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A comparative geochemical study of bituminous boat remains from H3, As-Sabiyah (Kuwait), and RJ-2, Ra'// al-Jinz (Oman)

This paper presents a geochemical analysis of fragments of bituminous amalgam from H3, As-Sabiyah (Kuwait), and RJ-2, Ra's al-Jinz (Oman). The fragments bear barnacles on one side and reed impressions on the other, and are thought to have been part of the coating of reed-bundle boats. The material from H3 dates to between 5300–4900 BC, while that of RJ-2 dates to 2500–2100 BC. Samples from both sites were geochemically compared to archaeological and ethnographic material from Kosak Shamali (northern Syria, *c.*5000–4400 BC), RH-5 (Oman, 4400–3500 BC) and Baghdad (central Iraq, 1900 AD).The composition of the bituminous amalgams was studied in detail. Rock-Eval Pyrolysis gave a measure of Total Organic Carbon in the samples, and allowed an initial comparison of the data sets using various parameters. Examination of the proportions of soluble and insoluble organic matter allowed an assessment of the quantity of vegetal matter added to the bitumen to make the bituminous amalgam. The composition of the Ra's al-Jinz material was studied using X-Ray Diffraction analysis and thin-section petrography, in order to assess the proportions of various minerals in the bituminous amalgams. It was concluded that the recipe for the bituminous mixture used to coat reed-bundle and wooden boats did not differ significantly from that commonly used to make 'mortar' for architectural purposes in Mesopotamia. Traces of animal fats or fish oils were not found in the analysed Ra's al-Jinz material, in contrast to previous hypotheses regarding the composition of the mixture. Comparison of the gross composition of extractable organic matter (the constituents of pure bitumen, soluble in chloroform or dichloromethane) showed the progressive effects of weathering on the samples. The isotopic composition of the bituminous material from H3 and the other sites was then compared to that of bitumen seeps and crude oils from Mesopotamia, Iran and Oman. The most significant result is that the material from As-Sabiyah originated in Kuwait, at a surface seep at Burgan, while the material from Ra's al-Jinz had a source in northern Mesopotamia.

Keywords: reed boats, bituminous coating, Kuwait, Oman, Iraq, Syria, mineralogical composition, bitumen origin, chemical composition, As-Sabiyah, Ra's al-Jinz, Baghdad, GC-MS, biomarkers, steranes, terpanes, carbon isotopic data on asphaltenes, Ubaid, Bronze Age.

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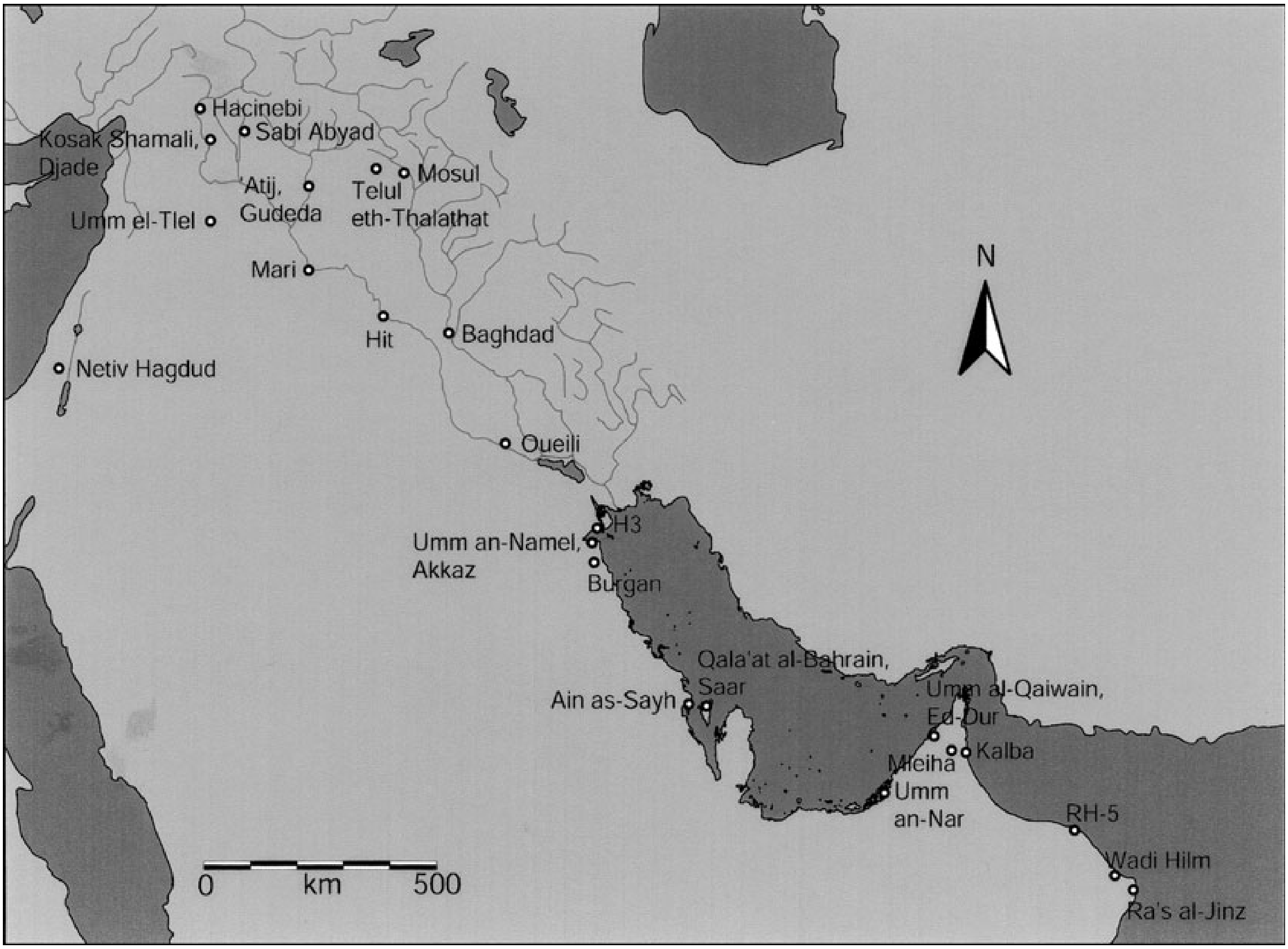

Fig. 1.
Map of the Middle East showing the location of sites and towns mentioned in the text.

Introduction

The recent discovery of Ubaid-period boat remains at H3, a coastal site in the As-Sabiyah region of northern Kuwait (Fig. 1), has given new impetus to the study of the origins of seafaring in the Arabian/Persian Gulf (1). The material culture of H3 indicates that its occupants were engaged in an exchange network which linked southern Mesopotamia and the Gulf region: its lithic industry, architecture and shell jewellery are Arabian Neolithic in character, but abundant Ubaid pottery and other Mesopotamian-style artefacts are present (2). The distribution of Ubaid-related material in the Gulf, chiefly pottery, has been discussed since the 1970s (3), and one leading interpretation is that the Mesopotamian material was transported by sea (4). Finds from H3, which include the bituminous fragments of Neolithic/Ubaid boats, as well as a model of a reed-bundle boat and a ceramic disc apparently showing a boat with a two-footed mast, strongly support the hypothesis that the relationship was indeed conducted by sea (5). Moreover, there are indications that the connection between southern Mesopotamia and the Gulf can be described as a true maritime trading relationship, of hitherto unsuspected complexity and stability (6).

The boat remains at H3 consist of pieces of bituminous material, including slabs with parallel reed impressions on one side and barnacles on the other. Some also bear string impressions (see below). It is proposed that these are the fragments of the waterproof coating which was applied to the exterior, and perhaps also to the interior, of reed-bundle boats (7). The coating would also have functioned as a tough and flexible protection against mechanical damage to the reed hull, as well as an anti-fouling agent (8). Historical and ethnographic sources show that the coating of reed and wooden boats with bitumen was common practice in the marshes of southern Iraq until recent decades (9), and there is sound archaeological evidence that bitumen-coated reed vessels were employed during the fourth and third millennia BC (see below). Mesopotamian cuneiform sources show that bitumen was used in large quantities to coat reed boats in the shipyards of southern Iraq during the late third and early second millennia BC (10).

The bituminous boat remains from H3 are Arabian Neolithic in date, contemporary with the Ubaid period in Mesopotamian chronology. They are currently the oldest known artefacts of their kind, dating to the centuries around 5000 BC (see below). They are very similar to later finds from the coastal site of Ra's al-Jinz in Oman, which date to the Bronze Age, *c.*2500–2100 BC (11). The Omani examples also show reed imprints on one side and barnacles on the other, but are larger, more numerous and better preserved. Unlike the examples from H3, some also bear impressions of wooden planks, and many show mat impressions, implying that during the Bronze Age the reed bundles were covered with mats before the application of the bitumen. Notwithstanding these differences, the morphological comparisons are good, and both sets of finds are interpreted as originating from seafaring boats.

Other coastal sites from the Gulf contain bituminous items which may have come from boats. At Qala'at al-Bahrain, on the north shore of Bahrain, a slab dated to Period IIb (*c.*2000 BC) shows impressions of reed bundles, tied together with a cord at an oblique angle (12). The other face of this triangular reed-impressed piece is flat and the bituminous mixture is tempered with organic material. According to the impression, this example may well have come from a reed-bundle boat (13), but no barnacles were observed, so the identification is tentative. The settlement on Umm an-Nar island also provides impressed pieces which are likely to have come from boats, in this case of the mid-late third millennium (14). As well as pieces with impressions of reed bundles, matting and wood, these include examples with parallel rope or string impressions comparable to those of H3 and Ra's al-Jinz (see below). Possible examples of the same date as the H3 material may occur at Sites C and D, Ain as-Sayh, located about 10 km south of Dhahran, Saudi Arabia (15). At Site C, bituminous fragments impressed with a woven reed pattern and 'reeding laced with fine, twisted, double stranded threading' were discovered. These remains, interpreted as matting in boat bottoms, do not show any barnacles, and their dating is problematic: Site C contained only one Ubaid sherd, along with another of later date (16).

Additional data from other areas in the Near East, including archaeological sites along the Euphrates and the Tigris rivers, provide examples of bituminous materials with reed imprints and traces of ropes, which are interpreted as remains of reed river-boats. Where the boats travelled on river systems, barnacles would not be present on the bituminous fragments. Consequently it is less certain that the selected bituminous pieces belonged to ancient boats. Included within this category is a fourth-millennium (3800 BC) example from Hacinebi, in southern Anatolia, on the Euphrates (17). The imprint, moulded on latex, clearly shows reed bundles (*Phragmites australis*) bound by ropes. This fragment dates to the early phase of the site, before the appearance of evidence for Uruk-period trading exchanges with southern Mesopotamia. An initial survey of the reports available for numerous archaeological sites from the Near East has yielded other examples which may belong to the river-boat category, namely bituminous slabs with reed and rope imprints from Kosak Shamali (18), also on the Euphrates River, in northern Syria.

The practice of coating boats with bituminous mixtures survived in Iraq until the last century, with the *quffah* or *guffah* (19), and the canoes called *tarada*. *Tarada* are presently built in the marshes of Southern Iraq (20) and *quffah* were still used to transport goods and people on the Tigris River at the beginning of the twentieth century. *Quffah* (cf. *quppu* in Assyrian, meaning plaited basket), were already used during the first millennium BC: they were described by Herodotus (484–425? BC) as the most outstanding curiosity of Babylonia. The *quffah* represented in relief on the walls of the Nimrud palace (860 BC) seem to be similar to the historical round coracle of Wales, or the present-day *thung* of Vietnam. Herodotus reported that the *quffah* were round, coated with leather and built in Armenia (21). He added that when these boats reached Babylon, leather was recovered from the hull and transported back to

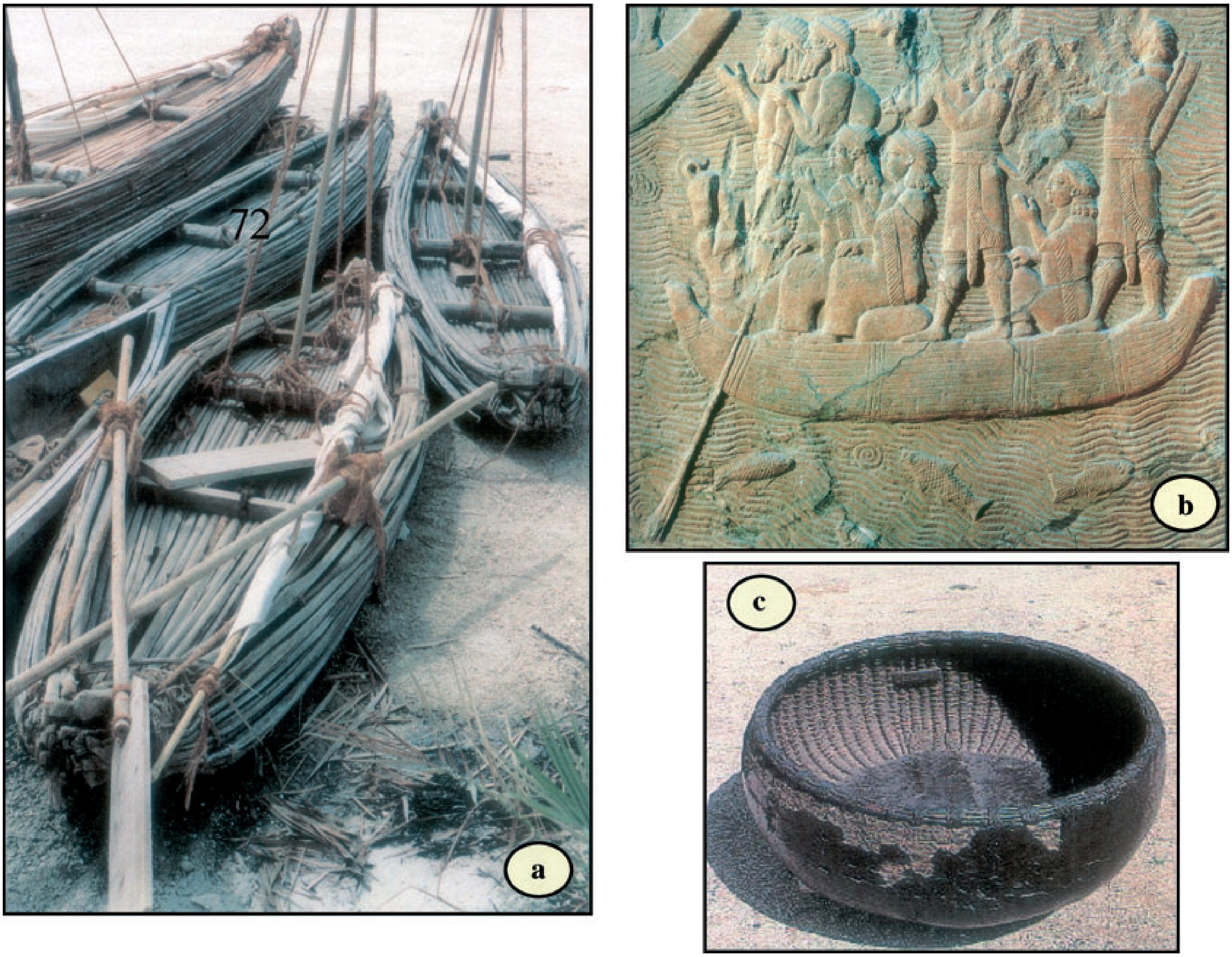

Fig. 2.
Reed- and palm-built boats of the Middle East. **a**. Small raft-boats (Arabic *shashat* or *shush*), made of the mid-ribs of date palm leaves, still used in the Gulf (photographed in Bahrain by J. Connan); **b**. Assyrian stone relief from the palace of Assurnasirpal at Nimrud (*c*.860 BC), northern Iraq, showing soldiers transported in reed or palm boats; **c**. *Quffah* of the Tigris River, made of plaited palm, wood and coated with a bituminous mastic (Musée de la Marine, Paris, reference no. 3 EX 9, diameter 163 cm, height 58 cm, gift from the Mission Française in Baghdad in 1901. Photograph from the catalogue of the exhibition 'A la rencontre de Sinbad', Musée de la Marine, 1994).

Armenia on donkeys. This information suggests that the leather was possibly not covered with bituminous mixture and consequently that this ancient *quffah* was slightly different from those working on the Tigris river at the beginning of the twentieth century. Recent *quffah* (Fig. 2c) were used as taxis to transport passengers and goods to supply markets or to unload cargoes with various goods, animals and even carriages. They were built with wood and palm, woven according to the basketry technique and were coated with a bituminous mixture. Such *quffah* were still operating in 1938 in Baghdad.

This paper presents a geochemical study of bituminous slabs from H3, As-Sabiyah and RJ-2, Ra's al-Jinz. These sites provide two groups of representative samples of the bituminous coating of ancient seafaring reed boats. These case studies are compared to data sets provided by samples from Kosak Shamali and Baghdad. The study was undertaken with several objectives:

1. To examine the gross composition of the bituminous mixtures, in order to determine what proportion is principally composed of bitumen, and document the mixtures' detailed composition, in

particular the input of mineral and organic additives.

2. To test the hypothesis that 6–9% tallow, i.e. animal fat, was incorporated into the mixture, as stated by Cleuziou and Tosi, and Rinaldi (22).

3. To identify the origin of this bitumen in order to document trade routes at each archaeological site.

4. To compare the various amalgams associated with the different archaeological examples, and with a contemporaneous counterpart represented by a sample from a *quffah* from the Tigris River, to find if significant and progressive changes occurred in the mixture through time.

Archaeological samples

H3, As-Sabiyah

Bitumen samples from twelve archaeological contexts at H3 were subjected to analysis. These were subdivided into fifteen samples, whose basic characteristics are summarised in Table 1. The first set (nos 1644 to 1650) comprised broken bituminous lumps (2–3 cm maximum) mixed with red sand. The size of the samples did not allow any vegetal imprints to be visible, with the exception of no. 1647. The second set included bigger fragments (nos 1771 and 1772), and showed large vegetal impressions (reed?) and barnacles. All the mixtures were heterogeneous and included minerals (sand grains, gasteropoda, shell debris, barnacles, clay?) and vegetal debris embedded in the bitumen. All samples were fragile and crumbly, and exhibited voids typically left by the dissolution of vegetal stems. These features suggest that the bituminous mixtures were severely weathered and micro-fissured, as documented by their permeability to water (23).

Before the analytical results are presented, it is necessary to contextualise the site and the bitumen.

H3 and its context

H3 is located on a low peninsula, now surrounded by mud-flats, on the north side of Kuwait Bay. Five seasons of excavation and survey took place between 1998 and 2004 (24). It is thought that the sea bordered the site during the time of its occupation, as a result of higher sea levels and/or the lesser deposition of sediments at that time (25). H3 would have been ideally located for maritime activities, at the edge of a natural harbour, facing a sheltered bay. The site had a short habitation history, and calibrated radiocarbon dates place the beginning of its occupation in the later part of the sixth millennium BC. Its use probably extended into the beginning of the fifth, and the longest likely date range for the bitumen samples used in this study is 5300–4800 BC (26). The actual date range may be very much shorter. The pottery is mainly Ubaid 2/3 (also known as Early Ubaid 3), perhaps developing into mature Ubaid 3 (27). A four-fold division of the site's sequence has been made, on stratigraphic and architectural grounds. The occurrence of bitumen within these periods is given in Figure 3 and Table 1.

The lithic technology, architecture and other aspects of H3's material culture align the site with the Arabian Neolithic, notwithstanding the presence of abundant Mesopotamian Ubaid artefacts. Its herding, fishing and gathering economy is typical of the coastal aspect of the Arabian Neolithic. The site is slightly unusual in that Periods 2–4 contain a cellular stone building complex (Fig. 4). The architectural complexity is largely due to repeated rebuilding, sometimes after short episodes of abandonment, consisting of additions and the subdivision of existing chambers. Although architecture of comparable complexity has not yet been excavated at other Arabian Neolithic sites, similar chambered structures are known from Shagra (Qatar), while recent investigations on the island of Marawah (Abu Dhabi) and at Kharimat Khor al-Manahil (inland Abu Dhabi) are beginning to show that cellular architecture is consistently associated with the Arabian Neolithic (28).

Description and quantification of the bitumen artefacts

Fifty-one pieces of bitumen from H3 are considered significant. This figure is intended to represent the number of individual slabs or chunks which were deposited and excavated. In reality, this number is likely to be no more than a close approximation: the material was exceedingly friable and frequently broken or cracked in the ground. During consolidation and reconstruction, it was not always possible to know exactly how many pieces had originally been laid down. A further complication is that thousands of small bitumen fragments and crumbs were scattered throughout the excavated deposits. To record and quantify all of these would have been

Table 1. Basic information on the analysed bituminous material from H3, As-Sabiyah.

sample number	site	estimated date of bitumen	Archaeological references: context	object	context description	period	sample	3D location	way of sampling	date of sampling	macroscopic description of sample analysed
1644	BAEK:H3	5300–4900 BC	1536	02	aeolian sand to the South of the building complex. Rich in artefacts, but a thick homogenous fill with no surfaces evident	4	bitumen	117.414/207.889/6.620	Hand picked	14/02/2001	crumbly bituminous lumps with sand, vegetal remains and some gaster-opoda filled with bitumen
1645	BAEK:H3	5300–4900 BC	1029	08	primary occupation debris in Chamber 1. Rich in bone, artefacts, bitumen	3	bitumen	not recorded	Hand picked	31/01/2001	crumbly bituminous lump with sand, vegetal remains and gasteropoda. Very similar to 1644. 1645 = bitumen enriched sample
1646	BAEK:H3	5300–4900 BC	1052	09	primary occupation debris in Chamber 1. 1052 is at a deeper level than 1029	3	bitumen	115.19/209.76/6.33	Hand picked	10/03/2001	similar to 1644 and 1645. 1646 = bitumen enriched sample
1647	BAEK:H3	5300–4900 BC	1020	04	upper fill of Chamber 17. Not primary occupation debris: it appears to be a deposit which formed when the chamber fell into temporary disuse	3	bitumen	111.969/208.416/6.539	Hand picked	05/02/2001	fairly crumbly brown-black mixture with few vegetal remains inside. Numerous traces of vegetal imprint at surface
1648a	BAEK:H3	5300–4900 BC	1021	01	fill of small compartment (Chamber 4). Contained two thin vertical slabs of bitumen, *c.*1 cm thick.	3	bitumen	not recorded	Hand picked	23/01/2001	assorted bituminous lumps
1648b	BAEK:H3	5300–4900 BC			Barnacles not evident, unclear if impressed or not aeolian sand and			not recorded	Hand picked		crumbly bituminous lumps without numerous vegetal debris inside
1649a	BAEK:H3	5300–4900 BC	1014	01	tumbled stones in Chamber 3. Not	3	bitumen	not recorded	Hand picked	22/01/2001	assorted bituminous lumps
1649b		5300–4900 BC			primary occupation debris: probably a mixture of collapse and occupation				Hand picked		big lumps of bituminous mixture with vegetal debris and sand
1649c		5300–4900 BC			material.				Hand picked		sand with lumps of bitu-minous mixture, remains of shells and vegetal debris
1650	BAEK:H3	5300–4900 BC	3034	14	primary occupation debris within Chamber 15. Chamber 15 was a work-ing area for lithics manu-facture, and other activities including shell jewellery manufacture.	3	bitumen	not recorded	Hand picked	28/02/2001	sand grains embedded in bitumen

1771	BAEK:H3	5300–4900 BC	1641	04	Chamber 27, red brown silty sand	3	bitumen	not recorded	Hand picked	04/03/2002	large imprint of 1.3 cm in diameter and holes of vegetal dissolution. Vegetal remains, quartz grains and barnacles in the mixture
1772	BAEK:H3	5300–4900 BC	1040	02	orange red silt and sand, post abandonment deposit	3	impressed bitumen fragmented (7× 9× 0.5 cm)	112.565/208.793/6.325	Hand picked	12/02/2001	large imprints of macro-vegetal remains (reeds?) within a black mixture with shell debris and quartz grains
1773	BAEK:H3	5300–4900 BC	1029	20	primary occupation debris in Chamber 1. Rich in bone, artefacts, bitumen	3	impressed bitumen	not recorded	Hand picked	31/01/2001	fairly crumbly black mixture with numerous quartz grains and vegetal debris, gasteropoda and other shell debris
1774	BAEK:H3	5300–4900 BC	1326	03	Chamber 33, occupation deposit	4	bitumen	121.36/209.35/6.45	Hand picked	17/03/2002	bituminous mixture with some vegetal remains, numerous quartz grains and shell debris
1775	BAEK:H3	5300–4900 BC	1668	01	silty sand, occupation south of buildings	3	bitumen	115.15/206.93/6.31	Hand picked	10/03/2002	bituminous mixture with vegetal remains, quartz grains and shell debris

Table 2. Typological breakdown of bitumen pieces from H3, As-Sabiyah.

Type of Bitumen Piece	Quantity
impressed bitumen, no barnacles visible	22
impressed bitumen with barnacles	17
bitumen fragment with no identifiable impressions or barnacles	8
string-impressed bitumen	4
sum	51

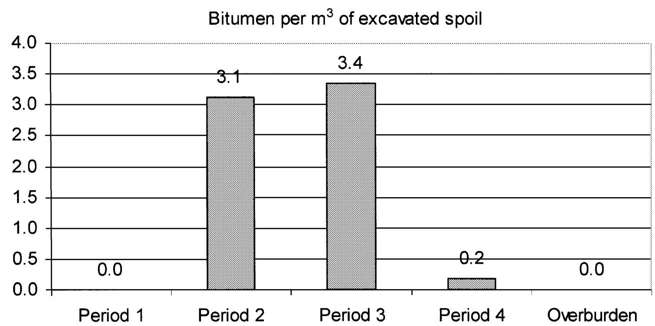

Fig. 3.
Chart showing chronological distribution of registered bitumen pieces at H3, As-Sabiyah.

an impossible and pointless task. A size limit was therefore imposed, at which a piece was considered to be worth counting: this was set at 3 cm (29). The samples submitted for destructive analysis in this study (Table 1) include damaged parts or unreconstructable examples of the fifty-one registered pieces, as well as other fragments which were too small to be included in the full quantification and registration process.

Figure 5 shows the size distributions of the quantified pieces. Most of the best-preserved and informative slabs measured between 5 and 8 cm across, with a thickness generally ranging between 1–2 cm, sometimes up to 3 cm (30). The largest pieces were around 20 cm long, but only 1 cm thick. One large and unusual piece was just under 5 cm thick. The shapes of the better-preserved bitumen pieces were, with exceptions, geometric, having approximately straight edges joining to make uneven polygons, usually with four or five sides (Fig. 6). This breakage pattern may reflect the underlying structure of the reed-bundle hull: perhaps a mesh of ropes was tied or sewn around the bundles, or the lashings holding the bundles together created such a pattern, and the bituminous coating fractured along the lines of the ropes.

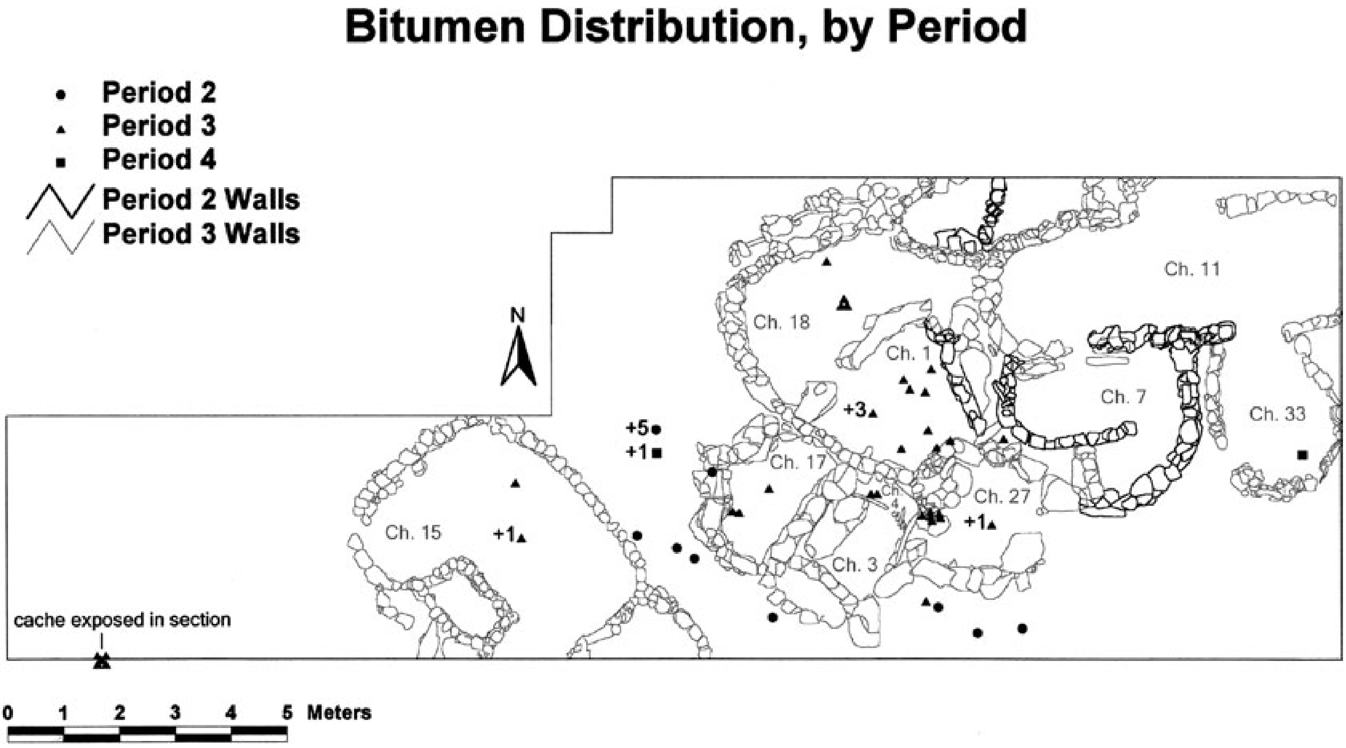

Fig. 4.
Simplified plan of main stone-built structures at H3, As-Sabiyah, with distribution of bitumen pieces. Period 4 additions and subdivisions are not shown. Coordinates were not available for eleven of the fifty-one bitumen finds: textual indicators on the figure are shown within the chambers and external areas where these were found (e.g. +5, +1).

The pieces of bitumen bore reed impressions and barnacles, as well as certain other features. Table 2 gives a breakdown of the characteristics of the assemblage. The eight fragments which did not display clear impressions or barnacles were mostly badly preserved. Seventeen slabs had both impressions and barnacles ('impressed barnacle bitumen'), equalling 33% of the assemblage (31). The impressions mostly consisted of parallel reeds, representing the surface of the reed bundles (Fig. 6a, c). Barnacles, identified as *Balanus trigonus* (Fig. 6b, d), never occur on the same side, indicating that they formed on submerged bitumen-coated reed structures, rather than forming on the slabs following the disintegration of such structures (32). Wood impressions were not noted, but one piece appears to show a mat impression. This underlines an important difference from the comparable Ra's al-Jinz slabs, which did show wood impressions, and many of which showed mat impressions (Fig. 7c). It is thought that mats were used to cover the hull of the Ra's al-Jinz boats before the application of the bitumen amalgam (33). The scarcity of mat impressions at H3 implies that this was not the case during the Neolithic/Ubaid period, or that mats were used much less extensively in the construction.

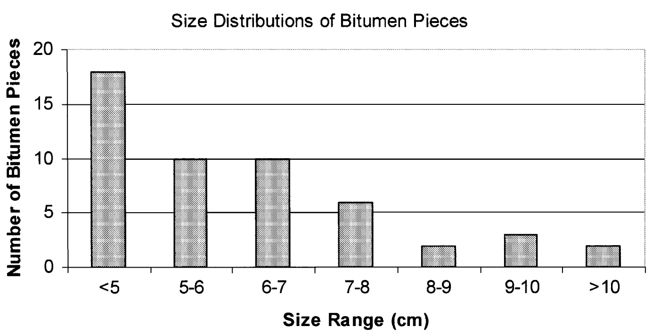

Fig. 5.
Chart showing size distribution of registered bitumen pieces at H3, As-Sabiyah.

Four pieces from H3 showed impressions of string or rope, 'string-impressed bitumen'. These are interpreted as impressions of the cords which held the reeds into bundles, and which lashed the

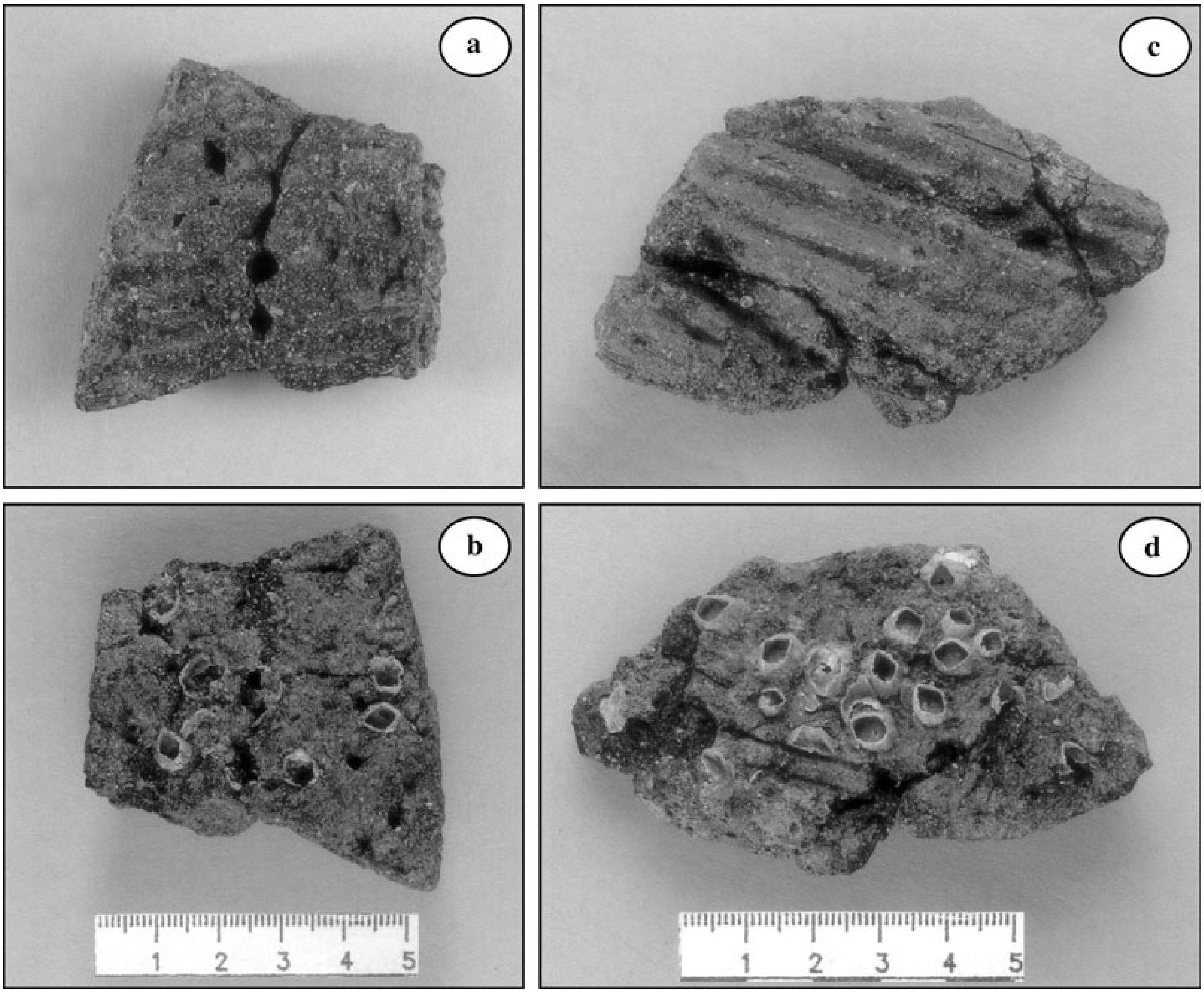

Fig. 6.
Bitumen slabs from H3, As-Sabiyah. **a**. Find no. 1029.09, dimensions 5.7 × 5.7 cm, 1.5–2.4 cm thick: inner surface, showing reed impressions (3–6 mm wide), and three 5 mm peg holes, which do not go all the way through. Note the mineral constituents in the bitumen; **b**. Outer surface of the same slab, exhibiting mature barnacles (6–7 mm); **c**. Find no. 1052.10, dimensions 8.7 × 4.8 cm, 1.4–2.4 cm thick: inner surface, showing reed impressions (5–7 mm wide); **d**. Outer surface of same slab, exhibiting mature barnacles (6–7 mm).

Table 3. Chronological distribution of bitumen at H3, As-Sabiyah, showing the number of pieces in each period, and the calculation of pieces per m^3 of excavated spoil in each period.

Site Period	Quantity of Bitumen	Volume of Spoil	Bitumen per m^3
Period 1	0	2116	0.0
Period 2	13	4172	3.1
Period 3	36	10745	3.4
Period 4	2	11598	0.2
Overburden	0	3188	0.0

bundles together to form a hull, as seen in Figure 2b. One piece showed three parallel ropes on the inner surface (Fig. 8), each slightly under 1 cm in diameter and consisting of a single thick twist of fine fibres, while the others showed impressions of string *c*.3 mm in diameter, made of two twisted strands of fibre.

Several of the pieces show small circular or uneven holes, usually less than 5 mm in diameter, and sometimes completely piercing the slab. This

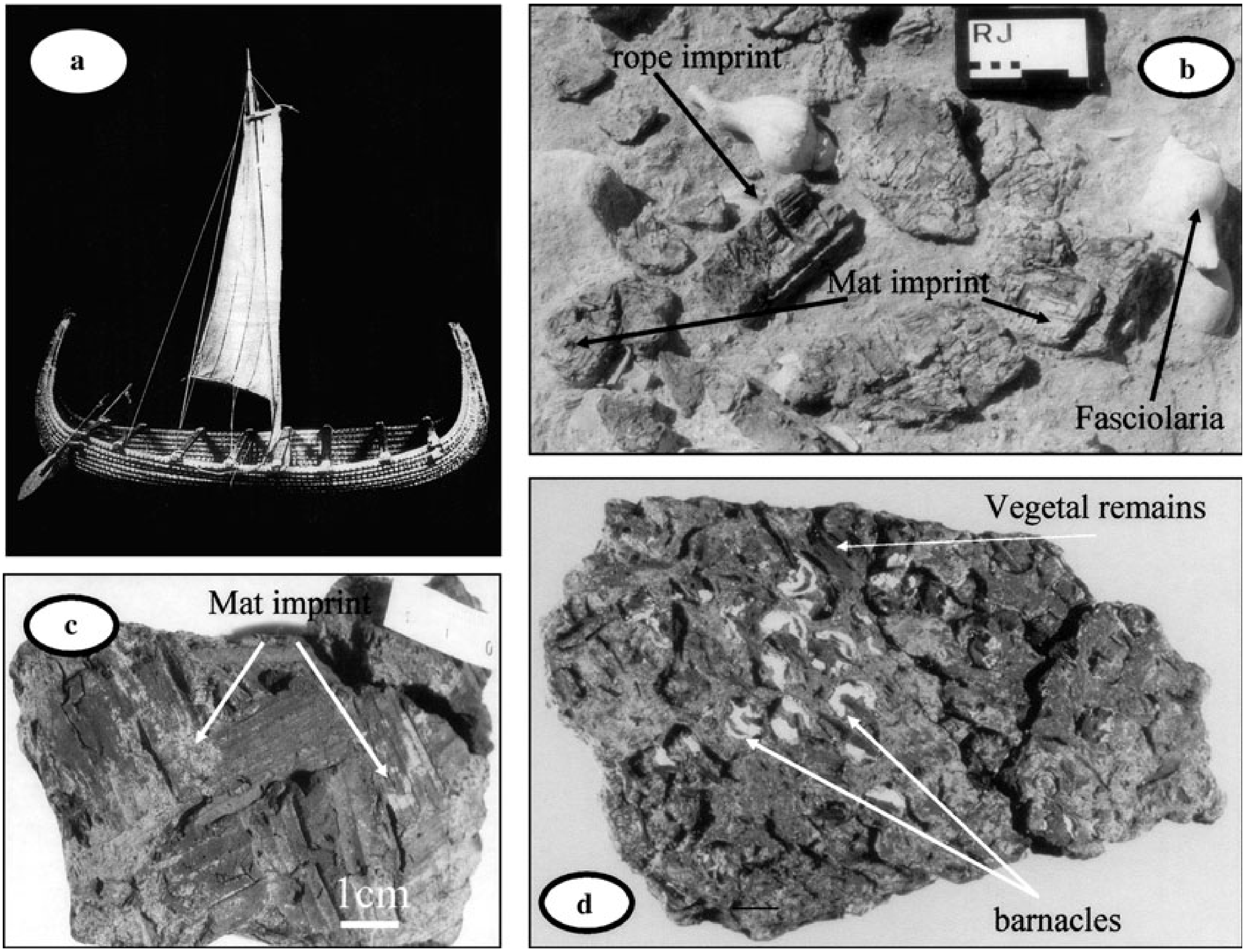

Fig. 7.
'Black boats of Magan': the bituminous slabs of Ra's al-Jinz (RJ-2, Oman); **a**. Scale 1/20 model of a Bronze Age reed boat, as proposed by Vosmer, Model of a Third Millennium BC Reed Boat (photo courtesy of Tom Vosmer); **b**. Bituminous slabs *in situ* at Ra's al-Jinz (RJ-2), in a shallow pit in Building I, Room 2, Period IIa (*c*.2500–2200 BC). In the centre of the picture, a fragment shows a rope impression, whereas two other fragments exhibit clear mat patterns (photo S. Cleuziou); **c**. Inner face of bituminous slab no. 725 (Building I, Room 2) with mat impression (photo J. Connan); **d**. Outer face of slab no. 182 (Building I, Room 6) showing encrusted barnacles and embedded vegetal remains (photo S. Cleuziou).

would negate the waterproofing properties of the coating, but in most cases these were not man-made. Marine boring organisms such as the teredo worm may have created some of them, necessitating the repair or removal of the coating. Others are likely to be pitting, resulting from post-depositional degradation and disturbance, including roots and burrowing insects. In one case, three evenly spaced holes, which do not pierce the slab, may indicate a row of small pegs or reeds protruding slightly from the bundle (Fig. 6a).

The majority of the slabs, including all the string-impressed and barnacle-encrusted slabs, are interpreted as the coating of reed-bundle boats. Most of the slabs which do not bear barnacles probably originated from parts of the vessels which were above the water-line, or inside the vessel. A few exceptions probably did not come from boats, however. These include at least one champagne-cork shaped piece, which is likely to have been a jar or bottle stopper, and had a hole or impression through which string could have passed to enable extraction.

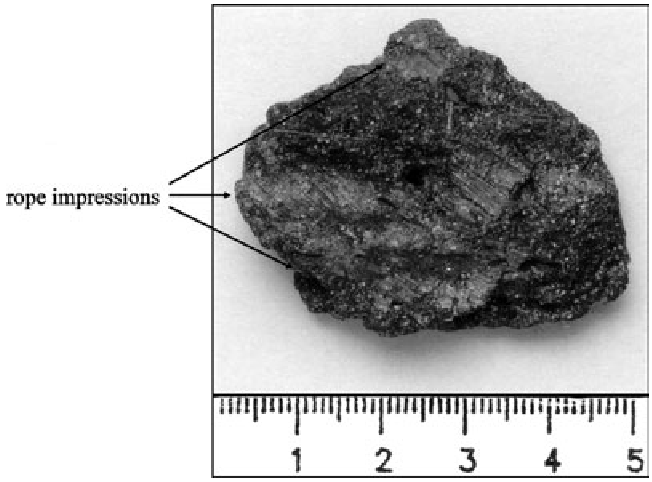

Fig. 8.
Example of a string/rope-impressed bitumen slab from H3, As-Sabiyah. Find no. 1049.01c, dimensions 4.8 × 3.6 cm, 1–2.5 cm thick. Three parallel impressions are visible, showing the imprint of three fine-fibred cords, *c.*7 mm wide when measurable. Only a fraction of the top impression survives. The outer face of this fragment did not show barnacles.

Another piece was misshapen and thick (4.5 cm), with no obvious outer or inner face, or surface impressions, although it was full of imprints of coarse vegetal matter which had been incorporated into it. This piece may have been a handful of amalgam which was prepared for use but not applied.

Examination of the bitumen showed that it was not pure, but mixed with other material to make a tough, adhesive and flexible amalgam. As well as the reed impressions, chopped vegetal matter, probably also reeds, left impressions within its fabric. In some cases, layers of reed impressions can be seen within the slab, perhaps indicating that reeds were applied onto the fresh bitumen during the application of the coating, which were then covered themselves with a second bitumen layer. Other inclusions include quartz sand, small gastropod and other shell fragments and barnacle fragments. Seed impressions were also noted, in three examples. The recipe used to make the amalgam is further discussed below.

Chronological and spatial distribution of the bitumen pieces from H3

The chronological distribution of the H3 bitumen shows a concentration in Periods 2 and 3 (Figs 3–4, Table 3). Although no slabs were found in Period 1, bitumen appears to have been present: an attempt to obtain a radiocarbon date from a Period 1 fire-pit suffered from contamination by ancient carbon. During Period 1, H3 was used as a campsite, with architectural remains restricted to numerous fire-pits. Contact with Mesopotamia was already occurring, however, perhaps by boat, as indicated by the presence of Ubaid pottery.

The appearance of quantifiable fragments of bitumen in Periods 2 and 3 perhaps indicates an intensification of boat-related activities and a closer involvement of the site's inhabitants in maritime trade. Although Period 2 commenced with the construction of stone walls, some of which survived into subsequent periods (e.g. those of Chamber 7), all thirteen Period 2 bitumen pieces were found in external sand and midden layers predating the western part of the central building complex, which had not yet been built.

The highest quantity of bitumen is associated with Period 3, which also saw the most extensive building activities, with the addition of a series of chambers to the western part of the central complex. The bitumen pieces of this period are strongly associated with the structures, with all but seven of the thirty-six being found inside the chambers. A particular concentration was found in Chamber 1 (eleven pieces), with four examples in the adjoining cell, Chamber 18, and six from Chamber 27.

The low quantity of bitumen in Period 4 may reflect a further change in the function of the site. Just two slabs were found, one in the paved Chamber 33, the other in sand above a collapse layer. Although the inhabitants were still involved in the maritime exchange network, judging from other artefact classes, activities directly relating to the boats may have diminished. It is possible that the falling sea-level inhibited direct access to the sea. People in the area may still have been involved with boats, but these activities may have occurred at an undiscovered locale, perhaps not far from H3 at a place now buried by sediments.

The construction of the stone architecture, particularly during Periods 2 and 3, and its chronological and spatial association with the bitumen, is likely to be intimately connected with the function of the site. Little is known, however, of the exact nature of the boat-related activities that took place at H3. The presence of the impressed and barnacle-covered pieces indicates simply that boats were stripped

Table 4. Basic information on the analysed bituminous material from RJ-2, Oman (2500–2100 BC), Kosak Shamali (5200–4300 BC) and Baghdad (1900 AD).

sample number	site	Country	Location: Building, Room, Sector, Level, etc.	sample reference	archaeological references	date range	Macroscopic description
148	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 5	RJ-2	2500–2300 BC	hard bituminous mixture with abundant vegetal debris, vegetal impressions at surface
149	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 15	RJ-2	2500–2300 BC	hard bituminous mixture with abundant vegetal debris, vegetal impressions at surface
150	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 38	RJ-2	2500–2300 BC	hard bituminous mixture with abundant vegetal debris, vegetal impressions at surface
151	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 46	RJ-2	2500–2300 BC	hard bituminous mixture with abundant vegetal debris, vegetal impressions at surface, white mineral in holes
725	Ra's al-Jinz	Oman	RJ-2 Building I?	sample from Claude Carrel, Elf Oman	RJ 2	2500–2300 BC	
756	Ra's al-Jinz	Oman	RJ-2	no reference	no references	2500–2300 BC	large chunk with voids (from dissolution of vegetal material), resembling bituminous mortar
757	Ra's al-Jinz	Oman	RJ-2 Build.III, Ro.4	bitumen 6	RJ-2 1988-QSQ 2111-F.N.14-B. 2038 O.266 -III-4	2500–2300 BC	1 cm black chunks with traces of vegetal matter inside
758	Ra's al-Jinz	Oman	RJ-2 Build.III, Ro.4	bitumen 10	RJ-2 1988-III-4	2500–2300 BC	brown black bituminous chunks
759	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 19	RJ-2 1986- ZJ 2- I-6	2500–2300 BC	large black chunks
760	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 21	RJ-2 1986- ZJ 2- I-6	2500–2300 BC	chunks with numerous vegetal impressions
761	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 63	RJ 2 1986- ZO- I-6	2500–2300 BC	vegetal impressions
762	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 84	RJ 2 1986- ZD- I-6	2500–2300 BC	chunks with vegetal impressions
763	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 85	RJ 2 1986- ZD 2- I-6	2500–2300 BC	chunks with vegetal impressions
764	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.6	bitumen 301	RJ 2 1986- ZE I-6	2500–2300 BC	numerous small pieces with vegetal impressions
765	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.12	bitumen 310	RJ 2- s.u. 343- I-12	2500–2300 BC	
766	Ra's al-Jinz	Oman	RJ-2 Build.II, Ro.17	bitumen 328	RJ 2 1987- QJW 860- II-17	2500–2300 BC	several bituminous chunks

767	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.4	bitumen 517	RJ 2- Z 6/4 2- I-4	2500–2300 BC	
768	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 518	RJ 2- I-2?	2500–2300 BC	small bituminous chunks
769	Ra's al-Jinz	Oman	RJ-2 Build.I, Ro.2	bitumen 533	RJ 2 1985- Z 15/3 I-2	2500–2300 BC	bituminous chunks with vegetal impressions
770	Ra's al-Jinz	Oman	RJ-2 Build.VII, Ro.6	bitumen 22?	RJ 2 1994 n.22- VII-6	2300–2100 BC	
771	Ra's al-Jinz	Oman	RJ-2 Build.VII, Ro.6	bitumen 31?	RJ 2 1994 n.31- VII-6	2300–2100 BC	
619	Ra's al-Jinz	Oman	RJ-2 Build.VIII, Ro.2	bitumen coating the interior of a potsherd (Mesopotamian origin)	RJ 2- 2765- 28/12/93- LWO 3- VIII-2 phase IIc	*c*.2300 BC	potsherd with bituminous crust inside, thin bituminous layer on the outside face
1378	Kosak Shamali	Syria	Sector A - Level 6		95KLS- AD4–11:sector A - Level 6	5100–4700 BC	black, hard sample with vegetal remains and mineral inside, large vegetal impression (reed?) at surface
1381	Kosak Shamali	Syria	Sector A - Level 10A		97KSL-AE5–22–9:sector A - Level 10A	5190–4800 BC	hard bituminous mixture with vegetal debris. Large vegetal impressions (reed?)
1385	Kosak Shamali	Syria	Sector B - Level 6		97KSL-BE7–34:sector B - Level 6	4550–4260 BC	hard black mixture with quartz grains but no vegetal debris. Large vegetal impressions (reed, wood?)
1073	Baghdad	Iraq	Musée de la Marine, Paris	inv.: 8 EX 9, given by the French Mission in Baghdad, 1901	*Quffah* of the Tigris River	1900 AD	lump of black bitumen. Homogenous aspect. No detectable vegetal remains

of their bitumen coating at or near the site. The find-spots of the bitumen pieces indicate a combination of loss/discard and deliberate storage. Most of the twenty-one pieces found outside the chambers may have been discarded, except for five found in a cache, stored vertically in a small pit on the southwestern side of the trench (Fig. 4). Other probable caches were found in Chamber 18, where three of the four pieces from that chamber were found stored together; Chamber 27, where six pieces were tightly grouped; and Chamber 4, where two very thin slabs were stored vertically. Some other single bitumen finds from inside the chambers may have been stored deliberately, though many of them are so small that they might be the products of larger slabs broken during storage, and thus lost or discarded.

The deliberate recovery and storage of material indicates an intention to re-use, perhaps for re-application to newly-built boats, or for repairing damaged ones. Bitumen was a valued raw material, the nearest source of which was around 100 km away, and recycling the bitumen would have been both technically possible and sensible (34). Burnt barnacle fragments visible in broken slabs show that in some cases the bitumen had been previously recycled. There is no reason why bitumen-coated reed-bundle boats could not have been repaired or constructed at the site using newly-brought or re-used bitumen. As this study shows, the bitumen itself was originally obtained from southern Kuwait, and it is possible that reeds grew close to the site during its occupation (35). There is no direct evidence of construction activity, however. Bitumen had many uses other than boat construction, and one artefact from H3 appears to be not a reed-bundle boat fragment, but a small jar-stopper. The bitumen could even have been recovered for use as fuel.

Ra's al-Jinz

The details published by Cleuziou and Tosi (36) on bitumen from RJ-2 can be summarised as follows. The corpus of archaeological bituminous materials comprises more than 200 slabs, with 100 additional smaller fragments. These include both impressed and unimpressed objects. Unimpressed objects are the most abundant and reach a weight of 2.7 kg in a loaf. These are thought to be the mixture prepared for storage. Impressions are either of mats (Figs 7b–c) or lashed reed bundles (Fig. 7b). The reeds were identified as *Typha sp*. and occasionally *Phragmites sp*. Bundles of reeds are laced with twisted ropes, and mats (Fig. 7c) are made of interwoven slit-cut reeds. Encrusted barnacles (Fig. 7d) occurred on 20% of the well-preserved material. As at H3, barnacles (in this case said to be *Balanus amphitrites*) are never present on the impressed surface or on the edges of the lumps. Their presence indicates that the bituminous lumps came from the coating of the hull in direct contact with sea water. Other bituminous pieces without barnacles are interpreted as belonging to that part of the coating of the boat which was never in contact with sea water. The excavated pieces are thought to be part of the bituminous coating, stored for re-use. Evidence of re-use is gained from the fact that barnacle fragments are sometimes found incorporated into the bituminous mixture, again comparable to the H3 material.

Basic data relating to the archaeological contexts of the Ra's al-Jinz samples, as well as some macroscopic descriptions, are listed in Table 4. Twenty-one samples of bituminous pieces from RJ-2 were selected for geochemical analyses. Nineteen came from the southern compound (Buildings I and III, especially Rooms 2, 4 and 6) and are representative samples from the bituminous envelope that coated reed boats. Two samples (nos 770 and 771) originate from the northern compound (Building VII, Room 6) and were excavated from a 60 cm-deep storage pit dug in the floor of the western corner of Room 6, which contained fifty-five bitumen slabs (37). This set of finds possesses specific characteristics, namely wood impressions on the bitumen slabs. This pattern raises a major question: did the parent boat with a wood-impressed pattern have a different origin? For example, could this boat have come from the Indus coastal area? The Indus region was rich in high-quality timber, unlike Oman or Mesopotamia, and such an hypothesis is reinforced by the high percentage of sherds imported from the Indus at RJ-2. If the hypothesis is valid, one might expect to identify a different bitumen used as a coating agent. The geochemical study of these specific samples was intended to explore this possibility.

To complete the data set, a sample of the bituminous crust coating the interior of a pot sherd was also analysed. The sherd was from a large buff ware jar, identified as a Mesopotamian product (38).

These jars are thought to be the vessels which were used to transport and store the bitumen (39). It was therefore important to determine whether the bitumen residue coating the inside of the sherd originated from Mesopotamia, in order to confirm the existence of a sea-borne trade in bitumen from Mesopotamia to Oman.

Kosak Shamali

The archaeological bituminous mixtures excavated from Kosak Shamali were published by Connan and Nishiaki (40). Among the various artefacts with bitumen (which include potsherds, flint blades, stones and bone tools), numerous relatively large flat slabs with reed (or palm?) imprints on one side were found in Level 6 of Sector A. These slabs (e.g. no. 1385, Fig. 9c) were unearthed from a stored position (for re-use?) in a chamber. Their average thickness is 11 mm (n = 28) which suggests that they are too thick to have originated from the waterproofing of the roof. The roof was apparently not built of reeds but of wood, using poplar, willow

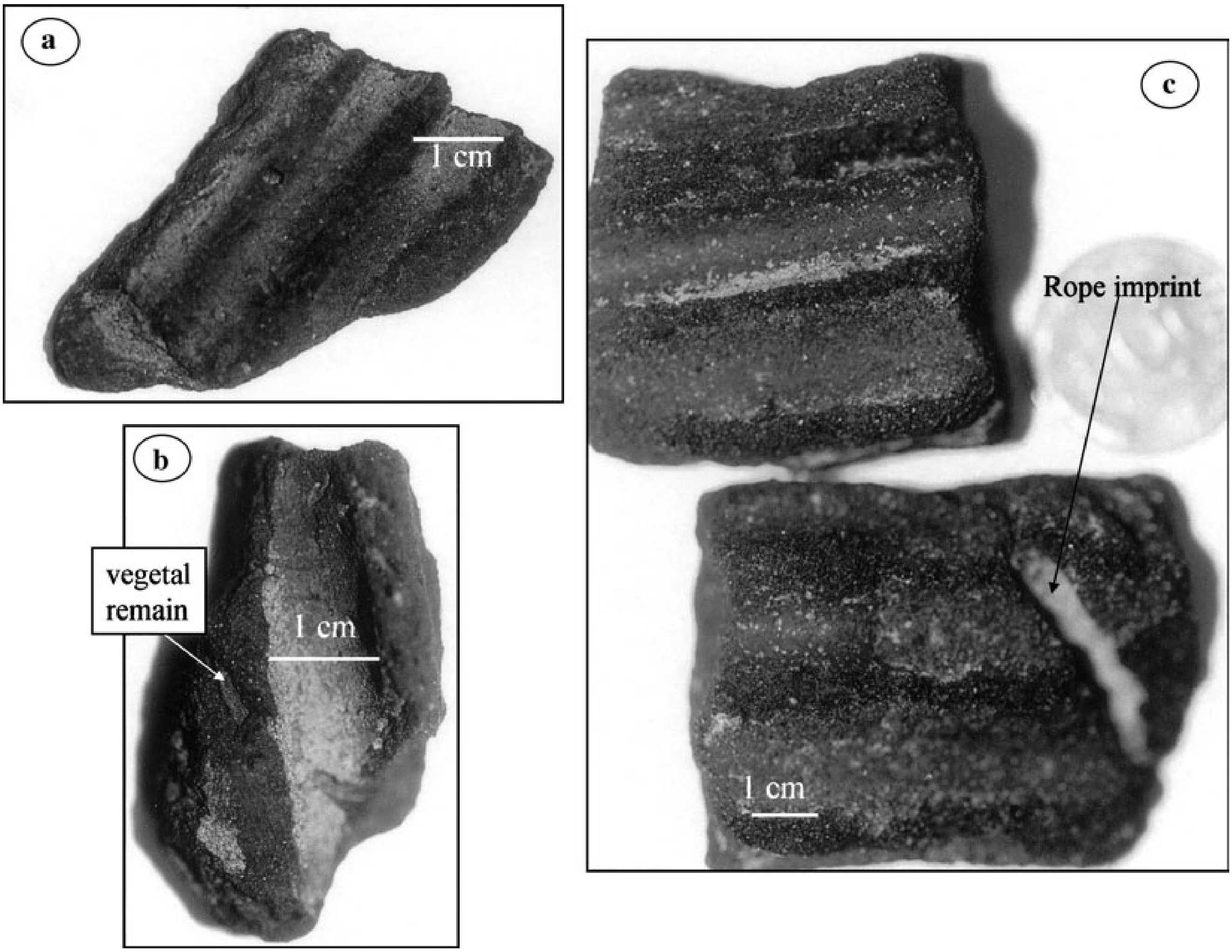

Fig. 9.
Presumed bituminous boat remains from Tell Kosak Shamali, on the Upper Euphrates (Syria); **a**. no. 1381 (Sector A, Level 10A, 'Early Ubaid', 5190–4995 BC); **b**. no. 1378 (Sector A, Level 6, 'Late Ubaid', 5100–4900 BC), from a fill covering mud-brick rooms of a burnt building with roof remains; **c**. no. 1385 (Sector B, Level 6, 'Post Ubaid', 4550–4405 BC), from the floor of Room B504 (BD7-46), which seems to have been a storage space for the preparation of pottery vessels for firing. Were the bituminous pieces intended to be used as fuel for firing pottery? See Koizumi T and Sudo H. The stratigraphy and architectures of Sector B of Tell Kosak Shamali. In: Nishiaki Y& Matsutani T, eds. *Tell Kosak Shamali, The Archaeological Investigations on the Upper Euphrates, Syria*. UMUT Monograph 1, The University Museum, The University of Tokyo, vol.1: 2001: 115–152.

and alder for roof beams, and branches of tamarisk to cover the space between the beams (41). The thickness of the Kosak Shamali samples, however, agrees with that of the slabs from RJ-2 and H3. Consequently, the Kosak Shamali samples may be considered to be the likely remains of the coating of reed (or wood, or palm) boats.

Basic information on the three samples analysed is listed in Table 4, including date range, provenance and macroscopic description, and photographs are shown in Figure 9. An outstanding characteristic of these samples is their hardness. The three samples are black, hard slabs with visible minerals (sand grains, quartz?). Number 1385 in particular appeared as a mixture of bitumen and sand (quartz?) grains, as in geological tar sands. A few samples (no. 1381 but not no. 1385) also have vegetal debris.

Baghdad

One sample from the bituminous coating of a recent *quffah* (Fig. 2c) was collected for analysis. The sample is a hard black lump, 1 cm thick in which no vegetal matter can be seen (Table 4).

Experimental methodology

The archaeological bituminous material was studied using the same analytical scheme applied in

Table 5. Rock-Eval data.

sample number	site	date range	S1	S2	S3	HI	OI	TOC	Tmax
1644	H3, As-Sabiyah	5300–4900 BC	5.71	82.14	5.53	315	21	26.0	427
1649a	H3, As-Sabiyah	5300–4900 BC	8.54	91.92	3.89	444	19	20.7	430
1771	H3, As-Sabiyah	5300–4900 BC	9.16	87.68	3.58	441	18	19.9	429
1772	H3, As-Sabiyah	5300–4900 BC	13.27	120.08	4.66	484	19	24.8	427
1773	H3, As-Sabiyah	5300–4900 BC	8.23	106.25	4.51	505	21	21.0	429
1774	H3, As-Sabiyah	5300–4900 BC	13.15	146.36	4.88	523	17	28.0	430
1775	H3, As-Sabiyah	5300–4900 BC	11.85	105.69	3.97	452	17	23.4	427
1073	Quffah, Baghdad	1900 AD	54.1	160.92	5.14	508	16	31.6	429
1378	Kosak Shamali	5100–4700 BC	13.1	59.3	4.6	446	34	13.3	430
1381	Kosak Shamali	5190–4800 BC	17.9	81.6	9.3	366	41	22.2	427
1385	Kosak Shamali	4550–4260 BC	9.8	41.8	4.33	441	45	9.5	431
148	Ra’s al-Jinz	2500–2300 BC	16.75	99.74	9.87	360	35	27.7	427
149	Ra’s al-Jinz	2500–2300 BC	21.01	115.18	9.90	388	33	29.7	429
151	Ra’s al-Jinz	2500–2300 BC	18.22	100.33	9.33	380	35	26.3	431
756	Ra’s al-Jinz	2500–2300 BC	9.71	92.57	9.42	343	34	27.0	430
757	Ra’s al-Jinz	2500–2300 BC	16.16	109.45	7.53	401	27	27.3	429
758	Ra’s al-Jinz	2500–2300 BC	15.28	97.71	8	353	28	27.6	429
759	Ra’s al-Jinz	2500–2300 BC	15	127.22	9.72	362	27	35.1	427
760	Ra’s al-Jinz	2500–2300 BC	13.12	100.87	9	360	32	28.0	427
761	Ra’s al-Jinz	2500–2300 BC	19.86	117.12	8.76	374	28	31.2	425
762	Ra’s al-Jinz	2500–2300 BC	10.66	102.93	8.13	368	29	28.0	432
763	Ra’s al-Jinz	2500–2300 BC	18.18	143.5	9.87	390	26	36.7	429
764	Ra’s al-Jinz	2500–2300 BC	18.65	105.97	7.92	383	28	27.6	429
765	Ra’s al-Jinz	2500–2300 BC	18.14	120.61	8.27	395	27	30.5	429
766	Ra’s al-Jinz	2500–2300 BC	15.48	98.53	7.56	378	29	26.0	428
767	Ra’s al-Jinz	2500–2300 BC	17.19	109.51	7.68	383	26	28.6	430
768	Ra’s al-Jinz	2500–2300 BC	15.62	107.5	7.75	361	26	29.7	428
769	Ra’s al-Jinz	2500–2300 BC	15.43	93.95	7.53	352	28	26.7	428
770	Ra’s al-Jinz	2300–2100 BC	20.25	121.29	8.18	376	25	32.3	426
771	Ra’s al-Jinz	2300–2100 BC	15.71	118.7	8.83	371	27	32.0	428
725	Ra’s al-Jinz	2500–2300 BC	17.82	95.25	8.84	361	33	26.4	428
619	Ra’s al-Jinz	*c.*2300	16.07	153.29	10.12	468	30	32.7	426

Key to abbreviations: TOC = Total Organic Carbon (as % by weight of sample); S_1 = Thermovaporised hydrocarbons (expressed in mg HC/g of sample); S_2 = pyrolysed hydrocarbons (in mg HC/g of sample); S_3 = CO_2 generated between 300 and 390°C (in mg CO_2/g of sample); HI = Hydrogen Index = S_2/TOCs (in mg HC/g TOC); OI = Oxygen Index = S_3/TOC (in mg CO_2/g TOC); Tmax = temperature of the maximum of the S_2 peak (in °C).

previous archaeometric studies (42). A detailed up-to-date flowchart with descriptions of each analytical technique and examples has been published (43), and analytical details can also be found in a recent paper devoted to the petroleum geochemistry of crude oils and source rocks in Kuwait (44).

Prior to the detailed chemical analysis, a binocular examination of each sample was undertaken on the raw samples. Petrographic analysis of thin sections was also conducted on some samples, in order to investigate the complexity of the heterogeneous mixture. X-Ray diffraction analysis, applied to the Ra’s al-Jinz material, allowed a quantitative measurement of the major minerals present in the bituminous mixtures. After the sampling procedure, which leaves fragments as references for further cross-checking, organic analyses were conducted, including screening techniques and detailed chemical and isotopic investigations. Several molecular ratios on steranes and terpanes, combined with isotopic criteria on asphaltenes ($\delta^{13}C$ and δD), were used to establish bitumen-to-bitumen and bitumen-to-oil seep correlations.

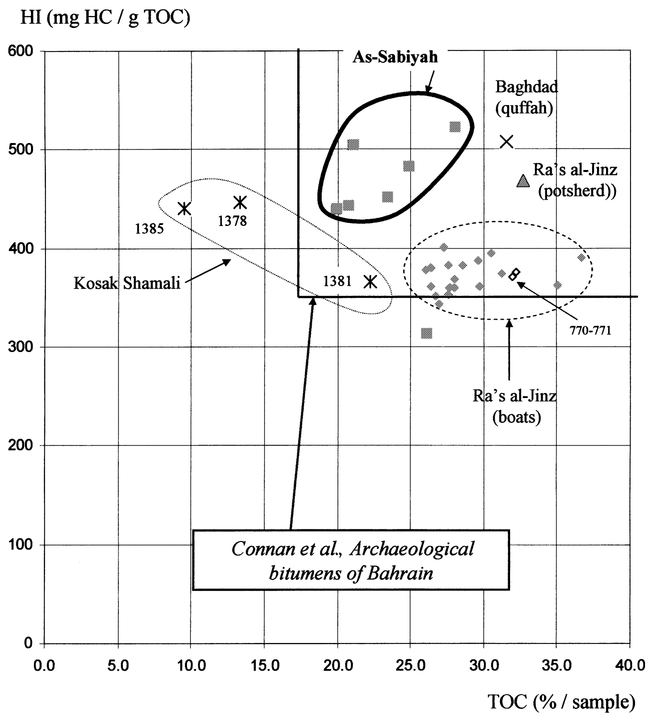

Fig. 10.
Hydrogen Index (HI), in mg of hydrocarbons (HC) per g of Total Organic Carbon (TOC) vs. TOC (as % by weight of raw sample), measured by Rock-Eval pyrolysis.

Results

Rock-Eval screening analysis: identification of bituminous mixtures

Rock-Eval Pyrolysis on whole samples was carried out as a screening technique, to compare the presumed bituminous mixtures from the different sites. The most important parameters deduced from the Rock-Eval analysis are listed in Table 5.

The plot of the Hydrogen Index (HI in mg HC/g TOC) as a function of Total Organic Carbon (TOC in %/sample) in Figure 10 shows that almost all samples fall within the area of archaeological bituminous mixtures defined by a previously analysed set of samples from Bahrain (45). Each case study, however (i.e. the material from each separate site), splits into separate groups indicating specific properties associated with each bituminous solution. In addition, all the bituminous fragments belonging to a single case study belong to the same population, showing an underlying homogeneity to the assemblages of each site.

Ra’s al-Jinz bituminous mixtures are rich in organic matter (having a higher TOC) with an average lower HI, perhaps because of enrichment with vegetal temper depleted in hydrogen. The bituminous slabs of Kosak Shamali display a significant depletion in organic matter. Within this case study one may identify two subgroups which reflect compositional changes: the increase of vegetal temper in no. 1381 decreases the HI and increases the TOC. The As-Sabiyah bituminous mixtures occupy an intermediate position and contain an organic matter richer in hydrogen, which suggests a predominant bitumen contribution. The coating of the Baghdad *quffah* is richer in TOC and HI, again being rich in bitumen.

Note that the slabs associated with wood impressions (Fig. 10, nos 770–771) at Ra’s al-Jinz are not significantly different from the slabs from reed boats. On the other hand, the bitumen mixture isolated from the Mesopotamian potsherd did not fall within that population, implying that it was not the final mixture which was prepared for coating boats. The mixtures used to coat boats were enriched with vegetal temper to improve the mechanical properties of the composite material, which served to lower the HI.

By considering another diagnostic diagram, namely HI vs. Tmax (Temperature of the S_2 peak maximum), the expected pattern is confirmed, with most data falling within the area previously defined for the archaeological bitumens of Bahrain (Fig. 11). Again sample nos 770 and 771 are included in the group comprising the coating of reed boats, whereas the inside coating of the Mesopotamian potsherd is obviously enriched in bitumen (higher HI and lower Tmax). The incorporation of chopped vegetal debris (straw, reed, palm) increases the Tmax of the whole mixture, as confirmed by Rock-Eval data acquired from RJ-2 samples that show an average Tmax of 433–436°C.

Mineralogical and petrographical analysis of RJ-2 samples

Certain RJ-2 samples were chosen for a detailed investigation of the bituminous mixtures. Thin sections perpendicular to the slab were prepared

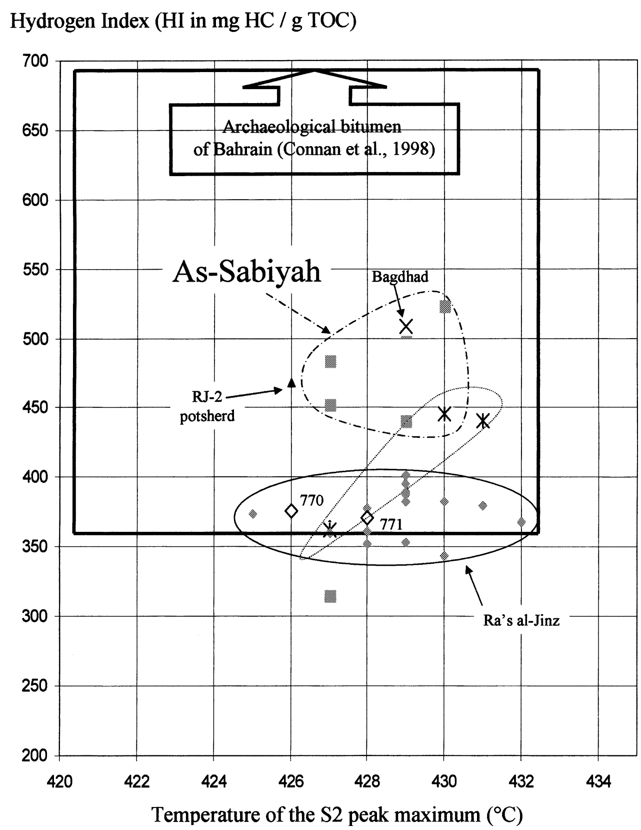

Fig. 11.
Hydrogen Index (HI), in mg of hydrocarbons (HC) per g of Total Organic Carbon (TOC) vs. Tmax (Temperature of the S_2 peak maximum, in °C).

from four samples (nos 148, 149, 150, 151) and examined by M. Veber. The four samples are very much alike and appeared to have been prepared according to the same recipe. Under microscopic examination, numerous pieces of vegetal debris are clearly visible inside the bituminous mixture (Fig. 12). Holes penetrating into the slab are mainly encountered on the edges of pieces. Their distribution in all directions results from the mixing procedure with bitumen and minerals, and documents an abundant vegetal contribution sometimes completely dissolved by weathering.

As a general statement, the mineral content of bituminous amalgams should be considered to have been deliberately added to the mixture. Minerals are only visible using a lens. The thin sections allow measurement of an average grain size of 150 μ, with carbonates dominating, mainly recrystallised calcite. Some quartz crystals with a granulometry lower than 50 μ are also present. The estimation of the total identifiable mineral contribution, using the petrographic evidence, is between 25–30%. If this figure is added to the nearly 25% contribution of unidentifiable material, which is likely to be clay minerals, then the proportions of inorganic matter (minerals) and organic matter (bitumen + vegetal temper) is approximately equal. This result is similar to that obtained by Cleuziou and Tosi (46).

Organic petrographical study confirmed the occurrence of bitumen maceral and provided evidence for the presence of carbonised vegetal pieces (47). Carbonised vegetal debris in the bituminous matrix is present for two possible reasons: fresh vegetal matter may have been carbonised during the heating procedure necessary for the preparation of the mastic; and ashes may have been incorporated as a mineral filler.

X-Ray Diffraction analysis was carried out to quantify the major minerals present in the RJ-2 bituminous mixtures, and in particular to cross-check the occurrence of gypsum ($CaSO_4$). This was reported by Cleuziou and Tosi to be a significant part of the mineral assemblage, at up to 33% of the raw material (48). The utilization of gypsum in such a mixture may have been intended to transform the mixture into a very hard and impermeable mass (49). According to X-Ray analysis of various archaeological bitumen samples, however, the addition of gypsum to bituminous mixtures was not

	% Bitumen extractable with chloroform	% Insoluble organic matter	% calcite	% dolomite	% quartz + halite + plagioclase	% undetermined
average composition	12.7	24	30	2.9	6.1	24.4

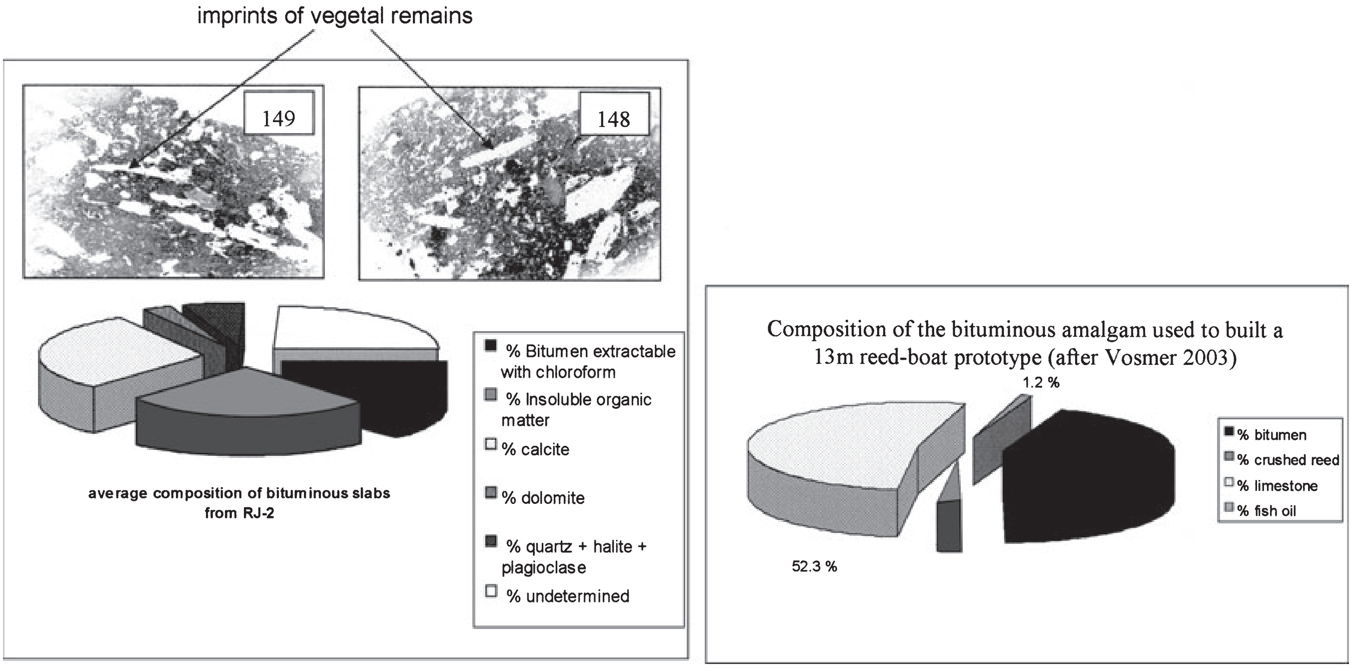

Fig. 12.
Thin sections and average composition of bituminous slabs from Ra's al-Jinz, compared with an artificial amalgam prepared to build a 13 m prototype in Oman. The table shows the average mineral content of selected RJ-2 slabs, according to X-Ray Diffraction analysis (mean values derived from Table 6). The bottom-left chart shows results from petrographic analysis. The bottom-right chart is derived from figures published in Vosmer, The Naval Architecture.

generally practised (50). It would therefore be surprising if such a high concentration of gypsum were incorporated into the mixture which was to be applied to the hulls of reed boats.

Results of the X-Ray Diffraction analysis are given in Table 6 and Figure 13. Firstly, no gypsum was detected in any sample (51). The major mineral additive is calcite (22–35%), as expected from examination of the thin sections. Calcite was also found to be the dominant mineral (41%) in a bituminous mixture scraped from a grey potsherd from Ra's al-Hamra (RH-5, pit HWD-O, 3500 BC)

Table 6. Mineralogical composition of a sample of bituminous slabs from Ra's al-Jinz, derived from X-Ray Diffraction analysis.

sample number	site	date range	% quartz	% calcite	% dolomite	plagioclases	gypsum or anhydrite	halite	pyrite
148	Ra's al-Jinz	2500–2300 BC	3	33	3	1	0	6	0
149	Ra's al-Jinz	2500–2300 BC	3	35	3	1	0	3	traces
150	Ra's al-Jinz	2500–2300 BC	4	38	1				
759	Ra's al-Jinz	2500–2300 BC	2	25	3	0	0	0	traces
760	Ra's al-Jinz	2500–2300 BC	2	22	3	1	0	2	traces
767	Ra's al-Jinz	2500–2300 BC	6	31	4	2	0	1	traces
770	Ra's al-Jinz	2300–2100 BC	3	28	3	1		0	0
771	Ra's al-Jinz	2300–2100 BC	4	28	3	1	0	0	traces

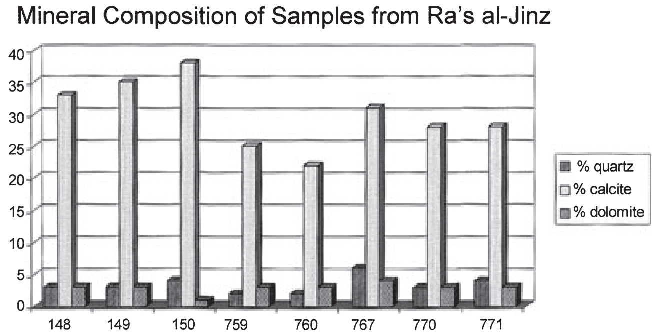

Fig. 13.
Chart of mineralogical composition of samples of bituminous slabs from Ra's al-Jinz, derived from X-Ray Diffraction analysis.

(52). Quartz and dolomite are much rarer in this analysis (Table 6, Fig. 13). Also noteworthy is the occurrence of halite (i.e. common salt, NaCl) in some slabs from the reed boat coating. This data is consistent with the use of these samples on the hull of reed boats, i.e. in direct contact with sea water. No halite was detected in those samples associated with wood impressions (samples 770, 771): these fragments of bituminous amalgam may have covered planks out of contact with sea water. Other than the NaCl, there is no significant difference in the mineral composition of the slabs associated with reed or wooden plank impressions.

Detailed analysis of organic matter

EXTRACTABLE ORGANIC MATTER VS. INSOLUBLE ORGANIC MATTER AND MINERALS

As a follow-up to the Rock-Eval analysis, which provided the Total Organic Carbon (TOC as percentage by weight of sample), Extractable Organic Matter (EOM = true bitumen) was isolated from selected samples from each case study, using chloroform or dichloromethane as a solvent, and weighed.

TOC values, obtained from the Rock-Eval Pyrolysis, were converted into values for Total Organic Matter (TOM as percentage of sample), calculated using the standard estimate that the average TOC is around 80% of the TOM. From these values and the measured proportion of Extractable Organic Matter (EOM), the amount of Insoluble Organic Matter (IOM) can be calculated. The results are presented in Table 7 and Figure 14. IOM has been taken as the sum of preserved vegetal remains and insoluble bituminous residues generated through oxidation of bitumen.

One must realise that the Total Organic Matter is underestimated in the case of As-Sabiyah and Ra's al-Jinz, as some vegetal components of the mixture have been lost by dissolution during weathering. However we believe that the present-day properties may reflect the past reality despite the weathering effects. One should be aware that it is impossible to evaluate the extent of degradation processes and their quantitative effects. Insoluble bitumen residue is formed whereas vegetal remains are removed.

Table 7 and Figure 14 confirm what was expected on the basis of the Rock-Eval Pyrolysis data, and highlight differences in the case studies. First of all, the coating of the recent *quffah* from Baghdad is based mainly on pure bitumen, without any important input of vegetal temper (the 4% IOM is very likely to be bitumen rendered insoluble by oxidation). This explains why the mixture appears as a very hard, homogenous, black, fine-grained solid, without significant evidence of weathering and oxidation in the matrix. Two samples from Kosak Shamali (nos 1378 and 1385), which had low TOC and higher HI (Table 5), are macroscopically similar to the *quffah* sample. In these samples, vegetal debris was not visible, and IOM comprised 19% of the Total Organic Material (Table 7, Fig. 14). This insoluble organic residue may also be composed of oxidised bitumen, the by-product of weathering. In ancient examples the percentage of this fraction has significantly increased to nearly 20% of TOM.

The last sample from Kosak Shamali (no. 1381), on the other hand, has more IOM (58%) than soluble bitumen (42%) (Table 7, Fig. 14), indicating a high level of surviving vegetal temper, estimated at around 39% of TOM (Table 8, Fig. 15). This is also the case in all the samples from Ra's al-Jinz, within which group there is no significant difference between slabs with reed or wood imprints. All the Ra's al-Jinz samples are brown and highly weathered, showing numerous voids left by the dissolution of chopped vegetal temper. They are still hard, though brittle: the abundance of vegetal debris (estimated at 47% and 53% TOM: Table 8, Fig. 15) distributed throughout the mixture has allowed the preservation of a certain cohesion. Samples with a similar aspect have been found at other archaeological sites of the Near East, as mortar in walls of temples and palaces (53). Integration of mineral and

Table 7. Quantitative measurement of the relative content of bitumen (EOM) and Insoluble Organic Matter (IOM) in the different bituminous mixtures used to coat reed and palm boats. Sample 1774 was excluded from the calculation of the average (mean) proportions, owing to an impossible IOM value (−0.9%), perhaps due to laboratory error.

sample number	site	date range	TOC (%/sample)	TOM (%/sample)	EOM (%/sample)	IOM (%/sample)	average TOM (%/sample)	average EOM (%/sample)	IOM (%/sample)	%EOM/TOM	%IOM/TOM
1644	H3, As-Sabiyah	5300–4900 BC	26.0	32.6	19.1	13.5	28.2	18.6	9.6	66	34
1649a	H3, As-Sabiyah	5300–4900 BC	20.7	25.9	8.9	17.0					
1771	H3, As-Sabiyah	5300–4900 BC	19.9	24.8	14.9	9.9					
1772	H3, As-Sabiyah	5300–4900 BC	24.8	31.0	19.5	11.5					
1773	H3, As-Sabiyah	5300–4900 BC	21.0	26.3	24.8	1.5					
1774	H3, As-Sabiyah	5300–4900 BC	28.0	35.0	35.9	−0.9					
1775	H3, As-Sabiyah	5300–4900 BC	23.4	29.2	24.7	4.5					
1073	Baghdad	1900 AD	31.6	39.5	38.1	1.4	39.5	38.1	1.4	96	4
1378	Kosak Shamali	5100–4700 BC	13.3	16.6	14.23	2.4	14.3	11.62	2.65	81	19
1385	Kosak Shamali	4550–4260 BC	9.5	11.9	9.01	2.9					
1378 and 1385	Kosak Shamali	5100–4260 BC		28.5	23.24	5.3					
1381	Kosak Shamali	5190–4800 BC	22.2	27.8	11.65	16.1	27.8	11.65	16.1	42	58
148	Ra’s al-Jinz	2500–2300 BC	27.7	34.6	14.4	20.2	36.9	12.7	24.2	34	66
149	Ra’s al-Jinz	2500–2300 BC	29.7	37.1	17.1	20.0					
757	Ra’s al-Jinz	2500–2300 BC	27.3	34.1	11.7	22.4					
759	Ra’s al-Jinz	2500–2300 BC	35.1	43.8	11	32.8					
762	Ra’s al-Jinz	2500–2300 BC	28.0	35.0	9.4	25.6					
770	Ra’s al-Jinz	2300–2100 BC	32.3	40.3	9.8	30.5	40.1	11.4	28.7	28	72
771	Ra’s al-Jinz	2300–2100 BC	32.0	40.0	13	27.0					

Key to abbreviations: TOC = Total Organic Carbon; EOM = Extractable Organic Matter with chloroform or dichloromethane; TOM = Total Organic Matter; IOM = Insoluble Organic Matter.

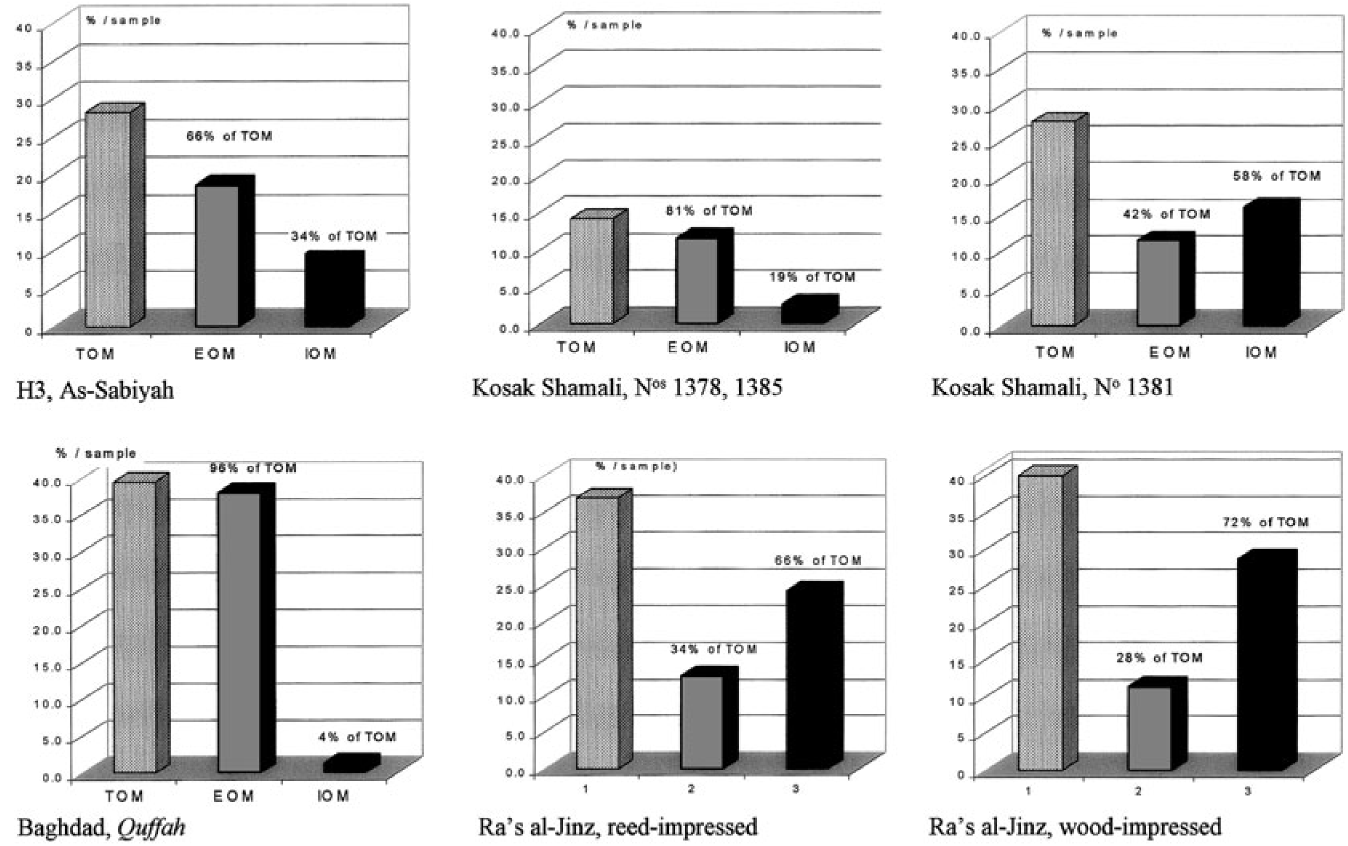

Fig. 14.
Average (mean) proportions of Total Organic Matter (TOM); Extractable Organic Matter, soluble in chloroform (EOM); and Insoluble Organic Matter (IOM).

organic data gathered from selected Ra's al-Jinz samples reveals the average composition of the bituminous amalgams used to coat reed (or reed and wood) boats (Fig. 12). Nearly 25% of the mixture is undetermined and may be constituted by clay minerals (soils) which were not analysed.

Table 8. Table giving breakdown of organic matter, showing average (mean) proportions of EOM (Extractable Organic Matter, i.e. soluble bitumen), IOBitumen (Insoluble Organic Bitumen), and IOMVegetal (Insoluble Organic Matter of Vegetal origin, i.e. surviving vegetal temper).

	EOM	IOBitumen	IOMVegetal
Kosak Shamali: 1378–1385	81	19	0
Kosak Shamali: 1381	42	19	39
Baghdad: quffah	96	4	0
Ra's al-Jinz: reed-impressed	34	19	47
Ra's al-Jinz: wood-impressed	28	19	53
As-Sabiyah	72	19	9

The H3 samples have a low average proportion of vegetal temper. The data on Table 7 aligns them with the *quffah* fragment and Kosak Shamali samples

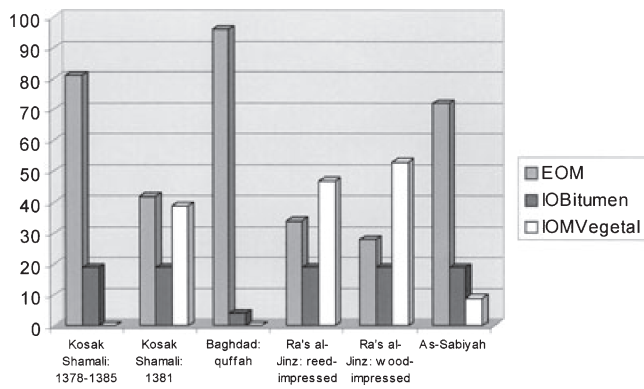

Fig. 15.
Breakdown of organic matter, showing average (mean) proportions of EOM (Extractable Organic Matter, i.e. soluble bitumen), IOBitumen (Insoluble Organic Bitumen), and IOMVegetal (Insoluble Organic Matter of Vegetal origin, i.e. surviving vegetal temper).

Table 9. Table giving proportions of Total Organic Matter (TOM); Extractable Organic Matter, soluble in chloroform (EOM); and Insoluble Organic Matter (IOM) within each H3 sample (1774 excluded).

sample number	TOM (%/sample)	EOM (%/sample)	IOM (%/sample)	%EOM/TOM	%IOM/TOM
1644	32.6	19.1	13.5	58.7	41.3
1649a	25.9	8.9	17.0	34.4	65.6
1771	24.8	14.9	9.9	60.0	40.0
1772	31.0	19.5	11.5	62.9	37.1
1773	26.3	24.8	1.5	94.4	5.6
1775	29.2	24.7	4.5	84.5	15.5

1378 and 1385, which did not display vegetal debris. In fact it is impossible to determine whether their present-day composition is largely due to the pristine mixture or to the intensity of weathering conditions. The presence of numerous voids left by vegetal matter in the fabric of these samples shows that vegetal temper was indeed used. A breakdown of the individual pieces from H3 (Table 9, Fig. 16) shows considerable variability in the proportions of Extractable Organic Matter (i.e. bitumen) and Insoluble Organic Matter (largely vegetal temper). This variability may partially be due to on-site taphonomic processes, e.g. variable exposure to water and plant or bacterial action, caused by proximity to the surface or protection by fallen stones. The initial restricted amount of vegetal temper combined with their probable extensive disappearance in the H3 samples through the effects of specific local weathering conditions, explains why these samples are extremely fragile and crumbly. Some large black fragments do show a predominance of the bituminous additive which normally protects the vegetal fragments, when present.

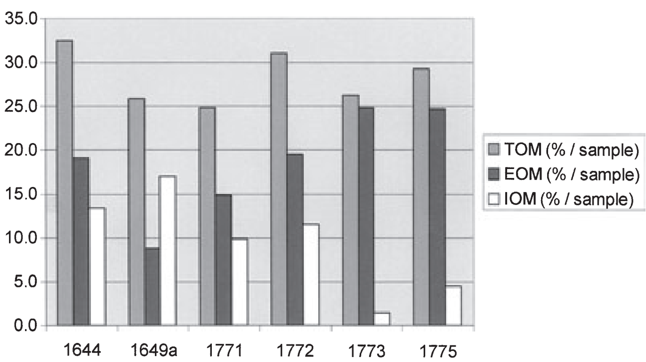

Fig. 16.
Proportions of Total Organic Matter (TOM); Extractable Organic Matter, soluble in chloroform (EOM); and Insoluble Organic Matter (IOM) within each H3 sample (1774 excluded).

Gross composition of Extractable Organic Matter (EOM)

The Extractable Organic Matter (EOM) was separated into four fractions ('saturates', 'aromatics', 'resins' and 'asphaltenes'), which were weighed. The gross composition of the extracts was calculated (Table 10) and presented in a ternary diagram ('saturates + aromatics' vs. 'resins' vs. 'asphaltenes'), reproduced in Figure 17.

In addition to archaeological samples, three samples from oil-stained sands outcropping at Burgan Hill, in inland Kuwait, were also analysed (Fig. 1). This is the area where deep Cretaceous oils of the Burgan field have migrated to surface through major faults (54). These oil seeps were, with those of Awali in Bahrain and Haushi in Oman, the only surface oil seeps accessible to inhabitants of the Gulf in antiquity (55). Their analysis in the present study is therefore crucial, as they may have been the bitumen source used by the inhabitants of H3 As-Sabiyah in the sixth/fifth millennia BC, two and a half millennia prior to the establishment of the better-known Bronze Age trade routes of the Gulf and Mesopotamia.

The samples (coordinates 28°55′N, 47°55′E), were taken from the area of surface seeps mentioned by H.R.P. Dickson (56), near the gathering centre of the Burgan oilfield, in the neighbourhood of the BG 399 well. They were collected on the 17th October 1989 by P. Fournier on Burgan Hill (90 m high), between 75 and 50 m in altitude. The bitumen occurs there in thin beds, without significant evidence of mining. On this hill, flint implements (scrapers, arrow heads, chipped flints) were also found (57). The bitumen samples, gathered before the war with Iraq, when many oil wells in the vicinity were set on fire, are not contaminated by carbonised by-products of the burning oil wells, which deposited a blanket of soot over the hill. The samples are therefore

Table 10. Gross composition of the extractable organic matter in archaeological samples and in the Burgan oil seeps.

sample number	site	% EOM/ sample	macroscopic description	% 'saturates'	% 'aromatics'	% 'resins'	% 'asphaltenes'	% 'resins + asphaltenes'
				sat10	aro10	res10	asp100	pol10
1644	H3, As-Sabiyah	10.8		10.3	8.4	34.2	47.1	81.3
1646	H3, As-Sabiyah	10.1		5.4	4.8	21.6	68.2	89.8
1649a	H3, As-Sabiyah	8.9		9.4	9.4	38.5	42.7	81.2
176	Burgan	10.6	outer surface: crust of homogenous black dry bitumen- inner surface quartz stuck to the bitumen	9.0	15.3	54.1	21.6	75.7
177	Burgan	4.8	pasty oil-stained sand, fairly consolidated	23.1	27.1	39.9	9.9	49.8
178	Burgan	2.4	brown sand with numerous quartz grains, splashes of bitumen on quartz grains, typical unconsolidated tar sand	31.0	31.0	30.8	7.2	38.0
1073	Baghdad	38.1		6.8	12.8	31.8	48.7	80.4
1378	Kosak Shamali	14.2		4.7	5.4	13.4	76.5	89.9
1381	Kosak Shamali	11.7		6.5	7.3	20.6	65.6	86.2
1385	Kosak Shamali	9.0		4.4	5.7	16.8	73.1	89.9
148	Ra's al-Jinz	14.4		7.4	1.7	34.2	56.7	90.9
149	Ra's al-Jinz	17.1		7.1	1.8	32.5	58.6	91.1
150	Ra's al-Jinz	15.1		7.3	1.1	40.1	51.5	91.6
151	Ra's al-Jinz	16.9		6.7	1.2	34.8	57.4	92.2
757	Ra's al-Jinz	11.7		6.0	3.0	40.3	50.7	91.0
759	Ra's al-Jinz	11.1		5.6	3.5	50.8	40.1	90.9
762	Ra's al-Jinz	9.4		6.1	4.8	51.0	38.0	89.0
770	Ra's al-Jinz	9.8		6.1	4.1	46.6	43.2	89.8
771	Ra's al-Jinz	13.0		5.7	4.4	51.3	38.5	89.9
619	Ra's al-Jinz	7.0		1.6	0.9	20.6	76.9	97.5

truly representative of the natural oil seeps of Burgan Hill.

Three samples were collected at or near the surface, from the oil-stained sand. Number 176, a black hard crust with weathering features (Fig. 18a), resulted from a concentration of bitumen at the surface (10.6% by weight of sample), caused by the melting of the oil under the seasonal high ambient temperatures (Figs 18b, c, f). In sample no. 177, the oil-stained sand was fairly hard but still plastic. It showed some bitumen concentration towards the surface (Fig. 18d) but no real bitumen-enriched crust. Sample no. 178 was soft and typical of a tar-sand, as exemplified by freshly excavated Athabasca tar-sand in Canada. The surface sample set was completed by oil-stained sands collected in a quarry opened in 1996 near Burgan Hill (no. 1057, Fig. 18e). This quarry revealed oil-stained sands and gas seeps in association with faults which allowed the migration of Burgan oil to the surface (58). These oil-stained sands were not exposed until recently when the quarry was opened. Consequently these samples are also uncontaminated by the soot generated by the oil-well fires of the first Iraq war.

Regarding changes in the macroscopic aspect of these oil seeps, one would assume there to be a sequence of progressively weathered counterparts of the Cretaceous oils found at depth in reservoirs of the Burgan field (59). Indeed the gross compositions of the oil seep samples (Table 10), as well as their molecular chemistry, confirm those assumptions: sample no. 178 does show unaltered C_{15+}alkanes with all n-alkanes present (Fig. 17), whereas no. 176 has lost its n-alkanes by biodegradation. Number 177 occupies an intermediate situation, with minute amounts of n-alkanes still detectable (Fig. 17).

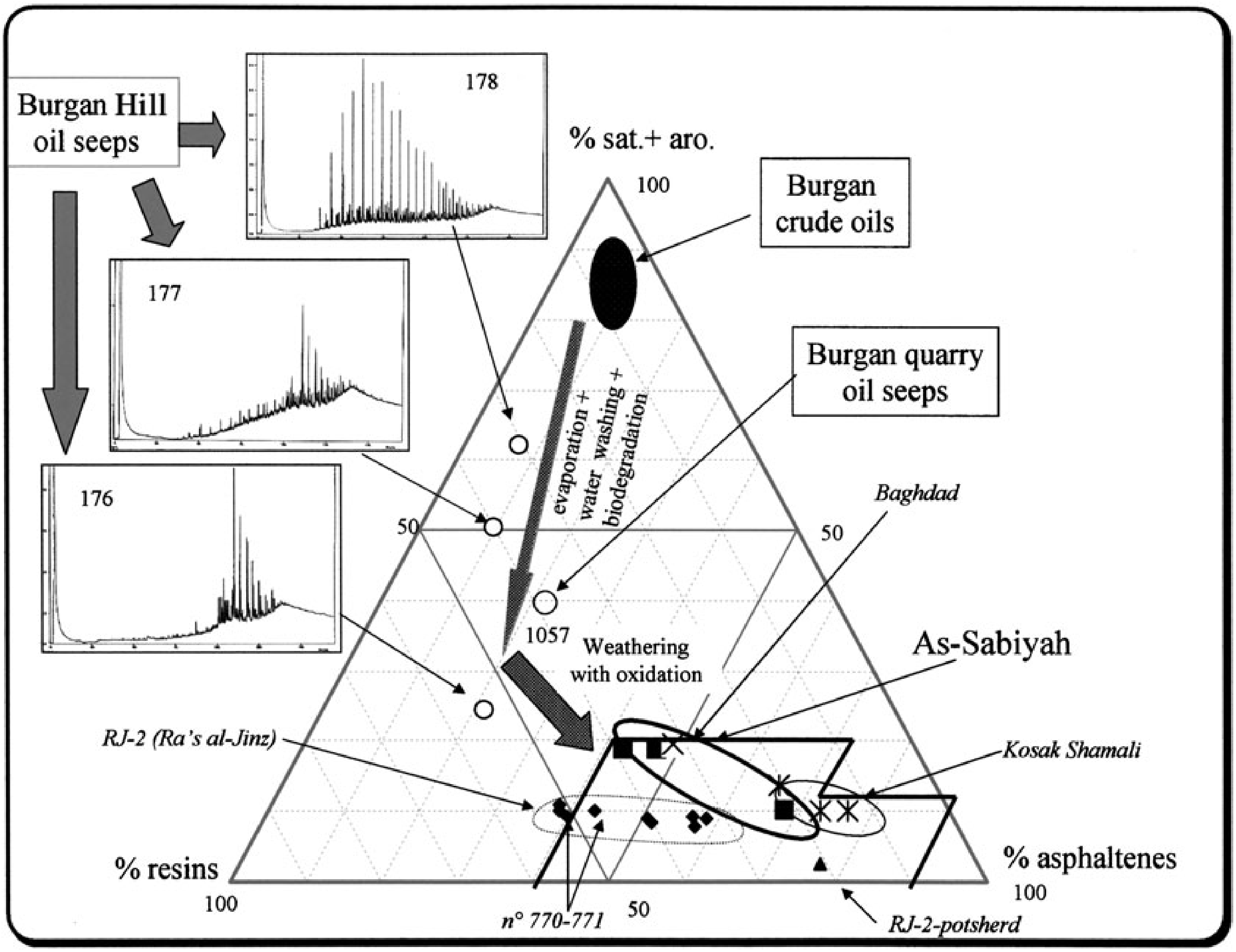

Fig. 17.
Ternary diagram of the gross composition of the organic matter extracted with chloroform or dichloromethane ('saturates + aromatics', 'resins' and 'asphaltenes'), giving a comparison between the bituminous samples from As-Sabiyah, Ra's al-Jinz, Baghdad and Kosak Shamali, and the oil seeps and crude oil from Burgan (Kuwait).

Analysis of C_{15+}aromatics, which did not reveal any pyrolitic polyaromatics such as fluoranthene and pyrene, confirmed that the samples are representative.

Figure 17 illustrates the difficulties encountered in finding the genetic origin of archaeological bitumen. Burgan crude oils represent the unaltered samples at depth and are the most hydrocarbon-enriched samples (more than 80%: Fig. 17) (60). Through evaporation, water washing, biodegradation of various intensities and some subordinate oxidation, hydrocarbons are reduced in surface oil seeps (see samples 178, 177, 1057 and 176). In this set of Burgan oil seeps, sample no. 176, from a bitumen-enriched crust, represents the most likely geological counterpart of the bitumen which is found in the bituminous material of H3 As-Sabiyah. The comparison of gross properties in Figure 17 shows, however, that even though this oil seep approaches the cluster of archaeological boat bitumens, it is still less weathered and oxidised than the archaeological samples. It appears that bitumen collected from surface oil seeps to prepare archaeological mixtures continued its evolution in the archaeological samples, under various degrees of weathering (evaporation, melting, oxidation, photo-oxidation, biodegradation). Archaeological samples are deeply depleted in hydrocarbons, especially C_{15+}aromatics, and asphaltenes

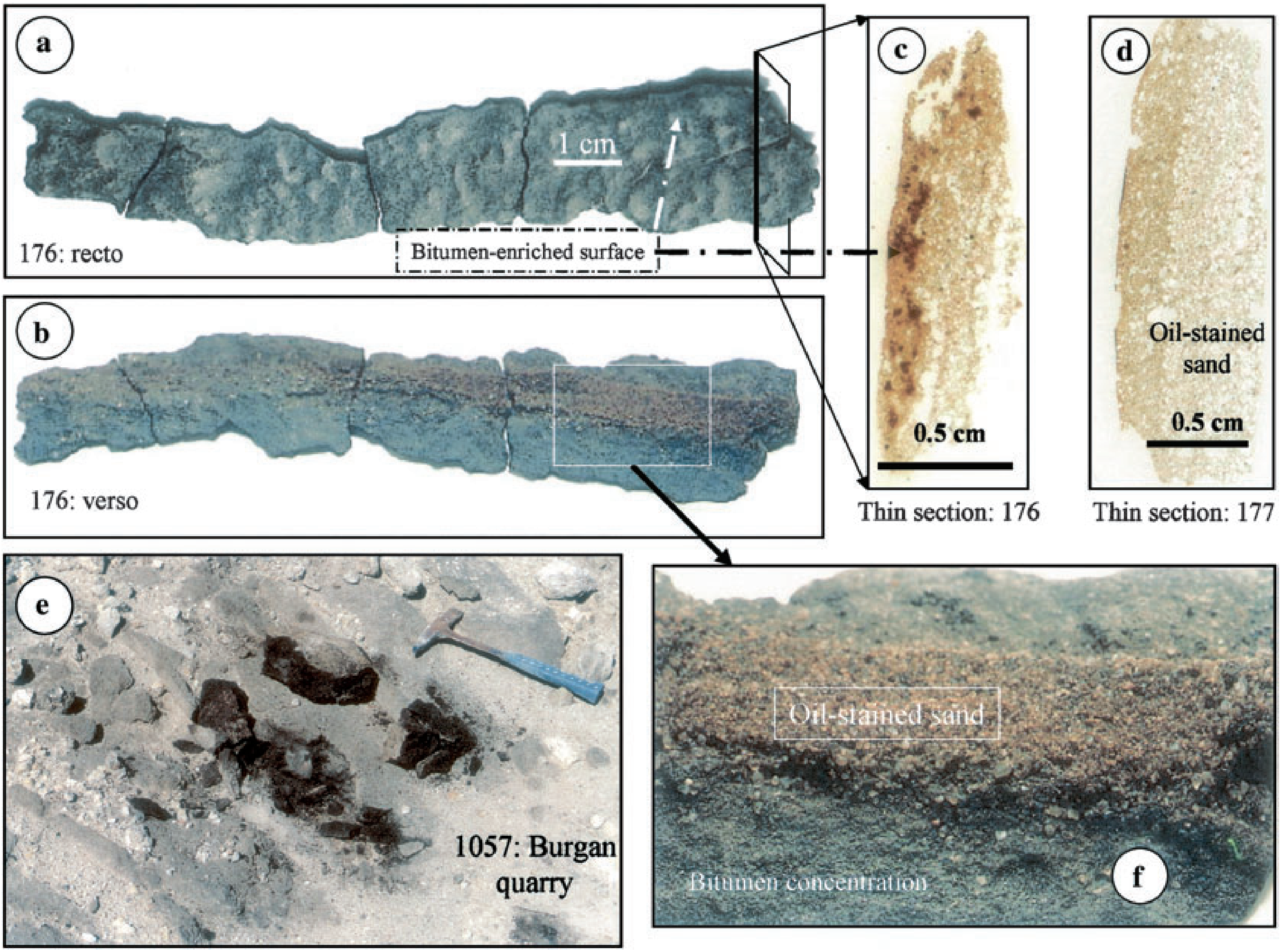

Fig. 18.
Oil seep samples from Burgan Hill (no. 176, no. 177) and the Burgan quarry (no. 1057): photographs of samples and thin sections; **a**. Sample no. 176: surface of the sample showing typical aspect of bitumen weathering; **b**. Sample no. 176: interior face documenting the concentration of bitumen at the surface and the tar-sand under the outer layer; **c**. Sample no. 176: thin section of the oil-stained sand with a clear concentration of bitumen towards the surface; **d**. Sample no. 177: thin section of a typical oil-stained sand sample. A slight bitumen concentration appears towards the surface; **e**. Oil-stained sand (sample no. 1057), outcropping in the Burgan quarry; **f**. Sample no. 176: close-up showing bitumen concentration and oil-stained sand.

are enhanced. The fact that those Burgan samples are less weathered and oxidised than no. 176 does not mean that similar samples were not primarily collected for boat-building, as the archaeological bitumens we analysed are the end-products of a long degradative history.

Origin of the bitumen indicated by isotopic data on asphaltenes

In previous papers, we underlined that carbon isotopic values of asphaltenes ($\delta^{13}C$ in ‰/PDB, Tables 11 and 13) provide reliable information on the origin of asphalts, because this parameter is not drastically modified by the intense weathering phenomena which affect the gross and the molecular compositions of bitumen in oil seeps and archaeological contexts. On the other hand, δD (‰/SMOW) of asphaltenes is not a source parameter, because this parameter is highly sensitive to alteration due to weathering processes. This alteration entails a major shift of δD towards heavier values, which means an enrichment in deuterium as seen in As-Sabiyah ($-50 < \delta D < -70$) and also in the Kosak Shamali and Oueili samples (Fig. 19). The occurrence of these

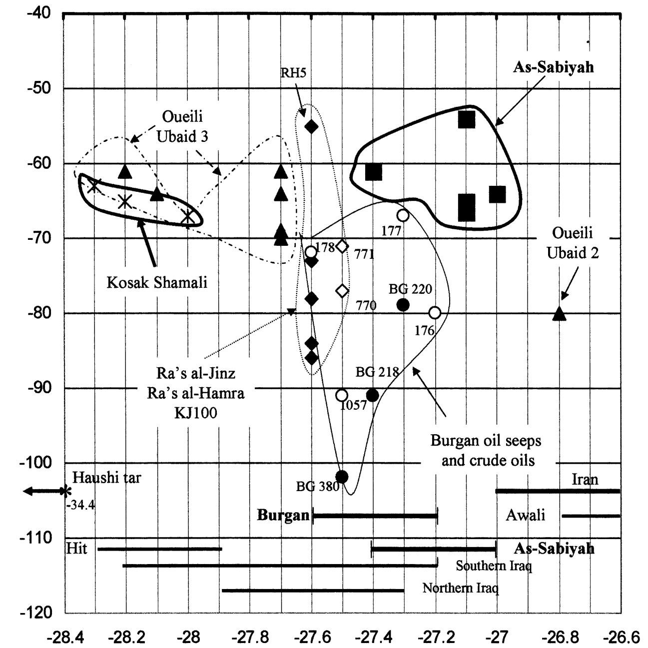

Fig. 19.
$\delta^{13}C$ vs. δD of asphaltenes: comparison of bituminous mixtures from reed boats from As-Sabiyah, Kosak Shamali and Ra's al-Jinz, together with archaeological samples from Tell el'Oueili (Ubaid 2 and 3), Ra's al-Jinz and Ra's al-Hamra, and geological references from Iran and Iraq.

heavy values agrees with what was previously observed in archaeological bitumens from Mesopotamia and Bahrain (61). Undegraded crude oils accumulated at depth, tar sands and oil seeps from the Burgan area do show higher values ($-65 < \delta D < -115$‰/SMOW). Consequently, the heavy values recorded for bitumen from Kosak Shamali, Oueili and As-Sabiyah confirm that these archaeological bitumens are heavily weathered. In that respect the samples from Ra's al-Jinz seem to be generally less altered, with lighter δD values ($-65 < \delta D < -85$‰/SMOW) (Fig. 19).

In order to gain information on the origin of bitumen, the $\delta^{13}C$ values (in ‰/PDB) must be acquired on a reliable organic fraction which represents the bitumen. Values on bulk samples, as used by Schwartz et al. (62), are unsuitable because they provide wrong references for the bitumen: they are extensively influenced by the carbonate content of the sample, as demonstrated in a previous paper (63). $\delta^{13}C$ values of asphaltenes do correspond to the bitumen and have been plotted as a function of δD values in Figure 19. As regional references we have added $\delta^{13}C$ data on asphalts and crude oils from Iran, northern Iraq, southern Iraq, Hit in Iraq, Awali in Bahrain (64) and from Burgan (this study). Comparison of $\delta^{13}C$ values leads to the following observations:

- There is only one source of bitumen for the As-Sabiyah bituminous slabs: the samples from H3 form a tight and discrete cluster.
- $\delta^{13}C$ values of As-Sabiyah partly match the data registered in oil seeps and crude oils from Burgan. Sample no. 176, is the closest to archaeological samples within the As-Sabiyah population. The incomplete overlapping of both $\delta^{13}C$ ranges may be due to a tiny shift of $\delta^{13}C$ values by weathering in archaeological samples, as observed elsewhere: in contrast to what was previously thought, the $\delta^{13}C$ values of asphaltenes are not unaffected by secondary alteration of bitumen, especially when this alteration is drastic as in the As-Sabiyah samples. The extent of this $\delta^{13}C$ shift remains small, however (0.2‰/PDB). Taking into account such a tiny shift, the Burgan Hill oil seeps are the likely source of the bitumen from H3, As-Sabiyah. Overlapping values from southern Iraq do correspond to crude oils at depth in reservoirs but not to surface samples.
- The Ubaid 2 and Ubaid 3 bitumens from Oueili, which are broadly contemporary with the As-Sabiyah material, have different origins, which are not the Burgan oil seeps. One might have expected that H3 shared the same source of bitumen with Oueili (65), judging from the evidence for an exchange relationship between As-Sabiyah and southern Mesopotamia, where Oueili is found. This hypothesis was disproved.
- The bitumen extracted from samples with reed or wooden plank impressions at Ra's al-Jinz, as well as the bitumen from two other sites in the neighbourhood along the coast (RH-5 and KJ100), belongs to a single genetic family.
- The bitumen of the unique tar-sand of Oman, which outcrops in the Haushi formation near the Safah oil field at the border with the United Arab Emirates, is not the source of the Ra's al-Jinz bitumen ($\delta^{13}C$ of asphaltenes $= -34.4$‰/PDB). This location has not been identified so far in archaeological bitumen from Oman (RH5, Wadi Hilm near Sur, Kalba, RJ-2) and the United Arab Emirates (Mleiha, Umm an Nar, Ed-Dur) (66).

Origin of bitumen based on sterane-terpane biomarkers and isotopic data on asphaltenes

'Saturates' were analysed by GC-MS (Gas Chromatography-Mass spectrometry) in order to examine sterane (*m/z* 217) and terpane (*m/z* 191) patterns, which are currently used to elaborate genetic parameters allowing the differentiation of various bitumen sources. As usual in archaeological bitumen, biomarker fingerprints display various degrees of alteration, ranging from almost unaltered patterns (State 0) to highly altered (State 8). At this highest level of alteration, both steranes and terpanes are significantly altered, but between States 0 and 7, terpane patterns are apparently preserved, and may be tentatively used to define genetic parameters reliably enough to identify the origin of the associated bitumen. One should remember, however, that terpanes may have been removed without entailing significant detectable changes in the patterns. This is the reason why we prefer to refer to patterns, and state that the terpanes are apparently not affected.

Samples from As-Sabiyah exhibit states of alteration between 4a and 6a which correspond to a moderate biodegradation of C_{27} and C_{28} steranes without alteration of terpanes (Table 11).

The review of regular sterane compositions (Table 12) represented in ternary diagrams (% C_{27}, % C_{28} and % $C_{29}\beta\beta$ steranes, Fig. 20) clearly differentiates the As-Sabiyah bitumens from their Burgan tar-sands and crude oil counterparts. The As-Sabiyah steranes are biodegraded and have lost C_{27} and C_{28} steranes (Figs 20a and 21). One geological sample (no. 176) which was identified as the most

Table 11. Summary of the characteristic properties of steranes and terpanes: evaluation of the degree of alteration.

sample number	location	steranes C_{21}–C_{22}	C_{27}–C_{29}	$C_{29}\alpha\alpha\alpha R$	C_{27}–C_{29}diast	terpanes tricyclopolypren.	C_{27}–C_{35}Hop.	degree of alteration
1644	H3	traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1644	As-Sabiyah	traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1645		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	4a
1646		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1647		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	4a
1648a		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1649a		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1649b		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1649c		traces	altered, less C27 and C28	unaltered	present, altered	altered, traces	unaltered	6a
1650		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1771		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1772		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1773		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1774		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1775		traces	altered, less C_{27} and C_{28}	unaltered	present, altered	altered, traces	unaltered	6a
1057	Burgan	unaltered	unaltered	unaltered	significant	present, low	unaltered	0a
53	oil seeps	altered	unaltered	unaltered	significant	altered, low	unaltered	1a
10		altered	unaltered	unaltered	significant	altered, low	unaltered	1a
176		altered	altered, less C_{27} and C_{28}	slightly altered	present, altered	altered, traces	unaltered	6b
177		altered	unaltered	unaltered	unaltered	altered, low	unaltered	1a
178		unaltered	unaltered	unaltered	unaltered	present, low	unaltered	0a
BG 220	Burgan	unaltered	unaltered	unaltered	significant	present, low	unaltered	0a
BG 218	oilfield	unaltered	unaltered	unaltered	significant	present, low	unaltered	0a
BG 380		unaltered	unaltered	unaltered	significant	present, low	unaltered	0a

Key to abbreviations: C21–C22 = C21 and C22 steranes; C27–C29 = C27 to C29 steranes; C29αααR = 5α,14α,17α-20R-24-ethylcholestane; C27–C29diast = C27–C29 diasteranes; tricyclopolypren. = tricyclopolyprenanes; C27–C35Hop. = C27 to C35 hopanes; degree of alteration: alteration of steranes and terpanes comprises 8 main degrees subdivided into 16 classes, 0 corresponds to no alteration, 6 to 8 to changes on steranes with a significant loss of C_{27} and C_{28} steranes, 8 is the higher state of degradation where terpanes are affected.

Table 12. Isotopic data on asphaltenes (δ^{13} Casp, δDasp) and biomarker ratios on steranes and terpanes of archaeological samples, crude oils (Burgan) and oil seeps (Haushi, Burgan). Absolute quantitation was carried out using deuterated standards (2,2,4,4-d4-5α-20R-24-ethylcholestane, 2,3-d2-17β,21α-30-normoretane) for sterane and terpane measurements.

sample number	location or site	date	depth	formation	δ_{13}Casp	δDasp	GC-MS	Tp1 Ts/Tm	Tp2 29:5/ 29αβH	Tp3 29αβH/ 30αβH	Tp20 mH/ hop	Tt26 23:3/ 24:4	T32 Tri/ pent.	Tp35 GCR/ 30αβH	TS40 27–30H/ 29St	TS41 Terp/ Ster	Tp42 seco/ hop	S51 27Sdia/ 27ααR	S57 27Sdia/ 29ααR	S63 27%	S64 28%	S65 29%	S66 Reg%	S67 Met%	S68 %Dia
1644	H3	5300–4900 BC			−27.4	−61	HP	0.24	0.07	1.23	0.16	0.47	0.02	0.13	16			0.4	0.08	5	30	65			
1645	H3	5300–4900 BC			−27.1	−54	HP	0.5	0.19	1.13	0.21	0.24	0.03	0.11	10.45	5.97	0.02	0.04	0.04	1	25	73	50	43	7
1646	H3	5300–4900 BC			−26.9		HP	0.5	0.18	1.11	0.19	0.22	0.02	0.11	11.64	6.02	0.04	0.14	0.03	0	26	74	51	43	6
1647	H3	5300–4900 BC					HP	0.19	0.08	1.02	0.22	0.43	0.02	0.2	12.49	5.2	0.12	0.2	0.09	12	26	61	52	45	3
1648a	H3	5300–4900 BC			−27		HP	0.24	0.09	1.06	0.21	0.22	0.01	0.18	10.21	5.79	0.15	0.36	0.02	3	27	69	53	43	4
1649a	H3	5300–4900 BC			−27.1	−65	HP	0.29	0.11	1.08	0.22	0.16	0.01	0.17	9.54	5.25	0.17	0.09	0.02	4	25	71	53	42	5
1649b	H3	5300–4900 BC					HP	0.28	0.11	1.08	0.21	0.26	0.02	0.17	9.52	5.28	0.16	0.31	0.02	3	28	69	53	43	5
1649c	H3	5300–4900 BC					HP	0.29	0.09	1.17	0.18	0.3	0.02	0.13	12.25			0.23	0.05	5	27	68			
1650	H3	5300–4900 BC			−27	−64																			
1771	H3	5300–4900 BC			−27.2																				
1772	H3	5300–4900 BC			−27.1	−66.5	HP	0.41	0.16	1.17	0.19	0.27	0.03	0.13	11.6			0.5	0.09	4	27	69			
1773	H3	5300–4900 BC			−27.2		HP	0.36	0.13	1.14	0.19	0.31	0.02	0.14	13.63			0.2	0.05	5	26	68			
757	RJ-2	2500–2300 BC			−27.6	−78	HP	0.1	0.07	0.96	0.23	0.37	0.02	0.22	17.71	6.24	0.13	0	0	26	23	51	64	36	0
759	RJ-2	2500–2300 BC			−27.6	−73	HP	0.12	0.07	0.96	0.24	0.7	0.02	0.25	14.98	5.26	0.17	0	0	27	24	49	56.1	43.9	0
762	RJ-2	2500–2300 BC			−27.6	−84	HP	0.12	0.07	0.94	0.23	1.04	0.02	0.22	15.29	5	0.17	0	0	23	24	53	58.2	41.8	0
770	RJ-2	2300–2100 BC			−27.5	−77	HP	0.12	0.05	0.88	0.3	0.68	0.02	0.2	9.62	2.24	0.16	0	0	22	24	54	51.1	48.9	0
771	RJ-2	2300–2100 BC			−27.5	−71	HP	0.12	0.07	0.88	0.25	0.6	0.02	0.23	10.63	4.09	0.25	0	0	23	25	53	54.6	45.4	0
772	KJ100	*c.*2500 BC			−27.6	−86	HP	0.16	0.08	1.11	0.3	0.37	0.02	0.26	26.88	9.39	0.14	0	0	21	22	57	48.4	51.6	0
619	RJ-2	*c.*2300 BC			−27.7		FIN	0.12	0.07	1.03	0.25			0.21	18	19	0.04	0	0	20	20	60	65	35	0
620	RH5	*c.*3400 BC			−27.6	−55	FIN	0.07	0.03	0.99	0.15			0.2	8.2	16.8	0.08	0	0	18	20	62	95	5	0
1073	Baghdad	1900 AD			−27.7		HP	0.24	0.11	1.03	0.27	0.76	0.06	0.23	7.55	3.54	0.23	0.12	0.09	30	27	43	63	36	1
1378	Kosak Shamali	5100–4700 BC			−28.3	−63	HP	0.16	0.09	1.23	0.17	6.1	0.18	0.53	11.8	2.9	0.11	0.22	0.19	26	30	44	44	55	1
1381	Kosak Shamali	5190–4800 BC			−28	−67	HP	0.13	0.09	0.99	0.28	2.45	0.09	0.33	9.2	4.2	0.1	0.11	0.05	26	26	48	52	47	1
1385	Kosak Shamali	4550–4260 BC			−28.2	−65	HP	0.25	0.15	1.03	0.23	5.63	0.41	0.63	8	1.7	0.77	3.32	3.59	25	26	49	37	58	5
125	Oueili	Ubaid 2?			−26.8	−80	FIN	0.62	0.11	0.97	0.29			0.09	4	4.5	0.11	0.75	0.25				69	24	7
21	Oueili	Ubaid 3			−27.7	−61	HP	0.17	0.09	1.01	0.35	0.43	0.02	0.26	7.7	4.6	0.13	0.07	0.04	11	25	64	42.9	55.8	1.3
22	Oueili	Ubaid 3			−27.7	−64	HP	0.17	0.08	1.11	0.29	0.57	0.03	0.21	11.9	7.2	0.11	0.08	0.07	27	25	48			
23	Oueili	Ubaid 3			−27.7	−70	FIN	0.11	0.09	0.96	0.22	0.43		0.2	13.9	14.3	0.07			20	20	60			
28	Oueili	Ubaid 3			−28.2	−61	HP	0.23	0.11	1.09	0.36	0.44	0.03	0.27	11.4	6.7	0.15	0.13	0.07	23	27	50	41	57	1.8
29	Oueili	Ubaid 3			−28.3	−63	HP	0.2	0.09	1.07	0.35	0.5	0.03	0.24	9.7	5.5	0.13	0.1	0.05	17	29	54	39	59	2
32	Oueili	Ubaid 3			−28.1	−64	HP	0.17	0.1	0.99	0.38	0.53	0.03	0.26	8.9	4.5	0.1	0.06	0.05	32	25	43	44	55	1
34	Oueili	Ubaid 3			−28	−68	HP	0.1	0.04	1.02	0.25	0.59	0.03	0.17	16.2	5.2	0.05	0	0	34	24	43	32	68	0
37	Oueili	Ubaid 3			−27.7	−69	HP	0.16	0.08	1.01	0.35	0.39	0.02	0.25	9.1	4.5	0.09	0	0	17	28	53	41	59	0
40	Oueili	Ubaid 3			−27.7	−69	FIN	0.17	0.12	1.05	0.18	0.53		0.23	18.19	15.75	0.06			31	21	48			
42	Oueili	Ubaid 3			−28	−67	HP	0.19	0.08	1.08	0.33	0.57	0.03	0.23	9.4	4	0.11	0.09	0.09	31	25	44	42	56	2
10	Burgan area	oil seep	surface				HP	0.55	0.12	1.34	0.22	0.33	0.03	0.1	12.6	4.85	0.14	0.32	0.33	35	18	46	59.1	38.5	2.4

Table 12. Continued

sample number	location or site	date	depth	formation	δ_{13}Casp	δDasp	GC-MS	Tp1 Ts/Tm	Tp2 29:5/ 29αβH	Tp3 29αβH/ 30αβH	Tp20 mH/ hop	Tt26 23:3/ 24:4	T32 Tri/ pent.	Tp35 GCR/ 30αβH	TS40 27–30H/ 29St	TS41 Terp/ Ster	Tp42 seco/ hop	S51 27Sdia/ 27ααR	S57 27Sdia/ 29ααR	S63 27%	S64 28%	S65 29%	S66 Reg%	S67 Met%	S68 %Dia
53	Burgan area	oil seep	surface				HP	0.55	0.12	1.19	0.21	0.36	0.03	0.1	12.7	4.94	0.12	0.26	0.2	32	20	48	58.8	39.3	1.9
176–1	Burgan hill	oil seep	surface		−27.2	−80	HP	0.47	0.12	1.22	0.19	0.31	0.02	0.09	11.52	5.34	0.12	0.2	0.06	9	24	66	51.4	46.4	2.3
177–1	Burgan hill	oil seep	surface		−27.3	−67	HP	0.42	0.09	1.25	0.16	0.41	0.03	0.08	14.31	4.02	0.1	0.26	0.22	35	18	47	51.3	46	2.7
178–1	Burgan hill	oil seep	surface		−27.6	−72	HP	0.5	0.09	1.32	0.19	0.6	0.04	0.09	12.9	3.63	0.11	0.27	0.29	35	19	46	55.1	42.5	2.4
1057	Burgan quarry	oil seep	surface		−27.5	−91	HP	0.33	0.18	1.02	0.22	0.61	0.05	0.13	6.99	3.26	0.22	0.3	0.21	34	22	44	55.5	42.9	1.6
BG 218 well	Burgan	crude oil	4683′	Burgan	−27.4	−91	HP	0.32	0.08	1.41	0.15	0.59	0.05	0.07	8.7	2.5	0.2	0.32	0.35	33	22	45	55.3	42.7	2
BG 220 well	oilfield	crude oil	4689′	Wara	−27.3	−79	HP	0.65	0.13	1.42	0.22	0.57	0.04	0.11	13.2	4.7	0.1	0.35	0.42	35	19	46	48.4	48.6	2.9
BG 380 well		crude oil	7100′	Minagish	−27.5	−102	HP	0.26	0.07	1.41	0.14	0.55	0.04	0.08	8.7	2.6	0.14	0.27	0.26	36	22	42	50	47	3
1821A	Haushi tar	oil seep	surface	Haushi	−34.3		Geomark	0.47		1.32		0.76		0.61						20	43	37			
1821B	Haushi tar	oil seep	surface	Haushi	−34.5		Geomark	0.46						0.61		3.8				20	40	40			
1821C	Haushi tar	oil seep	surface	Haushi	−34.2		Geomark	0.48		1.5		0.61		0.64		4.3				20	39	41			

Key to abbreviations: δ^{13} Casp = δ^{13} Casp (in ‰/PDB); δDasp = δDasp (in ‰/SMOW); Tp1 = Ts/Tm = 18α-22,29,30-trisnorneohopane/17α-22,29,30-trisnorhopane; Tp2 = 29:5/29αβH = 18α-22,29,30-norhopane/17α, 21β-30-norhopane; Tp3 = 29αβH/30αβH = 17α,21β-30-norhopane/17α, 21β-hopane; Tp20 = mH/Hop = methylhopanes/hopanes; Tt26 = 23/3/24/4 = C_{23} tricyclopolyprenane/C_{24} d-E-hopane; T32 = Tri/Penta = Tricyclic terpanes/Pentacyclic terpanes; Tp35 = GCR/30αβH = Gammacerane/17α,21β-hopane; TS40 = 27–30H/29St = C27αβH to C30αβH/29αααSt = C27 to C30-hopanes/C29αααSteranes; TS41 = Terp/Ster = m/z 191/m/z 217 = Terpanes/Steranes; Tp42 = seco/hop = secohopanes/hopanes; S51 = 27Sdia/27aaR = C_{27}diasterane/5α,14α,17α-20R-cholestane; S57 = 27Sdia/29aaR = C27Sdiastera/5α,14α,17α-20R-24-ethylcholestane; S63 = % 27βββSt = % 5α,14β,17β-20R-cholestane + 5α,14β,17β-20S-cholestane; S64 = 28βββSt = % 5α,14β,17β-20R-24-methylcholestane + 5α,14β,17β-20S-24-methylcholestane; S65 = 29βββSt = % 5α,14β,17β-20R-24-ethylcholestane + 5α,14β,17β-20S-24-ethylcholestane; S66 = Reg.% = % regular steranes; S67 = Met% = % methylsteranes; S68 = Dia% = % diasteranes.

Table 13. Isotopic data on asphaltenes, degrees of alteration of steranes and terpanes and some biomarker ratios in geological references from Iraq (northern area and Hit), Kuwait (Burgan oil field) and Oman (Haushi tar area).

Archaeol Number	well reference, location oil seep	type of sample	oil field	depth	formation	state of alteration	δ_{13}Casp	Tp1 = Ts/Tm	Tp35=GCRN/ 30αβH
16	Hit	oil seep		surface		0a	−28.2	0.18	0.27
135-1	Abu Jir	oil seep		surface		0a	−28.3	0.11	0.14
135-2	Abu Jir	oil seep		surface		0a	−28.3	0.13	0.15
231	Hit	oil seep		surface		0a	−28.3	0.1	0.23
232	Hit	oil seep		surface		0a	−28.3	0.13	0.23
695	Kilf 1	crude oil		6572′–6575′	Zubair	0a	−28	0.42	0.08
1352	Kilf 1	crude oil		6572′–6575′	Zubair	0a	−28	0.41	0.07
694	Fallujah 1	crude oil		2608–2610′	Pilsener	0a	−28.2	0.14	0.11
1351	Fallujah 1	crude oil		2608–2610′	Pilsener	0a	−28.2	0.13	0.09
443	Harbol	bitumen vein		surface		0a	−27.5	0.06	0.05
1356	Zakho	oil seep		surface		0a	−27.1	0.63	0.27
1482	Zhako	oil seep		surface		0a	−26.9	0.66	0.27
1483	Zhako	oil seep		surface		0a	−26.9	0.66	0.27
1357	Sara Sati	oil sand		surface		0a	−27.6	0.12	0.23
185	Fattah 1	oil seep		surface		0a	−27.8	0.16	0.15
186	Fattah 2	oil seep		surface		5a-7	−27.8	0.17	0.19
188	Fattah 4	oil seep		surface		0a	−28	0.09	0.09
1765	Al Fattah seep	oil seep		surface		0a	−28.5	0.13	0.1
1762	Hamman al-Aliel	oil seep		surface		0a	−27.8	0.18	0.05
1763	Qaiara	oil seep		surface		0a	−27.7	0.21	0.15
1764	Mishraq	oil seep		surface		0a	−28.2	0.2	0.16
209	Kifri	oil seep		surface		0a	−27.7	0.27	0.08
1099	Aman Hassan	bitumen vein		surface		0a	−28.5	0.17	0.25
687	Kirkuk 117	crude oil	Kirkuk	6880′	Quamchuqa	0a	−27.3	0.43	0.12
1348	Kirkuk 117	crude oil	Kirkuk	6880′	Quamchuqa	0a	−27.3	0.4	0.1
1354	Kirkuk 130	crude oil	Kirkuk	3516′	Kometan	0a	−27.7	0.31	0.11
1355	Kirkuk 131	crude oil	Kirkuk	3952–4057′	Quamchuqa	0a	−27.7	0.29	0.1
690	Damir Dagh 1	crude oil	Damir Dagh	5217–5272′	Shiranish	0a	−27.4	0.29	0.13
1349	Damir Dagh 1	crude oil	Damir Dagh	5217–5272′	Shiranish	0a	−27.4	0.26	0.11
1350	Bai Hassan 13	crude oil	Bai Hassan	4332′	Shiranish	0a	−27.1	0.2	0.11
1353	Bai Hassan 13	crude oil	Bai Hassan	5306–5430′	Quamchuqa/ Doka	0a	−27.8	0.17	0.11
176-1	Burgan hill	oil seep		surface		6b	−27.2	0.47	0.09
176-2	Burgan hill	oil seep		surface		6b	−27.2	0.52	0.13
177-1	Burgan hill	oil seep		surface		1a	−27.3	0.42	0.08
177-2	Burgan hill	oil seep		surface		1a	−27.3	0.46	0.12
177-3	Burgan hill	oil seep	Burgan	surface		1a	−27.3	0.44	0.13
178-1	Burgan hill	oil seep		surface		0a	−27.8	0.5	0.09
178-2	Burgan hill	oil seep		surface		0a	−27.8	0.43	0.13
1057	Burgan quarry	oil seep		surface		0a	−27.5	0.33	0.13
1709	BG 220	crude oil	Burgan	4689′	Wara	0a	−27.3	0.65	0.07
1710	BG 218	crude oil	Burgan	4683′	Burgan	0a	−27.4	0.32	0.11
1711	BG 380	crude oil	Burgan	7100′	Minagish	0a	−27.5	0.26	0.08
1680	Samsat	oil seep		surface		0a	−27.9	0.32	0.38
1821A	Haushi tar seep	oil seep		surface	Haushi	?	−34.3	0.46	0.61
1821B	Haushi tar seep	oil seep		surface	Haushi	?	−34.5	0.46	0.61
1821C	Haushi tar seep	oil seep		surface	Haushi	?	−34.2	0.47	0.64

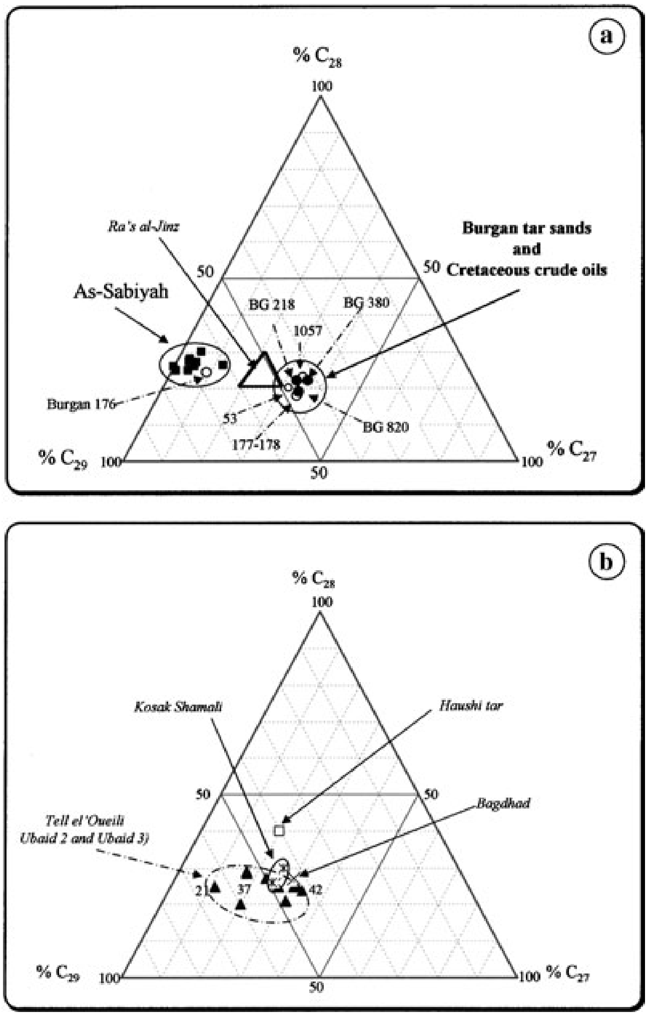

Fig. 20.
Ternary diagram giving the ββsteranes composition: comparison between samples from As-Sabiyah, Ra's al-Jinz, Kosak Shamali, Tell el'Oueli, Baghdad, together with geological references, namely Burgan crude oils and seeps (Kuwait) and Haushi tars (Oman).

weathered oil seep sample on the basis of gross composition data (Fig. 17), falls within the archaeological As-Sabiyah population (Fig. 20a) and has indeed lost C_{27}–C_{28} steranes (Fig. 21).

Most geological samples (e.g. oil seeps nos 177 and 178) do show characteristic unaltered sterane patterns (Fig. 22). Ra's al-Jinz archaeological bitumens show a similar situation (Fig. 20a), for their sterane patterns are also well preserved (Fig. 23). Note, however, that their sterane distribution (Fig. 20a) does not overlap the Burgan oil seep and crude oil cluster, suggesting that the source of the Ra's al-Jinz bitumen is different. The good preservation of steranes in the Ra's al-Jinz samples agrees with the good state of preservation of the Ra's al-Jinz raw samples, which is very likely to be related to the high amount of vegetal remains in the bituminous mixture. The mixtures from Baghdad (Fig. 24) and Kosak Shamali (67) are related to the well-preserved populations, but Oueili (Fig. 25) comprises various types of sterane, ranging from altered (e.g. sample 21) to well-preserved (e.g. sample 42).

Specific molecular ratios (e.g. Ts/Tm, GCRN/ $C30\alpha\beta H$: Tables 12 and 13), recognised previously as reliable genetic parameters for differentiating bitumen from various sources, were selected for a comparison of samples. These ratios have been compiled with $\delta^{13}C$ in Figures 26a and 27a. By reference to the basic information already provided by the $\delta^{13}C$ data on asphaltenes, we have restricted the source references to crude oils and oil seeps from northern Iraq (Fig. 28), Turkey (Samsat) and Kuwait (Burgan). Crude oils, mostly unaltered by biodegradation and weathering, are in some cases not directly comparable to oil seeps when these are altered, but sometimes they provide valuable data when oil seeps have unaltered steranes and terpanes.

A comparison of the data in Figures 26 and 27 allows the following conclusions to be made:

- The As-Sabiyah archaeological bitumen has a single source, probably the Burgan oil seeps which outcrop on Burgan Hill, *c.*70 km south of H3 as the crow flies.
- The bitumen of the Ubaid 2 and 3 periods from Oueili, contemporary with the As-Sabiyah material, does not have the same origin. In the Ubaid 2 period (only one sample), the bitumen came from Iran, whereas in the Ubaid 3 period, it came from Iraq, but apparently from two areas: south of Mosul (Fattah, Qaiyra, Misraq) and Hit.
- The bitumen of Ra's al-Jinz has a single source, and there is no difference between samples with reed or plank impressions. The bitumen coating a Mesopotamian potsherd at Ra's al-Jinz belongs also to the same genetic family as the bitumen found at Ra's al-Hamra (RH-5) and KJ100. The most likely origin for all this bitumen is northern Iraq (Fattah, Hammam al-Aliel). This bitumen is completely different from the Haushi tars of Oman which have an Infra-Cambrian origin in the Hufq formation (68).

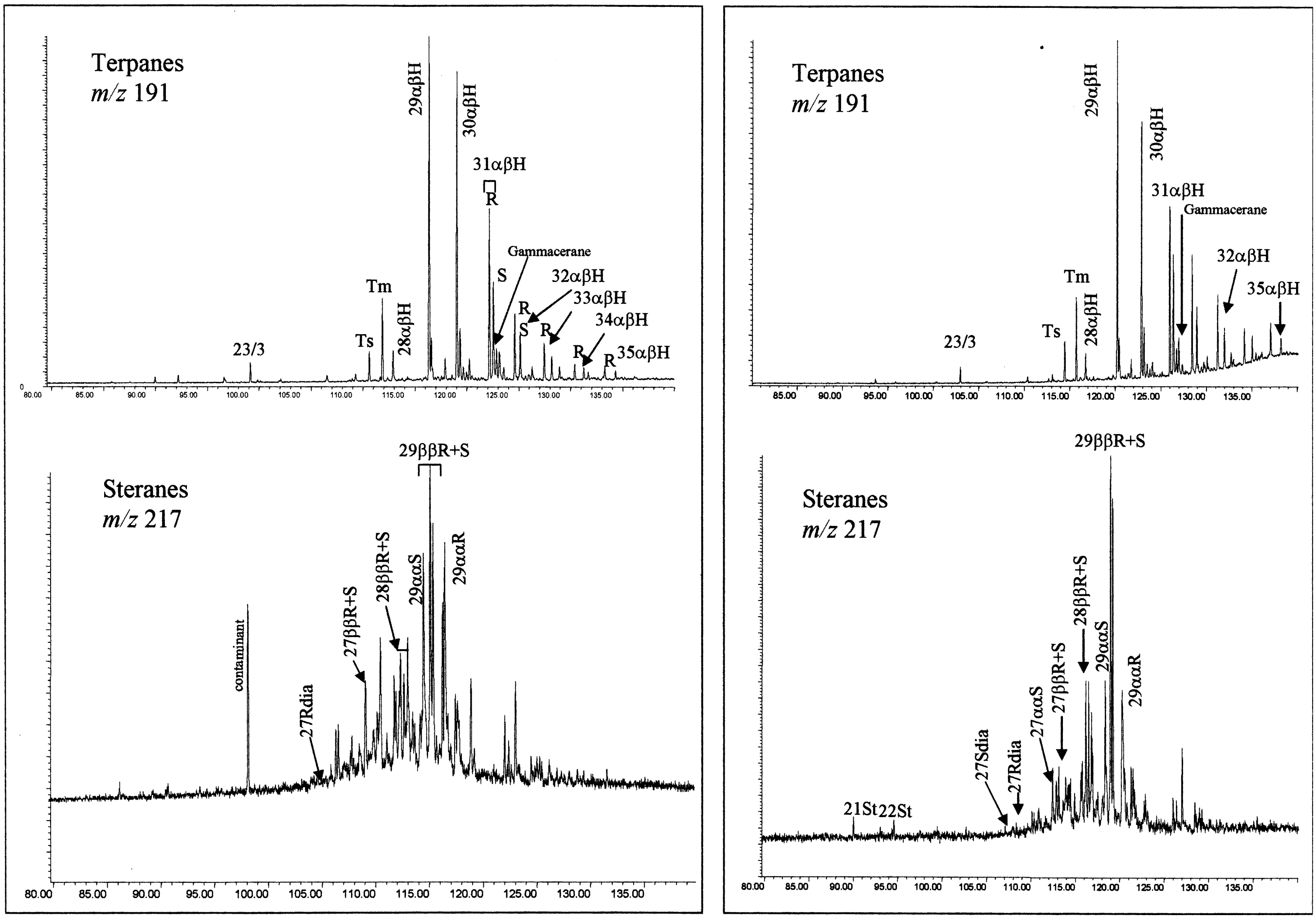

Fig. 21.
Distribution of steranes (*m/z* 217) and terpanes (*m/z* 191): comparison between As-Sabiyah (no. 1773) and Burgan oil seep (no. 176).

- The bitumen from the *quffah* of Baghdad is also probably from northern Iraq, south of Mosul (e.g. Qaiyra) or the Kifri area.
- The bitumen of Kosak Shamali is similar to Hit bitumen when considering Ts/Tm, but is different when referring to GCRN/30αβH, which approaches Samsat (Turkey) in one sample. Samsat or an unknown location in Turkey may therefore be the source.

Investigation of animal fats or fish oils in the RJ-2 bituminous mixture

In order to investigate the proposed addition of 6–9% tallow, i.e. animal fat, to the bituminous mixtures of Ra's al-Jinz, as stated by Cleuziou & Tosi and Rinaldi (69), a segment of a whole slab (no. 149: Fig. 29) was submitted to a specific analytical flow chart. This was to analyse the triacylglycerols which are characteristic biomarkers of animal fats, and the free fatty acids and combined alcohols which provide complementary information on lipids. The basic gross compositional data on hydrocarbons were cross-checked, and the extremely low amount of aromatic hydrocarbons (1% of total extract) was confirmed. This feature indicates that the bitumen was extensively oxidised, as usual in archaeological bitumens.

Triacylglycerols, which are the predominant constituents of animal fat, are contained in Polar Fraction 1 (Fig. 29). The direct injection of this fraction into the GC-MS and its analysis using the Chemical Ionisation (CI) mode with isobutane did not show the presence of triacylglycerols. A subsequent degradative treatment of this polar fraction by $LiAlH_4$ and $LiAlD_4$, which generate linear alcohols

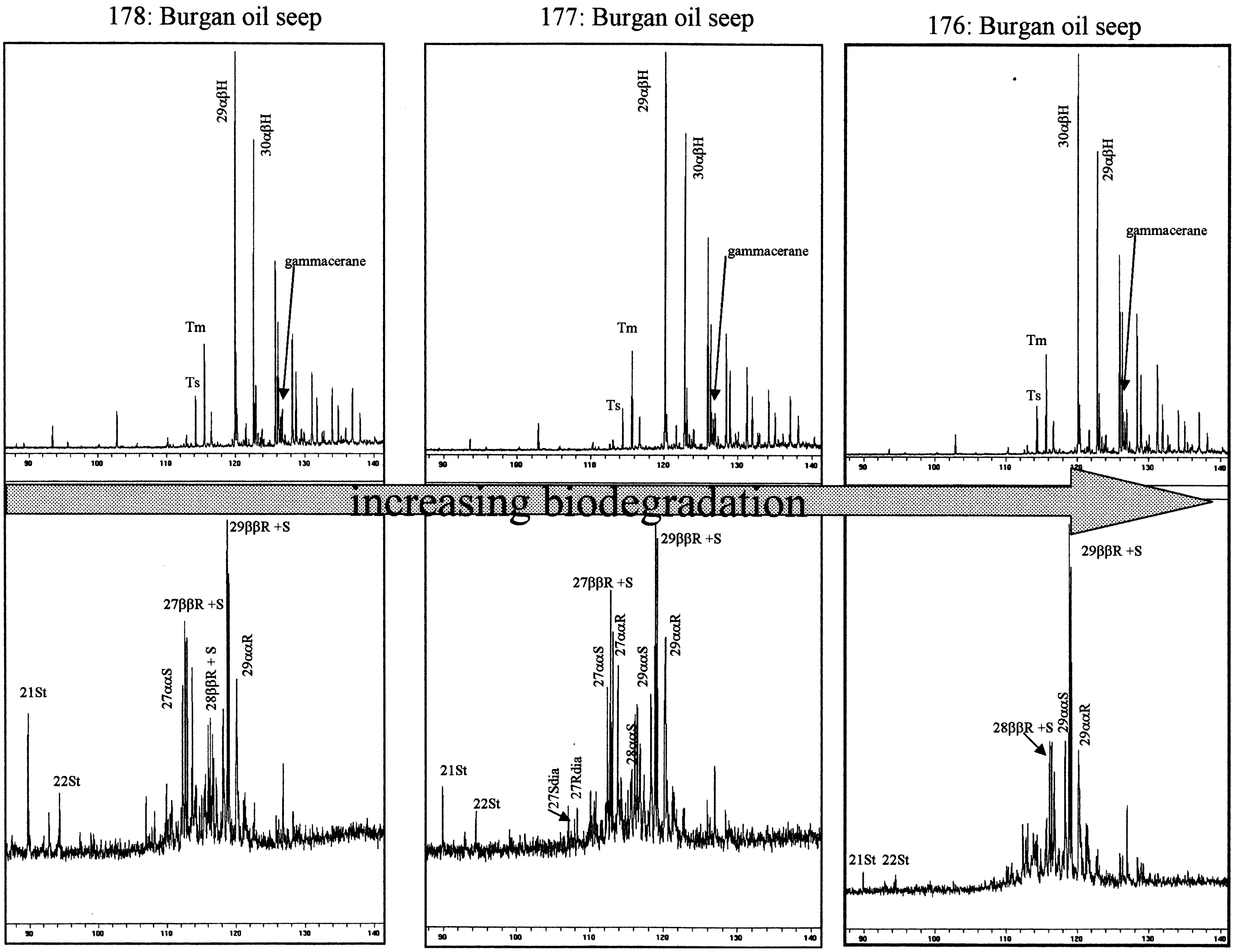

Fig. 22.
Comparison of oil seeps from Burgan Hill, showing the biodegradation of steranes between nos 177–178, which are preserved, and no. 176, which are biodegraded (loss of C_{27} and C_{28} steranes).

and linear deuterated alcohols, confirms that triacylglycerols are absent. Free fatty acids, converted into methyl esters and analysed by GC-MS, do not contain the typical fatty acids of animal fat, C_{15} and C_{17} linear and branched (70), but show a distribution covering a wide range C_9- C_{26}. This distribution, devoid of insaturates, in particular $C_{18:1}$, peaks at $C_{16:0}$ and shows an even predominance ($C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, $C_{20:0}$, $C_{22:0}$, $C_{24:0}$). This pattern suggests that the fatty acids, fairly oxidised, are largely produced by the vegetal input present in the bituminous mixture (C_9–C_{11}, $C_{16} > C_{18}$ and the predominance of even longer chain fatty acids C_{20}, C_{22}, C_{24}). A key conclusion of this study is therefore that there is no chemical evidence for the occurrence of animal fats or fish oils in the bituminous mixture of Ra's al-Jinz.

Discussion and conclusions

This geochemical study of bituminous material used to coat reed and wooden boats from the ancient Near East has answered questions concerning the detailed composition of the bituminous amalgams, the origin of the bitumen used in the different case studies, and the occurrence of animal fat or fish oil within the special amalgam used to waterproof seafaring and river boats.

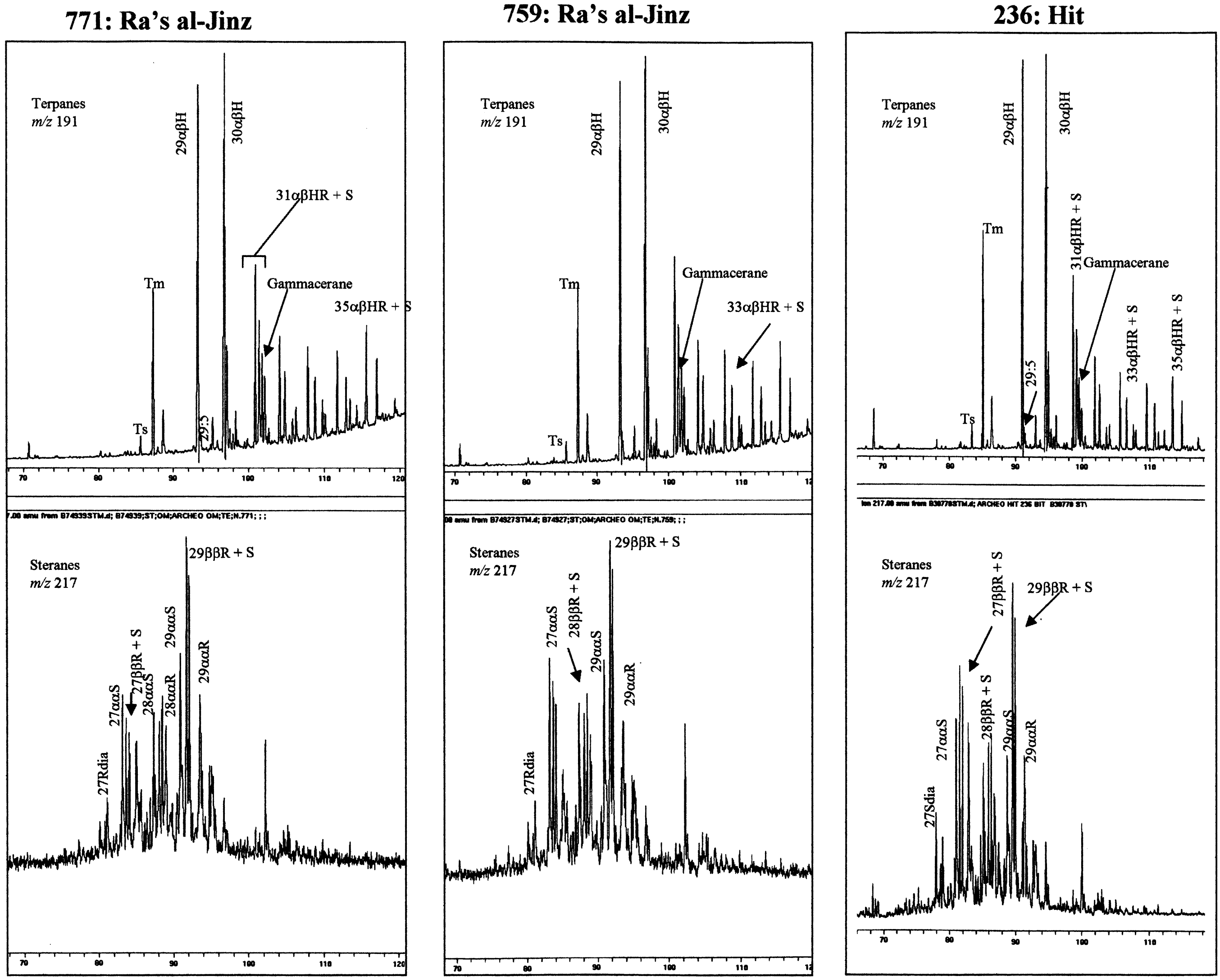

Fig. 23.
Distribution of steranes (*m/z* 217) and terpanes (*m/z* 191): comparison between Ra's al-Jinz samples (no. 771 and no. 759) and the oil seeps at Hit (no. 236) in Iraq.

It was found that the amalgams were generally made of a mixture of mineral and organic matter. The organic matter comprised a significant quantity of bitumen (10–35%) mixed with a variable contribution of vegetal matter. In some cases, for instance in Kosak Shamali, the vegetal input is lacking and the very hard mixture is mainly composed of sand and bitumen. Vegetal matter is also incorporated into most bituminous mortars used for building in Mesopotamia and the Gulf (71). The incorporation of fibrous vegetal debris (chopped straw, reed or palm) strengthens the bituminous mixture, which can also be referred to as bituminous amalgam or mastic (72), and prevents the mixture from sweating and flowing under high ambient temperatures. Fibrous materials entail a greater stability at high temperatures and normally allow a reduction in the amount of bitumen necessary.

As a general rule, ancient amalgams have a far greater quantity of bitumen. In modern mixtures the bitumen content averages 12–16%, and is manipulated at 180–200°C (73). In the archaeological bituminous mixtures, except for Kosak Shamali, the bitumen content is generally higher than 20%, and consequently they can be poured at lower temperatures. The addition of fibrous material reduces

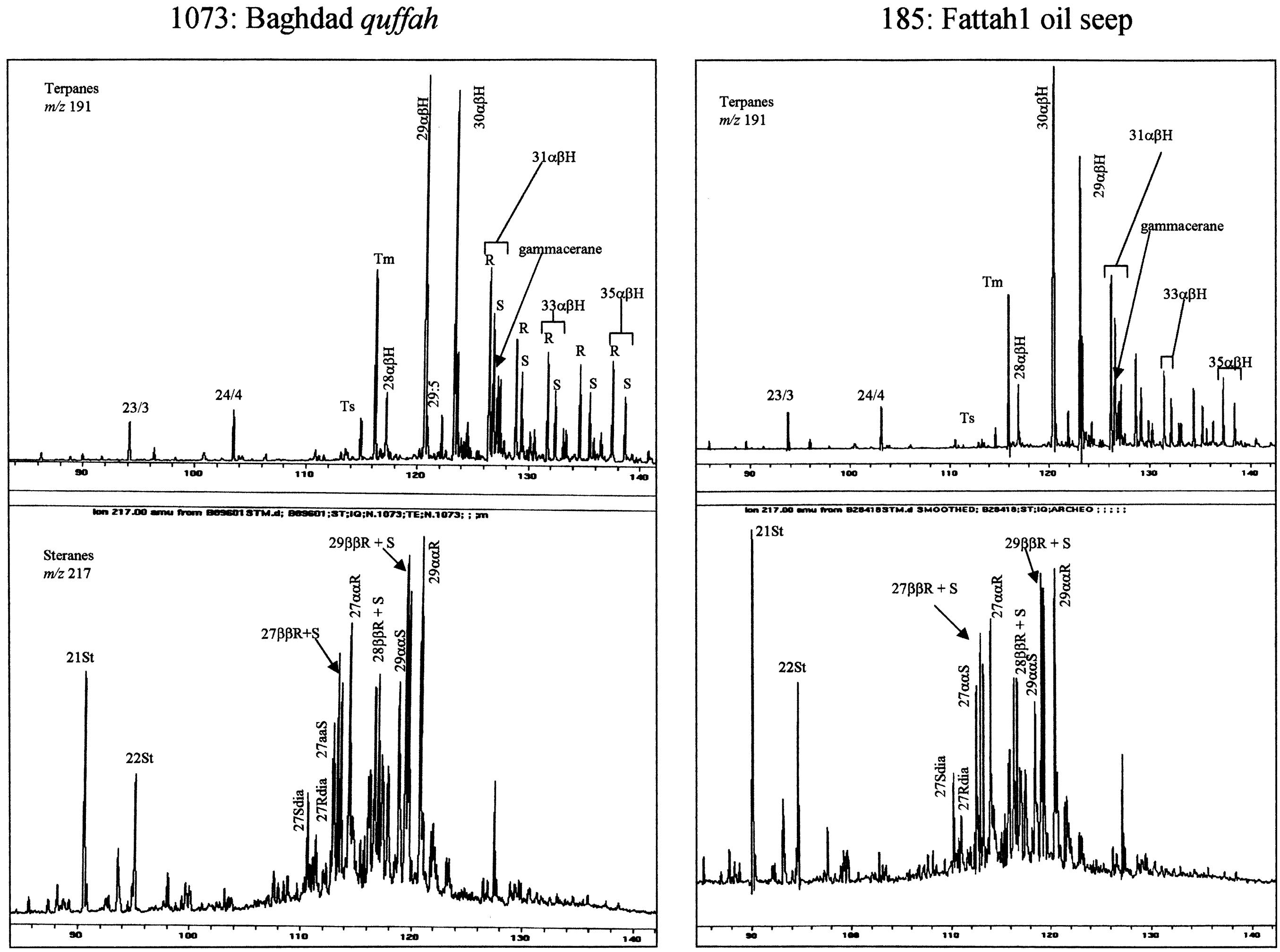

Fig. 24.
Distribution of steranes (*m/z* 217) and terpanes (*m/z* 191): comparison between a sample from the *quffah* of Baghdad (no. 1073) and the oil seep at Fattah (no. 185) in northern Iraq, south of Mosul.

fluidity but provides a greater stability after cooling to room temperature. The preparation of bituminous mortar by Forbes, using ancient recipes, resulted in mixtures which could be trowelled and tamped.

As a general statement, the study reveals that the bituminous amalgams used for coating boats were not found to have a specific composition designed for their specialised purpose. In fact, their composition matches the recipes which are widespread in the so-called mortars used for various waterproofing purposes, and for building operations on land. Such mixtures were used to reinforce and waterproof basketry and mats, as mortar in walls of temples, palaces or underground tombs, as bitumen lining on courtyard pavements, and as flooring layers in date presses (*madbasa*), among other purposes (74).

The suggested occurrence of animal fat or fish oil in the ancient amalgam from the Ra's al-Jinz reed boats would be exceptional, and therefore questionable and requiring verification. Careful examination of the evidence for the presence of animal fat, by applying the requisite analytical flow chart (Fig. 29), has led to the firm conclusion that no such material was incorporated into the bituminous mixture of Ra's al-Jinz sample no. 149.

The idea that animal or fish fats were added to the bituminous mixture may have been partly inspired by present-day practice in building seafaring vessels

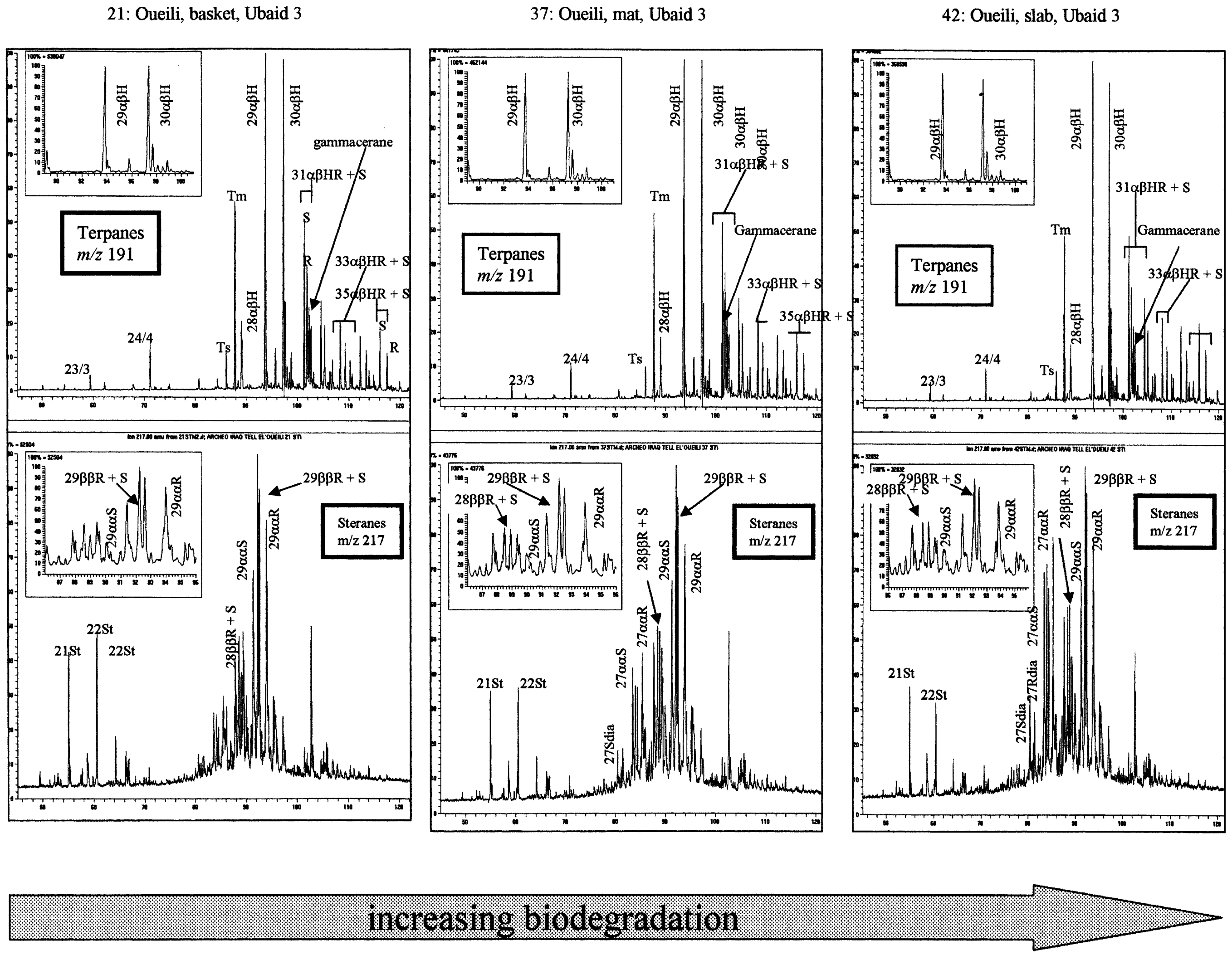

Fig. 25.
Distribution of steranes (m/z 217) and terpanes (m/z 191): comparison between Ubaid 3 samples from Tell el'Oueili. The fragmentograms illustrate a stepwise sequence of sterane biodegradation.

which travel in the Arabian Gulf and Indian Ocean today. For instance, according to a recent book about sailors from Kuwait 'a mixture of lime powder and animal fat was applied to the wooden hull to hinder the growth of barnacles below her waterline' during the construction of the *boom* Mohammadi II, which began in 1979 in an Indian shipbuilding village near Calicut (75). Among the fats which were used historically one may mention fish oil (shark in particular), ox tallow and palm oil. This recipe, however, relates to the protective layer which is painted over the hull of a wooden boat, which operates as an antifouling agent. It does not refer to the several-centimetre-thick coat of bituminous amalgam which was used to coat ancient reed-bundle boats (76).

Examination of the gross composition of various bituminous amalgams used to coat ancient reed-bundle vessels underlines the fact that different solutions were applied at different places and times. In general, vegetal temper was added, but sometimes, as in the *quffah* from Baghdad or in samples from Kosak Shamali, no vegetal additives were used. In the case of the *quffah*, the boat is a round basket used on the river (Fig. 2c). It is not submitted to the same constraints as a seafaring boat travelling across the Gulf or the Indian Ocean, and may have different requirements of its bituminous coating.

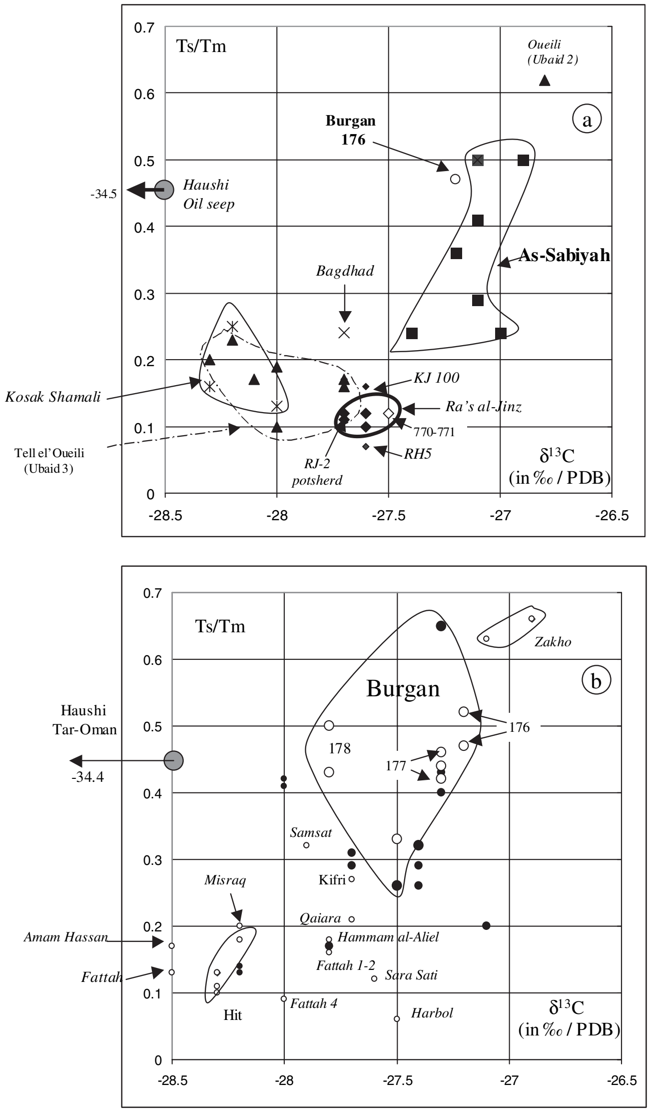

Fig. 26.
Appraisal of bitumen sources using a biomarker ratio on terpanes (Ts/Tm) and isotopic data on asphaltenes (δ^{13}C in ‰/PDB); **a**. Comparison between As-Sabiyah, Ra's al-Jinz, KJ100, RH5, Kosak Shamali, Baghdad and Tell el'Oueili. Burgan sample no. 176 and the Haushi tars are given as references; **b**. Comparison between oils seeps from Kuwait, northern Iraq and Hit.

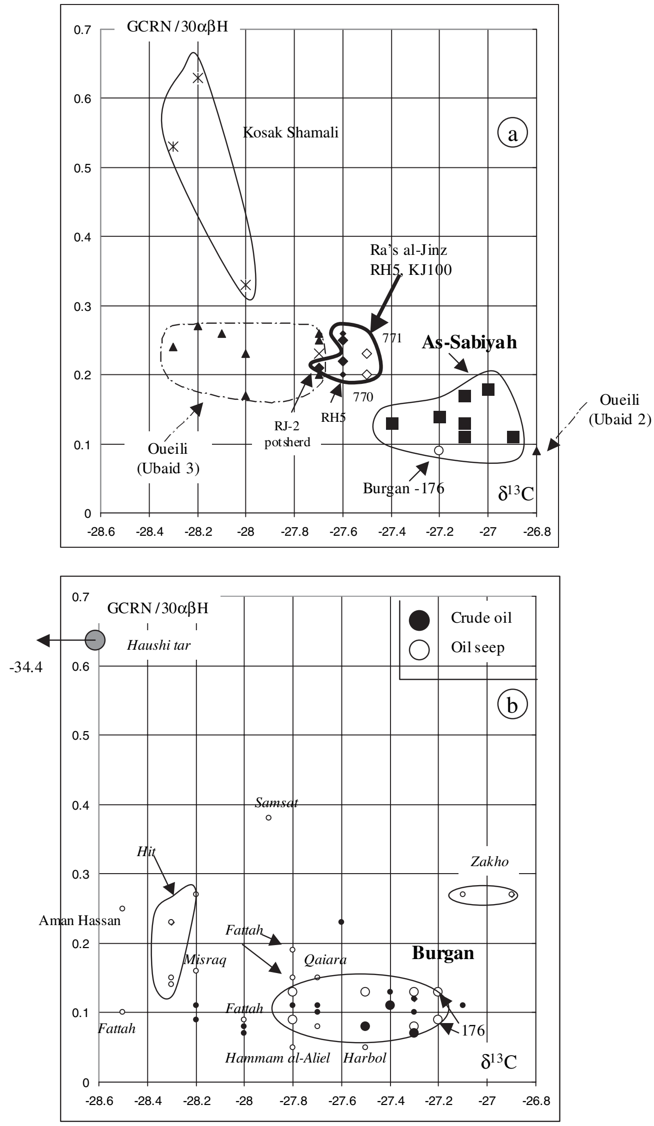

Fig. 27.
Appraisal of bitumen sources using a biomarker ratio on terpanes (Gammacerane/$C_{30}\alpha\beta$Hopane) and isotopic data on asphaltenes (δ^{13}C in ‰/PDB); **a**. Comparison between As-Sabiyah, Ra's al-Jinz, KJ100, RH5, Kosak Shamali, Baghdad and Tell el'Oueili. Burgan sample no. 176 and the Haushi tars are given as references; **b**. Comparison between oils seeps from Kuwait, northern Iraq and Hit.

Pure bitumen represents 96% of the total organic matter in the *quffah* mixture, which is very hard, and more than 1 cm thick. It would certainly ensure perfect waterproofing, but would lack the flexibility and tensile strength of a mixture with vegetal temper. Note that this ethnographic example is not fully comparable to archaeological samples because of its lesser state of alteration.

The bitumen content varies, but in general the amount was far in excess of what was absolutely necessary. The ratio between bitumen and vegetal debris fluctuates greatly in the samples, and the quantity of vegetal additive played a role in the preservation of the coherence of the amalgam through time. Bituminous mixtures incorporating a

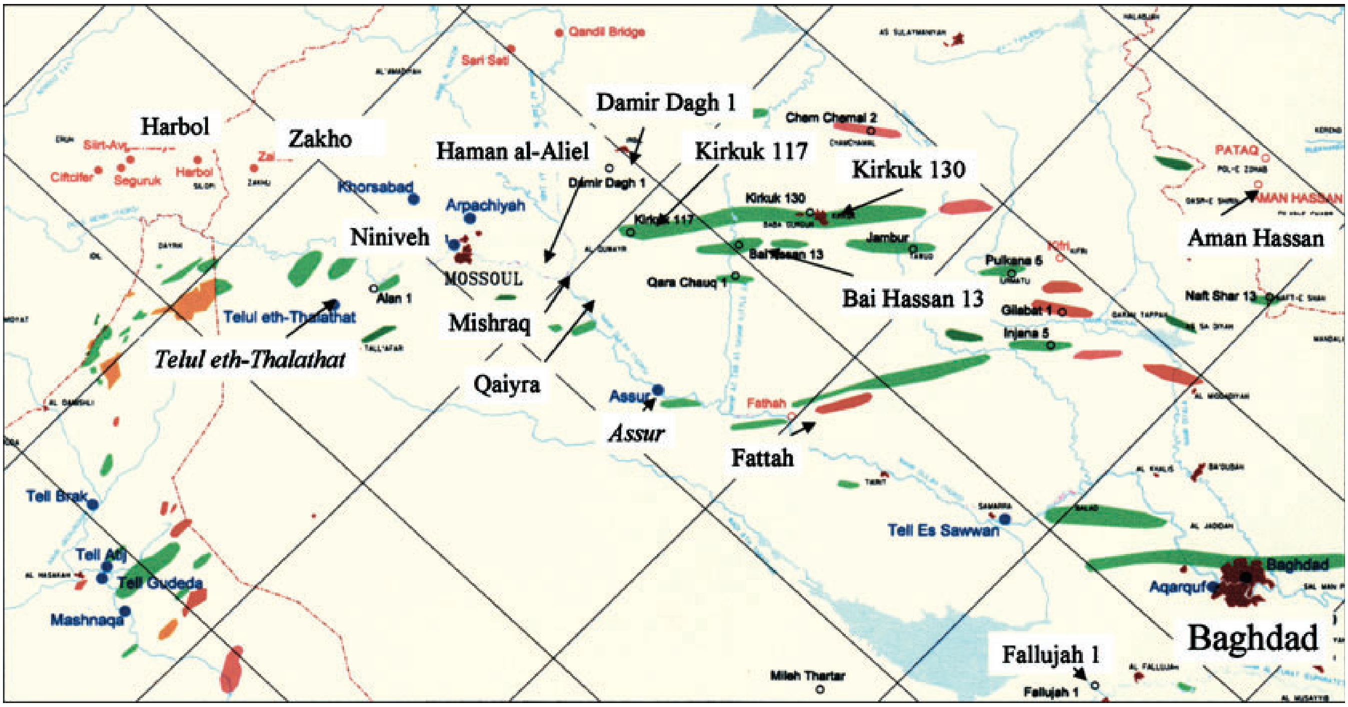

Fig. 28.
Map of northern Iraq giving the location of the oil fields and oil seeps used as references, and of some archaeological sites from which bituminous mixtures were analysed.

high quantity of vegetal debris would have been favoured for sea-going boats. This would have decelerated the progress of degradation, and improved the mechanical properties of the mixture. Such a situation was certainly adopted in Ra's al-Jinz, where abundant crushed vegetal material (reed?) was incorporated. The large quantity of surviving vegetal temper in the Ra's al-Jinz mixtures explains why those slabs were stronger and less friable than those from As-Sabiyah, which were probably depleted in vegetal additives when prepared, and additionally much more altered.

The quantities of Insoluble Organic Matter in the bituminous remains of reed boats from As-Sabiyah are higher than the *quffah* sample but lower than the Ra's al-Jinz slabs (Table 7). This implies that vegetal temper was used in the Ubaid-period amalgam, as evident from macroscopic examination, but possibly in lesser quantities than in the Bronze Age mixture of Ra's al-Jinz. The original proportion of vegetal temper was probably higher than recorded, however, as some would have been lost through weathering. The As-Sabiyah material is nearly 3000 years older than that of Ra's al-Jinz, and the pieces were subjected to more extreme environmental conditions, being located very close to the surface, in sands surrounded by salt flats, consequently with very heavy gypsum and halite salting. Considerable variation is evident within the samples from H3, As-Sabiyah, probably resulting from highly localised environmental conditions. One sample, no. 1773, showed a proportion of 94% Extractable Organic Matter to 6% Insoluble Organic Matter, indicating a very low proportion of surviving vegetal matter, despite voids left by vegetal temper being macroscopically visible. Another (1649a) showed 34% Extractable Organic Matter to 66% Insoluble Organic Matter, indicating a high proportion of surviving vegetal temper, in line with the Ra's al-Jinz average. This example may have been protected from fluctuations in moisture caused by sporadic rainfall by the tumbled stones in which it was found. The other samples from As-Sabiyah had no such protection, but were under sand only.

The natural degradation of the bitumen coating, which is amplified through time, would already have begun when the boats were at sea. Apart from the barnacles which colonised the surface, the forces

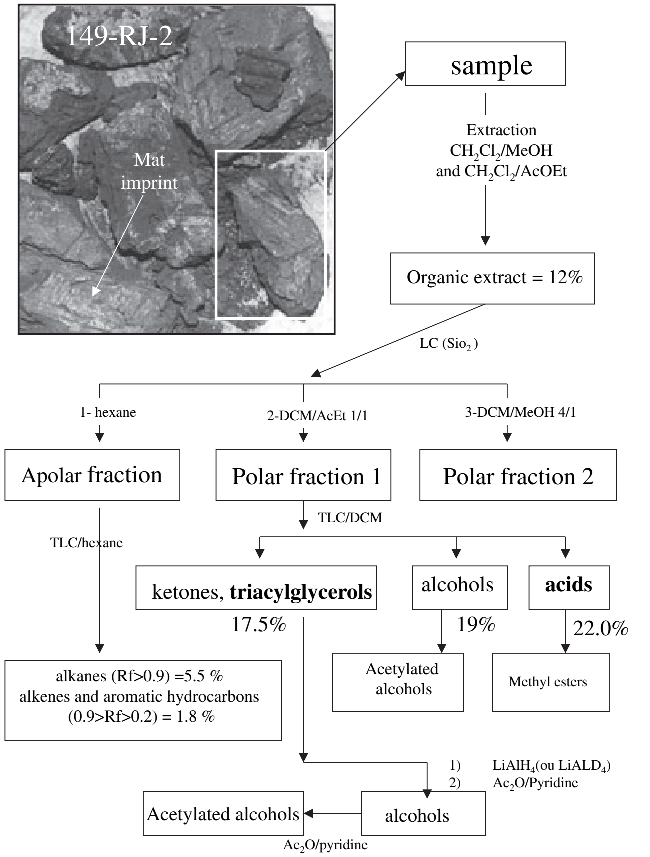

Fig. 29.
Investigation of animal fats in a bituminous slab from Ra’s al-Jinz (RJ-2): analytical flowchart and photograph of the sample (no. 149).

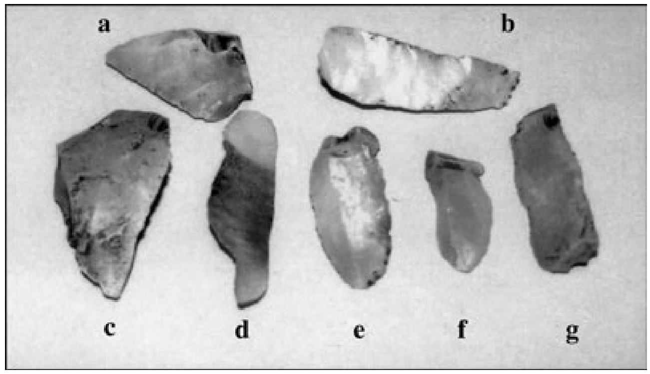

Fig. 30.
Photograph of flint implement from Burgan Hill, in a display cabinet within the National Museum of Kuwait, 1997. Black residues are visible, which may be bitumen used as a hafting adhesive.

applied by rough seas would eventually have opened macro- and micro-fissures in the coating, allowing salt water to penetrate and reach the reeds. Bituminous coatings would have had to be frequently restored, and when boats were no longer considered operational, the coating would have been recovered and stored for re-use. This explain why several caches of bituminous slabs were found stored in rooms at Ra’s al-Jinz, and in chambers and pits at H3, As-Sabiyah. Texts from the Isin-Larsa period confirm that boats were recoated with bitumen mixtures, and that used bitumen was stripped from boats which had finished sailing (77).

Another point worth mentioning concerns the origin of the As-Sabiyah bitumen. We have shown that the bitumen used to prepare the bituminous mixtures of As-Sabiyah has a local origin at Burgan Hill. In 1997, one year before the start of the As-Sabiyah excavations, Jacques Connan visited Dr. Fahad al-Wohaibi, then Director of the National Museum of Kuwait, and examined a small collection of flint implements from Burgan Hill, exhibited under glass in the small salvage rooms of the unreconstructed Museum. Due to past observation of bitumen-bearing flints from various archaeological sites in the Near East (78), Dr Connan looked for possible occurrences of bitumen traces on the artefacts.

Macroscopic examination of the available artefacts revealed traces of a black substance which is probably bitumen. A subsequent expert examination of the photographs gave encouraging results (79). Black traces appear at expected locations on artefacts a, b and e (Fig. 30), if bitumen was used as an adhesive in the hafting of these flint tools. It has not been possible to take better photographs or analyse the black traces to confirm the hypothesis. Indeed, it is questionable that geochemical analysis of these artefacts will produce reliable results, given that the Museum was burnt down during the first Gulf War, and that the bitumen on the flints has probably been carbonised. Nonetheless, the possibility remains that bitumen from Burgan Hill was used during the Arabian Neolithic period to haft flint implements, a hypothesis strengthened by the sourcing of the As-Sabiyah bitumen to the Burgan seeps. As noted above (and see note 57), a certain type of flint from H3, As-Sabiyah appears to be the same as that found at Burgan, and at two nearby sites known as Qurayn 1 and 2.

Concerning the origin of the bitumen, several sources were examined. The bitumen of the As-Sabiyah slabs, the oldest studied, was local and came from Burgan Hill, an inland source around 70 km south of As-Sabiyah as the crow flies. This bitumen is well differentiated from that of the Ubaid 3 period at Oueili which originates from northern Iraq (south of Mosul or Hit). At Kosak Shamali, on the Upper Euphrates, the bitumen seems to have come from Samsat, or an unknown oil seep in Turkey. Bitumen from Ra's al-Jinz and fourth-millennium sites in coastal Oman (RJ-2, RH-5 and KJ100) does not fit the Haushi oil seeps, near the border of Oman and the U.A.E., but matched bitumen from northern Iraq, south of Mosul (Fattah in particular). The bitumen stripped from reed and wooden boats at Ra's al-Jinz may originally have been imported from Mesopotamia by boat, in large pottery jars such as that found at RJ-2, also Mesopotamian in origin. In an alternative scenario, the boats dismantled at Ra's al-Jinz had originally been built elsewhere, perhaps in the shipyards of southern Mesopotamia. This is perhaps the more likely scenario, given the very large quantities of bitumen needed to coat an ocean-going reed-bundle vessel, which would have had to have been brought to Oman to build such a vessel there (80). The bitumen imported to Oman in jars may have been brought for repairs to the boats, and for some of the many other uses of bitumen.

The confirmation of a Burgan origin for the As-Sabiyah bitumen is in line with expectations regarding the history of exchange in the Gulf. During the Ubaid period, despite the long distance communications which brought ceramics from Mesopotamia to the Central Gulf and beyond, the volume of goods exported and exchanged would have been limited. In such a context, local sources would have been utilised whenever possible, especially in the case of the Burgan area, where resources included both bitumen and good-quality flint. That is not to say that bitumen was not transported over long distances during the Neolithic/Ubaid period, to areas which lacked surface seeps. Bituminous beads with bitumen from Iraq are found, for example, at an Ubaid-related Neolithic burial site in Umm al-Qaiwain, in the Lower Gulf (81).

Bitumen is found at fourth-millennium sites in Oman (e.g. RH-5, KJ100), but only becomes abundant in the Gulf region after the mid-third millennium BC, particularly at Ra's al-Jinz, when high volumes of goods were exchanged through the Gulf in an extensive and well-known maritime trading network. Regarding the specific occurrence of the slabs at Ra's al-Jinz, it is possible that boats were built from scratch there during the second half of the third millennium, using local reeds and imported northern Iraqi bitumen, and later dismantled. On the other hand, these boats may have been of Mesopotamian origin, i.e. they were built and coated with northern Iraqi bitumen in the boatyards of southern Mesopotamia, and later repaired in Oman with stored bitumen of the same origin, or simply dismantled.

Bitumen increases in frequency again during the Early Dilmun period (around 2000 BC), as documented by excavations at Failaka and Umm An-Namel in Kuwait (82), and Qala'at al-Bahrain and Saar in Bahrain (83). At this time, and during the second half of the third millennium, bitumen from Mesopotamia circulated over long distances, probably redistributed from Bahrain. The pattern of long-distance exchange of bitumen survived after the Early Dilmun Period, as the practice of using it for various purposes had become anchored in local traditions and technologies. Iranian bitumen also came to be implicated, documented at a Sasanian site on Akkaz island, Kuwait (84).

In contrast, at an earlier date, during the Ubaid Period/Arabic Neolithic, bitumen tended to be used in quantity only by those who had access to it locally, though it did circulate further in small quantities, in which case its use was apparently restricted to valuable artefacts, such as beads discovered in place around the neck of a buried individual at Umm al-Qaiwain. Large-scale export of bitumen did not occur until the establishment of commercial long-distance networks that traded in bulk goods, which did not become possible until the advent of complex urbanised societies during the Bronze Age.

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25. Carter, The Neolithic origins: 44. According to Dalongeville and Sanlaville, who carried out a detailed geomorphological study of sea-level change in the northern Gulf, there was a high stand of over +1 m between 6000 BC and 5500 BC (calibrated). Radiocarbon dates from H3 show that the site was occupied shortly after this, when sea level was falling but still above modern levels. See Dalongeville R & Sanlaville P. Confrontation des datations isotopiques avec les données géomorphologiques et archéologiques à propos des variations relatives du niveau marin sur la rive arabe du Golfe Persique. In: Aurenche O, Evin J & Hours F, eds. *Chronologies du Proche Orient*. Oxford: BAR Int Ser, 379/2: 1987: 567–583. In March, 2004, new geomorphological research was carried out by sea-levels experts from Durham University (Dr Ben Horton and Mr Matthew Wright). Cores were taken of the Holocene sediments in the infilled bay, and elsewhere along the coast of north Kuwait. Analytical work on this material is under way to test Dalongeville and Sanlaville’s results and establish a new high-resolution sea-level curve for the northern Gulf.
26. See Carter & Crawford, Fourth season’s work: Fig. 4. The maximum date range of the sampled H3 bitumen is calculated according to the following data: there are three radiocarbon dates relating to the lowest occupation at H3 (Periods 1 and 2), which are earlier than the bitumen samples (which are Period 3 and 4). AA-42171 (GU-9301) is from Period 1, calibrating to 5530–5320 BC at 95.4% probability, AA-52505(GU-10451) is from Period 1, calibrating to 5260–4950 BC at 95.4% probability. AA-52504 (GU-10450) is from Period 2, calibrating to 5260–4850 BC at 95.4% probability. These dates imply that the bitumen samples are later than 5260 BC. The highest pottery at H3, which is later than the bitumen samples, is Ubaid 2/3 or Ubaid 3. It is not Ubaid 4. At Oueili there are no C^{14} dates for the Ubaid 2 and 3 periods, but there is a series of five dates for the Ubaid 4. Two of these are from grain, and calibrate to 4893–4486 BC and 4725–4357 BC respectively (see Valladas H, Evin J & Arnold M. Datation par la méthode carbone 14 des couches Obeid 0 et 1 de Tell el Oueili (Iraq). In: Huot J-L, ed. *Oueili. Travaux de 1987 et 1989*. Paris: Editions Recherche sur les Civilisations, 1996: 381–390). These dates imply that the H3 bitumen is earlier than 4893 BC. The three other Oueili Ubaid 4 dates are from wood, and calibrate to an earlier range (mid-sixth–early fifth millennium BC). The wood may already have been old by the time it was burnt in the Ubaid 4 period.
27. Carter & Crawford, Fourth season’s work: 82–84.
28. For Shagra see Inizan M-L. *Préhistoire à Qatar: mission archéologique française à Qatar vol. 2*. Paris: CNRS, 1988. Details of excavations on Marawah (MR11) and Kharimat Khor al-Manahil can be found on the ADIAS website: http://www.adias-uae.com.
29. An apparent exception is a fragment showing a string impression (1040.02b), which is smaller than 3 cm across; it originally came from a much larger, crumbled piece which could not be reconstructed. The rest of the crumbled slab was analysed by Dr Connan as Sample 1772 in this report. During excavation, twenty-four further pieces smaller than 3 cm were recorded, none of which bore any particularly significant features. Although these records have been retained in the database, they are excluded from the quantitative analyses given here.
30. This thickness compares well to that of the Ra’s al-Jinz material, which generally has a thickness of 1–3 cm. Vosmer, Ships in the ancient Arabian Sea: 236.
31. This figure of 33% is slightly higher than that given for the Ra’s al-Jinz

slabs, where 20% of the slabs are said to have borne barnacles. Vosmer, Ships in the ancient Arabian Sea: 235.

32. *Balanus trigonus* is found throughout the Gulf, and forms in quiet water at low tide level or below. It can reach the size of the examples seen on the H3 slabs in 2–6 months. Identification and information kindly provided by Emily Glover.
33. Vosmer, Ships in the ancient Arabian Sea: 236.
34. See Schwartz M & Hollander D. Annealing, distilling, reheating and recycling: Bitumen processing in the ancient Near East. *Paléorient* 26/2: 2001: 83–91, for an excellent discussion of the process and consequences of recycling bitumen.
35. A palaeobotanical study (palynology and phytolith analysis) of the soils and a bitumen sample from H3 is currently being undertaken by Dr Adrian Parker (Oxford Brookes University). This may reveal whether reeds grew nearby, and which reeds were used in making the bitumen amalgam.
36. Cleuziou & Tosi, Black boats: 748–754; Cleuziou & Tosi, Ra's al-Jinz and the prehistoric coastal culture: 63–64.
37. Cleuziou & Tosi, Ra's al-Jinz and the prehistoric coastal culture: 63.
38. Méry S & Schneider G. Mesopotamian pottery wares in Eastern Arabia from the fifth to the second millennium BC: A contribution of archaeometry to the economic history. *PSAS* 26: 1996: 93.
39. Cleuziou & Tosi, Ra's al-Jinz and the prehistoric coastal culture: 66.
40. Connan & Nishiaki, The bituminous mixtures of Tell Kosak Shamali.
41. Nishiaki, personal communication, February 2003.
42. Connan J & Deschesne O. *Le Bitume à Suse*. Paris: Éditions de la Réunion des Musées Nationaux and Elf Aquitaine, 1996; Connan J. Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations. *Philosophical Transactions of the Royal Society of London B* 353: 1999: 33–50.
43. Connan J. L'archéologie moléculaire et isotopique des bitumes, brais et goudrons de bois. In: Miskovsky J, ed. *Géologie de la Préhistoire*. Paris: Association pour l'Étude de l'Environnement Géologique de la Préhistoire, 2002: 1045–1056.
44. Abdullah FH & Connan J. Geochemical study of some Cretaceous rocks from Kuwait: comparison with oils from Cretaceous and Jurassic reservoirs. *Organic Geochemistry* 33: 2002: 125–148.
45. Connan et al., The archaeological bitumens of Bahrain.
46. See Cleuziou & Tosi, Black boats: 755, Table 64.1.
47. J-L. Faggionato, personal communication. Additionally, at least one piece of bitumen from H3 contains a carbonised grain.
48. Cleuziou & Tosi, Black boats: 755, Table 64.1.
49. Cleuziou & Tosi, Black boats: 755, Table 64.1.
50. Connan J. Quelques secrets des bitumes archéologiques de Mésopotamie révélés par les analyses de géochimie organique pétrolière. *Bull Centres Rech Explor-Prod. Elf Aquitaine* 12/2: 1988: 759–787.
51. This contradicts the results on Ra's al-Jinz bitumen, conducted by Dr Giuseppe Scala and published by Cleuziou & Tosi, Black boats: 755, Table 64.1.
52. Cleuziou S & Tosi M. The south-eastern frontier of the ancient Near East. In: Frifelt K & Sørensen P, eds. *South Asian Archaeology 1985*. London: Scandinavian Institute of Asian Studies Occasional Papers, 4: 1989: 15–47.
53. Forbes, *Studies in Ancient Technology*; Connan, Quelques secrets des bitumes archéologiques; Connan & Deschesne, *Le Bitume à Suse*; Connan et al., Archaeological bitumens of Bahrain; Marschner RF, Duffy LJ & Wright HT. Asphalts from middle eastern archaeological sites. *Archaeological Chemistry 2*. Chicago: American Chemical Society, 1978: 150–171; Marschner RF, Duffy LJ & Wright HT. Asphalts from ancient town sites in Southwestern Iran. *Paléorient* 4: 1978: 97–112.
54. Carman GJ. Structural elements of onshore Kuwait. *GeoArabia* 1/2: 1996: 239–266.
55. Connan et al., The archaeological bitumens of Bahrain: 145. Bahra, the location of a modern oil well in Kuwait, only *c*.25 km from As-Sabiyah, has in the past been cited as a possible bitumen source. Analysis by Dr Connan has since shown that the surface staining is not in fact an oil seep, but an accumulation of organic matter produced by methanotrophic bacteria living on CH_4, which escapes to the surface through faults.
56. Dickson HRP. *Kuwait and her Neighbours*. London: Allen and Unwin, 1956. Lorimer also mentions the Burgan seeps, explaining that 'bitumen exudes from the ground in a hollow near the Burqan hill'. See Lorimer JG. *Gazeteer of the Persian Gulf, Oman and Central Arabia. Volume 2: Geographical and Statistical*. Calcutta: Government Printing Office, 1908: 1066.
57. It was not possible for members of the British Archaeological Expedition to visit the area of bitumen seeps and flint scatters at Burgan Hill. However, lithic material from Burgan in a collection at the National Museum of Kuwait was examined by Dr Heiko Kallweit. The tools belong to the Arabian Neolithic tradition, implying contemporaneity with H3. Certain tools and flakes from H3 appear to be made of the same stone as the Burgan collection, and it is likely that a common source can be found a few kilometres south of Burgan, possibly at a hill known as Qurayn (given the site code Qurayn 1), which is thickly scattered with natural raw flint nodules of the same macroscopic appearance. Another extensive flint site is located nearby, named Qurayn 2, which is covered with small mounds of chipped flint of the same appearance. This may be another source and a core preparation area. Collections were taken from Qurayn 1 and Qurayn 2, for laboratary analysis and comparison with selected material from H3. Provisionally, it seems likely that the inhabitants of H3 visited the Burgan area not just to collect bitumen, but also to gather high-quality flint for tool-making.
58. Connan J, Lacrampe-Couloume G, Adam P, Albrecht P & Abdullah FH. Unexpected organic geochemistry in the two famous oil/gas seepage of Kuwait: Evidence of activity of methanotrophic bacteria at surface, *Book of Abstracts, part I, 19th International Meeting of Organic Geochemistry*,

6–10 September 1999. Istanbul, 1999: 59–60.

59. Abdullah & Connan, Geochemical study of some Cretaceous rocks.
60. Abdullah & Connan, Geochemical study of some Cretaceous rocks.
61. Connan, Quelques secrets des bitumes archéologiques; Connan et al., The archaeological bitumens of Bahrain.
62. Schwartz M, Hollander D & Stein G. Reconstructing Mesopotamian exchange networks in the fourth millennium BC: Geochemical and archaeological analyses of bitumen artifacts from Haçınebi Tepe, Turkey. *Paléorient* 25/1: 1999: 67–82.
63. Connan & Nishiaki, The bituminous mixtures of Tell Kosak Shamali.
64. Connan et al., The archaeological bitumens of Bahrain.
65. Connan J, Breniquet C & Huot J-L. Les objets bituminés de Tell el Oueili. Des témoins de la diversité des réseaux d'échanges commerciaux de l'Obeid 0 à l'Uruk récent. In: Huot J-L, ed. *Oueili, Travaux de 1987 et 1989*. Paris: Éditions Recherche sur les Civilisations, 1996: 413–430.
66. Connan J & Mouton M. Study of some bituminous lumps of Mleiha: Preliminary results. In: Mouton M, ed. *Mleiha I. Environnement, stratégies de subsistance et artisanats*. Lyon: TMO, 29: 1999: 245–264; Connan J, unpublished results.
67. Connan and Nishiaki, The bituminous mixtures of Tell Kosak Shamali.
68. Grantham PJ, Lijmbach GWM & Posthuma J. Geochemistry of crude oils in Oman. In: Brooks J, ed. *Classic Petroleum Provinces*. London: Geological Society Publications, 50: 1990: 317–328; Richard PD, Nederlof PJR, Terken JJM & Al-Ruwehy N. Integrated Haushi hydrocarbon study in North Oman. *GeoArabia* 3: 1998: 146–147; Richard PD, Nederlof PJR, Terken JJM & Al-Ruwehy N. *Generation and retention of hydrocarbons in the Haushi Play, North Oman: GeoArabia* 3: 1998: 493–506; Pollastro RM. *Ghaba Salt Basin Province and Fahud Salt Basin Province, Oman—Geological overview and total petroleum system*. Denver: U.S.Geological Survey open-file reports, 99-50-D: 1999.
69. Cleuziou & Tosi, Black boats of Magan: 755; Rinaldi, Some interesting results.
70. Tchapla A, Méjanelle P, Bleton J, Goursaud S & Mourer R. A propos de l'homme de Lyon: Matériaux des baumes d'une momie de l'époque Ptolémaïque conservée au Muséum d'histoire naturelle de Lyon. *Encyclopédie religieuse de l'univers végétal* 1: 1999: 445–487.
71. Forbes, *Studies in Ancient Technology; Connan*, Quelques secrets des bitumes archéologiques; Connan & Deschesne, *Le Bitume à Suse*; Connan et al., Archaeological bitumens of Bahrain.
72. Forbes, *Studies in Ancient Technology*.
73. Forbes, *Studies in Ancient Technology*.
74. Forbes, *Studies in Ancient Technology*; Connan, Quelques secrets des bitumes archéologiques; Connan et al., Archaeological bitumens of Bahrain; Marschner, Duffy & Wright, Asphalts from middle eastern archaeological sites: 150–171; Marschner, Duffy & Wright, Asphalts from ancient town sites: 97–112.
75. Marafie HMR & Al Rashoud CF. *Kuwait's age of sail, Pearl divers, Sea captains and Shipbuilders Past and Present*. Kuwait: Al-Hashemi II Publications, 1993.
76. There is an Ur III text from Girsu of the late third millenium BC, quoted by Cleuziou and Tosi, Black Boats: 746, which lists materials used for building reed and wooden boats. This text mentions 595 litres of fish oil in conjunction with large quantities of bitumen, reeds, ropes, wood and other materials. The purpose of this fish oil is not stated but the text is used as evidence that fish oils were used in boat-building in antiquity. This interpretation can be questioned, on the grounds that the fish oil was not necessarily incorporated in the mixture used to cover the hull of reed boats. Similar problems exist when referring to texts relating to *ad-kub*, the craftsmen working with reed. Such texts often list bitumen, alkali and gypsum. Gypsum mixed with bitumen is reported in CAD G, p.54–55 but such a mixture has not been identified in our study. What is alkali (*naga*)? Is it calcite? Translation problems may be responsible for uncertainties in the true identification of this mineral, as underlined by G. Petrequin in his memoir *Le bitume en Mésopotamie aux époques néo-sumériennes et paléo-babylonienne d'après les sources cunéiformes*. Université de Paris I, 1989. The grouping of products in a list is not a proof that they were incorporated together into a mixture. Experimental variations on the recipe for bitumen amalgam were conducted by Dr Rinaldi, and by Tom Vosmer and his team when building experimental reconstructions of reed-bundle vessels in Oman and Ravenna. They found that fish oil or animal fats aided the adherence of the bitumen amalgam to the structure of the vessel, whether wood or reed: see Vosmer, The Magan Boat Project: 54. Bituminous mixtures without fish oil, however, also provide an adhesive amalgam, which could have been applied as the coating of reed boats. Such mixtures are widespread in the ancient Near East, used as a waterproofing agent.
77. The repair of a boat is quoted in Babylonian inscriptions in a text in the Yale Babylonian Collection (BIN X, 129, F 4). The salvage of used bituminous mixture from a boat is mentioned in WMAH 3, R VI, 25.
78. These sites include Umm el-Tlel, Kosak Shamali, Djadé el-Mughara, Tell Sabi Abyad II, Tell Atij, Gudeda and Mari in Syria, Telul Eth-Thalathat II in Iraq, and Netiv Hagdud in Israel. See Boëda E, Connan J, Dessort D, Muhesen S, Mercier N, Valladas H & Tisnerat N. Bitumen as a hafting material on Middle Palaeolithic artefacts. *Nature* 380: 1996: 336–338; Connan, Use and trade of bitumen; Connan & Nishiaki, The bituminous mixtures of Tell Kosak Shamali; Connan & Deschesne, Le Bitume à Suse. For a reference to the flint collection from Burgan, see Calvet Y. The Dilmun Culture at its border with Mesopotamia. In: Cleuziou S, Tosi M & Zarins J, eds. *Essays on the Late Prehistory of the Arabian Peninsula*. Rome: Serie Orientale Roma, 93: 2002: 257–271.
79. Examination by E. Boëda (Nanterre University, Paris X).
80. According to Vosmer, The Naval Architecture: 154, a 13 m reed-bundle boat capable of carrying *c*.6.5 tonnes of cargo would require around 1650 kg of pure (refined) bitumen, to which 1950 kg mineral matter must be added

to compensate for the refinement. Mineral material, found in the archaeological bituminous amalgams, occurs naturally in the neighbourhood of most sites. Its incorporation into the mixture limits the consumption of bitumen, which may have been imported from a distance, therefore being a valuable commodity. If this was so, then the raw bitumen needed to coat such a vessel would weigh 3600 kg.

81. Phillips, Prehistoric Middens and a Cemetery from the Southern Arabian Gulf. In: Cleuziou, Tosi & Zarins, *Essays on the Late Prehistory of the Arabian Peninsula*: 176, n. 12.
82. Connan, unpublished.
83. Connan et al., Archaeological bitumens of Bahrain.
84. Connan J & Gachet J. The bituminous mixtuers of Akkaz: a Partho-Sasanian site of Kuwait, in preparation.