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A geochemical study of bituminous mixtures from Failaka and Umm an-Namel (Kuwait), from the Early Dilmun to the Early Islamic period

Jacques Connan[1] and Robert Carter[2]
[1]Laboratoire de Géochimie Bioorganique, UMR 7509, CNRS, 25 rue Becquerel, 67200–Strasbourg, France
e-mail: connan.jacques@wanadoo.fr

[2]Archaeology Department, Durham University, South Road, Durham, DH1 3LE, UK
e-mail: racbahr@hotmail.com

This paper is the last in a series presenting geochemical analyses of fragments of bituminous mixtures excavated from archaeological sites in Kuwait. The first was devoted to bituminous boat remains from the Ubaid-related Neolithic site of H3, As-Sabiyah, while the second dealt with bituminous amalgams from the Partho-Sasanian site of ᶜAkkaz, a former island now joined to the south side of Kuwait Bay. This, the third, refers to bitumen-bearing samples from two other islands, Failaka and Umm an-Namel, and covers a time span including the Early Dilmun period, the Kassite period and the Hellenistic to Early Islamic periods. The composition of the bituminous amalgams was studied in detail. The proportions of soluble and insoluble organic matter as well as vegetal organic matter were evaluated. Mineralogical composition by X-Ray diffraction and thin-section analysis was used to estimate the mineral input in the bituminous mixtures. It can be confirmed that the recipes used in the preparation of these bituminous amalgams comply with those traditionally used in antiquity, as seen at many sites in Mesopotamia and the Gulf. Analysis of the soluble organic matter, and especially its ''saturates'' fraction, provided sterane and terpane distributions and the measurement of diagnostic molecular ratios. These data, complemented by the isotopic composition of asphaltenes, allowed the identification of the sources of the bitumen, by calibration with numerous references from Iran and northern Iraq (oil seeps, bitumen from archaeological sites). It was established that the bitumen from Failaka and Umm an-Namel was mainly imported from central Iraq (Hit-Abu Jir) and northern Iraq (around Mosul). One sample of oil-stained sand, dating to the Early Dilmun period, originated from Burgan and thus documents small-scale imports from inland Kuwait. These results, and those of previous analyses, agree with the geopolitical context of the Early Dilmun, Kassite and Hellenistic periods, and the maritime trade routes that linked Mesopotamia to the settlements of the Gulf and beyond. The paper concludes with an overview of recent bitumen provenance analyses, and discerns chronological patterns in the distribution of Iraqi and Iranian bitumen in the Gulf and Indian Ocean, from the Neolithic to the Islamic periods.

Keywords: bituminous mixtures, Kuwait, Failaka, Umm an-Namel, biomarkers, steranes, terpanes, carbon isotopic data on asphaltenes, Dilmun, Hellenistic, Kassite, Islamic, Ikaros, GC-MS, mineralogical composition, bitumen origin, chemical composition

Introduction

Bituminous mixtures are widespread in ancient civilizations of the Near East, especially in Syria, Iraq and Iran. As demonstrated in previous studies, bitumen from northern Iraq is known from sites in southern Mesopotamia, as well as Bahrain, which is believed to have been a transit place between Mesopotamia and present-day Oman (1). The island of Failaka, known as Ikaros in Hellenistic times, played a key role as a first stop on the seafaring route to the East. Here, bitumen remains were unearthed from different periods ranging from the Early Dilmun to the Islamic periods. Bitumen was also found on Umm an-Namel island (Early Dilmun and Parthian periods), located just off the main seafaring route on the south side of Kuwait Bay.

This paper presents a geochemical study of bituminous samples from Failaka and Umm an-Namel (Fig. 1). The study was undertaken with several objectives:

- to examine the gross composition of the bituminous mixtures, in order to determine what proportion is principally composed of bitumen, and to document the mixture's detailed composition, in particular the input of mineral and organic additives;
- to identify the origin of the bitumen in order to document the trade routes incorporating the two sites;
- to explore the function of certain ceramic vessels, and their role in the treatment and storage of organic materials;

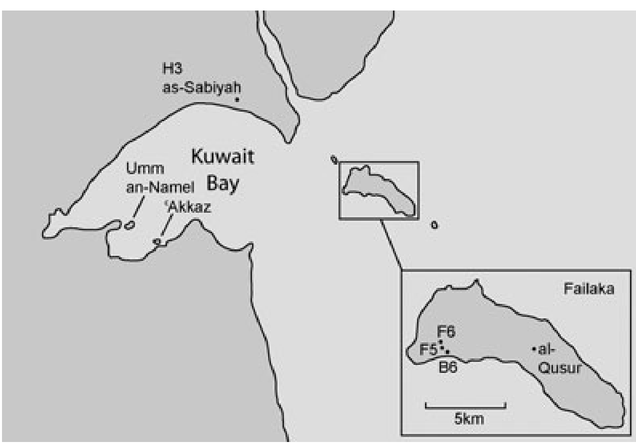


Fig. 1.
The location of sites in Kuwait, which have provided bitumen samples for analysis.

- to complete the regional history of the bitumen trade for this particular area of the Gulf by adding new key results to the data already obtained from As-Sabiyah (5300–4800 BC) and ᶜAkkaz (first century AD and 600 AD) (2);
- to permit an overview of the bitumen trade with regard to previous studies by J. Connan of bituminous material from numerous sites in the Gulf and Indian Ocean region, from the Neolithic to the Islamic periods.

The archaeological samples

Thirty bituminous samples from Failaka and nine bituminous mixtures from Umm an-Namel Island were subjected to geochemical analyses in order to study their gross composition and to try to determine the bitumen origin. Their field references and their archaeological contexts are listed in Table 1. In addition, five further samples were derived by extracting residues from within or adhering to the surface of potsherds associated with some of the samples (Table 2).

On Failaka, the samples were taken from two Hellenistic sites (B6 and F5), an Early Dilmun and Kassite site (F6) and an early Islamic site (al-Qusur), while on Umm an-Namel samples were taken from a slightly earlier horizon of the Early Dilmun period and the Parthian period. This is a considerable date range (potentially 2100 BC–1000 AD), and the analysis is thus well positioned to study bitumen usage and procurement over a long period of time. If the samples are counted by period (excluding the subsamples listed in Table 2):

- fifteen are Early Dilmun (ten from F6, five from Umm an-Namel)
- three are Kassite (from F6)
- sixteen are Hellenistic (eight from F5, seven from B6, one from an uncertain location)
- two are Parthian (from Umm an-Namel)
- one is Early Islamic (from al-Qusur)
- two are of unknown date (from Umm an-Namel).

Most of the samples belong to well-known categories excavated from other archaeological sites (Table 3):

- thin films or thick coats of bituminous mixtures covering the interior face of potsherds (Type 1: fifteen samples, Figs 2f–g, 3 and 4);

Table 1. Basic information on the analysed bituminous material from Failaka and Umm an-Namel.

database number	Site	date range	mixture type	sample reference	locus	layer	level	excavation campaign	description of archaeological context	macroscopic description of sample
11	Al-Qusur	700–800 AD	7					Failaka 84	surface	spindle whorl. Black, hard, bituminous mixture with numerous grains of carbonate, metallic rod in the middle
1	B6	205–140 BC	1			UF 48	III-IV	Failaka 83	jar in UF 48	piece of jar with thin film of bitumen inside, some traces of bitumen outside, close to the neck of the jar
2	B6	200–150 BC	1			UF 53	III-IV	Failaka 83	ground (3)	3 pieces of jars, two pieces of neck with bitumen inside, one piece of jar with bitumen on both sides
3	B6	200–150 BC	1			UF 49		Failaka 83		2 pieces of jar with bitumen inside and outside
4	B6	175 BC	1			??		Failaka 84		one piece of jar with bitumen inside and outside
14	B6	250 BC	4			UF 44		Failaka 83		big lumps of bitumen (3 cm thick) with numerous vegetal debris inside, brown, fairly hard. Numerous holes due to the dissolution of vegetal debris. Stains the fingers
15	B6	250 BC	4	F83 2030		UF 32		Failaka 83	door 112, ground (2)	big lumps of bitumen (3 cm thick) with numerous vegetal debris inside, brown, fairly hard. Numerous holes due to the dissolution of vegetal debris. Stains the fingers
13	B6?	205–140 BC	1			UF 6–7		Failaka		several pieces of jar with bitumen inside
152	F5	200–140 BC	9	F86 H1516	H88	UF H136	III-IVA	Failaka 86	disturbed soil on an occupation level, under H130-ground H90	hard, black, with numerous mineral grains without vegetal debris
153	F5	164–140 BC	8	F86 H1427	H87	UF H132	IVA	Failaka 86	in the ‘‘enclosure’’ H104 used for bitumen work. Infilling on Surface H94.	big lump, hard, brown with weathering figures and few vegetal debris
154	F5	164–140 BC	8	F86 H1222	Tower NW	sounding 8	IVA?	Failaka 86	Sounding 8, Tower NW. Infilling at the time of rebuilding?	very big lump of black-brown hard material without vegetal debris inside. Wood or palm imprint on surface
994	F5	150 BC	7		H 140	UF H169	end of IVB	Failaka	infilling of a plastered vessel (basin 140) with a bituminous bottom in room H126	big lump (3 cm thick) on a potsherd. Hard with weathering features

Table 1. Continued.

database number	Site	date range	mixture type	sample reference	locus	layer	level	excavation campaign	description of archaeological context	macroscopic description of sample
996	F5	164–140 BC	8	F86 H1435	H 87	UF H135	IVA	Failaka 86	Surface H94, a refill of Surface H197	big lump of bitumen (3 cm thick) coating egg-shaped bottom of a local jar
998	F5	205 BC	8	F88 H2705	H 87	UF H244	III	Failaka 88	Surface H197, at the level of a brick bench in NW corner of the room	heterogeneous sample: crust of bitumen on potsherd, hard round lump
999	F5	205–140 BC	8	F88 H2720	H126		III	Failaka 88		numerous brown lumps without vegetal debris, with weathering features. It was stuck on the drainpipe, towards the shoe - a waterproofing agent?
1000	F5	150 BC	8		H130	UF H168	IVB	Failaka 87	infill of ground H143	thick brown plaque with weathering figures, no visible vegetal debris
5	F6	1400–1300 BC	1	F84 1031		UF 3		Failaka 84	infillings	fragment of a jar with a thick coat of bitumen inside. Numerous quartz grains in the bituminous mixture
6	F6	1400–1300 BC	6	F84 1067		UF 7		Failaka 84	infillings	lumps of bitumen mixture, brown, soft with round grains (quartz?), some vegetal remains and a shell piece. Mortar type
7	F6	1400–1300 BC	7	F84 1178		UF 17		Failaka 84		bituminous mixture with mineral matter (round quartz grains), hard, black
8	F6	2000–1700 BC	4	F84 1214	308	UF 26		Failaka 84		lump of bitumen mixture, hard, black, with numerous vegetal debris, some round quartz grains
52	F6	2000–1700 BC	4	F85 1602		UF 86		Failaka 85		lumps of bitumen with some vegetal debris, black, falling in powder. Stains the fingers
988	F6	2000–1700 BC	4	F86 1754	337	UF 108		Failaka 86		500 g of brown lumps with vegetal debris
989	F6	2000–1700 BC	4	F87 2200	345	UF 131		Failaka 87		500 g of brown bituminous mixture with numerous vegetal debris. Big lump of bitumen on the outside of a potsherd
990	F6	2000–1700 BC	4	F86 1663		UF 95		Failaka 86	well stratified	
991	F6	2000–1700 BC	4	F86 1829		UF 115		Failaka 86	infillings	
992	F6	2000–1700 BC	4	F86 1785		UF 112		Failaka 86		100 g of brown material with numerous vegetal debris. Mortar type
997	F6	2000–1700 BC	6	F88 2539	381	UF 171		Failaka 88		brown lumps, hard, with minerals, without vegetal debris

993a	F6	2000–1700 BC	18	F86 1822		UF 118		Failaka 86		bitumen with numerous quartz grains, looks like an oil-stained reservoir
993b	F6	2000–1700 BC	4	F86 1822		UF 118		Failaka 86		brown lumps, soft, with numerous vegetal debris
958	Umm an-Namel	2100–2000 BC	4		C VIII c1	Depth 35 cm	1st level	Umm an-Namel 85	North of trench	Brown bituminous mixture with visible vegetal debris, stains the fingers
959	Umm an-Namel	2100–2000 BC	9		C VIII		1st level	Umm an-Namel 85	North of trench	Black bituminous mixture with rush imprint (sealing mixture?)
960	Umm an-Namel	2100–2000 BC	7		C VIII c1/c	0–56 cm		Umm an-Namel 90		Black bituminous mixture, hard with a vacuolar structure (degas-sing?)
1112	Umm an-Namel	100 BC–200 AD	1		BIXc1/WB	27–40 cm		Umm an-Namel 90	western side	bituminous mixture (thick-ness = 0.5 mm) coating the inter-ior face of a beige potsherd (thickness 18 mm)
1113	Umm an-Namel	2100–2000 BC	1		C VIII c1/c	from depth 66 to 78 cm		Umm an-Namel 90	end of the trench	black layer (thickness = 0.5 mm) with a carbonised aspect covering the interior face of a red potsherd (thickness = 4 mm)
1114	Umm an-Namel	undated	1		CVII/a1/5	90 to 104 cm		Umm an-Namel 90	from all parts of the square	thick bituminous crust (thick-ness = 3 mm) on the interior face of a beige potsherd (thick-ness = 15 mm)
1115	Umm an-Namel	undated	1		CVIIa1/1	from depth 90 to 110 cm		Umm an-Namel 90	the northern part 2 × 2 m	thick bituminous crust (thick-ness = 2–3 mm) on the interior face of a red potsherd (thick-ness = 18 mm)
1116	Umm an-Namel	100 BC–200 AD	1		BIXc1	surface		Umm an-Namel 85		thin bituminous layer (thick-ness = 0.5 mm) on the interior face of a beige potsherd (thick-ness = 7–9 mm)
1117	Umm an-Namel	2100–2000 BC	1		CVIII c1 mixed			Umm an-Namel 90	pile	black layer (1–2 mm) on the interior face of a pink potsherd (thick-ness = 5–7 mm)
995		150 BC	1	F86 H138				Failaka 86		bitumen inside a potsherd

Table 2. Aliquots (subsamples) derived from existing samples by scraping or by extraction from crushed potsherds.

database number	original sample number	mixture type	excavation campaign	date range	site	nature of sample
1245	1	1	Failaka 83	205–140 BC	B6	scraping of thin coat of bituminous material inside potsherd
1248	1	30	Failaka 83	205–140 BC	B6	extract from half of the cleaned, crushed potsherd
1246	2	1	Failaka 83	200–150 BC	B6	scraping of thin coat of bituminous material inside potsherd C
1247	5	30	Failaka 84	1400–1300 BC	F6	extract from cleaned, crushed pot sherd
1222	1117	30	Umm an-Namel 90	2100–2000 BC	Umm an-Namel	extract from cleaned, crushed pot sherd

Table 3. Types of bituminous mixture.

Mixture Type	Former Type	Description
1	1a	Bitumen on the interior face of a potsherd
2	1b	Bitumen on the exterior face of a potsherd
3	2	Mat or basket or tool handle
4	3a	Brown mortar: mixture of mineral, bitumen and vegetal debris (straw?)
5	3b	Black hard mortar: mixture of small vegetal debris (straw?), bitumen and mineral
6	4a	Brown crumbly mixture without vegetal debris
7	4b	Black hard mixture without vegetal debris
8	4c	Brown hard mixture without vegetal debris
9	5	Black mixture with reed or wood imprint
10	6a	Bitumen on the interior surface of a sarcophagus
11	6b	Bitumen on the exterior surface of a sarcophagus
12	7	Bitumen in a *madbasa* (date syrup press)
13	8	Bitumen as boat caulking
14	9	Bitumen as glue on flint implement or terracotta
15	10	Natural asphalt or natural bitumen
16	11	Bitumen as mixture of a spindle whorl
17	12	Bitumen mixture of a bead
18	13	Bitumen mixed with quartz grains resembling an oil-stained reservoir
19	14	Carbonised organic matter
20	15	Massive pure bitumen
21	16	Ash
22	17	Bitumen mastic = bituminous rock
30	25	Residue extracted from crushed potsherd

- mortar-type, comprising brown mixtures of bitumen, mineral matter and vegetal debris, fairly crumbly (Type 4: eleven samples, Figs 2b, 2h);
- black or brown mixtures without vegetal debris (Type 6–8: eight samples, Fig. 2d–e);
- hard black mixtures with reed or wood impressions (Type 9: two samples, Fig. 2c).

To complete the list we have two special samples: sample no. 11 is a spindle whorl showing a metallic rod in its axis (Type 16 as a spindle whorl and Type 7 as composite material, Fig. 2d–e); and sample no. 993a (Type 18, Fig. 2a–b) appears to be a geological sample, in this case a tar sand from the Burgan area, inland Kuwait. Some other well-preserved samples from the Hellenistic fortress F5, which were not subjected to analysis, are shown on Fig. 5. These include pieces with mat or basket impressions, as well as material adhering to pottery.

B6, Failaka: the Hellenistic shrine, third and second centuries BC

In the Hellenistic beach sanctuary on Failaka (Site B6), bitumen was observed as a thin film coating the interior jars for waterproofing but also as thick crusts of stored bituminous amalgam (3). These

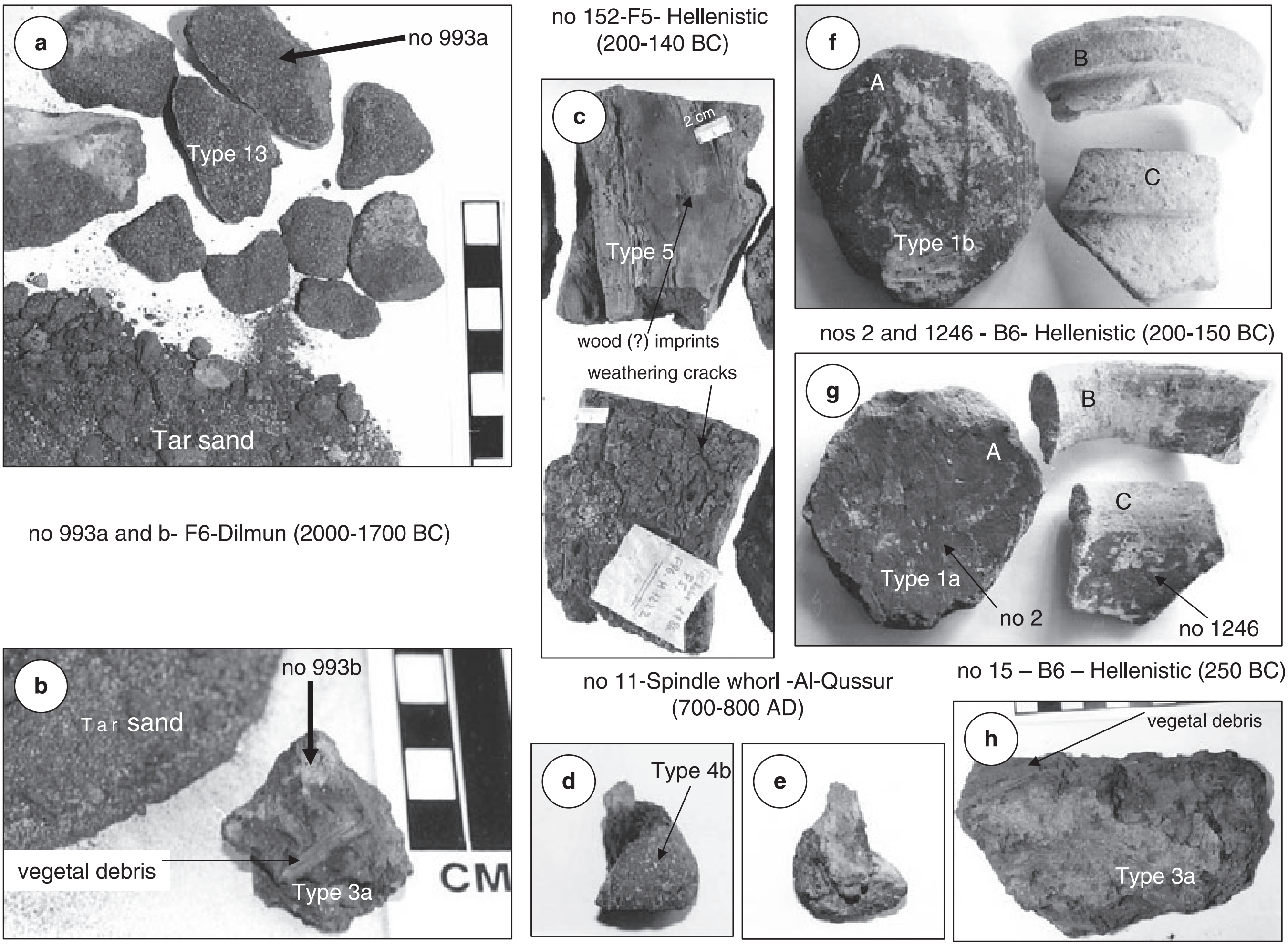


Fig. 2.
Examples of bituminous samples from Failaka. **a.** sample no. 993a (Site F6, Early Dilmun) exhibits a typical aspect of oil-stained sand (Type 18); **b.** sample no. 993b (Site F6, Early Dilmun) illustrates a mortar-type mixture with vegetal debris (Type 4); **c.** sample no. 152 (Site F5, Hellenistic) shows plank imprints on one side and weathering cracks on the other side (Type 9); **d–e.** sample no. 11 is a spindle whorl (Al-Qusur, Early Islamic) which was prepared using a hard mixture of bitumen and minerals (Type 7); **f–g.** samples A, B and C (Site B6, Hellenistic) are bitumen-coated potsherds. Sample A (no. 2 and no. 1245) is a spoon-like potsherd that was probably used to process bituminous mixtures. Samples B and C (no. 1246) are potsherds with a thin film of bituminous mixtures on the interior face; **h.** sample no. 15 (Site B6, Hellenistic) belongs to the mortar-type category (Type 4) and contains vegetal debris.

mixtures may have been transported in the jars themselves, though it should be noted that an illustrated example of a jar coated with bitumen is described as a ''local jar'' (4). Bitumen pieces were also found covering parts of the floor of the building during its second phase (5). The analysed samples from B6 include both bitumen adhering to pottery (sample nos 1–4, 13) and larger lumps (sample nos 14–15), which may have been scattered or stored in the building. B6 was apparently a small shrine to Artemis, dated by the excavators to the third and early second centuries BC (6). Despite the sacred context its finds included domestic refuse such as net weights and spindle whorls. The bitumen and associated pottery are therefore as likely to relate to every-day activities as to ritual behaviour.

F5, Failaka: the Hellenistic fortress, third and second centuries BC

Similar conclusions can be drawn with the jars excavated from the Hellenistic fortress F5 on Failaka (storage jars with a thick bituminous crust at the bottom: Fig. 5a). F5 was originally a square fortifi-

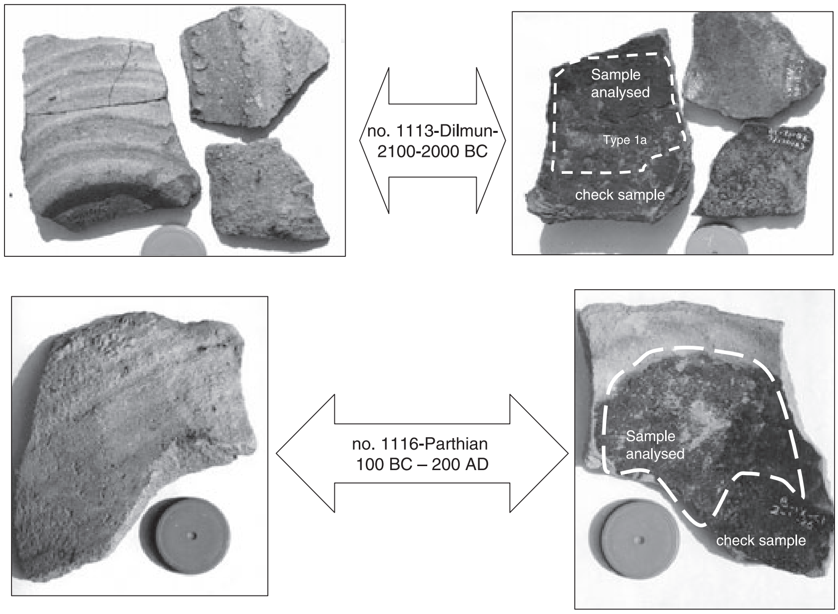


Fig. 3.
Examples of potsherds from Umm an-Namel. Sample no. 1113 (Early Dilmun) is a potsherd covered by a black coating, with a carbonised aspect. Sample no. 1116 (Parthian) shows a thicker bituminous crust coating the interior face.

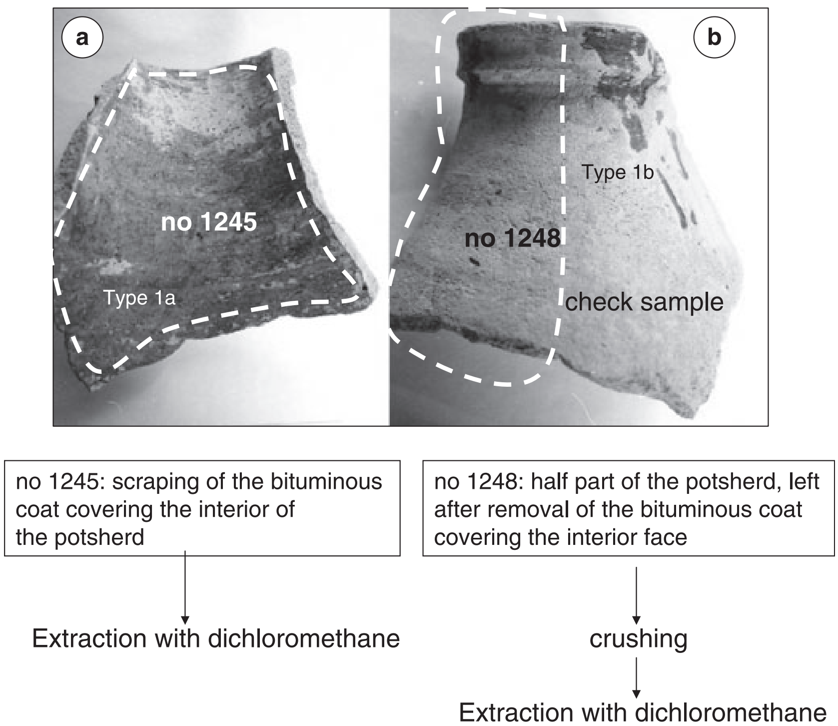


Fig. 4.
A two-step procedure to investigate the organic matter trapped inside potsherds. **a.** sample no. 1245 is collected by scraping the interior face of the potsherd; **b.** sample no. 1248 is isolated by extracting the cleaned potsherd which was crushed.

cation measuring just under 60 × 60 m, founded in the early third century BC, and enclosing temples, public buildings and domestic housing. It was later expanded and refortified with a moat (7). The site appears to have functioned both as a small Seleucid garrison and a fishing village.

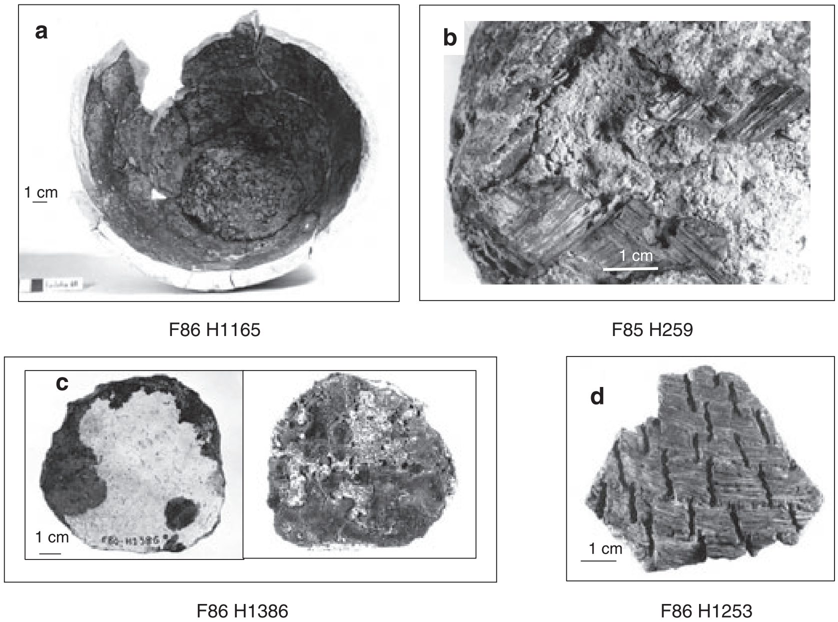


Fig. 5.
Examples of bituminous artefacts found in the Hellenistic fortress F5, Failaka (photographs and sample information from J. Gachet). **a.** F86 H1165, Locus H68-UF H115, Surface H82 (courtyard). Thick bituminous mixture at the bottom of a local jar, *c.* 164–140 BC; **b.** F85 H259, Locus H 6-UF H19, Surface H37 (courtyard). Bottom of a basket with traces of interwoven straw, found with numerous artefacts including bitumen-bearing jars, *c.* 150 BC; **c.** F86 H1386, Locus H 88-UF H127. Big sherd of local jar, cut into a circular shape. Thick crust of bitumen covering one face and smearing the other face. This shape of potsherd is thought to be a kind of spoon used to process the bituminous mixture, *c.*164–140 BC; **d.** F86 H1253, Locus H 88-UF H123. Infilling of surface with sand and ashes. Bituminous mixture with mat imprint, *c.* 164–140 BC.

In this complex many pieces of bitumen show imprints of basket weaving (Fig. 5b). In the southeast corner of one room, Locus H87, a small enclosure was cleared out, about 1.30 m in diameter, containing blocks of bitumen. Locus 87 dates to Period 3 (late third–mid-second century BC) and is interpreted as a bitumen workshop and warehouse (8). It has been described as follows: ''Thick and large pieces of bitumen were found inside, as well as numerous fragments of jars covered with bitumen, some having possibly been used as spoons [see Fig. 5c]; there were many traces of bitumen around and we may assume some kind of processing of bitumen in that area'' (9). Bitumen, present as thick coats in numerous jars or as blocks in the enclosure, is associated with oyster shells, net weights, earthenware and fish bones, and is clearly related to fishing activities. The bitumen stored and possibly processed therein may have been used to coat fishing vessels: large pieces of bitumen with plank imprints (Fig. 2c) may testify to this, although it has been suggested that bitumen was used to coat roofs or terrace structures, also resulting in such impressions (10). The boat interpretation remains hypothetical because barnacles were not identified on these fragments, in contrast to those seen on samples from As-Sabiyah and Ra's al-Jinz (11).

In addition to the exceptional discoveries (the workshop for bitumen processing) and common occurrences (e.g. the numerous jars), there were various other occurrences of bituminous matter at F5: as a thick crust covering the broken neck of the terracotta head of a woman (F87 H 2510, not included in this study) (12); as a waterproofing agent at the bottom of a basin (sample no. 994) (13); and as a sealing agent and mortar in some buildings.

F6, Failaka: the Bronze Age tower-temple, *c.* 2000–1700 and 1400–1300 BC

Thirteen of the samples originated from a large building of uncertain function on mound F6. This was a thick-walled square structure, *c.* 20 × 20 m, surrounded by a platform or terrace. The paucity of pottery and other finds argues against a domestic function, and the excavators tentatively suggest that it was some kind of tower-like temple (14). This structure was built during the Early Dilmun period, in the early second millennium BC. The associated pottery (Period Vc) and material below its floor (Periods Va, Vb) compare to City II material from Qala'at al-Bahrain (15) and Periods 1, 2A and 2B on Failaka, indicating a date of *c.* 2000–1700 BC.

The building was reused or continued to be used into the Kassite period. The excavators date this later phase, Period IV, to the mid-second millennium, although the limited quantity of published pottery suggests affinity with Højlund's Periods 4A–4B, giving a slightly later date of *c.* 1400–1300 BC (16).

Ten of the relevant samples date to the Early Dilmun phase of the building. Where the locus is provided it can be shown that these were all from interior fills of the building, Period Vc, except for sample 8 (Locus 308), which was from an external ashy soil, also Period Vc (17). The other three, samples 5–7, were from Kassite levels.

Other examples of bituminous material from the F6 tower-temple include bitumen used to plug a hole in a vase body (F 84.1184) (18), and a fragment of sculpture representing the top of an animal thigh with stylised muscle design (F 84.1309) (19). This sculpture, found in levels predating the tower-temple and thus dated to the first centuries of the second millennium BC, is described as a black bituminous stone, very much like the "bitumen mastic" of masterpieces from Susa exhibited in the Louvre Museum (20). This sculpture is clearly an export from the Susa area, for this particular bituminous material is rare and only outcrops at Ghali Kuh, just under 150 km from Susa (21). Similar materials exist elsewhere but they are very distant, found in southeastern Turkey in the asphaltite veins of the Siirt area. A Susian origin for the Failaka sculpture, if confirmed by further analyses, would add a new example to the short list of those which have been identified outside Susa, so far mainly discovered in Mesopotamia (22).

Umm an-Namel Island: Early Dilmun and Parthian, *c.* 2100–2000 BC and 100 BC–AD 200

Umm an-Namel is an island off the south side of Kuwait Bay just west of Kuwait City (see Fig. 1). Most of the nine samples came from a trench excavated in 1985 and 1990 by the National Museum of Kuwait under the direction of Dr Fahad al-Wohaibi. Remains dating to the Bronze Age and the Parthian period were uncovered. The Bronze Age remains are reported to include an installation of ovens dated to the Early Dilmun period, with traces of associated settlement remains (23). The pottery includes chain-ridged sherds (see Fig. 3). According to Højlund, most of the chain-ridge sherds from Umm an-Namel belong to his type B55B, which is almost entirely found from the City Ib to the early City IIb at Qala'at al-Bahrain (24). This suggests a date earlier than the occupation of Failaka, where chain-ridges are not found, probably between 2100 and 2000 BC. Five samples came from these layers.

No details of the Parthian levels are published. Two samples came from these layers. The remaining two samples from Umm an-Namel are undated.

Al-Qusur: Early Islamic village site, seventh–tenth centuries AD

One of the samples, no. 11, consisted of a bitumen spindle whorl picked up from the surface of al-Qusur (see Fig. 2d–e). This is a large village site in the centre of the island, dated to the eighth century AD (25). Nothing significant can be said about its context other than that it provides a sample probably dating to the Early Islamic period.

Experimental methodology

Residue analysis

A preliminary two-step analytical procedure was adopted to identify the goods that were stored or processed inside the ceramic vessels, which had been waterproofed with bituminous mixtures. In the first step, the bituminous coat from the interior face of the potsherd was scraped off and analysed (no. 1245, Fig. 4a). In the second step, the cleaned potsherd was crushed and extraction was made with dichloromethane (no. 1248, Fig. 4b) to examine any possible organic residue trapped within the potsherd matrix. Those samples analysed to explore this particular issue are listed in Table 2. The results of this analysis are given below under the section entitled *The possible uses of some ceramics from Umm an-Namel and Failaka*.

Compositional, mineralogical and isotopic analyses

The archaeological bituminous material was studied using the same analytical scheme applied in previous archaeometric studies (26). A detailed, up-to-date flowchart with descriptions of each analytical technique and examples has been published (27), and analytical details can also be found in a recent paper devoted to the petroleum geochemistry of crude oils and source rocks in Kuwait (28).

Prior to the detailed chemical analysis, a binocular examination of each sample was undertaken on the raw samples. Petrographical analyses of thin sections as well as X-Ray Diffraction analyses were also conducted on several samples to allow a quantitative measurement of the minerals present in the bituminous mixtures. After the macroscopic examination, 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 (δ^{13}C and δD), were used to establish bitumen-to-bitumen and bitumen-to-oil seep correlations. During that phase of the work available data on natural oil seeps were compiled. The detailed analysis of chemicals trapped within the porous matrix of selected potsherds was carried out using GC-MS and GC-C-IR-MS, entailing measurements of δ^{13}C values of individual compounds.

Results

Rock-Eval screening analysis: basic characterisation of bituminous mixtures

Rock-Eval pyrolysis on whole samples, including some crushed potsherds, was carried out as a screening technique to get an initial insight into the organic mixtures present. The most important parameters, deduced from the Rock-Eval analysis, are listed in Table 4.

The plot of the Hydrogen Index (HI in mg HC/g TOC) as a function of Total Organic Carbon (TOC in %/sample) in Fig. 6 shows that most samples fall within the area of archaeological bituminous mixtures defined previously by sets of samples from Bahrain (29), Kuwait (30), Mari and Susa (31).

Data collected on three aliquots (subsamples) of sample no. 993 (Fig. 2a–b) reflect the heterogeneities occurring in the sample bag. Sample no. 993a contained less than 8.9% TOC with an HI of 523, whereas sample no. 993b had 32.0% TOC for a reduced HI of 434. The third subsample (no. 993) occupied an intermediate position between these two extremes. The differences between sample nos 993a and 993b are entirely consistent with the expected nature of each aliquot: sample no. 993a was evidently a geological oil-stained sand containing tar with a high HI, whereas sample no. 993b (Fig. 2b) was an archaeological mixture or amalgam, in which HI is reduced due to the input of vegetal debris, and which is enriched in bitumen compared to the natural tar sand of sample no. 993a. Such enrichment is common within the archaeological population of bituminous amalgams, which show between 20% and 40% TOC. Note also that the tar sand aliquot, sample no. 993a, appears to have a different geographical origin to that of sample no. 993b (see below), despite the fact that both were recorded as the same sample during the excavation process.

Sample nos 1246 and 2 also illustrate the heterogeneities of samples collected in the same bag at excavation (Fig. 6). This heterogeneity is seen in Fig. 2f–g. The bituminous mixture on potsherd C (sample no. 1246) is much less abundant than on potsherd A, and consequently TOC values may be reduced by 50% when sampling these contrasting situations.

Sample nos 960 and 1113, from Umm an-Namel, are located outside the main cluster, being depleted in hydrogen (Fig. 6). This is consistent with macroscopic observations, which suggest burning: the coating of sample no. 1113 has a black, sooty aspect (see Fig. 3), while numerous vacuolar structures are likely due to degassing inside sample no. 960. Evidently a portion of carbonised bitumen is present in both samples.

Lastly, note the very low amount of organic matter, which has migrated inside the potsherds of sample nos 1248 and 1247 (Fig. 6). This organic matter seems to be depleted in hydrogen.

By considering another diagnostic diagram, namely HI vs Tmax (Temperature of the S2 peak maximum), the previous conclusions are confirmed: most data fall within the area previously defined for the archaeological bitumens of Bahrain (Fig. 7). Again, sample nos 1113 and 960 fall outside the range of most samples: their HI is lower, with a

Table 4. Rock-Eval data.

sample number	site	date range	mixture type	TOC (% by weight of sample)	S1 (mg HC/g of sample)	S2 (mg HC/g of sample)	S3 (mg CO_2/g of sample	HI (mg HC/g of TOC	OI (mg CO_2/ g TOC	Tmax (°C)
11	Al-Qusur	700–800 AD	7	22.61	28.47	120.55	6.66	533	29	429
2	B6	200–150 BC	1	38.32	20.31	164.28	12.38	428	32	428
4	B6	175 BC	1	8.16	4.13	40.26	1.97	493	24	426
14	B6	250 BC	4	32.01	23.83	124.93	10.41	390	32	426
15	B6	250 BC	4	24.38	15.19	90.64	8.31	371	34	426
1245	B6	205–140 BC	1	9.86	2.10	28.53	6.92	289	70	422
1246	B6	200–150 BC	1	18.78	9.44	86.36	5.09	459	27	425
1248	B6	205–140 BC	30	0.18	0.12	0.34	1.23	189	683	427
13	B6?	205–140 BC	1	29.36	19.25	133.63	7.93	455	27	427
152	F5	200–140 BC	7	20.10	15.57	100.36	4.05	499	20	424
153	F5	164–140 BC	8	28.57	32.79	132.42	5.58	463	19	424
154	F5	164–140 BC	8	33.04	30.45	132.67	6.94	401	21	426
994	F5	150 BC	7	26.46	21.54	115.98	5.56	438	21	425
996	F5	164–140 BC	1	22.95	25.35	99.44	4.96	433	22	423
998	F5	205 BC	1	26.36	24.80	114.64	5.27	435	20	425
999	F5	205–140 BC	8	29.93	32.96	131.32	6.40	439	21	426
1000	F5	150 BC	8	31.31	29.38	127.46	6.15	407	20	425
6	F6	1400–1300 BC	6	12.65	7.06	58.47	3.79	462	29	423
7	F6	1400–1300 BC	7	22.57	15.58	104.15	7.79	461	34	427
8	F6	2000–1700 BC	4	26.38	12.77	119.66	6.8	453	25	431
52	F6	2000–1700 BC	4	22.46	10.11	86.86	8.48	386	37	432
988	F6	2000–1700 BC	4	22.74	15.15	89.46	4.31	393	19	429
989	F6	2000–1700 BC	4	27.23	14.30	109.34	4.96	402	18	430
990	F6	2000–1700 BC	4	24.96	13.87	96.93	4.89	388	20	428
991	F6	2000–1700 BC	4	25.61	15.18	96.42	5.18	376	20	426
992	F6	2000–1700 BC	4	25.95	17.22	101.60	4.67	392	18	428
993	F6	2000–1700 BC		18.98	13.09	84.78	3.23	446	17	428
997	F6	2000–1700 BC	6	21.34	16.56	90.53	4.27	424	20	428
1247	F6	1400–1300 BC	30	0.40	0.15	0.52	1.00	130	250	429
993a	F6	2000–1700 BC	18	8.90	7.33	46.52	3.80	523	43	428
993b	F6	2000–1700 BC	4	32.05	14.60	139.20	8.80	434	28	429
995	Failaka	150 BC	1	35.24	27.76	151.78	6.87	431	19	427
958	Umm an-Namel	2100–2000 BC	4	28.37	16.25	103.16	5.61	364	20	432
959	Umm an-Namel	2100–2000 BC	9	24.59	15.77	91.12	5.34	371	22	433
960	Umm an-Namel	2100–2000 BC	7	16.00	5.28	36.81	3.63	230	23	438
1112	Umm an-Namel	100 BC–200 AD	1	36.94	24.44	171.20	8.70	463	24	426
1113	Umm an-Namel	2100–2000 BC	1	20.70	5.91	57.95	5.76	280	28	436
1114	Umm an-Namel	undated	1	24.50	11.60	109.25	5.67	446	23	426
1115	Umm an-Namel	undated	1	21.24	8.80	92.17	4.38	434	21	427
1116	Umm an-Namel	100 BC–200 AD	1	32.85	18.69	153.69	7.92	468	24	426
1117	Umm an-Namel	2100–2000 BC	1	18.49	7.84	85.88	4.18	464	23	428

Key to abbreviations: TOC = Total Organic Carbon; S1 = thermovaporised hydrocarbons; S2 = pyrolysed hydrocarbons; S3 = CO_2 generated between 300 and 390°C; HI = Hydrogen Index; OI = Oxygen Index; Tmax = Temperature of the maximum of the S2 peak.

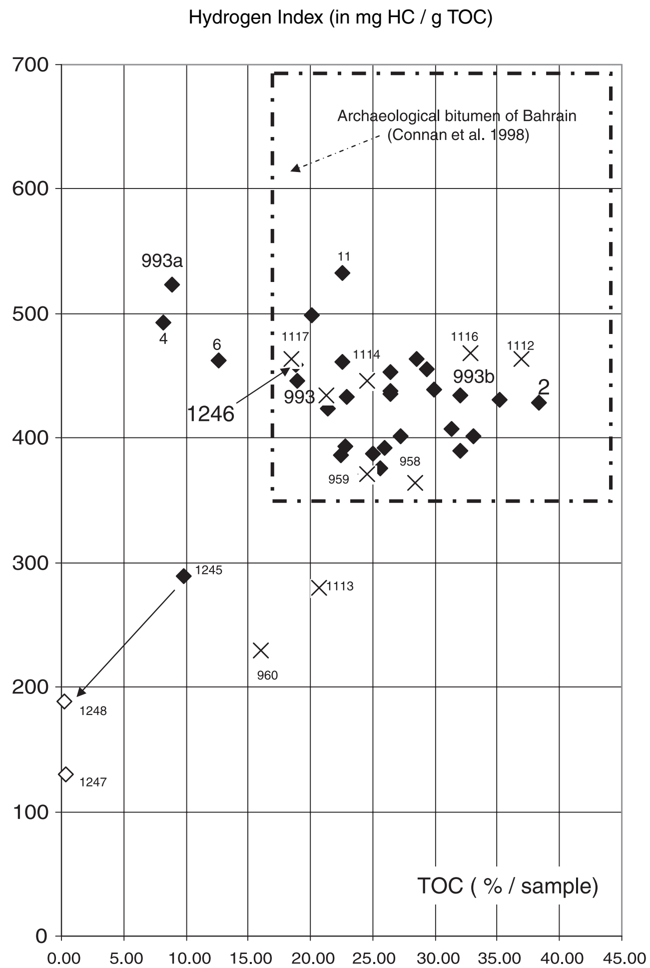


Fig. 6.
Hydrogen Index (HI), in mg of hydrocarbons (HC) per g of Total Organic Carbon (TOC) vs TOC (as % by weight of raw sample), measured by Rock-Eval pyrolysis.

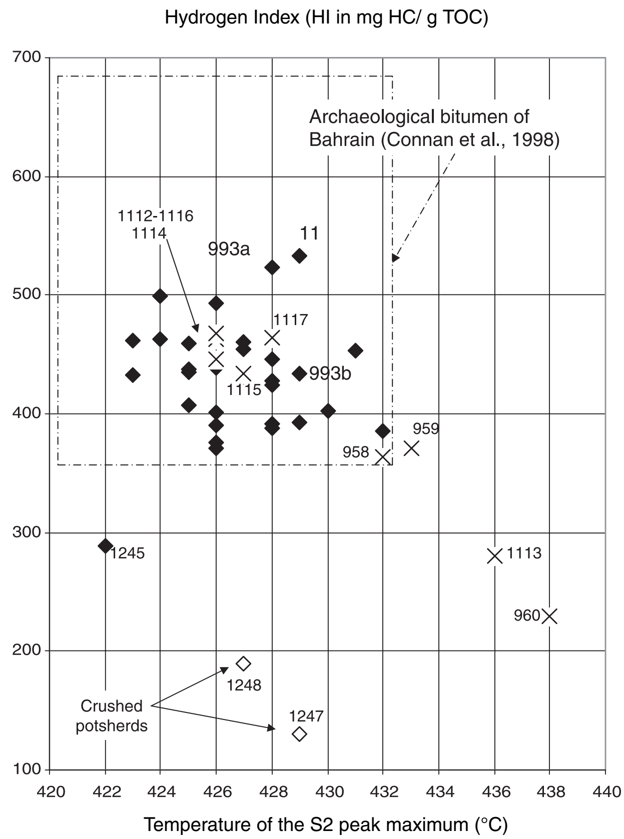


Fig. 7.
Hydrogen Index (HI), in mg of hydrocarbons (HC) per g of Total Organic Carbon (TOC) vs Tmax (Temperature of the S2 peak maximum, in °C).

higher Tmax. These characteristics fully confirm the explanation that both contain carbonised organic matter. The potsherd residues (sample nos 1248 and 1247) are also set apart from the archaeological bitumen, with lower HI but comparable Tmax. This information will be revisited later when the molecular data is discussed.

In order better to understand the bulk pyrolysis data, several cross plots were experimentally drawn. No relationship was apparent between the HI (Hydrogen Index), the OI (Oxygen Index in mg CO_2/g TOC), the mixture type and the sample date. The plot of Tmax vs the mixture types (Fig. 8) provides some clue to explain the possible variations of some Rock-Eval parameters. As expected Tmax was found to be generally higher in vegetal-containing mixtures while HI tends to be lower. Sample no. 11, the spindle whorl, was likely to have been prepared using bitumen with no vegetal input (Figs 7–8).

Mineralogical and petrographical analysis of Failaka samples

Several samples from Failaka were selected to examine their mineralogical additives by X-Ray Diffraction analysis. Thin sections, perpendicular to the slab (Fig. 9a), were prepared for three samples (nos 152, 153, 154) and examined by M. Veber. At first glance, the whole thin section of sample no. 153, shown here as an example, is dominated by a bitumen background (Fig. 9b). At a higher magnification, carbonates and quartz are visible (Fig. 9c). Quartz grains are rounded with a granulometry of 350 μ and carbonates are mainly bioclasts (foraminifera and lamellibranchia, Fig. 9d). Bioclasts were also found in mortars, plasters and adhesives

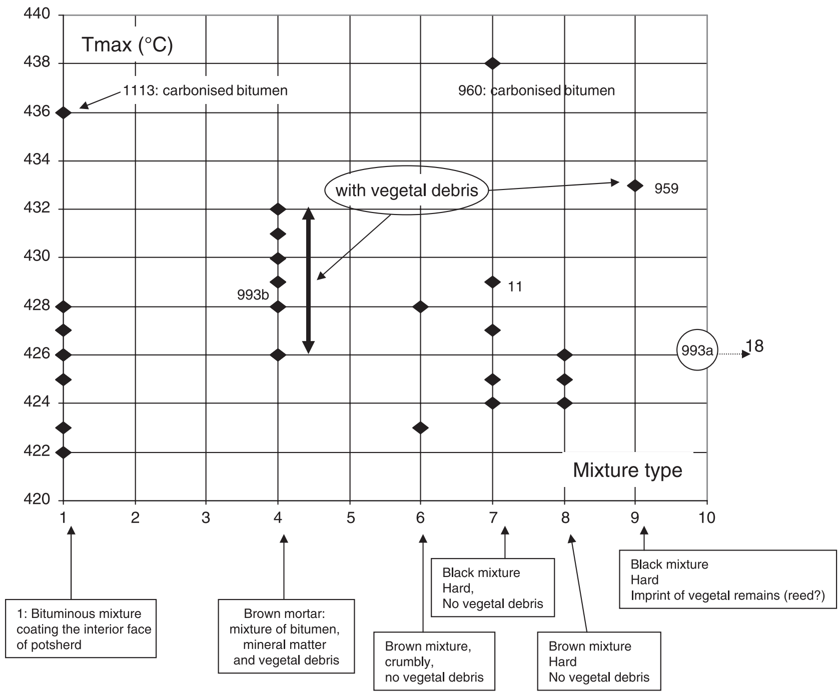
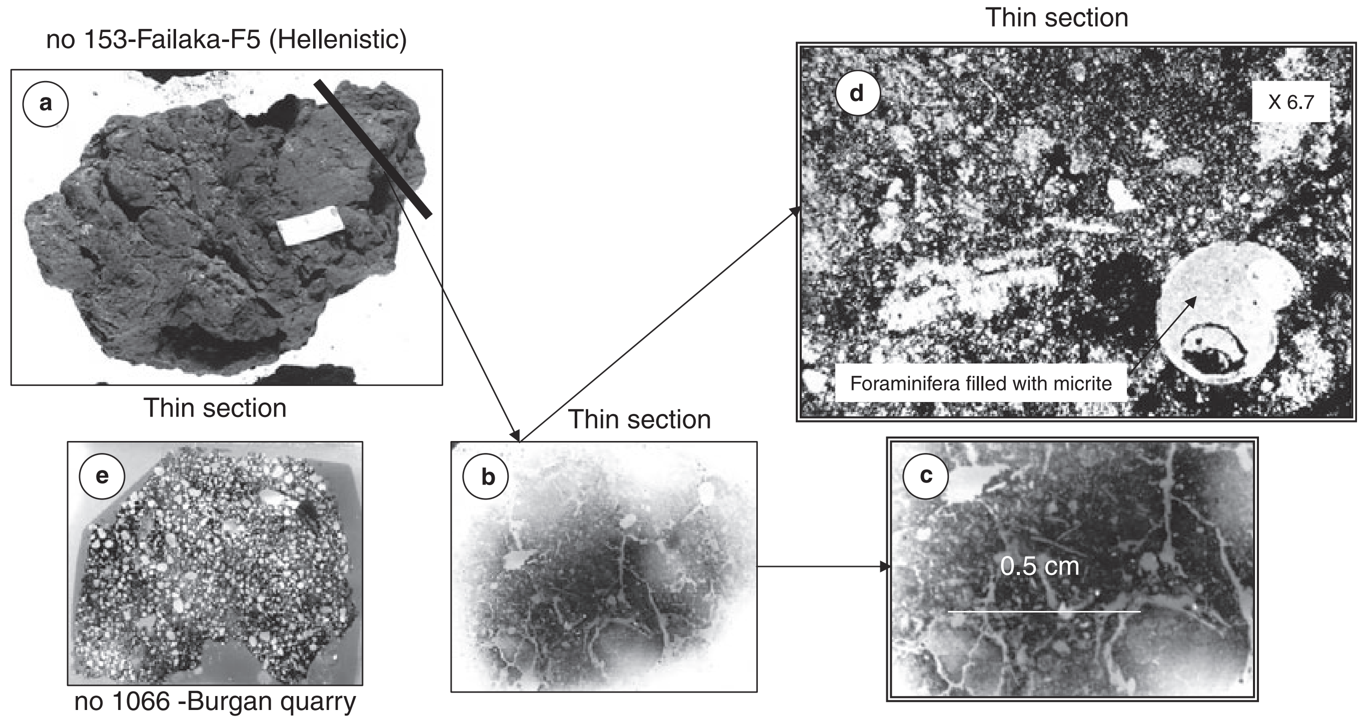


Fig. 8.
Tmax (Temperature of the S2 peak maximum, in °C) vs mixture type.

used on the floors, walls and pipework of Bronze Age archaeological remains on Failaka (32). In the carbonates, some dolomitisation has taken place.

The archaeological bituminous mixtures show a clearly contrasting pattern when compared to outcropping natural tar sands from the Burgan area. In these geological tar sands, rounded quartz grains (granulometry of 350–500 μ) predominate in the thin section (no. 1066, Fig. 9e). Consequently, sample no. 153, found in an enclosure thought to be a workshop where it was prepared, seems to have been manufactured by mixing bitumen with quartz and carbonate sands from the Failaka outcrops and beaches. At this stage of the study an input of Burgan tar sands should not be excluded. However, the amount of true bitumen, higher than 30%, indicates that the mixture was necessarily enriched by the addition of pure bitumen, for the oil-stained sand from Burgan never shows more than 10% bitumen. These hypotheses will be revisited when other information is presented.

The mineralogical composition of some of the archaeological bitumens from Failaka and of tar sand samples from the Burgan area were compared using X-Ray Diffraction analysis (Table 5). The plot of % calcite + dolomite as a function of % quartz (Fig. 10a) clearly differentiates the tar sands of the Burgan area from the archaeological samples. Archaeological sample compositions are highly diversified and the carbonate content varies from 0% to 60%. Evidently the carbonates in the bituminous amalgams were deliberately added, and Burgan tar sands may in theory have been used as an additive (hence the quartz input?) to prepare the mixtures. The addition of Burgan tar sand is not necessary, however, as quartz is available on Failaka, as demonstrated by its identification in mortars (33). The plot of the percentage of major identified minerals (calcite + dolomite + quartz) vs mixture types (Fig. 10b) reveals a marked trend: the mineral content increases from Type 1, mainly comprising thin films of bituminous matter covering the interior face of potsherds (except sample no. 13), to Type 18, which are tar sands. This property suggests that the thin films scraped from potsherds are mainly composed of bitumen and baked clay from the pottery, whereas other archaeological samples are mixtures that have been processed by combining bitumen, tar sands (?), clay and beach sands.



sample number	location	quartz	carbonates	estimated Minerals %/ thin section	calcite%	quartz%	feldspath %
153	Failaka	rounded quartz with a granulometry of 350µ	sand formed of bioclasts: foraminiferas, lamellibranchia	10	30	70	
176	Burgan hill	well sorted rounded quartz 300-500µ (eolian sand?) and 50µ		65		80	20

Fig. 9.
Comparison of thin sections and mineral composition of one mortar-type sample from Failaka and Burgan oil-stained sandstones. **a.** sample no.153 (F5, Hellenistic); **b.** thin section of sample no.153; **c.** zoom of thin section b; **d.** thin section of sample no.153 at higher magnification (×6.7) showing foraminifera filled with micrite. Table of data with mineralogical composition estimated from thin sections.

Detailed analysis of organic matter

Extractable Organic Matter (EOM) vs Insoluble Organic Matter (IOM)

Insights into the composition of the organic matter were gained by taking into account the % TOM (% Total Organic Matter = % Total Organic Carbon × 1.25), the % EOM (% Extractable Organic Matter measured by dichloromethane extraction) and the % IOM (% Insoluble Organic Matter = TOM–EOM). The results, listed in Table 6, are presented in Fig. 11 as a function of mixture types. In that figure, samples containing carbonised organic matter were discarded and Type 1 was split into two subgroups: thin films on one side, thick coats on the other side. The results (Figs 11a–b) confirm the validity of the distinction: in thin films the IOM predominates (average 68.8%) whereas in thick coats the situation is reversed, with bitumen largely dominant (24.8% IOM). It appears that thin films on potsherds are particularly rich in oxidised bitumen that has been largely converted into insoluble matter, whereas thick coats are likely to be the remains of manufactured bituminous amalgams stored in jars, as also seen at [c]Akkaz (34).

Figures 11d–e provide a comparison of bituminous amalgams with and without apparent vegetal debris. Compositions are variable in both groups but, as expected, Insoluble Organic Matter tends to

Table 5. Mineralogical composition of selected samples from Failaka, with a comparison with oil-stained sands from Burgan.

sample number	location	Mixture type	% quartz	% calcite	% dolomite	% calc.+dolo.
11	Al-Qusur	7	6	38	6	44
1	B6	1	5	13	0	13
2	B6	1	6	17	0	17
3	B6	1	16	6	0	6
4	B6	1	4	0	0	0
14	B6	4	16	23	1	24
15	B6	4	8	31	5	36
13	B6?	1	4	39	2	41
53	Burgan	18	80	1	0	1
1056	Burgan quarry	18	61	0	0	0
1057	Burgan quarry	18	55	17	0	17
1062	Burgan quarry	18	55	11	2	13
1066	Burgan quarry	18	72	0	0	0
152	F5	9	33	15	1	16
153	F5	8	11	51	6	57
5	F6	1	17	15	2	17
6	F6	6	21	11	3	14
7	F6	7	16	18	0	18
8	F6	4	11	18	2	20
52	F6	4	9	19	2	21

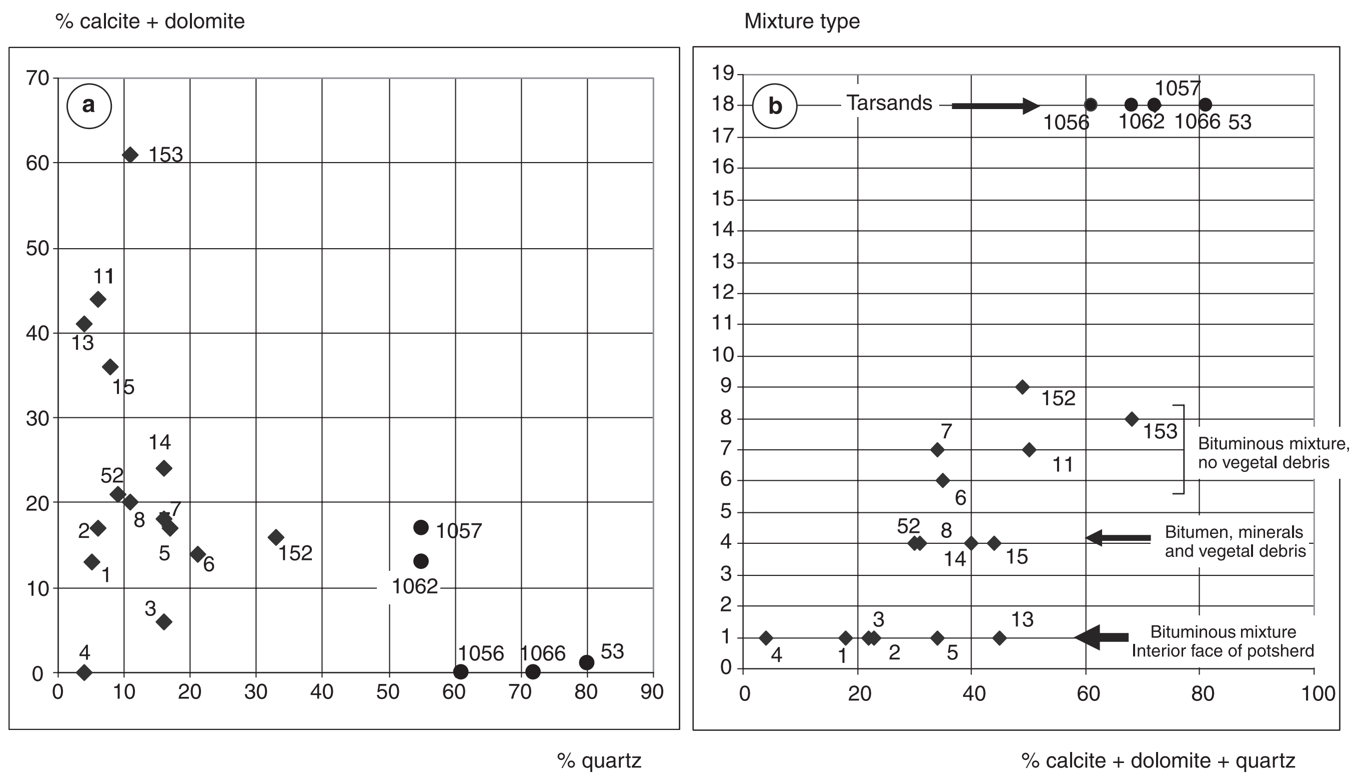


Fig. 10.
Mineralogical composition and mixture type. **a.** % calcite + dolomite vs % quartz; **b.** mixture type vs % calcite + dolomite + quartz.

be higher in types that show obvious vegetal remains. The archaeological tar sands (Fig. 11c), well consolidated and preserved, contain just 12% insoluble bitumen. The exceptions are crushed potsherds (Fig. 11f) and the thin films coating potsherds (Fig. 11a), which are particularly enriched

Table 6. Quantitative measurement of the relative content of Bitumen (EOM) and Insoluble Organic Matter (IOM) in the bituminous mixtures of Failaka and Umm an-Namel.

sample number	mixture Type	site	% TOC/ sample	% TOM/ sample	% EOM/ sample	% IOM/ sample	% EOM/ TOM	% IOM/ TOM	% IOMBit/ IOM	% IOM Vegetal/IOM
2	1	B6	38.3	47.9	15.9	32.0	33.2	66.8	66.8	0
4	1	B6	8.2	10.2	4.7	5.5	46.1	53.9	53.9	0
14	4	B6	32.0	40.0	28.5	11.5	71.2	28.8	27	1.8
15	4	B6	24.4	30.5	14.2	16.3	46.6	53.4	27	26.4
1245	1	B6	9.9	12.3	1.7	10.6	14.2	85.8	85.8	0
1248	30	B6	0.2	0.2	0.0	0.2	15	85	85	0
13	1	B6?	29.4	36.7	26.7	10.0	72.8	27.2	27.2	0
152	7	F5	20.1	25.1	19.5	5.7	77.5	22.5	22.5	0
154	8	F5	33.0	41.3	39.1	2.2	94.8	5.2	5.2	0
6	6	F6	12.7	15.8	9.0	6.8	56.9	43.1	43.1	0
7	7	F6	22.6	28.2	9.4	18.8	33.3	66.7	66.7	0
8	4	F6	26.4	33.0	14.7	18.3	44.6	55.4	27	28.4
52	4	F6	22.5	28.1	9.4	18.7	33.5	66.5	27	39.5
988	4	F6	22.7	28.4	16.6	11.8	58.4	41.6	27	14.6
992	4	F6	26.0	32.4	13.0	19.4	40.1	59.9	27	32.9
1247	30	F6	0.4	0.5	0.2	0.3	39.4	60.6	60.6	0
993a	18	F6	8.9	11.1	9.8	1.4	87.8	12.2	12.2	0
993b	4	F6	32.1	40.1	24.9	15.2	62.1	37.9	27	10.9
958	4	Umm an Namel	28.4	35.5	7.5	28.0	21.0	79.0	27	52
959	9	Umm an Namel	24.6	30.7	3.3	27.5	10.7	89.3	27	62.3
960	7	Umm an Namel	16.0	20.0	6.3	13.7	31.5	68.5	68.5	0
1112	1	Umm an Namel	36.9	46.2	45.6	0.6	98.8	1.2	1.2	0
1113	1	Umm an Namel	20.7	25.9	24.1	19.6	24.1	75.9	75.9	0
1114	1	Umm an Namel	24.5	30.6	20.5	10.1	67.1	32.9	32.9	0
1115	1	Umm an Namel	21.2	26.6	13.1	13.5	49.2	50.8	50.8	0
1116	1	Umm an Namel	32.9	41.1	31.3	9.8	76.2	23.8	23.8	0
1117	1	Umm an Namel	18.5	23.1	20.1	3.1	86.8	13.2	13.2	0
1222	30	Umm an Namel	36.6	45.7	1.0	44.7	2.2	97.8	97.8	0

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

in Insoluble Organic Matter. The surface and the interior of potsherds seem to concentrate the resistant polymerised organic matter.

The estimation of an average percentage of insoluble bitumen in archaeological samples of this set has been established by using data from samples that are devoid of visible vegetal organic debris. This average has been found to be around 27% of IOM. This value, which is higher than the value found in the geological tar sand sample no. 993a (12% IOMBit/IOM: Fig. 11c), is quite comparable to the previous estimation carried out in the As-Sabiyah study (35) in which the IOMBit was estimated to be 20% of IOM. On the basis of this average value, the percentage of IOMVegetal was deduced (Table 6). A plot of the results in a ternary diagram (% IOMBit, % IOMVegetal, % EOM, Fig. 12) shows no particular differences between the Failaka and Umm an-Namel samples. Similar types of bituminous materials are found at both sites, but two outstanding features can be mentioned:

- samples with detectable vegetal remains, and especially sample no. 993b, all derive from the remains of used bituminous mixtures, whereas all the other samples originate from crusts covering the interior face of potsherds;
- samples from on and within potsherds are similar when the layer is very thin (e.g. sample nos 1 and 1248, respectively adhering to the surface of and extracted from the interior of the same sherd), but differ widely when the coat is thick (e.g. sample nos 1117 and 1222, respectively adhering to and from inside the same sherd, but with very different proportions of IOMBit and EOM).

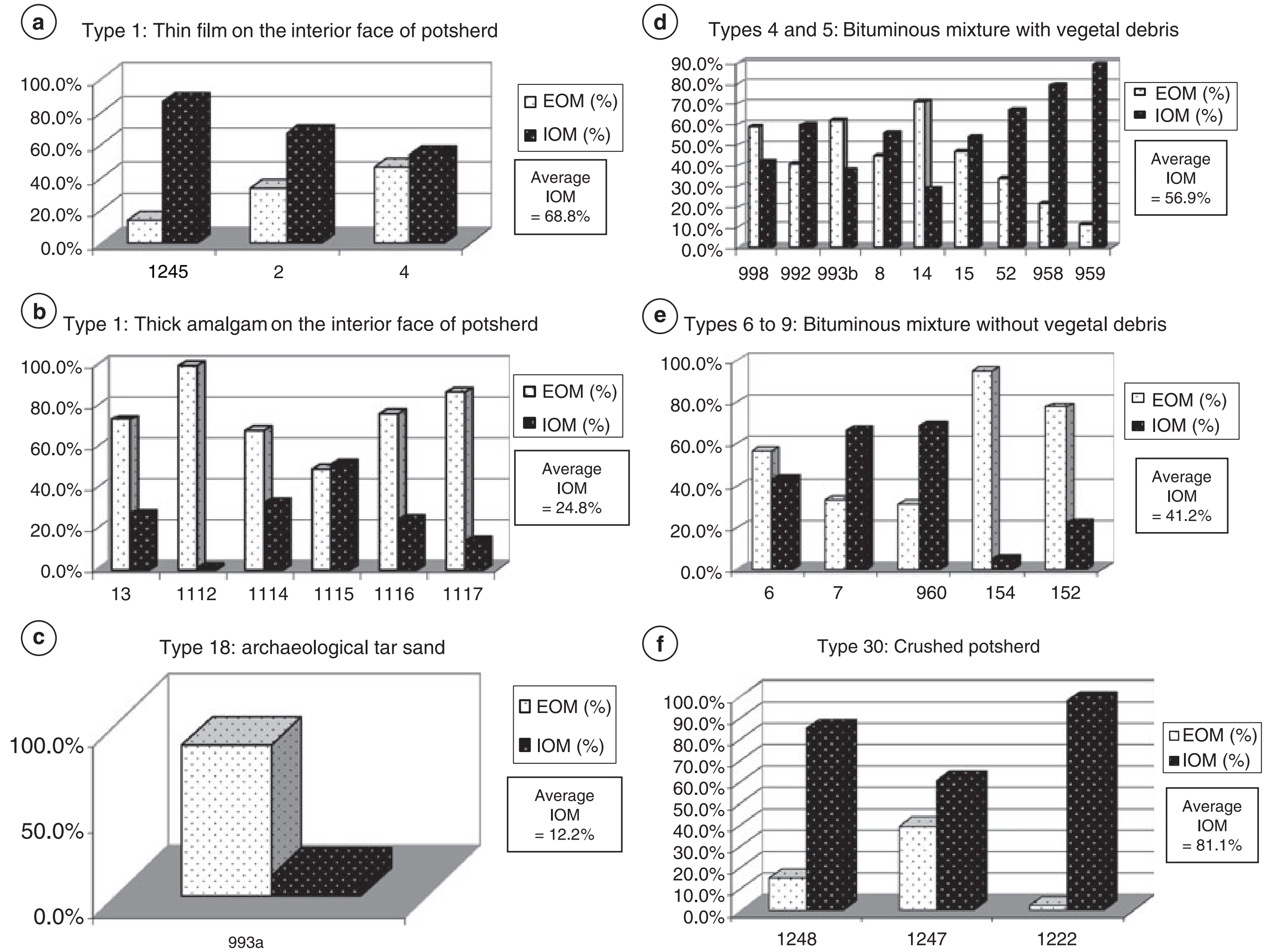


Fig. 11.
EOM (Extractable Organic Matter, i.e. soluble bitumen) and IOM (Insoluble Organic Matter, i.e. IOBitumen = insoluble bitumen + IOMVegetal = insoluble organic matter of vegetal origin) in the various types of samples; **a.** Type 1: thin film on the interior face of potsherd; **b.** Type 1: thick amalgam on the interior face of potsherd. **c.** Type 18: archaeological tar sand; **d.** Types 4 and 5: bituminous mixture with vegetal debris; **e.** Types 6 to 9: bituminous mixture without vegetal debris; **f.** Type 30: crushed potsherd.

These results lead to the following observations:

- firstly, the bitumen-enriched mixtures present on potsherds may be the remnants of pristine bituminous mixtures which were stored or transported in jars, or used to waterproof them, whereas the bituminous mixtures with vegetal debris are materials which were reprocessed for various applications, especially for use as mortar in buildings;
- secondly, insoluble polymerised organic matter concentrates at the interface with or within the potsherd, through a combined effect of cracking and oxidation.

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. This was in order to provide basic data that are indicative of the nature of the sample. In geological oil seeps the amount of saturates and aromatics is generally much higher than in archaeological bitumens. Through weathering of geological bitumen, which entails biodegradation, oxidation, evaporation, water washing, photo-oxidation, etc., the aromatics are severely affected and converted into

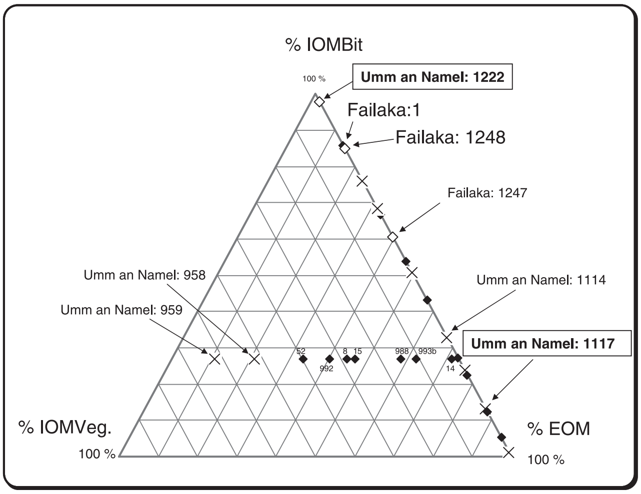


Fig. 12.
Composition of Organic Matter in a ternary diagram: % IOMBit vs %IOMVeg. vs % EOM.

resins and mainly asphaltenes. Consequently the gross composition often discriminates an archaeological bitumen, which was severely transformed by oxidation-biodegradation and is often extremely rich in asphaltenes, from a natural asphalt or bitumen, which may have been biodegraded but not oxidised.

The gross compositions of the extracts were calculated (Table 7) and presented in a ternary diagram (''saturates + aromatics'' vs ''aromatics'' vs ''asphaltenes''), reproduced in Fig. 13. In addition to the archaeological samples, three samples (nos 176, 177, 178) from oil-stained sands outcropping at Burgan Hill in inland Kuwait and three samples (nos 1056, 1057, 1062) collected in 1996 from the surface in an open quarry close to Burgan Hill were added as reference samples for geological tar sands. The results obtained from crushed potsherds (sample nos 1245, 1247, 1248, 1222) were also included in the synthesis, to be compared with their archaeological bituminous mixtures.

The results shown in Fig. 13 indicate the following:

- all the archaeological samples cluster within the area previously defined as the zone of typical archaeological bitumens. The asphaltenes largely predominate whereas hydrocarbons are minor constituents. Of particular interest is that sample no. 993a, which was expected to behave like a geological sample, possesses a gross composition similar to the archaeological sample no. 993b. This suggests that weathering has strongly affected it and has induced the same gross compositional changes seen in its archaeological neighbours. Although apparently a tar sand and resembling a geological sample, sample no. 993a should also be considered an archaeological sample due to its archaeological context, and as such its gross properties result from transformations since the Early Dilmun period;
- freshly collected geological samples, on the other hand, are well differentiated from the archaeological samples and still contain significant amounts of hydrocarbons, especially aromatics. This means that if they were already biodegraded, as underlined in a previous paper (36), their degradation by weathering and especially oxidation was of limited extent;
- as a general statement, the amount of hydrocarbons in the potsherd extracts is much greater than in the bituminous mixtures coating their interior faces (e.g. sample nos 1245 and 5, sample nos 1222 and 1117, sample nos 1248 and 1245).

The origin of the bitumen, as indicated by isotopic data on asphaltenes

Carbon isotopic values of asphaltenes ($\delta^{13}C$ in ‰/PDB, Table 7) provide reliable information on the origin of asphalts, because this parameter is not drastically modified by the intense weathering phenomena that affect the gross and the molecular composition of bitumen in oil seeps and archaeological contexts. In contrast, δD (in ‰/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 all archaeological samples from the Kuwaiti sites, namely [c]Akkaz (37), As-Sabiyah (38), Failaka and Umm an-Namel (see Fig. 14). The heavy values recorded in samples from the four archaeological sites confirm that the bitumens are heavily weathered. In this respect sample nos 993a and 993b do not exhibit different behaviour, as weathering has equally altered the presumed geological sample from Burgan.

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 that represents the true bitumen. Values on bulk samples, as used by Schwartz, Hollander and Stein (39) are unsuitable because they provide false references for

Table 7. Gross composition of the extractable organic matter and isotopic data of asphaltenes from archaeological samples from Failaka and Umm an-Namel.

sample number	mixture type	site	Sat10	Aro10	Res10	Asp100	$\delta^{13}c_{asp}$	δD_{asp}
11	7	Al-Qusur					−27.7	−70
1	1	B6	3.3	2.4	43.9	50.4	−27.9	−58
2	1	B6	3.9	2.0	32.8	61.3	−27.9	−49
3	1	B6	2.1	2.7	43.1	52.1	−27.9	−58
4	1	B6	1.5	1.5	38.2	58.8	−27.9	−61
14	4	B6	2.5	1.9	20.8	74.8	−28.0	−56
15	4	B6	2.6	2.5	28.0	66.9	−28.1	−56
1245	1	B6	4.5	8.3	48.4	38.8	−28.0	−81
1248	30	B6	13.3	9.5	71.4	5.8	−27.9	−83
13	1	B6?	2.9	1.7	26.1	69.3	−27.8	−56
53	18	Burgan	14.5	17.4	57.2	10.9	−27.2	−80
176	18	Burgan	9.0	15.3	54.1	21.6	−27.3	−67
177	18	Burgan	23.1	27.1	39.9	9.9	−27.6	−72
178	18	Burgan	31.0	31.0	30.8	7.2		
1056	18	Burgan	17.8	26.1	50.1	6.0	−27.7	
1057	18	Burgan	10.9	29.4	40.7	19.0	−27.5	−91
1062	18	Burgan	16.1	22.0	28.9	33.0	−27.5	
152	7	F5	2.6	2.4	21.6	73.4	−27.8	−65
153	8	F5	4.7	5.2	26.3	63.8	−27.8	−63
154	8	F5	4.8	2.4	19.3	73.5	−27.8	−63
988	4	F5	2.5	4.4	20	73.1	−28.0	−73
996	1	F5	2.2	2.7	14.1	80.7	−27.5	−69
999	8	F5	3.1	5.2	12.3	79.4	−27.6	−79
5	1	F6	2.1	1.6	33.1	63.2	−27.8	−51
6	6	F6	3.3	0.9	26.6	69.2	−27.9	−58
7	7	F6	3.1	1.6	27.3	68.0	−28.3	−56
8	4	F6	3.3	3.5	37.2	56.0	−27.7	−64
52	4	F6	5.7	3.0	34.4	56.9	−28.1	−64
992	4	F6	3.3	4.6	28	64.1	−27.9	−78
1247	30	F6	5.6	5.5	69.4	19.5	−27.5	−68
993a	18	F6	1.5	3.9	20	74.6	−27.5	−75
993b	4	F6	2.2	3.4	16.2	78.2	−28.1	−71
958	4	Umm an Namel	3.6	4.1	35.8	56.5	−27.6	−75
959	9	Umm an Namel	4.0	4.7	36.9	54.4	−27.7	−61
960	7	Umm an Namel	3.1	7.4	40.2	49.3	−27.2	−65
1112	1	Umm an Namel	3.1	5.7	8.7	82.5	−28.1	−57
1113	1	Umm an Namel	4.6	8.0	42.9	44.5	−27.6	−62
1114	1	Umm an Namel	2.2	3.5	17.4	76.9	−28.2	−56
1115	1	Umm an Namel	2.5	3.9	18.5	75.1	−28.2	−62
1116	1	Umm an Namel	2.0	2.4	14.3	81.3	−28.2	−58
1117	1	Umm an Namel	1.2	2.6	16.8	79.4	−27.7	−54
1222	30	Umm an Namel	5.0	5.8	41.4	47.8	−27.4	−58

Key to abbreviations: Sat10 = % ''saturates'' in extract; Aro10 = % ''aromatics'' in extract; Res10 = % ''resins'' in extract; Asp100 = % ''asphaltenes'' in extract; δ^{13}Casp = δ^{13}C of asphaltenes (in ‰/PDB); δDasp = δD of asphaltenes (in ‰/SMOW).

the bitumen: they are extensively influenced by the carbonate content of the sample as demonstrated in a previous paper (40). δ^{13}C of asphaltenes do correspond to bitumen and have been plotted as a function of δD of asphaltenes (Fig. 14) and the date of the samples (Fig. 15).

Figure 14 illustrates the striking difference between bitumens of Failaka, As-Sabiyah and ^{c}Akkaz. The Sabiyah material has been identified as originating from Burgan, inland Kuwait (41), while the archaeological bitumens from ^{c}Akkaz originate from Iran, probably Luristan (42). The plot of δ^{13}C of

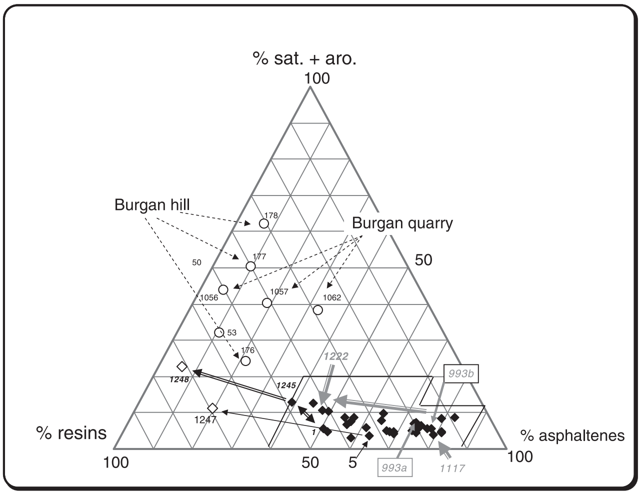


Fig. 13.
Ternary diagram of the gross composition of the organic matter extracted with chloroform or dichloromethane (''saturates + aromatics'', ''resins'' and ''asphaltenes''), giving a comparison between the bituminous samples of Umm an-Namel and Failaka including the crushed potsherds and the oil seeps from Burgan (Kuwait).

asphaltenes as a function of the sample date (Fig. 15), along with the δ^{13}C range of oil seeps from Iran, Iraq and Kuwait, suggests some additional comments:

- sample no. 993a falls within the range of Burgan oil seeps;
- samples from Failaka do not show any trends from the Dilmun period to the Kassite, Hellenistic and even Early Islamic periods. Values fall within the range of oil seeps both in Iran (Deh Luran area) and in Iraq (northern area);
- the samples from Umm an-Namel did not come from the same source during the Early Dilmun and Parthian periods;
- examination of δ^{13}C of asphaltenes does not completely solve the problem of the origin of the bitumen from Failaka and Umm an-Namel, but it already indicates that it did not have a local Kuwaiti source (with one possible exception), and that it was not imported from Khuzistan, Iran.
- at this stage of the analysis, northern Iraq and the Hit area, as well as the Luristan Province of Iran, are all good candidates to be the source of bitumen. Subsequent genetic parameters are therefore needed to upgrade this pre-diagnostic and trace the source.

The origin of the bitumen, as indicated by sterane and terpane biomarkers and isotopic data on asphaltenes
''Saturates'' were analysed by GC-MS (Gas Chromatography-Mass Spectrometry) in order to exam-

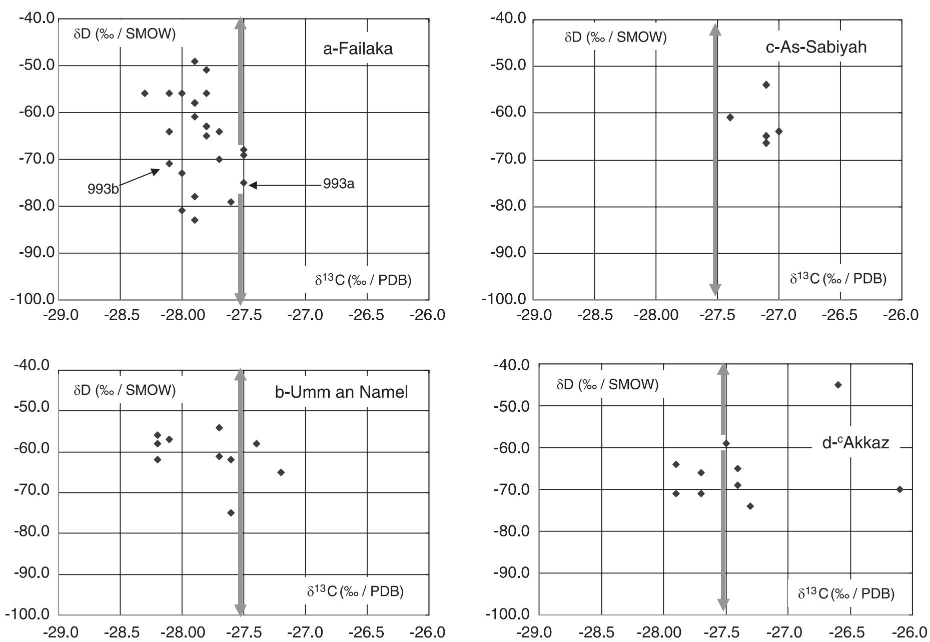


Fig. 14.
δ^{13}C vs δD of asphaltenes from several archaeological sites in Kuwait; **a.** bituminous mixtures from Failaka; **b.** bituminous mixtures from Umm an-Namel; **c.** bituminous mixtures of As-Sabiyah; **d.** bituminous mixtures of ^{c}Akkaz.

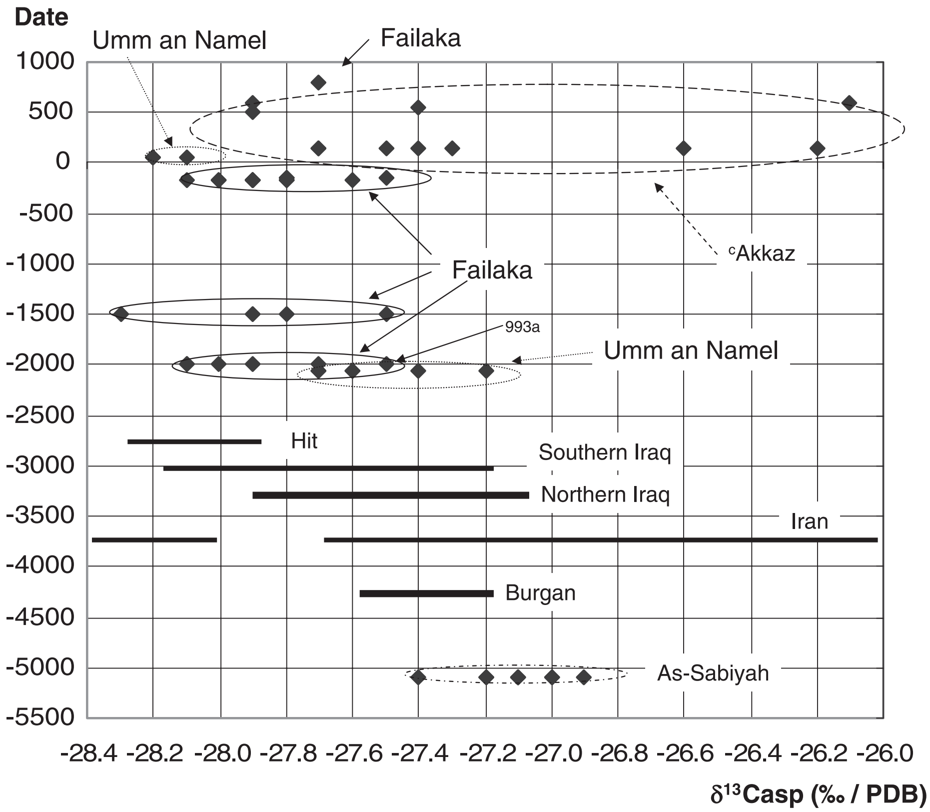


Fig. 15.
δ^{13}C of asphaltenes from archaeological sites from Kuwait as a function of the sample date: comparison to oil seep references from Iraq, Iran and Kuwait.

ine 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 bitumens, biomarker fingerprints display various degrees of alteration (Table 8) from almost unaltered patterns (State 0) to moderately altered ones (State 6). Between States 0 and 6, terpane patterns are apparently preserved, and may be used to define genetic parameters reliable enough to identify the origin of the associated bitumen. One should remember, however, that terpanes might 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 these patterns are apparently not affected.

The review of regular sterane composition (Table 9), represented in ternary diagrams (% C_{27}, % C_{28} and % C_{29} ββsteranes, Fig. 16), show that the Failaka (Fig. 16a) and Umm an-Namel (Fig. 16b) archaeological samples cluster within the same area of the diagram. As a general rule, steranes extracted from the crushed potsherds (sample nos 1248, 1247, 1222) are less altered than steranes isolated from bitumen coating their interior face (sample nos 1245, 5 and 1117). In other words, bitumen trapped within the porosity of the potsherd is better preserved than bitumen in direct contact with the local environment.

As already mentioned, sample no. 993a is different from sample no. 993b. It falls close to the archaeological samples from As-Sabiyah and within the area including sample no. 176, from Burgan (Fig. 16a). Comparison of sterane and terpane patterns (Fig. 17) of sample nos 993a–b with the Burgan oil seep sample no. 176, which is the closest to archaeological bitumens, reveals similarities with sample nos 993a and 176, but differences with sample no. 993b. As striking are differences between the Tm to Ts ratios and the Gammacerane to C31αβhopaneR ratios. However, even if sample no. 993a resembles sample no. 176, the match is not perfect, as the two samples do not have the same state of alteration: sample no.

Table 8. Summary of the characteristic properties of steranes and terpanes from Failaka and Umm an-Namel: evaluation of the degree of alteration.

sample		Steranes			Diasteranes	Terpanes			degree
number	site	C_{21}-C_{22}	C_{27}-C_{29}	C_{29} αααR	C_{27}-C_{28}diast	tricyclopolypren.	oleanane	C_{27}-C_{35}Hop.	of alteration
11	al-Qusur	present	no alteration	unaltered	absent	low-traces	absent	no alteration	0a
1	B6	almost absent	less C27	unaltered	absent	altered	absent	no alteration	4a
2	B6	almost absent	less C27	unaltered	absent	altered	absent	no alteration	4a
3	B6	almost absent	less C27	unaltered	traces	altered	absent	no alteration	6a
4	B6	almost absent	almost no C27	unaltered	present-traces	absent	absent	no alteration	6a
14	B6	present	almost no C27	unaltered	absent	low-altered?	absent	no alteration	5a
1245	B6	absent	less C27	unaltered	absent	altered	absent	no alteration	4a
1248	B6	present-altered	less C27	altered	absent	altered	absent	no alteration	4b
13	B6?	present	less C27	unaltered	absent	low-altered?	absent	no alteration	4a
152	F5	present	almost no C27	unaltered	absent	low-altered	absent	no alteration	5a
996	F5	present	almost no C27	unaltered	absent	low-altered?	absent	no alteration	5a
999	F5	present	almost no C27	unaltered	absent	low present	absent	no alteration	5a
5	F6	present	almost no C27	unaltered	absent	present	absent	no alteration	6a
6	F6	absent	less C27	unaltered	present	absent	absent	no alteration	4a
7	F6	present	less C27	unaltered	absent	altered?	absent	no alteration	2a
8	F6	present	almost no C27	unaltered	absent	present	absent	no alteration	6a
52	F6	altered	almost no C27	unaltered	absent	low-altered	absent	no alteration	6a
988	F6	present	almost no C27	unaltered	absent	present	absent	no alteration	5a
992	F6	present	less C27	unaltered	absent	low-present	absent	no alteration	3a
1247	F6	present-altered	almost no C27	unaltered	absent	altered	absent	no alteration	6a
993a	F6	altered	almost no C27	unaltered	absent	low-altered	absent	no alteration	6a
993b	F6	present	less C27	unaltered	absent	low-altered?	absent	no alteration	3a
958	Umm an Namel	present	almost no C27	unaltered	absent	low-altered?	absent	no alteration	5a
959	Umm an Namel	present	almost no C27	unaltered	absent	low-altered?	absent	no alteration	5a
960	Umm an Namel	present	less C27	unaltered	absent	altered	absent	no alteration	4a
1112	Umm an Namel	altered	slightly altered?	unaltered	absent	low-altered?	absent	no alteration	1a
1113	Umm an Namel	altered	no alteration	unaltered	absent	absent	absent	no alteration	2a
1114	Umm an Namel	altered	almost no C27	unaltered	absent	altered	absent	no alteration	6a
1115	Umm an Namel	altered?	almost no C27	unaltered	absent	altered	absent	no alteration	6a
1116	Umm an Namel	absent	altered	unaltered	absent	altered	absent	no alteration	4a
1117	Umm an Namel	absent	almost no C27	unaltered	absent	altered	absent	no alteration	6a
1222	Umm an Namel	altered	less C27	unaltered	absent	low-altered	absent	no alteration	4a

Key to abbreviations: C_{21}-C_{22} = C_{21} and C_{22} steranes; C_{27}-C_{29} = C_{27} to C_{29}steranes; C_{29}αααR = 5α,14α,17α-20R-24-ethylcholestane; C_{27}-C_{29}diast. = C_{27}-C_{29}-diasteranes; tricyclopolypren. = tricyclopolyprenanes; C_{27}-C_{35}Hop. = C_{27} to C_{35} 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.

993a is more degraded than its geological counterpart. Taking into account the effect of this secondary alteration, one should reasonably consider that the archaeological sample no. 993a was imported from Burgan to Failaka.

Most archaeological samples from Failaka and Umm an-Namel do not exhibit the molecular characteristics of the Burgan oil seeps, but show patterns compatible with the oil seeps of northern and central Iraq. Fig. 18 illustrates these similarities in a comparison of samples from Failaka (no. 15) and Umm an-Namel (no. 1112) with an oil seep (no. 135) from Hit-Abu Jir in central Iraq. In order to investigate more precisely this hypothesis and to

Table 9. Biomarker ratios on steranes and terpanes of archaeological samples from Failaka and Umm an-Namel. Absolute quantitations were 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	site	date	Tp1	Tp2	Tp3	Tp20	Tt26	T32	Tp35	TS40	TS41	TP42	S51	S57	S63	S64	S65	S66	S67	S68
11	al-Qusur	700–800 AD	0.13	0.09	0.92	0.34	0.38	0.02	0.24	8.13	4.12	0.09	0.03	0.02	26.4	23.9	49.7	55.8	43.1	1.10
1	B6	205–140 BC	0.13	0.07	1.01	0.27	0.25	0.01	0.27	22.98	17.84	0.07	0.00	0.00	21.6	22.1	56.4	42.3	57.0	0.71
2	B6	200–150 BC	0.15	0.07	0.94	0.29	0.24	0.01	0.21	11.86	7.84	0.06	0.02	0.01	20.3	20.2	59.5	57.1	42.2	0.76
3	B6	200–150 BC	0.20	0.09	1.00	0.35	0.48	0.02	0.28	18.83	19.54	0.14	0.53	0.22	19.2	22.3	58.5	36.3	62.2	1.52
4	B6	175 BC																		
14	B6	250 BC																		
15	B6	250 BC	0.15	0.11	0.94	0.36	0.46	0.03	0.29	9.37	11.07	0.11	0.06	0.02	10.6	26.0	63.4	43.3	55.8	0.87
1245	B6	205–140 BC	0.14	0.08	1.00	0.35	0.17	0.01	0.29	14.95	9.81	0.06	0.03	0.01	23	23	54	54	45	1
1248	B6	205–140 BC	0.16	0.07	0.92	0.33	0.95	0.03	0.21	8.97	3.59	0.10	0.19	0.13	27	22	50	50	48	2
13	B6?	205–140 BC	0.21	0.09	1.28	0.34	0.34	0.03	0.27	25.82	11.75	0.26	0.17	0.04	18.3	24.9	56.8	36.3	61.8	1.91
152	F5	200–140 BC																		
153	F5	164–140 BC	0.17	0.09	1.09	0.37	0.56	0.04	0.21	10.07	4.54	0.23	0.14	0.03	7.1	28.0	64.8	54.3	44.6	1.10
154	F5	164–140 BC																		
996	F5	164–140 BC	0.25	0.14	1.18	0.47	0.44	0.07	0.29	13.45	3.92	0.43	0.12	0.04	15	26	59	48	50	2
999	F5	205–140 BC	0.27	0.16	1.08	0.53	0.49	0.09	0.36	10.60	3.82	0.55	0.13	0.05	8	29	62	40	57	2
5	F6	1400–1300 BC	0.24	0.14	1.31	0.38	0.57	0.05	0.22	11.38	5.67	0.24	.	.	1.4	27.0	71.7	40.3	58.4	1.31
6	F6	1400–1300 BC	0.17	0.08	0.99	0.23	0.53	0.02	0.20	12.57	3.38	0.15	1.42	0.48	21.8	22.6	55.6	31.4	65.9	2.76
7	F6	1400–1300 BC	0.15	0.09	0.97	0.34	0.68	0.03	0.24	8.30	4.43	0.09	0.04	0.02	21.1	23.4	55.6	55.9	43.2	0.91
8	F6	2000–1700 BC	0.18	0.07	1.11	0.26	0.24	0.02	0.20	14.58	5.88	0.12	0.17	0.01	1.4	22.4	76.1	43.3	55.3	1.39
52	F6	2000–1700 BC	0.16	0.09	0.94	0.30	0.26	0.02	0.25	13.66	7.31	0.12	.	.	6.3	23.9	69.8	39.8	59.4	0.85
988	F6	2000–1700 BC	0.20	0.13	0.91	0.49	0.37	0.04	0.29	7.12	4.33	0.14	0.08	0.02	13	28	60	53	46	1
992	F6	2000–1700 BC	0.18	0.14	0.88	0.47	0.40	0.03	0.36	7.62	4.10	0.14	0.07	0.04	19	26	55	49	50	1
1247	F6	1400–1300 BC	0.24	0.12	1.23	0.38	0.53	0.05	0.18	11.16	5.08	0.30	0.29	0.07	12	23	65	51	47	2
993a	F6	2000–1700 BC	0.33	0.13	1.08	0.52	0.14	0.03	0.21	8.33	3.89	0.40	0.11	0.03	2	24	74	44	55	1
993b	F6	2000–1700 BC	0.16	0.12	0.94	0.46	0.56	0.04	0.32	6.60	3.86	0.14	0.00	0.00	16	27	57	54	46	1
958	Umm an Namel	2100–2000	0.16	0.09	0.94	0.32	0.27	0.02	0.22	10.14	5.83	0.09	0.07	0.01	3.4	25.3	71.3	53.6	45.2	1.26
959	Umm an Namel	2100–2000	0.15	0.13	0.89	0.40	0.36	0.02	0.30	7.90	5.27	0.11	0.06	0.01	4.1	28.1	67.9	52.3	46.2	1.51
960	Umm an Namel	2100–2000	0.11	0.07	0.89	0.25	0.23	0.01	0.20	15.57	6.46	0.06	0.02	0.02	17.3	24.9	57.8	55.9	42.7	1.41
1112	Umm an Namel	100 BC–200 AD	0.13	0.09	0.84	0.36	0.57	0.02	0.27	12.64	5.30	0.20	.	0.04	24.5	22.5	53.1	48.4	50.2	1.40
1113	Umm an Namel	2100–2000	0.14	0.10	0.88	0.27	0.49	0.02	0.25	13.98	5.77	0.13	.	0.06	22.1	24.1	53.7	47.6	50.2	2.21
1114	Umm an Namel	100 BC–200 AD	0.18	0.08	0.92	0.35	0.32	0.02	0.31	9.27	5.35	0.15	.	0.01	2.5	21.3	76.2	52.1	47.3	0.51
1115	Umm an Namel	100 BC–200 AD	0.12	0.14	0.91	0.42	0.57	0.03	0.33	7.74	4.44	0.21	.	0.01	7.9	28.0	64.0	52.6	46.7	0.69
1116	Umm an Namel	100 BC–200 AD	0.11	0.09	1.00	0.30	0.26	0.01	0.27	15.59	8.28	0.13	0.06	0.02	23.2	24.7	52.1	52.3	46.7	0.97
1117	Umm an Namel	2100–2000	0.21	0.10	1.11	0.34	0.35	0.02	0.24	7.98	3.14	0.49	.	0.03	2.3	18.4	79.3	51.4	47.6	0.95
1222	Umm an Namel	2100–2000	0.18	0.08	1.30	0.23	0.22	0.02	0.18	16.73	7.78	0.16	0.04	0.01	16.7	21.5	61.8	48.5	50.2	1.4

Key to abbreviations: Tp1 = Ts/Tm = 18α-22,29,30-trisnorneohopane/17α-22,29,30-trisnorhopane; Tp2 = 29:5/29αβH = 29Ts/17α,21β-30-norhopane; Tp3 = 29αβH/30αβH = 17α,21β-30-norhopane/17α,21β-hopane; Tp20 = mH/Hop = 2α-methylhopanes/hopanes; Tt26 = 23:3/24:4 = C_{23}tricyclopolyprenane/C24–17,21-secohopane; T32 = tric/pent = tricyclopolyprenanes/triterpanes; Tp35 = GCRN/30αβH = Gammacerane/17α,21β-hopane; Tp37 = OLN/30αβH = 18α-oleanane/17α,21β-hopane; Ts40 = 27–30H/29st = 27–30hopanes/29steranes; Ts41 = *m/z* 191/*m/z* 217 = total terpanes/total steranes; Tp42 = 29+30SH/29 + 30αβH, 29 + 30 secohopanes/17α,21β-30-norhopane + 17α,21β-hopane; S51 = 27Sdia/29ααR = 27S-diasterane/5α,14α,17α-20R-24-ethylcholestane; S57 = 27Sdia/29αααR = C27diaste/5α,14α,17α-20R-24-ethylcholestane; S63 = %C27ββ = % 5α,14β,17β-20S+20R-cholestane; S64 = %C28ββ = 5α,14β,17β-20S+20R-24-methylcholestane; S65 = %C29ββ = 5α,14β,17β-20S+20R-24-ethylcholestane; S66 = Reg (*m/z* 218) = % regular steranes αββ determined by *m/z* 218; S67 = Met(*m/z* 232) = % methylsteranes determined by m/z 232; S68 = Dia(*m/z* 259) = % diasteranes determined by *m/z* 259.

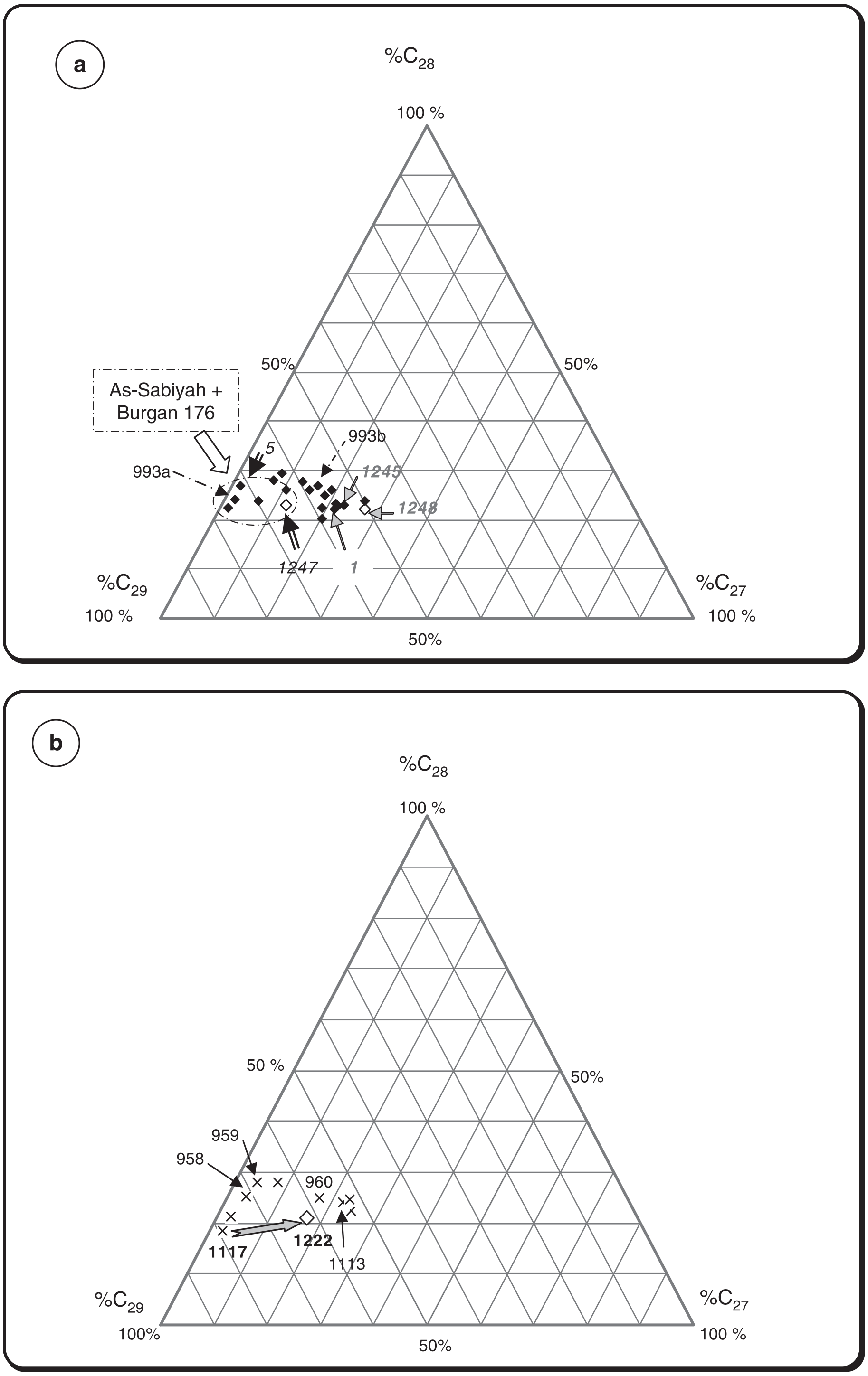


Fig. 16.
Ternary diagram giving the ββsteranes composition: comparison between samples from Failaka, Umm an-Namel, As-Sabiyah, together with geological references from Burgan (Kuwait).

confirm the relationship, molecular ratios were acquired and compared. These ratios are listed in Table 9.

Specific molecular ratios (e.g. Ts/Tm, GCRN/C30αβH), recognised previously as reliable genetic parameters for differentiating bitumen from various

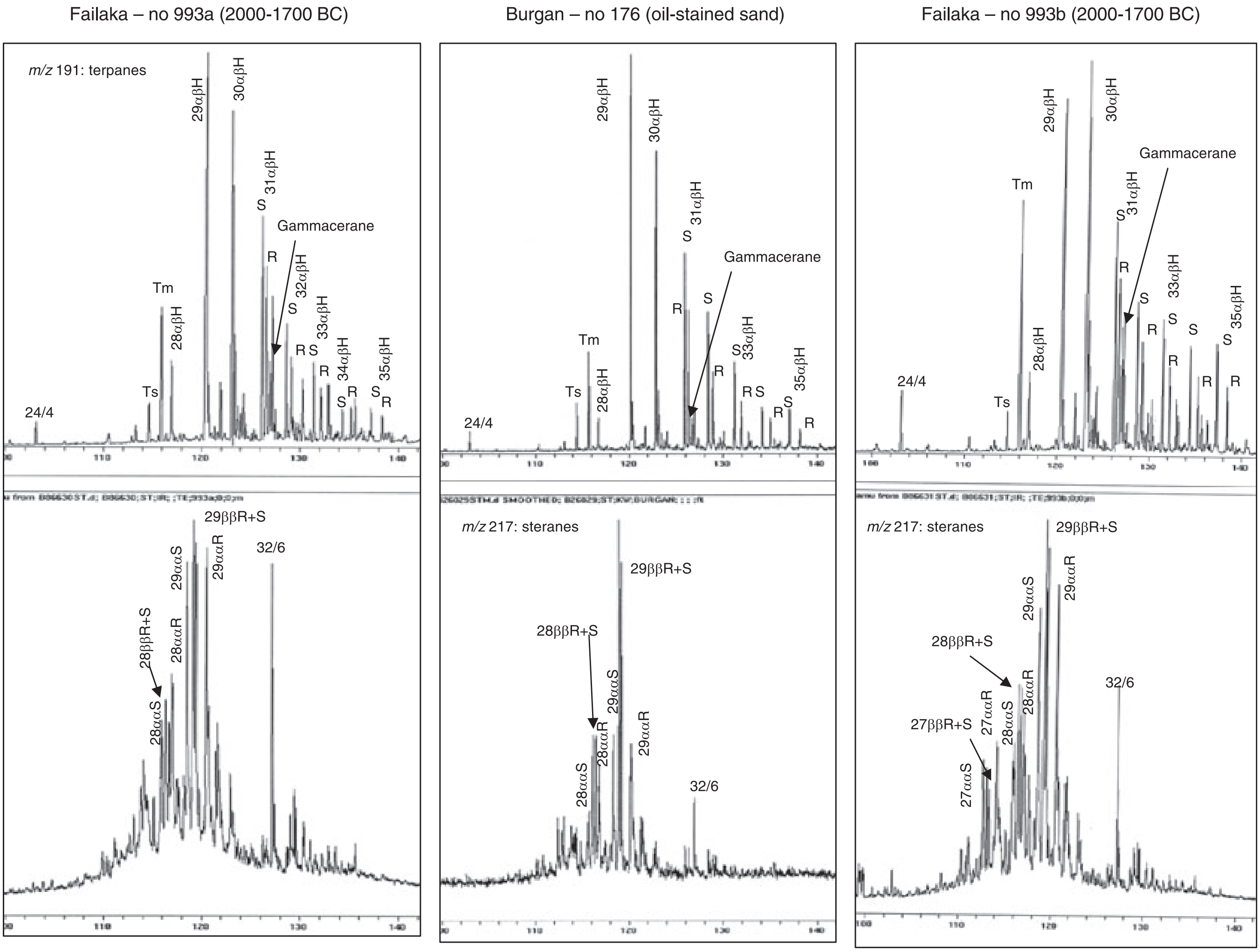


Fig. 17.
Distribution of steranes (*m/z* 217) and terpanes (*m/z* 191): comparison between Failaka (no. 993a and no. 993b, Dilmun, 2000–1700 BC) and Burgan oil seep (no. 176).

sources, were selected for a comparison of samples. These ratios were compiled with δ^{13}C in Figs 19 and 20. As references to trace bitumen back to its source, we have included in these figures data on oil seeps from Iraq, Kuwait and Iran (Luristan Province exclusively), and archaeological bitumen from sites in northern Iraq, As-Sabiyah, Kuwait, and two archaeological sites in the Luristan Province of Iran. The location of the oil seeps and archaeological sites is shown on Fig. 21.

The molecular ratios of the Failaka and Umm an-Namel samples are completely different from what was recorded in archaeological bitumen from As-Sabiyah (Figs 19b–c, 20b–c). One bitumen only (sample no. 993a) exhibits molecular characteristics that approach those of Burgan and As-Sabiyah (Figs 19a–c, 20a–c). Consequently sample no. 993a is probably a geological sample from Burgan, which has been subsequently oxidized to acquire the gross properties of archaeological bitumens. Other bitumens from Failaka and Umm an-Namel do not exhibit the molecular characteristics of oil seeps from Luristan in Iran (Figs 19b and d), as it seemed purely on the basis of their sterane-terpane patterns, but are in agreement with the characteristics of oil seeps (Fig. 19a) and archaeological bitumens of the Mosul area of northern Iraq (Fig. 19c) and Hit-Abu Jir (Figs 19a, 20c).

One remarkable feature is that the match in molecular ratios is better when considering bitumen

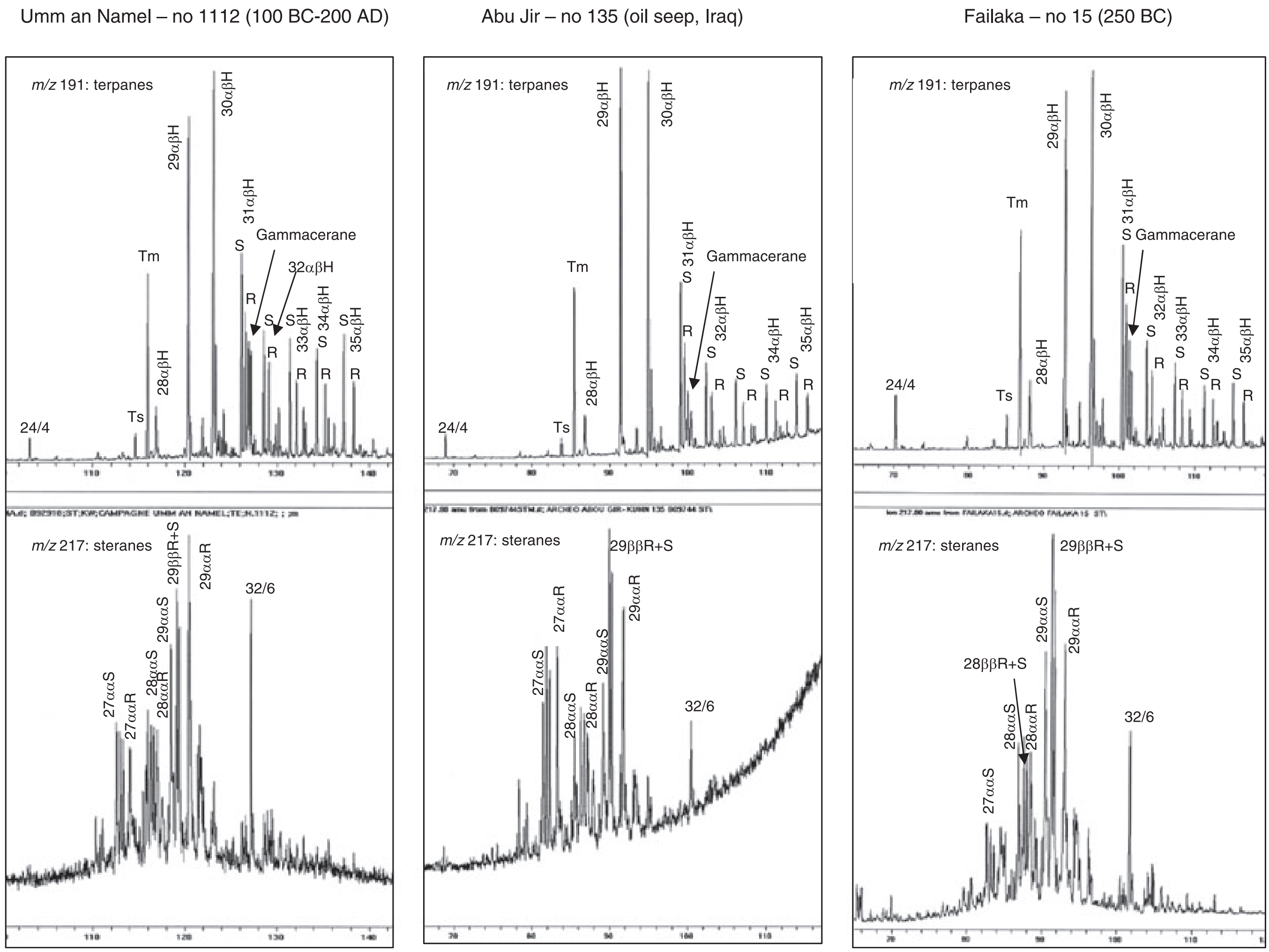


Fig. 18.
Distribution of steranes (*m*/*z* 217) and terpanes (*m*/*z* 191): comparison between Umm an-Namel (no. 1112, 100 BC–200 AD), Failaka (no. 15, 250 BC) and Hit-Abu Jir oil seep in Iraq (no. 135).

from archaeological sites rather than oil seeps. This reconfirms that, in many cases, oil seeps are not the end products which are eventually analysed as archaeological bitumens: molecular changes still continue after the incorporation of the oil seep material into bitumen amalgams. This again highlights the difficulties encountered when trying to correlate oil seeps with archaeological bitumens, as discussed recently in another paper (43).

Nonetheless, despite some discrepancies, for instance in the GCRN/C_{30} $\alpha\beta$H ratio, which tends to be higher in archaeological bitumen due to the preferential removal of C_{30} $\alpha\beta$H (44), the origin of bitumens from Failaka and Umm an-Namel can be delineated. It came from two different sources, the Hit-Abu Jir area (samples from Failaka F6, F5, B6 and the Parthian levels of Umm an-Namel) and the Mosul area in northern Iraq (the Early Dilmun levels of Umm an-Namel). At first glance the Sultan-Pol Doktar bitumen appears as a potential candidate, as its molecular and isotopic ratios match those of archaeological samples. This possibility should be ruled out, however, as these bitumens occur in outcrops as solid matter with a melting point higher than 300°C. In addition, their extractable bitumen represents between 6 and 18% of the raw sample. Consequently, this solid bitumen would not have been suitable for the preparation of the bitumen amalgams unearthed at archaeological sites, and is unlikely to have been mined and exported from Iran at this time.

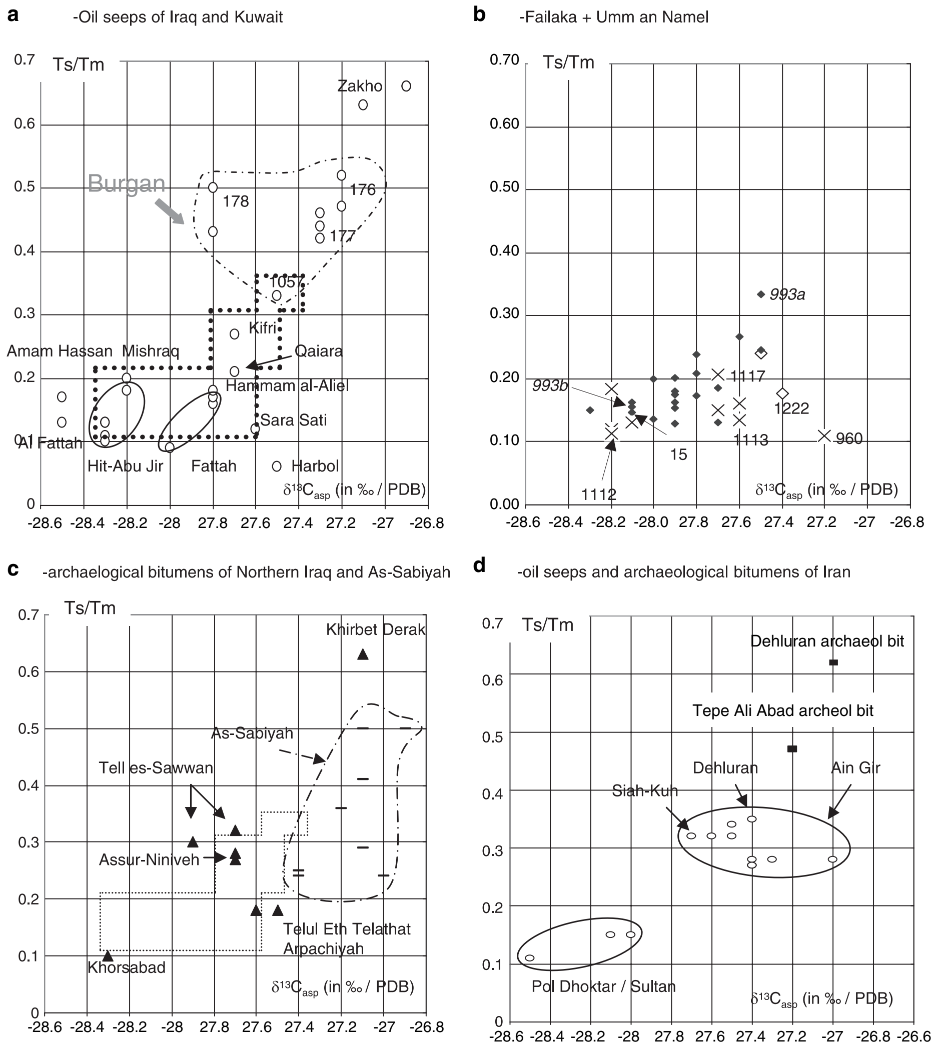


Fig. 19.

Appraisal of bitumen sources using a biomarker ratio on terpanes (Ts/Tm) and isotopic data on asphaltenes ($\delta^{13}C$ in ‰/PDB). **a.** comparison between oil seeps of Iraq and Kuwait; **b.** comparison between Failaka and Umm an-Namel; **c.** comparison between archaeological bitumens of northern Iraq and As-Sabiyah samples; **d.** comparison between oil seeps and archaeological bitumens of Iran.

The possible uses of some ceramics from Umm an-Namel and Failaka

The GC (Gas Chromatography) and GC-MS (Gas Chromatography-Mass Spectrometry) analysis of C_{15+}aromatics of the bituminous mixtures isolated from Umm an-Namel potsherds showed two types of molecular patterns: typical spectra of altered bitumen (sample nos 1112, 1114, 1115, 1116) identified by diagnostic families of biomarkers, namely triaromatic steroids (*m/z* 231), 8,14 monoaromatised secohopanoids (*m/z* 365) and benzohopanes (*m/z* 191); and specific fingerprints (sample nos 1113, 1117 and 1222) in which a series of low molecular weight components are strongly apparent (Table 10).

GC-MS analysis of C_{15+}aromatics from the second family (sample nos 1113, 1117, 1222) allowed the identification of two main features: a complete series of sesquiterpenoids based on the cadinane skeleton in the low molecular range (45); and the main biomarkers characteristic of degraded bitumen in the high molecular range of the C_{15+}aromatic fraction (Fig. 22). Sesquiterpenoids with the cadinane skeleton occur primarily in volatile oils and vegetal gums but also in some marine algae (46). The degradation pathway of biomass precursors through burning (Fig. 23) is oxidation to cadalene (47), as indeed suggested by the results obtained on the Umm an-Namel samples (sample nos 1113, 1117 and

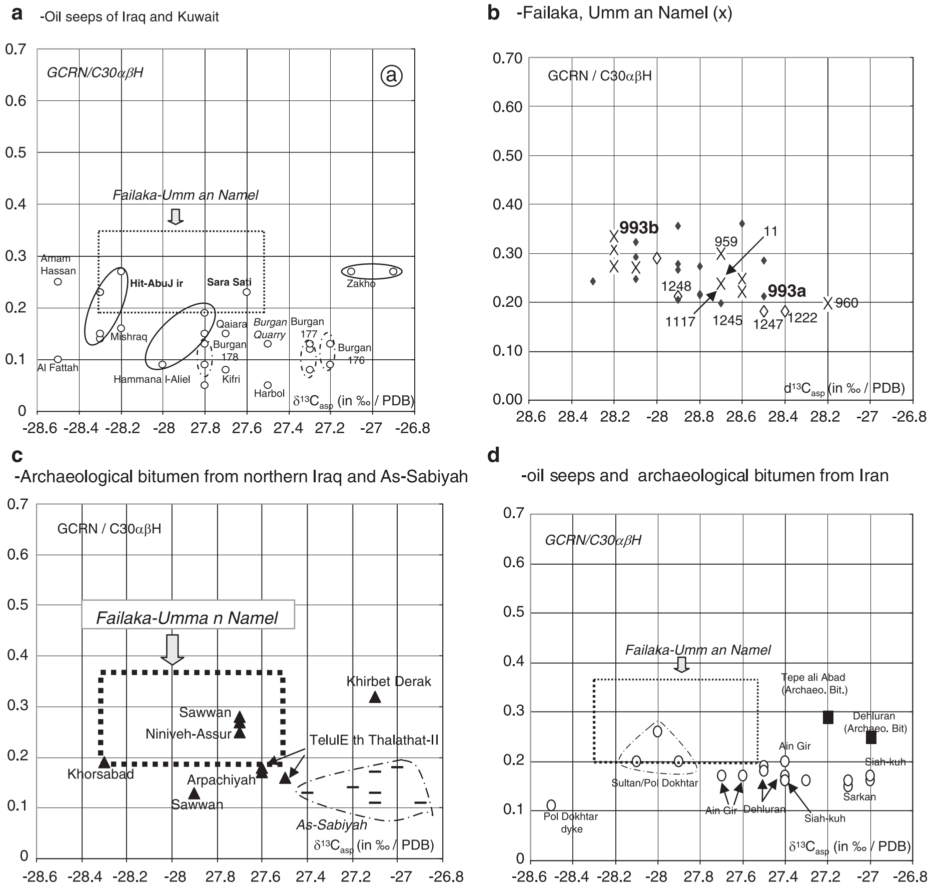


Fig. 20.
Appraisal of bitumen sources using biomarker ratio on terpanes (GCRN/C30αβH = Gammacerane/17α,21β-hopane) and isotopic data on asphaltenes ($\delta^{13}C$ in ‰/PDB); **a.** comparison between oil seeps of Iraq and Kuwait; **b.** comparison between Failaka and Umm an-Namel; **c.** comparison between archaeological bitumens of northern Iraq and As-Sabiyah samples; **d.** comparison between oil seeps and archaeological bitumens of Iran.

1222: Table 10, Figs 3 and 24). Both bituminous samples coated the interior face of Dilmun pottery, and in sample no. 1113 we have evidence of carbonised material within the thin shiny black layer (see HI, Fig. 7). A comparison between the bitumen coatings and the extract from crushed potsherds allows us to cross-check the occurrence of specific compounds within the porous matrix of the potsherds. Sesquiterpenoids with cadinane skeleton are not restricted to the outer bituminous coat, but have also penetrated the potsherd itself, and are better preserved than expected (Fig. 24). The acquisition of the $\delta^{13}C$ values of individual molecules by linking an isotope-ratio mass spectrometer to a gas chromatograph with online combustion of the eluting compounds to CO_2 and H_2O (GC-C-IR-MS) gave values for individual sesquiterpenoids compounds of between −30 and −38 ‰/PDB. These values, which correspond to a significant depletion of the ^{13}C isotope, are in agreement with the published literature (48) for sesquiterpenoids, and confirm that these molecules were biosynthesised via the mevalonic acid pathway (MVA pathway). The sesquiterpenoids are quantitatively dominant in the C_{15+}aromatic fraction, as the bulk isotope values reach −33 and −32 ‰/PDB, whereas the C_{15+}aromatics associated with the bitumen input possess values around −27/−28 ‰/PDB.

The identified sesquiterpenoids are unfortunately not specific enough to ascribe a specific plant contribution to their signatures, which are additionally largely the result of oxidation reactions during heating. However, the results suggest that the vessels in which such a characteristic molecular

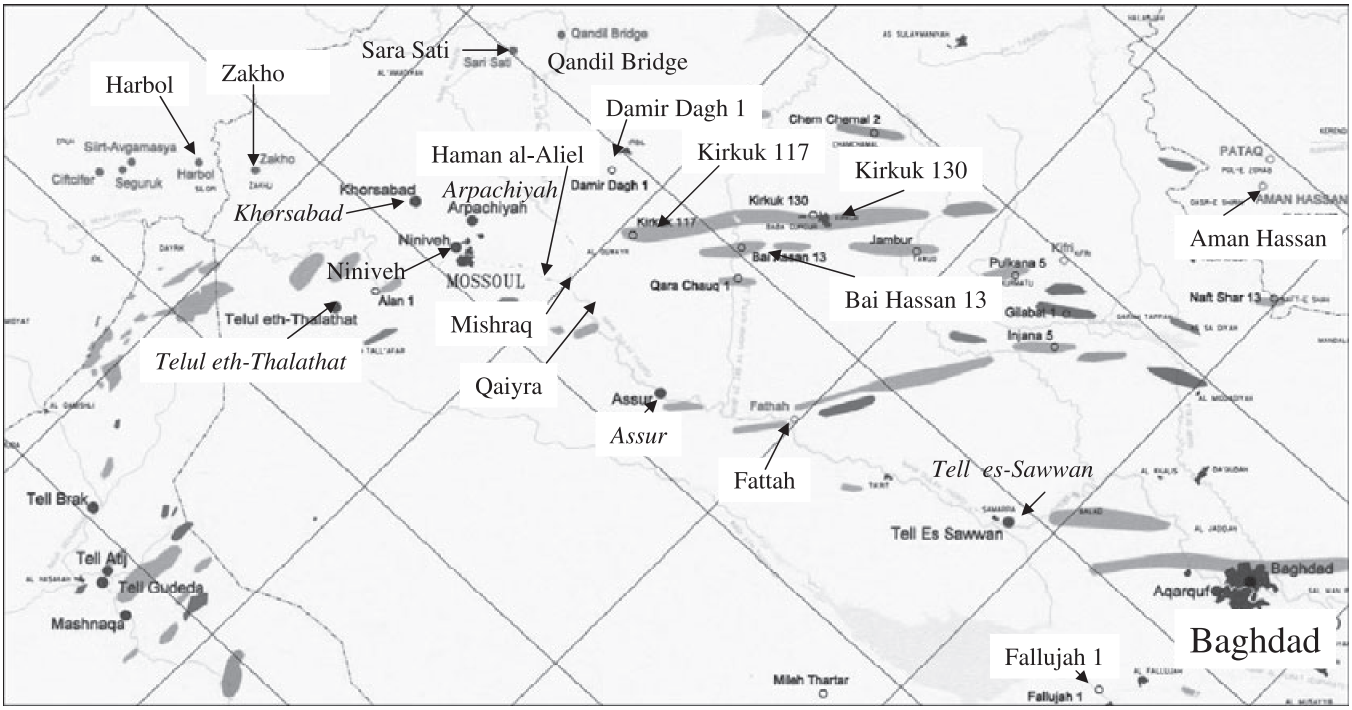


Fig. 21.
Map of northern Iraq giving the location of the oil fields and oil seeps used as references, and of some archaeological sites from which bituminous mixtures were analysed.

fingerprint was found were used to prepare plant extracts, probably by heating vegetal matter with water. Such activities might include cooking vegetables or cereals, or other processing procedures. This would be in line with the archaeological context, which included oven installations and other settlement remains, and the analysed pottery may therefore have been from cooking vessels. The heating was high enough to carbonize a part of the bitumen and generate the diaromatised sesquiterpenoid cadalene. The occurrence of T-alkylbenzenes in almost all samples (Table 10) may result from this carbonisation procedure, as they were observed to have a close relationship with the occurrence of ash within bituminous amalgams (49). They may alternatively be allochtonous contaminants from anthropogenic activities (i.e. the combustion of petroleum), because they can be detected in bituminous samples stored in museums (in artefacts from Susa stored in the Louvre Museum for example). Regarding their formation through the combustion of petroleum, they were identified in abundance within the marine sea-floor sediments of Kuwait Bay after the great oil-field fires at the end of the First Gulf War (50).

A similar approach was adopted to investigate the possible occurrence of vegetal biomarkers in two potsherds from Failaka (sample nos 1245 and 1248, derived from sample no. 1, Hellenistic; and sample no. 1247, derived from sample no. 5, Kassite). Sample no. 1 was probably from the illustrated storage jar (see Fig. 4), with unknown contents. Gas chromatographic traces of C_{15+}alkanes and C_{15+}aromatics from sample nos 1245 and 1248 (Fig. 25) show a significant concentration of light ends inside the potsherd. The occurrence of a complete series of n-alkanes between n-C_{13} and n-C_{21} in sample no. 1248 is mainly due to the increased combustion input marked by the occurrence of enhanced T-alkylbenzenes in the C_{15+}aromatics of this sample (Fig. 25). This potsherd, stored in the Louvre Museum, contains phthalates, which are well-known plasticisers (Fig. 25). These phthalates have migrated inside the potsherd. Apart from these obvious anthropogenic contaminants, some probable indigenous components (Fig. 26) were identi-

Table 10. Summary of the results of the GC-MS analysis from the C15+aromatic fraction of potsherds from Failaka and Umm an-Namel.

					aromatic families							comments
sample number	lab number	site	date	crust of bitumen	Sesquiterpenoids	esters + ketones + other molecules of plant origin	T-alkylBZ	DBT	Triaromatic steroids	8,14 Monoaromatized Secohopanoids	Benzohopanes	interpretation
1245	B97981	B6	205–140 BC	thin film of bitumen	absent		present	present-low	present-traces	present	present-trace	bitumen + carbonised input + contaminant
1248	B99819	B6	205–140 BC	potsherd crushed	absent		abundant	present	present-traces	present	present-trace	bitumen + carbonised input + contaminant
1247	B98783	F6	1400–1300 BC	potsherd crushed	absent	present	abundant	present	present-traces	present	present - trace	bitumen + carbonised input + contaminant + plant extract
1112	B92918	Umm an Namel	100 BC–200 AD	significant	absent		present	absent	present-traces	present	present-altered?	typical spectum of a bitumen
1113	B92919	Umm an Namel	2100–2000 BC	carbonised? crust of bitumen	abundant		absent	absent	present	present	present	bitumen + essential oil contribution
1114	B92920	Umm an Namel	undated	thick crust of bitumen	absent							typical spectrum of bitumen by GC
1115	B92921	Umm an Namel	undated	thick crust of bitumen	absent							typical spectrum of bitumen by GC
1116	B92922	Umm an Namel	2100–2000 BC	significant crust	absent		present	absent	present-traces	present	present	bitumen
1117	B92923	Umm an Namel	2100–2000 BC	crust of bitumen	abundant		present	absent	present-traces	present	present-altered?	bitumen + essential oil contribution
1222	B97941	Umm an Namel	2100–2000 BC	potsherd crushed	abundant		absent	absent	present-traces	present	present -altered	bitumen + essential oil contribution

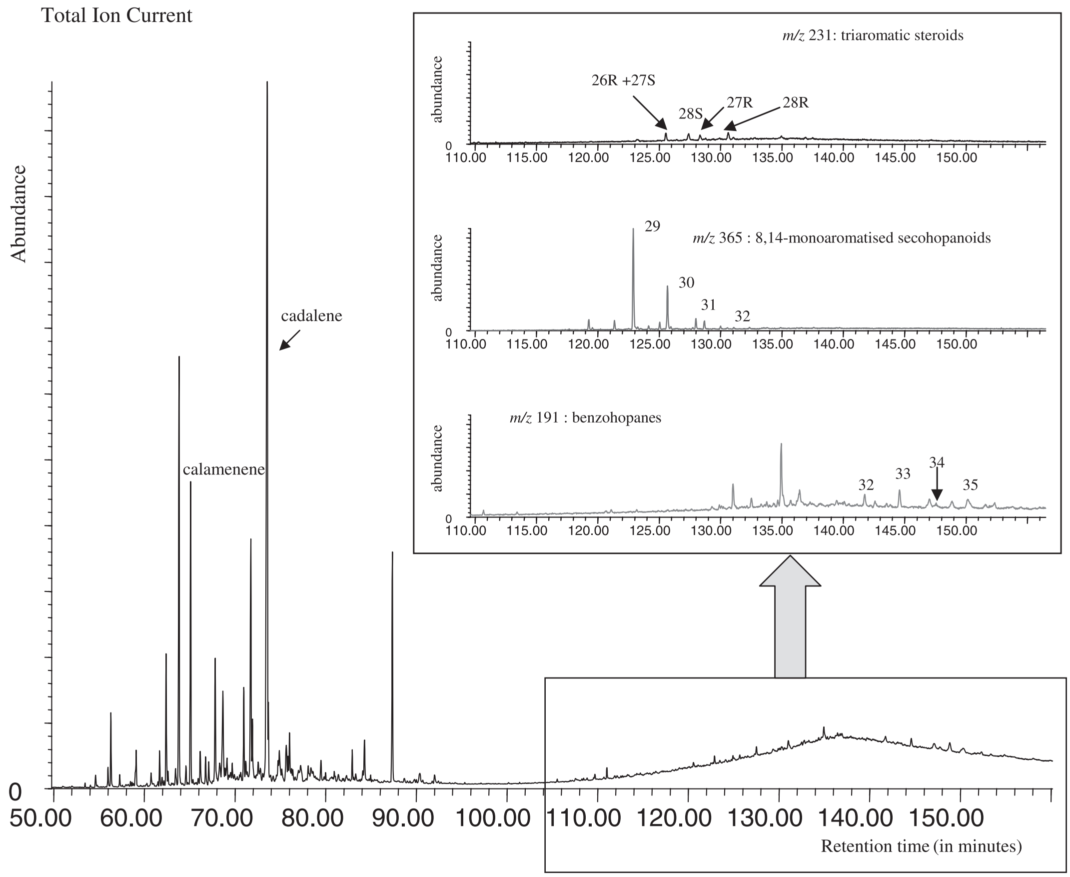


Fig. 22.
Total ion current, *m/z* 231 (triaromatic steroids), *m/z* 365 (8,14-monoaromatised secohopanoids) and *m/z* 191 (benzohopanes) of the C_{15+}aromatic fraction of sample no. 1222 (crushed potsherd of Umm an-Namel) showing the plant sesquiterpenes (calamenene, cadalene) and the bitumen biomarkers (benzohopanes, triaromatic steroids, 8,14 monoaromatised secohopanoids).

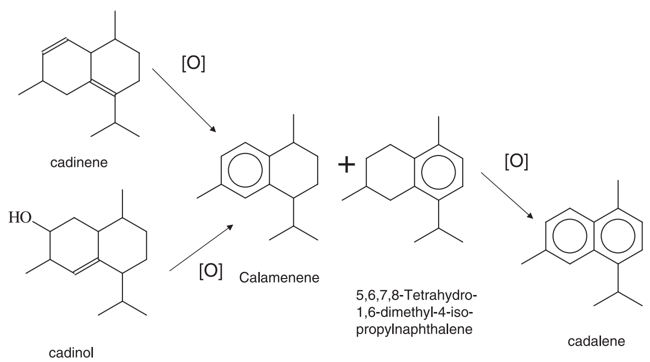


Fig. 23.
Scheme for the alteration of sesquiterpenoid precursor to aromatic hydrocarbons (after Simoneit, 1998).

fied, namely isopropyl- and myristyl-myristate, 6,10,14-trimethyl-2-pentadecanone, linear long chain esters and squalene. Myristic acid occurs widely in vegetable glycerides (e.g. as a major component of nutmeg), 6,10,14-trimethyl-2-pentadecanone is widespread in plant species and squalene is found in many vegetable oils (e.g. palm oil, cottonseed oil, rapeseed oil) (51). In addition chlorinated hydrocarbons ($C_6H_6Cl_6$, $C_{14}H_8Cl_4$, $C_{14}H_9Cl_5$ = o,p′-DDT) were found, especially in sample no. 1245, i.e. at the surface of the potsherd. These compounds, which are insecticides, are obvious contaminants introduced during the storage of samples in the Louvre Museum. A group of compounds occurring in the light ends zone is difficult to interpret. They are present in all three Failaka samples and are therefore suspected to be pollutants. In addition to these compounds of various origins, some biomarkers of bitumen (e.g. 8,14 monoaromatised secohopanoids, Fig. 26) were identified.

To conclude, the Failaka potsherds exhibit three main origins for the chemicals identified: anthropogenic pollutants (plasticisers, pesticides, combus-

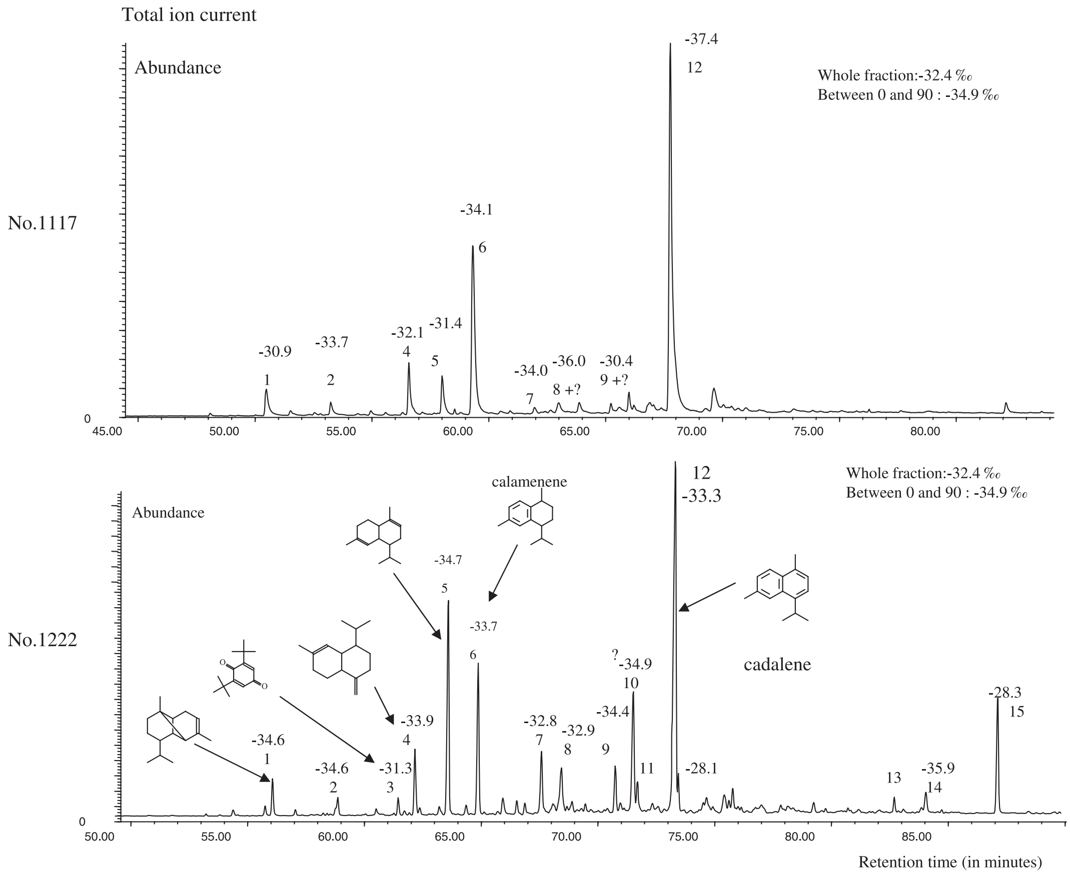


Fig. 24.
Total ion current (partial) showing the sesquiterpene distributions: comparison of two samples from the same potsherd (Umm an-Namel, Dilmun, 2100–2000 BC): the bituminous coat inside the potsherd (no. 1117) and the extract of the same potsherd cleaned and crushed (no. 1222).

tion by-products); bitumen; and vegetal constituents. The latter chemicals, unfortunately widespread in the vegetable kingdom, do not allow us to determine the exact nature of the vegetal content. Nonetheless, the results suggest that the pottery was used to store or treat vegetal matter.

Discussion and conclusions

The bituminous mixtures

As we have stressed, the bituminous mixtures from Failaka and Umm an-Namel, ranging in date from the late third millennium BC to the Islamic period, do not differ from those of other Near Eastern sites. Their compositions underline the conventional and conservative nature of traditional bitumen processing, and illustrate the means by which bitumen was incorporated with vegetal matter and mineral into amalgams for use in coating mats and basketry, for mortar preparation and perhaps for coating or caulking boats. The mineralogical composition of the Failaka samples indicates the deliberate addition of minerals available on the beaches of Failaka, particularly carbonates.

The use on boats, though known from other sites (52), is suggested by the abundance of bituminous material associated with artefacts related to fishing activities at F5 during the Hellenistic period. By tradition, however, the Greeks did not use bitumen for caulking or coating their boats but pitch, i.e. tar produced from the heating of conifer wood, or a mixture of beeswax and pitch called *zopissa,* as identified on archaic boats (sixth century BC) from the ancient harbour of Marseille in France (53). Notwithstanding the lack of discoveries of ancient Hellenistic hulls in the Gulf — according to Vosmer we have no archaeological data at all on Hellenistic ships in the Gulf or western Indian Ocean (54) — it

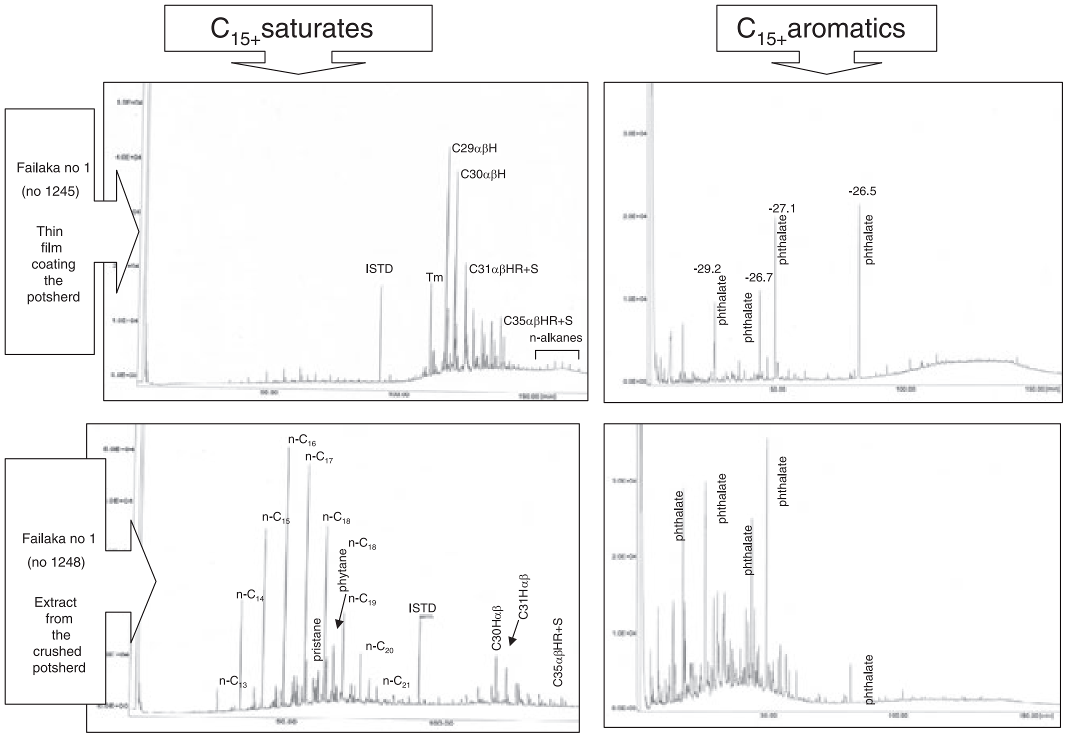


Fig. 25.
Total ion current of the C_{15+}alkanes and the C_{15+}aromatics of two samples from the same potsherd (Failaka, Hellenistic, B6, 205–140 BC): the bituminous coat inside the potsherd (no. 1245) and the extract of the same potsherd cleaned and crushed.

remains possible that bitumen was used instead of pitch in the area. This hypothesis is not currently supported by the occurrence of any barnacles on the bitumen pieces from F5. Moreover, according to Callot, Gachet and Salles (55) the most common Arabian (and Indian?) vessel was the sewn-plank boat until Classical times (56), and bitumen is not thought to have been used on sewn boats. Finally, the wood impressions on some of the bitumen pieces from F5 may have been from bitumen-coated roofing or terraces, as suggested by the excavators (57).

Among the archaeological samples from the Early Dilmun tower-temple on F6, an oil-stained sand from Burgan was identified. The occurrence of this geological sample, which has reached a similar degree of oxidation to its archaeological counterparts, testifies that oil-stained sand was imported to Failaka from Burgan during the early second millennium BC. It is remarkable that this source was known but not much used. The Burgan bitumen has had specific uses in the local context, determined by its specific properties, which may have made it less visible in the archaeological and analytical record. It may simply have been considered inferior to the Hit material: if such an oil-stained sand had been intended to be used in the ways described above, it would have had to be combined with additional bitumen (e.g. from Hit) to enrich the mixture, as its natural oil content does not exceed 10%. The resulting molecular and isotopic properties would be composite and it would be impossible to disentangle the contribution of each bitumen source in the mixture. Additionally, Burgan's inland location may have made it less economical than the Hit bitumen, which was distant but more accessible by sea and river, as well as being purer.

The corpus of samples from potsherds represented a significant part of the sample set. Such samples could be subdivided into two groups, which showed different properties: thin films coating the interior face and thick crusts. The former samples were generally bitumen-enriched and represent the remains either of relatively pure bitumen coats used to waterproof pottery, or of pure bitumen transported as a trade item in the pots. The latter samples often showed vegetal debris and are interpreted as the stored remains of processed bituminous amalgams.

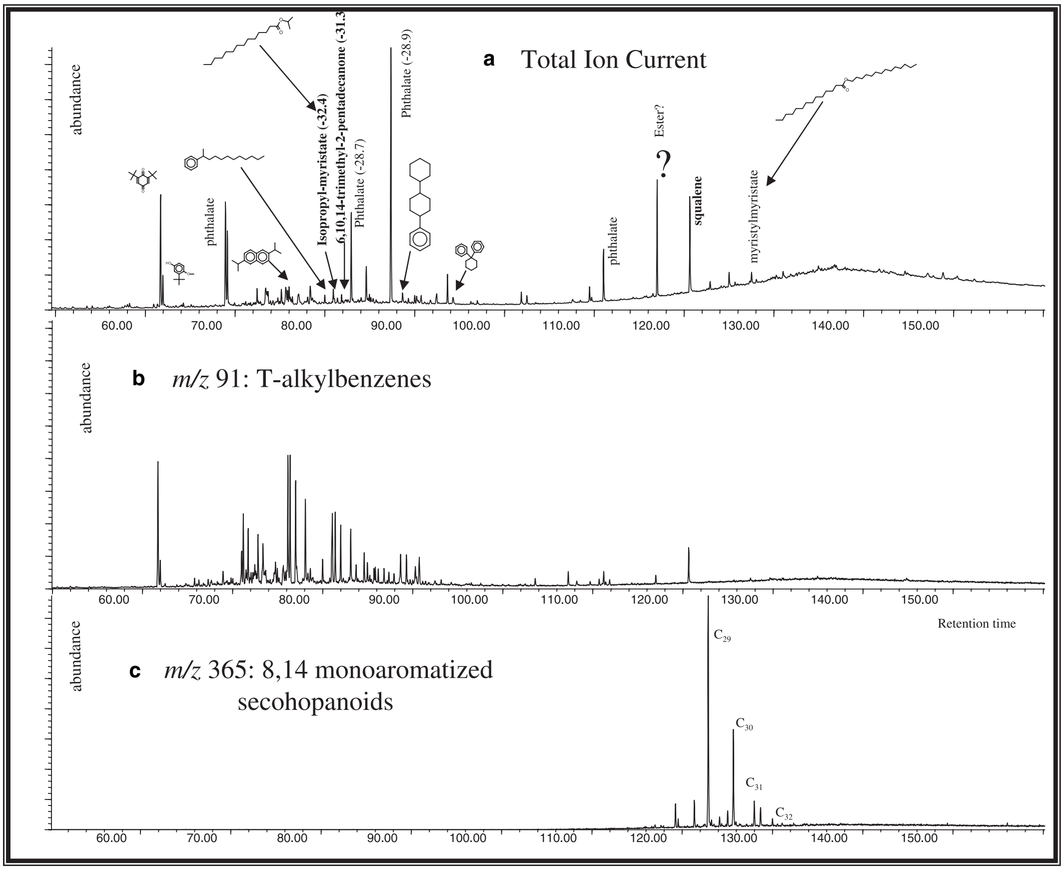


Fig. 26.
GC-MS analysis of the C_{15+}aromatics from sample no. 1248. **A.** total ion current; **B.** *m/z* 91 (T-alkylbenzenes); **C.** *m/z* 365 (8,14-monoaromatized secohopanoids).

Finally, the spindle whorl from al-Qusur had an unusual composition consisting of a hard mixture of bitumen and minerals, appropriate to its function.

Bitumen origins and trade routes

A key result of this study is the identification of the origin of the bitumen imported to Failaka and Umm an-Namel between the Early Dilmun and Early Islamic periods. Apart from the Burgan tar sand sample, it originated from northern Iraq (Mosul area) and central Iraq (Hit-Abu Jir area). The occurrence of bitumen from these areas has previously been demonstrated at several sites in southern Mesopotamia, namely Tell el'Oueili (58), Larsa and Tello, as well as in Saudi Arabia (59), Bahrain (60), the U.A.E. (al-Buhais) (61) and Oman (Ra's al Jinz – RJ 2) (62).

These results complete the general history of bitumen in the Kuwait area. In the earliest recorded instance (Neolithic/Ubaid period, *c.* 5000 BC), the inhabitants of As-Sabiyah used bitumen from Burgan Hill, inland Kuwait, to coat their reed-bundle boats. The occupation of Kuwait is then poorly documented until the late third and early second millennia BC, when first Umm an-Namel and then Failaka emerged as active participants in the Dilmunite trade through the Gulf, probably acting as a maritime staging post on the way to Bahrain (Fig. 27). As we have shown, bitumen from northern Iraq was used at Umm an-Namel and bitumen from central Iraq (Hit-Abu Jir) was subsequently used on Failaka, although the Burgan source was still apparently known.

This commerce is in line with the evidence from Bahrain, which was receiving bitumen from Iraqi sources at the same time (see below). Indeed, the Iraqi bitumen reaching Bahrain in the early second millennium BC is very likely to have passed through Failaka. Abundant evidence shows a thriving and highly cosmopolitan community on Failaka from *c.* 2000 BC onwards, which certainly functioned as a maritime staging post on the trade route linking the Mesopotamian states and empires to the polities of the Gulf, and ultimately to the Indus Valley civilization. Close connections with both southern Mesopotamia and Bahrain are demonstrated not only by the mixture of Mesopotamian and Dilmun-style pottery on Failaka (63), but also by the use of Mesopotamian cuneiform script (64), and by the glyptic record, in which Dilmun seals display elements of Mesopotamian iconography (65). Umm an-Namel may have played a similar role during the late third millennium, though it is a much smaller site on a smaller island.

This linking role continued into the later second millennium, when Kassite-period Failaka was host to a ''palace'' at F6 as well as the still-extant tower-temple, with domestic housing and another temple at F3 (66). Bahrain itself appears to have been under Mesopotamian control at this time (67), and it is probable that Failaka was used as a staging post and depot, which connected the Kassite Empire with its dependencies in the Central Gulf region. The continuing

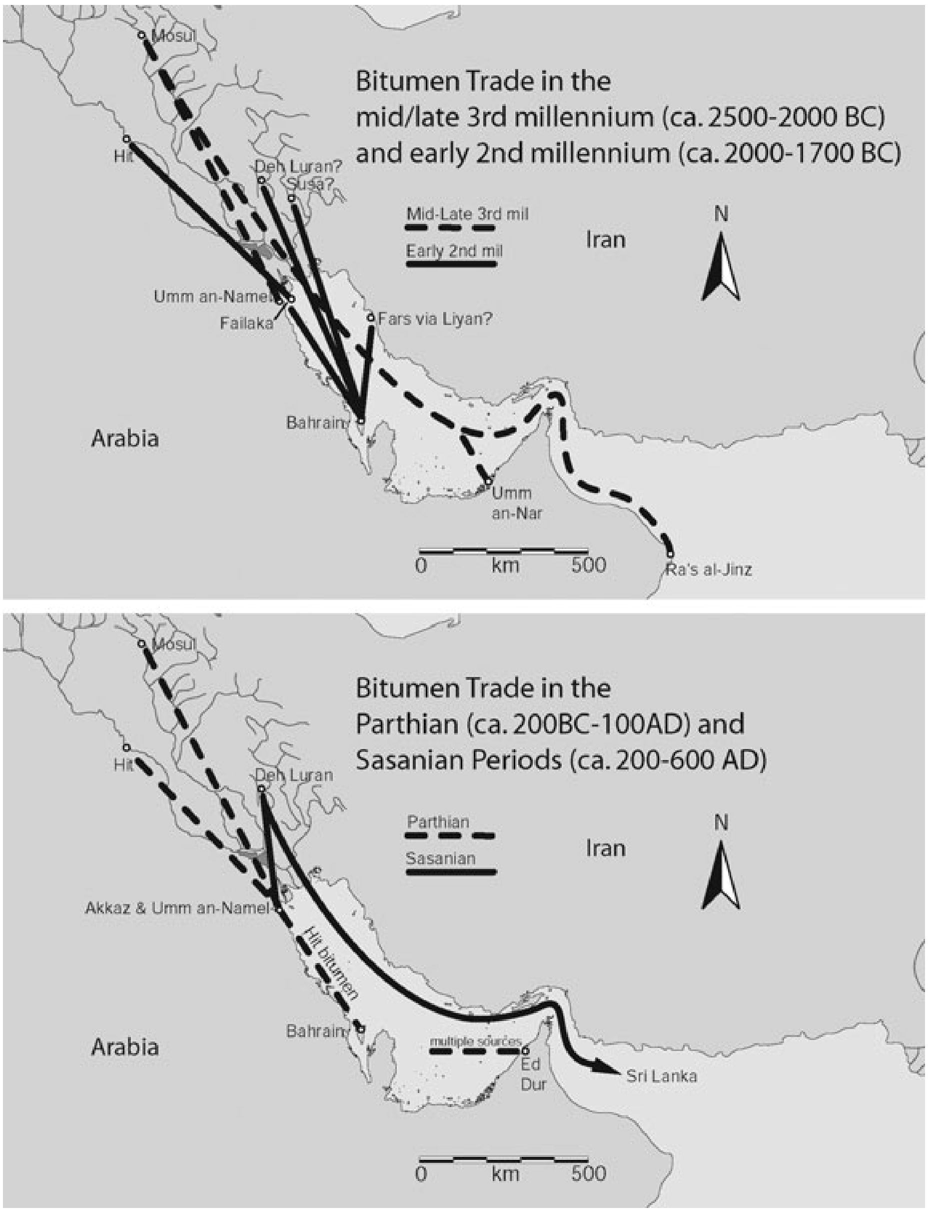


Fig. 27.
Bitumen trade routes in the Gulf and Indian Ocean during the Bronze Age and Partho-Sasanian Periods.

Table 11. Table summarising the provenance of archaeological bitumens from the Gulf and Indian Ocean, from the Neolithic to the Islamic periods, as analysed by Jacques Connan.

Site	reference	Region	date (older)	mean date for chart	probable bitumen source	number of samples	comments
H3-As-Sabiyah	Connan et al. 2005	Kuwait	5300–4900 BC	5100 BC	Kuwait: Burgan oil seeps	15	
UAQ2	Phillips 2002:176, n.12	U.A.E.	5000 BC	5000 BC	Iraq: Hit/Abu Jir	2	
Ain As-Sayh-site C	McClure and Al-Shaikh Arab.arch.epig 1993:4:107–125	Saudi Arabia	4500–4000 BC or later	4250 BC	Northern Iraq	1	date may be as early as 5000–4500 BC, but possibly later: 3rd mil pot also found at site
Umm an-Nar	Frifelt	Abu Dhabi	2600–2400 BC	2500 BC	Northern Iraq	1	bitumen on floor of the warehouse
RJ2, Ra's al-Jinz	Connan et al. 2005	Oman	2500–2300 BC	2400 BC	Northern Iraq: Fattah Hammam al-Alliel	22	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	2500–2000 BC	2250 BC	Iraq: probably northern Iraq	5	
Saar	Connan et al. 1998	Bahrain	2100–2000 BC	2050 BC	Iran	1	
Umm an Namel	this study	Kuwait	2100–2000 BC	2050 BC	Northern Iraq	5	
Failaka-F6	this study	Kuwait	2000–1700 BC	1850 BC	Iraq: Hit/Abu Jir	9	
Failaka-F6	this study	Kuwait	2000–1700 BC	1850 BC	Kuwait: Burgan oil seeps	1	
Buri	Connan et al. 1998	Bahrain	2000–1700 BC	1850 BC	Iran	1	
Karranah	Connan et al. 1998	Bahrain	2000–1700 BC	1850 BC	Iran	3	
Saar	Connan et al. 1998	Bahrain	2000–1700 BC	1850 BC	Iran	13	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	2000–1700 BC	1850 BC	Iraq	3	
F6, Failaka	this study	Kuwait	1400–1300 BC	1350 BC	Iraq: Hit/Abu Jir	3	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	1400–1300 BC	1350 BC	Iraq: Hit/Abu Jir	14	2 of them identifed as from Hit Abu Jir; others probably also
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	700–600 BC	650 BC	Iraq: Hit/Abu Jir	2	1 of the 2 identified as from Hit/Abu Jir
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	400BC	400 BC	Iraq	5	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	400BC	400 BC	Iran: Khuzestan and Fars	2	1 of the two identified as from Khuzestan/Fars
F5&B6	this study	Kuwait	300–100 BC	200 BC	Iraq: Hit/Abu Jir	16	
Umm an Namel	this study	Kuwait	100 BC–200 AD	50 AD	Iraq: Hit/Abu Jir	2	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	100 BC–200 AD	50 AD	Iraq: Hit/Abu Jir	4	1 of the 4 identified as from Hit/Abu Jir
Ed-Dur	Connan: unpublished results	E.A.U (Umm al Qaiwain)	0–100 AD	50 AD	Northern Iraq	9	
Ed-Dur	Connan: unpublished results	E.A.U (Umm al Qaiwain)	0–100 AD	50 AD	Iran: Luristan	7	
Ed-Dur	Connan: unpublished results	E.A.U (Umm al Qaiwain)	0–100 AD	50 AD	Iran (Khuzestan-Fars)	2	
Ed-Dur	Connan: unpublished results	E.A.U (Umm al Qaiwain)	200–400 AD	300 AD	Northern Iraq	1	
+^{c}Akkaz	Connan, 2007, TMO in press	Kuwait	100–600 AD	350 AD	Iran: Luristan	35	source in Luristan is probably Ain Gir-Dehluran - Siah Kuh
Sri Lanka	Stern et al, 2007 in press	Anuradhapura	200–1000 AD	600 AD	Iran: Luristan	9	
al-Qusur	this study	Kuwait	700–800 AD	750 AD	Iraq: Hit/Abu Jir	1	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	1200–1500 AD	1350 AD	Iran	3	
Qala'at al-Bahrain	Connan et al. 1998	Bahrain	1200–1500 AD	1350 AD	Iraq	5	

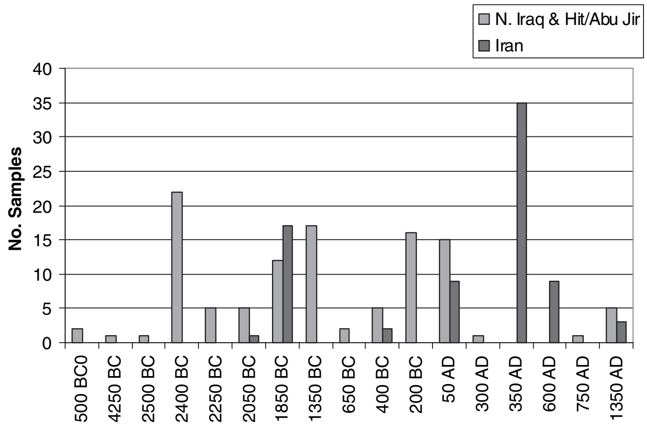


Fig. 28.
Chart summarising the Iraqi and Iranian provenance of analysed bitumen samples through time.

presence of Mesopotamian bitumen on both Failaka and Bahrain is therefore in line with expectations.

In the Hellenistic period, Failaka (Ikaros) was part of the Seleucid empire. Antiochos 1st (281–241 BC) initiated the control of the Gulf, and the start of the third century BC saw the construction of the fortress at F5 (68). It has been theorised that the Greeks built a fleet to secure the Gulf, and that this may have been based at Failaka (69). If so, it is possible that the fleet was maintained and caulked with bitumen there, hence the bituminous mixtures and bitumen workshop on F5. Note, however, the reservations outlined above with regard to the lack of barnacles on these samples, and the doubts surrounding Greek use of bitumen for this purpose. Whatever the case, Failaka remained a strategic node linking Mesopotamia with the Gulf, and the presence of Iraqi bitumen is expected.

From a regional perspective, these new data document the continuity of the Mesopotamian supply through time, and the importance of the main trade routes starting from northern Iraq, following the Euphrates and the Tigris, down to the main cities of southern Mesopotamia, then through or past Failaka and along the southern coast of the Gulf. The distribution of this bitumen ultimately reached Oman in the Bronze Age (Ra's al-Jinz). Further work is required to establish the extent of the distribution of Iraqi bitumen in later periods, but it seems possible that it was transported beyond Failaka and the Gulf, and into the wider Indian Ocean trading system.

The persistent use of Iraqi bitumen, frequently identifiable as being from northern Iraq or the Hit area, reflects a strong Gulf-wide trend, as shown by Table 11 and Figs 27–28, which summarise the results of a decade's work on bitumen from the Gulf and the Indian Ocean. The almost continuous export of this bitumen transcends the rise and fall of political or cultural-historical entities. The prevalence of Hit bitumen in particular reflects that site's unique position as an apparently inexhaustible bitumen source on the major transport route connecting Mesopotamia with the Gulf and more distant maritime trading networks.

There is an underlying complexity, however, demonstrated by the presence of bitumen from various Iranian sources at different times and places (Table 11). Although the Failaka data show a relatively linear trading network persisting through time (initially from northern Iraq via the Tigris, then central Iraq via the Euphrates, to Failaka and beyond), this pattern is specific to Failaka, and reflects its geographical position near the outlet of the great Mesopotamian river transport system. In fact, multiple bitumen sources from Iran as well as Iraq fed into the Gulf, coming to prominence at different times. It is possible that, compared to the Iraqi sources and especially Hit, source areas in Iran did not enjoy such easy access to reliable riverine and maritime routes, and therefore a single Iranian source did not consistently feature in the bitumen trade in the way that the northern Iraqi sources and then the Hit area appear to have done. The popularity of the Hit bitumen may additionally have been enhanced by its relative purity and its natural occurrence in a solid state, which allowed it to be easily transported and readily transformed into amalgams for various purposes.

The bitumen trade in the Gulf and Indian Ocean through time

Bearing in mind the limitations imposed by small sample sizes from certain sites and time spans, Table 11 and Figs 27 and 28 allow the following observations to be made on a period-by-period basis.

The Ubaid/Neolithic period

As outlined in a previous study (70), local sources seem to have been used where possible during the sixth and fifth millennia BC. Thus the bitumen from H3, As-Sabiyah in northern Kuwait, originated from Burgan, in southern Kuwait. There is, however, evidence of material from more than one distant source being brought into the Gulf. Bitumen beads from a Neolithic burial in Umm al-Quwain originated from the Hit source in Iraq (71), while bitumen from an Ubaid-related site in Saudi Arabia, Ain as-Sayh C, also appears to be Iraqi, this time from northern Iraq. Thus, as early as the Neolithic, bitumen from three very different areas, hundreds of kilometres apart, was being utilised in the Gulf region.

Given the use of bitumen to coat boats capable of long-distance travel by sea, it is to be anticipated that further bitumen from Burgan and/or Iraq, and perhaps also Iran, might in the future be identified at coastal Neolithic sites in the Central Gulf or beyond, and perhaps also on the Iranian shores.

The Bronze Age, third to mid-second millennia BC

One of the best-represented periods, both in terms of numbers of samples and sites, is the earlier Bronze Age, up to the third quarter of the second millennium BC. During the first part of this period, prior to and during the first two centuries of the Early Dilmun period of Bahrain and Failaka, northern Iraqi sources appear to have dominated the trade, with such material being identified at Umm an-Namel, Umm an-Nar (Abu Dhabi) and Ras al-Jinz (Oman). Bitumen from the latter includes boat remains (perhaps therefore indicating trade in goods other than bitumen itself) but also bitumen lining a jar. Whether or not the material in the U.A.E. and Oman travelled through or bypassed the site at Umm an-Namel is not known.

At around 2000 BC the northern Iraqi source appears to be replaced by the Hit-Abu Jir source, and there is thenceforth evidence for multiple routes and relationships. Iraqi bitumen is found in third- and early second-millennium contexts in Oman, Bahrain (Qala'at al-Bahrain) and Kuwait, and it can sometimes be pinpointed to Hit-Abu Jir. Iranian bitumen also first appears at around this time, first being found in a late third-millennium context at Saar, Bahrain, and then being plentiful in early second-millennium Saar and a range of contemporary Bahraini sites. It has been previously observed that the bitumen used at the urban centre of Early Dilmun, Qala'at al-Bahrain, was Iraqi, whereas that of the outlying village sites (Saar, Buri, Karanah) was Iranian (72) and that this may reflect parallel exchange systems (73). Certainly, from a geographical position, Bahrain was well placed to trade with both Iraq (presumably through Failaka after 2000 BC) and Iran. Dilmun-related finds from Susa and Liyan, an urban centre on Bushehr, and Kaftari pottery from Bahrain and Failaka, all indicate connections between Dilmun and Iran at this time (74) and this is reflected in the Bahraini bitumen record. Interestingly, however, only Iraqi bitumen has been identified on Failaka at this time (apart from the anomalous Burgan tar sand sample). Assuming a representative sample, this suggests that western Iranian bitumen (e.g. from Luristan and Khuzestan) was bypassing Failaka, despite Failaka being en route from western Iran to Bahrain. Alternatively, western Iranian bitumen was not being exported into the Gulf at all, but instead, the Iranian bitumen on Bahrain travelled directly to Bahrain from different parts of Iran, for example from Fars and beyond via Liyan.

The Late Bronze Age, mid- to late second millennium BC

During the Kassite period the only evidence from Bahrain and Kuwait is for bitumen from Iraq, which in the case of Failaka can be narrowed down to Hit-Abu Jir. The prevalence of Iraqi bitumen at this time may reflect the policies of the Kassite rulers of Babylonia, who controlled much of the Gulf, including Bahrain, following their conquest of the Sealands (75). They may have deliberately restricted access to resources outside their control, for political and economic reasons. More data would be required to confirm this pattern: although the number of samples for this period is reasonable, the samples are from only two sites (F6, Failaka and Qala'at al-Bahrain). No samples are available from sites comparable to the smaller Bahraini sites that had earlier displayed Iranian bitumen.

The early first millennium BC and the Achaemenid period

Data is lacking for the early and mid-first millennium BC, although two samples, the origin of one of which could be pinpointed at Hit, show that Iraqi bitumen (again Hit-Abu Jir) was entering Bahrain during the Neo-Assyrian or Neo-Babylonian period (*c.* 700/600 BC). Both Iraqi and Iranian material then co-occurs during the Achaemenid period (samples of *c.* 400 BC at Qala'at al-Bahrain), perhaps reflecting Bahrain's absorption into the Persian Empire at this time.

The Hellenistic period

Evidence for the Hellenistic period is restricted to the material studied here from Kuwait, which originated from Hit-Abu Jir. Although there is a reasonable number of samples, it is all from the one small island of Failaka, so firm conclusions can not be drawn regarding the wider bitumen trade in the Gulf.

The Parthian and Sasanian periods

Once again material from a wide variety of bitumen sources made its way into the Gulf. A few samples from the Parthian period, from both Failaka and Qala'at al-Bahrain, originated from Iraq, with positive identifications for Hit. Others from a small tell on ^{c}Akkaz, a tiny island just 6 km to the southeast of Umm an-Namel, reveal a trade link with the Luristan province of western Iran (76). This site, dated from the beginning of the first century AD to the end of the sixth century AD (i.e. covering the later Parthian and the whole of the Sasanian period), was used at a time when Failaka did not appear to have been occupied (77). Further Iranian bitumen, this time from both Luristan and Khuzestan, has been identified at ed-Dur in the U.A.E. In fact, Ed-Dur shows a wide mixture of bitumens, with material from the northern Iraqi source making its first confirmed appearance since the third millennium BC. This reflects its status as a thoroughly cosmopolitan port close to the entrance to the Gulf.

The international flavour of the Gulf trade and strengthening of long-distance trade routes encompassing the Indian Ocean, which eventually culminated in direct trade with China during the late Early Islamic period, is reflected by the presence of western Iranian bitumen at Anuradhapura in Sri Lanka, between the third and the ninth century AD (78).

During the Parthian and Sasanian periods much of the archaeological bitumen is associated with torpedo jars, i.e. bitumen-lined or bitumen-carrying amphorae. This is true at ^{c}Akkaz, where the bitumen was identified as being from Iran. Torpedo jars are sometimes assumed to be of Mesopotamian origin rather than Iranian, and further analyses of their bitumen, combined with examination of their ceramic petrography, would be extremely useful.

The Islamic period

By the Early Islamic period, a single sample from al-Qusur shows that Hit bitumen was still traded in the Gulf. Later Islamic attestations show that both Iraqi and Iranian bitumen was used at Qala'at al-Bahrain in the medieval period. The most recent evidence comes from reports by twentieth-century observers who note the continuing use of bitumen from Hit in the marshes of southern Iraq (79).

Overview

During the Neolithic, bitumen from both local (Burgan bitumen at H3 As-Sabiyah) and distant sources (Hit bitumen at Umm al-Quwain) was used in the Gulf. During the Bronze Age, northern Iraqi bitumen was initially used, but was supplanted towards the end of the third millennium by bitumen from Hit-Abu Jir and Iran. Iranian bitumen from several sources, and Iraqi bitumen from Hit-Abu Jir, then continued to be important in the succeeding millennia. Certain places, such as Early Dilmun Bahrain and Parthian ed-Dur, show a wide variety of bitumens from different regions, reflecting their status as entrepôts. Failaka and Umm an-Namel, on the other hand, tend to show simpler patterns, indicative of their role as staging posts linking the Gulf with routes up the Tigris (to northern Iraqi sources) and the Euphrates (to Hit-Abu Jir).

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