3.9.2. Bitumen provenience

by Thomas Van de Velde

Introduction

Several bitumen samples from the 2008-2012 excavations in Tell F6 were sent to Ghent for geochemical analysis in order to determine their origin. In the Near East, bitumen surfaces naturally at several locations and raw material from these seepages was extracted by humans for a variety of purposes. The material was especially practical as an adhesive but was also used frequently for its waterproofing properties. It has been used in architecture as a mortar or to waterproof reed mats, for the lining of pottery, repairing pottery, as a material used to make stoppers/corks, to waterproof baskets, to enhance and waterproof the hull of boats etc.

Bitumen samples from several archaeological sites in the Arabian Gulf have been sourced in the past and most came from the same seepages as the bitumen used in Mesopotamia and Iran (Van de Velde in preparation, Connan and Carter 2007, Connan *et al.* 2005, Connan *et al.* 1998, Connan and Van de Velde 2010, Connan unpubl., Van de Velde *et al.* 2015). These are to be located in northern Iraq (around Mosul), at Hit (Iraq, middle Euphrates river), the Dead Sea, the Burgan Hill in Kuwait, and a variety of seepages in western Iran (fig. 1093)

Bitumen on Bronze-Age Failaka

We can mark the 21st century BC as an important era for both Bahrain and Failaka, for it is then that the settlements on the islands start to become major players in the trade and interregional contacts that characterise the Bronze Age in the Arabian Gulf. The fate of the island of Failaka is closely intertwined with that of Bahrain as it is also here, on this strategically-located island in the upper Gulf, that we find strong manifestations of the Dilmun culture. It is especially the work of the Danish pioneering excavations (1958-1963), the following French missions (1983-1988) and the work of the Kuwaiti-Slovak missions (2004-2008) that uncovered the Bronze Age on this island (Calvet and Gachet 1990, Salles 1984, Calvet and Salles 1986, Kjærum and Højlund 2013, Højlund 1987, Benediková and Barta 2009, Barta *et al.* 2008). These teams and excavations worked respectively at the Bronze Age sites of Tell F3, Tell F6, Site G3, and Al-Khidr (fig. 1094).

At all these sites an abundance of bituminous material was found but the bitumen from Tell F3, Tell F6, and Site G3 has never been studied and is only sparsely mentioned in publications as the following review will show.

In House 26 in Tell F3 (dated c. 1850-1800 BC) the plastered surface of a small trough is said to have traces of bitumen (Kjærum and Højlund 2013 p. 81). From Site G3, a dwelling site north of Tell F6, two pottery sherds with traces of bitumen inside are mentioned (Salles 1984 fig. 28:68 & fig. 30:92).

More evidence of bitumen presence and usage is mentioned from the area of the temple in Tell F6 excavated by the French mission and dated to the end of the 3rd and beginning of the 2nd millennium BC. Several zones both inside and outside the structure yielded layers with shapeless lumps of bitumen. Unfortunately, there is no information available as to what sort of artefacts these bitumen lumps originally belonged, the easily-decaying nature of bituminous material obviously attributes to that. Beside the bitumen lumps, a "*zone de déchets de bitumen*" is mentioned (locus 389) (Calvet and Gachet 1990). The excavation report does not give any further information on this context, but it is thus possible that bitumen was worked in the immediate surroundings of the temple.

Bitumen was also attested in close context with pottery (Pic 2008: catalogue nos. 8, 43, 140, 168, 229, 241, 249, 250). This could either have been as a lining of the vessels, or a remnant of the storing/transporting/working of bituminous material.

Noteworthy is a sculptured piece made from a black bituminous stone from the temple at Tell F6 (Calvet and Pic 1986 p. 76-77). The material was originally identified as an artificial 'stone' and named "*mastic de bitume*" (Connan and Deschesne 1996). It was, however, later identified as a natural-occurring rock from the Sargelu formation in Iran (Connan 2012 p. 156-177) and should not be considered as actual bitumen.

It is clear from the French excavation reports from Tell F6 that bitumen was found frequently on the site. No detailed study on this material has been performed, however, making it hard to make any claims on its use or to make an assessment on quantities.

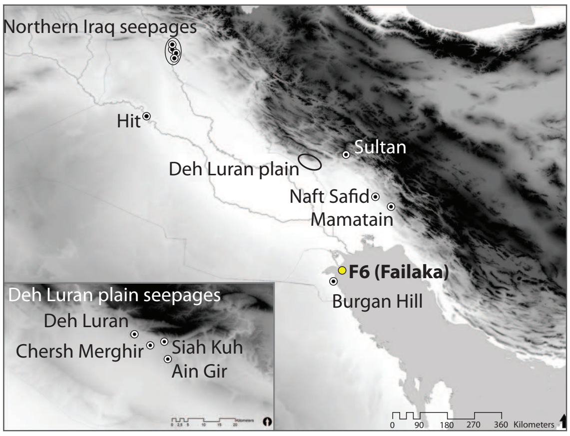

Fig. 1093. Map showing the bitumen seepages mentioned in the text. For a complete overview of all bitumen seepages in Antiquity see Connan & Van de Velde (2010) & Connan (2012).

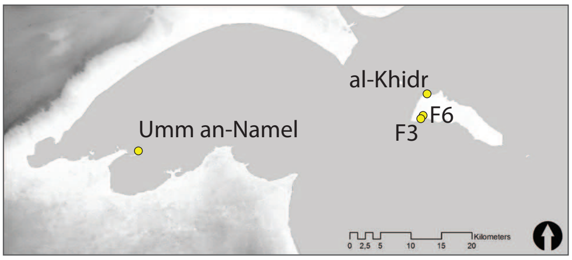

Fig. 1094. Dilmun-period sites with evidence of bitumen usage.

Conversely, excavations at Al-Khidr have revealed a Dilmun-period settlement with massive amounts of bitumen used in a domestic context, and the finds from here have been properly analysed and published (Benedikova and Barta 2009). Al-Khidr was excavated by a joint Kuwaiti-Slovak team for four campaigns. The site is identified as a dwelling site similar to Tell F3. All bitumen finds from Al-Khidr have been quantified, registered and, where possible, identified. Around 200-230 kilograms of bitumen was recovered from the site, including bitumen-coated baskets and cordage, seal impressions, bottle stoppers, or just plain shapeless lumps. There are even occurrences of bitumen layers (largely in contexts with pottery or with stones in walls), between building stones as bonding materials, and thick bitumen crusts in large earthenware vessels (Belenová-Štolcová 2010). The evidence could also point towards bitumen processing on the site and the thick crusts in vessels could also be evidence of transporting.

In general, there is a lot of evidence for the use and working of bitumen at several Bronze Age sites on the island of Failaka although the material has been unevenly studied and published. The excavations at Al-Khidr show that bitumen was used for a multitude of purposes and this is supported by the excavations presented here (see above Højlund p. 210).

The origin of the bitumen from Failaka

As yet, only bitumen from the French missions at Al-Qusur, Site B6, Tell F5 and Tell F6 has been analysed to obtain information on its geological origin, the latter site being the only Bronze Age site. Geochemical tests have been conducted on thirteen bitumen samples from the Bronze Age levels at Tell F6, three from the Middle Dilmun Period (ca. 1400-1300 BC) and ten from the Early Dilmun levels (ca. 2000-1700 BC). All of these samples originated from the Hit area in Iraq, with the exception of one sample which came from the Burgan Hill bitumen seepage (Kuwait) (Connan and Carter 2007) (fig. 1093). There is, however, also proof that Iranian bitumen was used at the Dilmun settlement at Saar and in several tumuli from the same period (Connan *et al.* 1998, Van de Velde in preparation). It seems that bitumen from several seepages and source areas was exported to several Dilmun settlements simultaneously, although it looks apparent that raw materials from the Hit seepages was not used in this area prior to 2000 B.C.

Bitumen samples from F6 (Kuwaiti-Danish campaigns)

Several bitumen samples from the 2008-2012 excavations in Tell F6 were selected for geochemical screening to determine their geological origin. Bitumen from several trenches and deposits were chosen in order to investigate whether or not bitumen suppliers changed through time (fig. 1095). Faint impressions are visible on several samples, but in all cases these are too small or not enough pronounced to allow any detailed identification.

The viscosity of natural bitumen does not allow the material to be properly worked, therefore a temper was added (Forbes 1964, Connan and Van de Velde 2010). These additives were not studied in detail but rather macroscopically checked. There was nothing noteworthy for most of the samples; most samples had the typical brownish-black colour, often tempered with sand. Samples 9 and 10 however are extraordi-

Sample	ID	Phase	δ13C	Ts/Tm	GCRN/C_{30}	GCRN/31R	OLN/C_{30}	Source
1	A123-X482	4	-27,05	0,26	0,14	0,41	0,04	Mixture?
2	A179-X474	4	-27,88	0,22	0,14	0,4	/	Deh Luran plain
3	A180-X493	4	-26,97	0,26	0,12	0,36	0,07	Mixture?
4	A220-X725	2	-26,54	0,36	0,13	0,4	0,1	Mixture?
5	A206-X615	3	-27,32	0,25	0,15	0,47	0,05	Mixture?
6	A209-X668	3	-27,5	0,2	0,19	0,51	/	Deh Luran plain
7	A215-X760	3	-27,49	0,29	0,19	0,49	/	Deh Luran plain
8	A218-X743	3	-27,51	0,24	0,14	0,42	/	Deh Luran plain
9	E87-X349	6		0,33	0,08	0,24	/	Deh Luran plain?
10	A140-X280	6		0,34	0,08	0,25	/	Deh Luran plain?
11	E119-X541	5	-26,77					Mixture?
12	E122-X535	6	-27,8					Deh Luran plain?
13	E67-X554	7	-27,83					Deh Luran plain?
14	J18-X79	1	-27,32					

Fig. 1095. Archaeological samples used in this research. Measured values of δ13C and molecular ratios Ts/Tm (18α(H)-22,29,30-trisnorneohopane/17α(H)-22,29,30-trisnorhopane), GCRN/C30 (Gammacerane/C30αβ-hopane), GCRN/31R (Gammacerane/ C3122R hopane), OLN/C30 (Oleanane/C30αβ-hopane). NM= no measurement.

nary because of the presence of complete shells in their matrix (fig. 1096). Crushed-shell inclusions are attested quite frequently in bitumen mixtures, but these can be considered as intrusive in the initial matrix (i.e. sand) that was used to create a bitumen mixture rather than a deliberate addition. The shells present in samples 9 and 10 have been identified as members of the *Potamididae* family, a species closely associated with mud flats and mangroves. These shells are only visible on one side of the lumps, in both cases the backside is free of any inclusions, and in one case (sample 9) elongated impressions are visible. These imprints are about 2 to 5 mm wide and probably derive from reed bundles.

It is unlikely that shells were added deliberately to the bitumen mixture as that would not enhance its physical characteristics in any way, it would actually make it more porous. So either the shells in this bitumen are an accident (for example the spilling of bitumen on a shell-covered surface), or they became part of the bitumen by a physical process. There are strong indications for the usage of bitumen in naval architecture and it is not impossible to imagine shells being impressed into the bitumen coated hulls of boats when they were moored in the mangroves. Bitumen was also a product which was quite often reused and in some cases there is evidence of the stripping of bitumen from boats with the aim to store these for later re-use (Connan *et al.* 2005, Carter 2010). This could also have been the case for the bitumen samples 9 and 10 from Tell F6.

Analytical methods

Sample preparation

The idea on sourcing archaeological bitumen was tested and published for the first time in 1978 (Marschner *et al.* 1978) and further refined by Nissenbaum and Connan (Nissenbaum *et al.* 1980, Nissenbaum *et al.* 1984, Rullkotter *et al.* 1985, Rullkotter and Nissenbaum 1988, Connan 1988, Connan and Deschesne 1992, Connan *et al.* 1992). The techniques used by these and other researchers rely on those developed for the petroleum industry and have proven to be effective on archaeological samples as well. These techniques embody the identification and quantification of individual molecules from the saturated hydrocarbon fraction, and stable carbon isotope analysis ($\delta^{13}C$) on the asphaltenes fraction. Bitumen consists of two more chemical fractions (resins and aromatics), which do not contain useful parameters for identifying their source.

As stated above, archaeological bitumen is generally an artificial mixture consisting of pure bitumen and a temper. Evidently, the bitumen needs to be isolated from the added ingredients prior to analysis. Archaeological samples were crushed and put in a vial for solvent extraction by dichloromethane:methanol (3:1 ratio, 1,5 ml per gram of sample). The vial was put in an ultrasonic bath and centrifuge, after which the liquid fraction was recovered. This process was repeated twice.

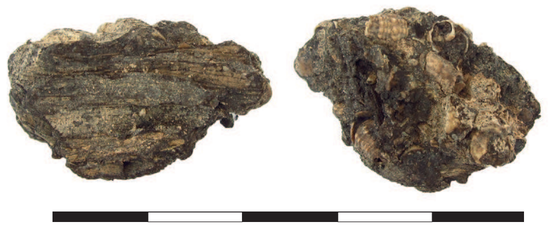

Fig. 1096. Bitumen sample 9 bearing shell inclusions. Note the parallel impressed lines on the backside (left photo) and the shells on the front.

Asphaltenes can be defined as the heaviest components of petroleum and are insoluble in light n-alkanes (e.g. hexane) but soluble in organic compounds (e.g. dichloromethane) (Goual 2012). Therefore the solvent was removed from the sample by evaporation after which n-hexane precipitation was used to isolate the asphaltenes fraction. Standard column chromatography was used for separation of the saturated hydrocarbon fraction (Peters *et al.* 2005a p. 200).

Stable Carbon Isotope analysis parameters

EA-IRMS (Elemental Analysis – Isotope Ratio Mass Spectrometry) was used on the asphaltenes fraction. The carbon isotopic composition of the asphaltenes fraction was determined using an elemental analyser (ANCA-SL, PDZ Europa, UK), coupled to an isotope ration mass spectroscopy (IRMS) (20-20, SerCon, UK). The isotopic composition of natural samples (i.e. not synthetic isotopic enrichment) is reported relative to an international reference, using the so called 'δ' scale and is typically expressed in ‰.

$$\delta^{13}C = \frac{\left[\frac{^{13}C}{^{12}C}\right]_{sample} - \left[\frac{^{13}C}{^{12}C}\right]_{VPDB}}{\left[\frac{^{13}C}{^{12}C}\right]_{VPDB}}$$

For C the international reference is Vienna Pee Dee Belimnite (VPDB), which has a carbon isotopic ratio of 0.0111802 (± 0.0000028). The measured values of all samples can be found in fig. 1095.

GC-MS analysis parameters

GC-MS analysis (gas chromatography-mass spectrometry) was conducted on the saturated hydrocarbon fraction in order to determine and quantify biomarkers. These complex organic compounds are derivations of the original organic materials from which bitumen is formed, containing source-specific information (Peters *et al.* 2005b, Peters *et al.* 2005a). A Hewlett-Packard 6890-5973 GC-MS system equipped with an Agilent Technologies HP-5MS column (30m x 0.25mm ID, 0.25µm) was used with Helium as a carrier gas (gas flow of 1.5 ml/min). One microliter of sample dissolved in CH_2Cl_2 was injected (in splitless mode). The oven temperature increased incrementally from 40°C to 250°C at 6°C per minute, and from 250°C to 300°C at 2°C per minute. The temperature was then held at 300°C for 30 minutes. The terpane fingerprint (m/z 191) was used to identify and quantify individual molecules present in the samples (fig. 1097). Due to the nature of the samples it is impossible to use a purely quantitative approach, therefore molecular ratios are used in fingerprinting rather than individual compounds.

For both techniques several replicate analyses of samples were conducted to cross-check consistency of the measurements. No discrepancies were identified. If a sample was measured more than once, the average of all measurements was calculated and used for further analyses and interpretation. The measured values can be found in fig. 1095.

The origin of the F6 samples

The geologic origin of the sample was investigated using the information from the terpane fingerprints and the values obtained through stable carbon isotope analysis on the asphaltenes fraction. The $\delta^{13}C$ values of all samples are too high to contain any bitumen from the Hit area. In several samples (samples 1, 3, 4 & 5) 18α-oleanane was observed. The base for this compound is angiosperms and originates in the Triassic Period or earlier and is for this region mainly linked to oils originating from the Padbeh source-rock formation in Iran (Peters *et al.* 2005b p. 572, Connan 2012 p. 117).

Fig. 1098 shows several cross-plots combining several parameters; the molecular ratios Ts/Tm and 18α-oleanane/C_{30}αβ-hopane, but also the values retrieved from stable carbon isotope analysis. The bitumen from Tell F6 seems to cluster nicely together with bitumen samples from the Hellenistic period site of Akkaz, which have been published in detail (Connan 2011). The exact source of these samples has not been established as their genetic parameters do not match any of the reference seepages, nor any other archaeological bitumen. It has therefore been suggested that this bitumen was either a mixture between two types of bitumen (one from the seepages on the Deh Luran

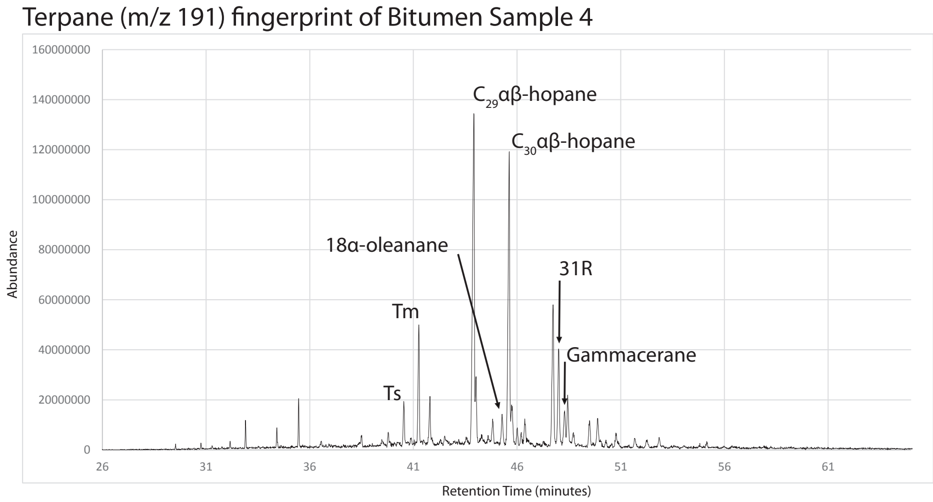

Fig. 1097. Terpane fingerprint of bitumen sample 4.

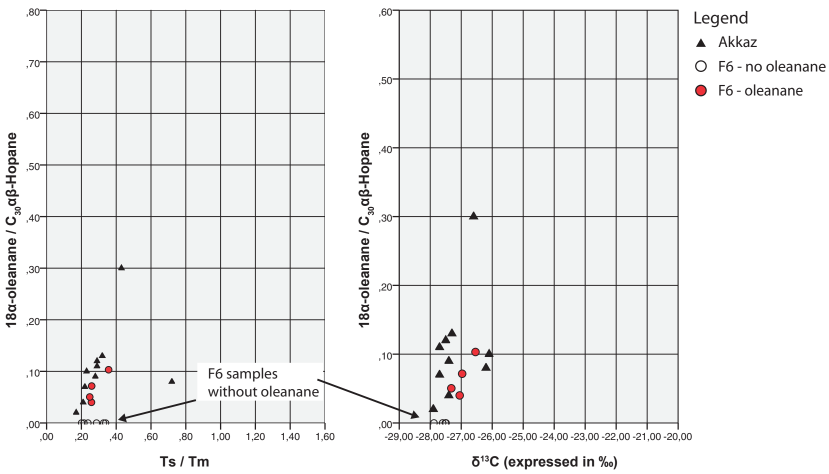

Fig. 1098. Cross-plots of Ts/Tm vs. 18α-oleanane/C30αβ-hopane (left) and δ13C vs. 18α-oleanane/ C30αβ-hopane. The bitumen samples from Tell F6 seem to correlate with those from Akkaz (molecular ratios and δ13C retrieved from Connan 2011).

plain mixed with oleanane-containing bitumen) or alternatively this bitumen came from a yet-unidentified seepage (Connan 2011). We should however mention that the Tell F6 bitumen does not match those from Akkaz on all parameters, the Gammacerane/ C_{30}αβ-hopane ratio[24] for instance is remarkably higher in the samples from Akkaz and the range in which the Akkaz bitumen $\delta^{13}C$ values fall is much wider (fig. 1099). Of course, the extreme wide range of $\delta^{13}C$ values in the Akkaz samples could be an indication of the presence of bitumen from multiple seepages.

If the bitumen from Akkaz is indeed a mixture of raw material from different seepages (one with a genetic pattern reminiscent of those from the Deh Luran plain and one containing oleanane), it is striking that the 18α-oleanane/C_{30}αβ-hopane ratio is very similar in both datasets. That would indicate that the composition of the mixtures is similar, which would be quite coincidental considering the 2000 year gap between the two sites. In that respect, it seems more likely that the bitumen from both sites were extracted from an unidentified seepage. The deviating Gammacerane/C_{30}αβ-hopane, the wide $\delta^{13}C$ range of the Akkaz samples, and the fact that as of yet no oleanane-containing bitumen with a $\delta^{13}C$ of asphaltenes within the -28/-27‰ range has been identified in bitumen samples (Connan 2011) on the other hand conflict with this hypothesis.

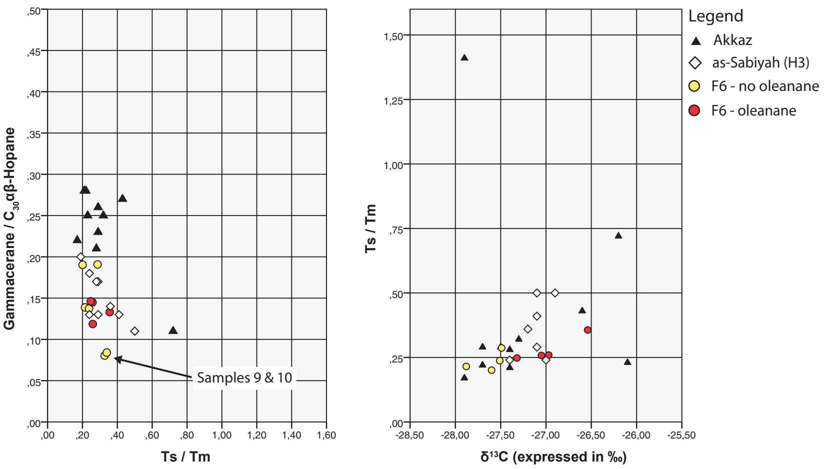

Fig. 1099. Cross-plots of Ts/Tm vs. Gammacerane/ C30αβ-hopane and δ13C/ vs. Ts/ Tm. The bitumen samples excavated at the Neolithic site of as-Sabiyah have been identified as coming from the Burgan Hill (Kuwait).

From the ten bitumen samples which have been subjected to GC-MS analyses, only 4 showed a presence of oleanane. The same genetic parameters as described above were used to identify the source of the other 6 samples. Both molecular ratios and $\delta^{13}C$ match with bitumen from Susa, which lacks oleanane and has been identified as coming from one of the seepages on the Deh Luran plain.[25] Bitumen from the Burgan Hill shows a very similar molecular pattern (Connan 2010, Connan *et al.* 2005), but as illustrated in fig. 1099, the $\delta^{13}C$ of this bitumen does not match with the values from the Tell F6 samples. Consequently, we can securely state that the Tell F6 bitumen samples without oleanane are coming from one of the seepages on the Deh Luran plain. The same type of bitumen has also been identified in archaeological bitumen samples from Bronze Age tumuli in the A'ali burial field in Bahrain (Van de Velde in prep.) and possibly also in the archaeological bitumen samples from Saar Settlement (Connan *et al.* 1998).

If the bitumen containing oleanane are mixtures, then it would make sense that one of the components is material from the seepages on the Deh Luran plain as the molecular parameters (Ts/Tm, Gammacerane/C_{30}αβ-hopane, Gammacerane/C_{31}22R hopane) between the two groups show great similarities (fig. 1099). There is, however, a distinction between the two groups based on the $\delta^{13}C$ measurements, which are lower in the samples without oleanane. This, however, does not necessarily mean anything as this value of course could be influenced by the addition of bitumen from another seepage.

For three samples no molecular data was retrieved and only $\delta^{13}C$ is available. The values of samples 12 & 13 are both low in number (-27,8‰ and -27,83‰) and correlate with the $\delta^{13}C$ of the samples coming from the Deh Luran plain. Sample 11 on the other hand shows a relatively low $\delta^{13}C$ (-26,77‰) in such a degree that it falls within the range of the samples containing oleanane and should therefore probably be placed in the same group.

Samples 9 & 10 are outliers in the dataset (fig. 1099) and do not seem to belong to either of the two groups defined above. These two samples do not exhibit any oleanane and are characterised by their low Gammacerane/C_{30}αβ-hopane. Alteration of the Gammacerane/C_{30}αβ-hopane parameter is possible because of biodegradation of the sample. Unfortunately no isotopic data is available for these samples. Either this bitumen comes from an unidentified seepage, or we are encountering a chemically alteration of the samples. It is remarkable that these samples do not only distinguish themselves from the rest of the dataset because of their molecular ratio, but also because of the high number of shell inclusions (cf. supra). It remains most likely that this bitumen shares the same origin as the other non-oleanane containing samples, i.e. one of the seepages on the Deh Luran plain.

Bitumen sample J18

One specific feature that was excavated at Tell F6 was a stone set pit (J16, figs. 36 and 1095: Sample 14) with a very fine-grained black deposit at the bottom. It was thought that this pit was a fire pit specifically for the heating and processing of bitumen, hence the black colour of the lower deposit, and a sample was taken for geochemical screening. GC-MS on this sample revealed a very obscure chromatogram lacking all the distinctive peaks identified in bitumen. However, $\delta^{13}C$ on this sample gave a value of -27,32‰, which correlates nicely with that of bitumen. Previous experimental work on bitumen revealed that the recycling – or more specifically, the reheating – of bitumen caused the evaporation of entire compound classes, yet that the isotopic signature on the asphaltenes remains the same independent of the duration of the reheating of the sample (Hollander and Schwartz 2000). If the fire-pit discussed here was indeed used as an installation for the working of bitumen, its contents would naturally be subject to numerous processes of (re-) heating, causing the archaeological sample to behave like it does on the chemical analyses. So quite possibly, the black deposit in the stone set pit is the silent witness of bitumen processing, but we should not take this for granted as no bitumen-specific molecules could be identified. Unfortunately, the experimental work discussed above does not include detailed chromatograms and consequently it was impossible to compare those results with that of sample J18, nor was it possible in the current research to duplicate a similar test.

Conclusion

Thirteen bitumen samples from the 2008-2012 excavations at the Bronze Age site of Tell F6 on Failaka have been investigated with the aim to determine their original seepage. GC-MS analysis was conducted on ten samples, and stable carbon isotope analysis on eleven. Using these analytical techniques, it was possible to identify two different main groups in the bitumen dataset, discriminated by either the absence or presence of oleanane – a chemical molecule only present in bitumen coming from the Padbeh source rock formation (Iran). The group of samples containing oleanane shows close resemblance to a group of bitumen samples from the Hellenistic site of Akkaz. No specific origin for these samples was given, but it was suggested that this bitumen was either a mixture of raw materials from different sources, or coming from an unidentified seepage. The latter option being the most plausible. The other group of bitumen samples from F6, lacking oleanane, is coming from one of the bitumen seepages on the Deh Luran plain (Iran). The dataset knows two true outliers, samples 9 and 10, for which no reference data was found. It is most likely that this bitumen is also coming from the Deh Luran plain.

As Iranian bitumen has been identified in several Dilmun-period datasets from both Failaka and Bahrain, it should come as no surprise that this type of material is also found at Tell F6. Remarkable, however, is the difference in bitumen between the Tell F6 bitumen datasets from the French and the Kuwaiti-Danish missions. Most of the material from the French excavations of the temple is Iraqi in origin (Hit-area), whereas one sample was identified as coming from the Burgan Hill seepage (Kuwait).

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