

# The bitumen of Tell Brak from the Middle Uruk (c.3500 BC) to Late Bronze Age (c.1280 BC): origin and trade routes

## Abstract

13 archaeological samples, dated from the Middle Uruk period (c.3500 BC) to the Late Bronze age (c.1280 BC), were analyzed by geochemical techniques in order to identify bitumen and to attempt to find its origin. Extracts do show that the samples are characteristic archaeological bitumens. Bitumens of Tell Brak were compared to some other archaeological asphalts, to crude oils and natural asphalts. Utilization of carbon isotopes on asphaltene and biomarkers namely steranes and terpanes allowed us to identify two main areas of bitumen supply, Hit on one side along the Euphrate river, northern Iraq on the other side.

**Keywords:** bitumen, Tell Brak, origin, archaeological samples, natural asphalts, crude oils, steranes, terpanes, carbon isotopes, deuterium isotopes, asphaltene

Volume 3 Issue 6 - 2018

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**Received:** October 02, 2018 | **Published:** November 26, 2018

## Introduction

Bitumen belongs to the list of common raw materials which has been extensively used in Mesopotamia, Elam and the Gulf until the Neolithic period (7000-6000 BC). Evidence of earlier use has been recently documented in the Syrian desert<sup>1-3</sup> near el Known where the bitumen-coated flint implement, dated 70000 BC (Middle Palaeolithic) have been unearthed. Since the pioneering works by Forbes,<sup>4</sup> Marschner and Wright<sup>5</sup> and Marchner et al.<sup>6</sup> several studies were conducted on archaeological sites from present day Iraq, Iran and the Gulf, using efficient analytical techniques of petroleum exploration. A review, summarizing the various aspects of the use and trade of bitumen in antiquity and prehistory has been recently published.<sup>7,8</sup> When an archaeologist find a presumed bituminous mixture, the recurrent questions that spring to his mind are: Is-it a real bituminous mixture? How much bitumen was used? What other additives were mixed with the bitumen? Where did the bitumen come from? At a particular location, were there any changes in sources of bitumen through time? Do these identified trade routes agree with other historical data, especially the geopolitical and cultural framework? This last question has been addressed with success in some well documented case histories spanning a rather large period of time and presenting a satisfactory bank of samples. Such demonstrative examples refer to case studies on Tell el 'Oueili in southern Iraq<sup>9</sup> and more recently on various archaeological sites of Bahrain.<sup>10</sup> A complete study, recording the situation in Kuwait through time from 5000 BC to 700 AD, is also available.<sup>11-14</sup>

At present no data have been published on archaeological sites along the Rhabur river and this study of the bituminous mixtures from Brak will be the first one in the area. The only recent study, published on archaeological bitumens of the Near East refers to results from Hacinebi along the Euphrates, at the border between Turkey and Syria.<sup>15,16</sup> However the conclusions of these studies should be regarded with much caution for, as we will be demonstrating in this paper, the isotopic parameters used for tracing the source of the bitumen are not valid for largely obscured by mineral matrix effect. The present paper will summarise the geochemical results acquired on 13 archaeological samples from Brak and will discuss these data in the light of references issued from Northern Iraq, South-West Turkey and Hit.

## Archaeological samples

13 archaeological samples presumed to be composed of various bituminous mixtures were selected for analysis. The sample set spans a rather long period of the historical record at Brak, starting with the Middle Uruk occupation, c.3500 BC, and ending at the Late Bronze age around c.1280 BC. The basic information related to each sample is given in Table 1 with its macroscopic description which was carried out prior to any chemical investigation. The sample set covers a wide variety of sample types which are currently recorded in archaeological sites from the Middle East namely : bitumen crusts in the interior of potsherds (n° 1126, Figure 1) or on the lip (n°1224) or in the exterior of potsherd (n° 1126, Figure 1), bitumen coating on a wall cone which is probably a remain of glue (n°1127, Figure 1), bituminous coating of mats (n°1175) or baskets (n°1176), bituminous mixtures with numerous vegetal remains which looks like mortars (n°1122 and n°1123), cakes of bituminous mixtures thought to be possibly stored raw material (n°1128, Figure 1; n°1125), hard bituminous mixtures with reed and possibly rope impressions (reed boats? roofs? n°1025, n°1177), hard black sealing agent (n°1026, Figure 1), bituminous mixture without obvious vegetal remains (n° 1125 and n°1124).

## Experimental

The archaeological bituminous materials were studied using the same analytical scheme applied in previous studies.<sup>9,17</sup> A detailed up-to-date flowchart with a description of each analytical technique has been presented with some examples in Connan.<sup>18</sup> A binocular description of each sample was carried out prior to the detailed chemical analysis. In the present study a petrographical analysis was not undertaken for the samples appeared to be quite classical in regard of our past experience. After the sampling procedure which keep aliquots of check samples (see n°1126 in Fig.1), chemical analyses including screening techniques such as Rock-Eval pyrolysis and detailed investigations in particular molecular analysis of hydrocarbons and isotopic analysis of the asphaltene were conducted. Several diagnostic molecular biomarkers especially on terpanes and isotopic criteria on asphaltene ( $\delta^{13}C$ ) were used to establish bitumen-to-bitumen and bitumen-to-crude oil correlations.

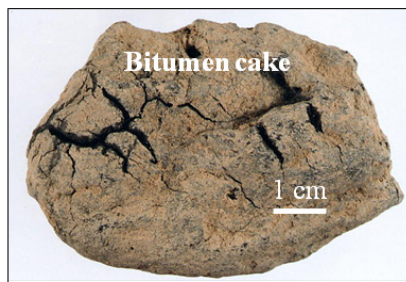
**Table 1** Basic information about the samples

Sample number	Date		Date of sampling	Archaeological references	Area, locus	Comments on period	Sample type	Macroscopic description
	Max	Min						
1128	-3500		27-05-1997	A cake of bitumen (in which the bitumen was possibly transported or stored?)	TW 730	Middle Uruk	4c	A big lump of "bitumen" with weathering cracks
1126	-3400			a sherd from a "flower pot" with bitumen	TW 710. A pit contemporary with the earliest Late Uruk level at Brak	Early Late Uruk (possibly Late Middle Uruk)	1a	bitumen crust coating the interior of the sherd
1127	-3200			Wall cone	probably from the Eye Temple	Late Uruk (possibly later)	1b	bitumen coating on one end of the wall cone
1124	-3200		22-04-1997	Bitumen?	TW 627. A level which lies at the top of the Late Uruk walls	either right at the end of the Late Uruk occupation, or slightly earlier than sample 1025 (TW 287)	4b	hard and black bituminous mixture without obvious vegetal remains
1125	-3200		30-04-1997	"Bitumen" lump	TW 627. A level which lies at the top of the Late Uruk walls	either right at the end of the Late Uruk occupation at Brak, or slightly earlier than sample 1025 (TW 287)	4c	bitumen mixture. Extremely hard rock
1025	-3000	-2900	season 1992	Register n° 5496	TW 287, level 8/9	Level 10 contains Jamdat Nasr pottery	3b or 5	Black sample with numerous weathering cracks and reed (?) impressions
1026	-2900		season 1991	Register n° 5218	TW 249, in "construction level" for level 6, it can come from earlier fill	ED I in southern Mesopotamian terms but the fact that the bitumen was incorporated within the fill beneath the building	3b	Hard black cake with weathering cracks and some vegetal remains
1123	-2900		16-04-1997	Bitumen showing a reed mat impression on the bottom, sample 2	TW 605. This is a level which has been cut by the pit TW 605 (sample 1) and is earlier in date	should be dated around or not long after 3000 BC	4c or 2	brown mixture, fairly hard, with long vegetal remains
1122	-2900		14-04-1997	A large circular piece of bitumen (with string impression?), sample 1	TW 606. Pit of early 3rd millennium date, probably not far in time from the original sample 1026 from TW 249	post -Jamdat Nasr and pre-Ninivite 5	3a	brown sample with numerous big vegetal remains inside

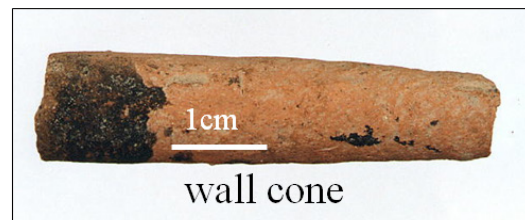
Table Continued...

1175	-2300	-2200	Matting impression	Akkadian monumental building, Room 30, locus SS 585	Early Bronze age	2	bituminous mat, well preserved
1176	-2300	-2300	Basket impression	room 3 in the south building of Late Akkadian, area FS, locus FS 1525, one construction level later than sample 1175	Early Bronze age	3b and 2	very black surface with numerous vegetal remains
1224	-1950		Sherd	southern type of pottery but could possibly be made in the north	Isin-Larsa period or sometimes referred as Early Old Babylonian	1b	bitumen coating on the sherd lip, traces of bitumen in the interior
1177	-1280		Matting impression and burnt wood	burnt roof collapse in the Mittanni Palace, room 11	Late Bronze age Mittanni	4b	two types of sample. The type selected for analysis show imprints of vegetal remains (reeds?)

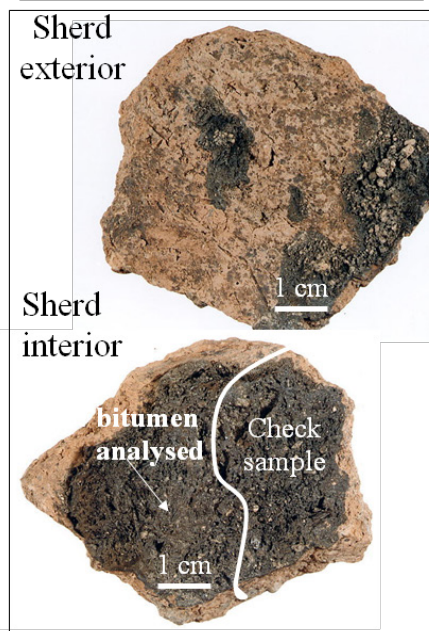
1128  
3500  
BC



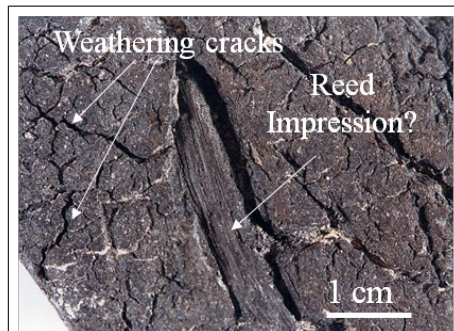
1127  
3200  
BC



1126  
3400  
BC



1025  
3000-2900  
BC



1026  
2900  
BC

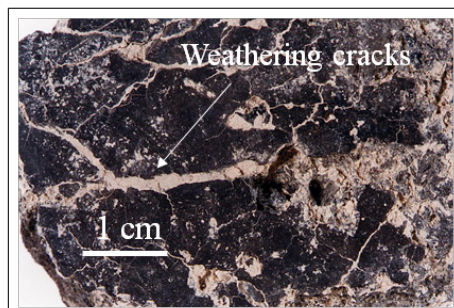


Figure 1 Pictures of some samples.

## Results

### Recognition of bituminous mixtures by Rock-Eval screening techniques of Bahrain 10

The Rock-Eval pyrolysis of the raw samples has been applied on all samples except on samples n°1127, 1175, 1176, 1224 and 1177. The most important parameters obtained are listed in Table 2. Among the samples analysed we have not found any pure raw bitumen as identified previously in Mashnaqa and Mari. All the samples belong to the so-called “archaeological bitumen” family, i.e. they are all bituminous mixtures processed by mixing bitumen with mineral matter and organic debris. Their TOC (Total Organic Carbon), HI (Hydrogen Index), and Tmax (temperature of the maximum of the S2 peak corresponding to Hydrocarbons released by pyrolysis) are fully consistent with the data obtained on “archaeological bitumen” of Bahrain (Figure 2).<sup>19</sup> Obviously the sample n°1128, referred as a bitumen cake (Figure 1) and thought to be representative of the possible form under which the bitumen is transported, is already a manufactured sample, possibly stored to be subsequently used. One should again notice that the current bitumen richness chosen at Brak is similar to what is currently used elsewhere in the Near East: TOC are ranging from 10 to 40 % as commonly observed. To summarise, the bituminous mixtures analysed at Brak are classical archaeological bitumens of the Near East.

### Gross composition of the dichloromethane extract

As a follow up of the Rock-Eval screening analysis, the samples are extracted with dichloromethane and this extractable organic matter (= true bitumen) is subsequently separated into 4 fractions (“saturates”, “aromatics”, “resins” and “asphaltenes”) which are weighted. Gross compositions of extracts are calculated (Table 3) and represented in two classical ternary diagrams reproduced in Figure 3 & Figure 4. All samples, except the sample 1224 which is much richer in both saturated and aromatic hydrocarbons (Figure 3), fall within the area defined as characteristics of archaeological bitumens.<sup>9,10</sup> The sample 1224 which coats the lip of a potsherd as a thin film is much more like a natural asphalt and may have been applied as a pure material on the pottery. The low quantity recovered has not allowed us to evaluate its purity. All these basic gross composition data confirms that the extractable organic matter is bitumen which has been biodegraded and oxidised.

### Presumed origin of the bitumen assumed by carbon isotopic data on asphaltenes

In previous papers, we pointed out that the carbon isotope value of asphaltenes (Table 3) (Table 4) provides reliable genetic information on crude oils and asphalts for this parameter is not significantly affected by intense weathering processes which have deeply modified the gross composition of the archaeological bitumens, leading to reduced amount of both saturates and aromatics.  $\delta D$  (in ‰/SMOW) of asphaltenes is not a source parameter for it was found to be very sensitive to alteration processes which have significantly modified the bitumen. This alteration entails a major shift of  $\delta D$  towards heavier values which means an enrichment in deuterium, as seen herein in the sample set ( $-54 < \delta D < -77$  ‰/SMOW, Table 3). The occurrence of this heavy value range confirms what has been seen in archaeological bitumen everywhere and especially in Bahrain. Unbiodegraded crude

oils, collected from reservoir at depth, do show much lighter values ( $-75 < \delta D < -120$  ‰/SMOW). Consequently heavy values are again showing that archaeological bitumens of Brak are deeply weathered oils.

$\delta^{13}C$  (in ‰/VPDB) of asphaltenes from Brak have been plotted as a function of the date of samples in Figure 5. References, collected on crude oils from subsurface oil fields (Table 4) (Figure 6), natural asphalts outcropping at surface (Table 4) (Figure 6), and on natural asphalts from Hit (Figure 6),<sup>10</sup> were incorporated in Figure 5. At a first glance, the distribution pattern of Tell Brak suggests two possible main origins for bitumen. The main source seems to be located in northern Iraq whereas the secondary one is the famous natural asphalt deposit of Hit-Abu Jir, along the Euphrates. Apparently, both sources coexist in the oldest samples, between 3500 and 3000 BC whereas the northern source was only identified in younger samples, between 2300 and 1280 BC.

One should notice that  $\delta^{13}C$  values of asphaltenes recorded in both archaeological and reference samples varies between  $-28.3$  and  $-26.9$  ‰/PDB, i.e. within a very narrow range of less than 1.5‰/PDB. These results are fully consistent with what has been reported in our previous papers,<sup>9,10,17,19</sup> but contrast with what was published by Schwartz et al.<sup>15</sup> These authors report  $\delta^{13}C$  values of so-called “archaeological bitumens”, i.e. in fact raw bulk samples, between  $-10$  and  $-28$  ‰/PDB and consider these values as representative for the bitumen itself. This assumption is fully wrong for the analyses performed on the bulk raw bituminous samples do not provide reliable  $\delta^{13}C$  values for the total organic carbon and more precisely for its bitumen sub-fraction. In fact, this bulk measurement gives only a  $\delta^{13}C$  average value of the bituminous mixture which is a garbage-type sample constituted of many different components including mineral and organic ones. One should also remember that the organic matter itself is often a mixture of bitumen, vegetal debris (reed, straw) and carbonised materials from ashes. The bulk values, measured on whole samples, are consequently largely influenced by the mineral matrix present and significant shifts should be expected when carbonates are abundant. Marine carbonates possess  $\delta^{13}C$  values around 0<sup>20</sup> whereas petroleum (crude oils, bitumen, natural asphalts) values cover the  $-20/33$  ‰ range.<sup>21</sup> Occurrences of various mixtures of bitumen and minerals, especially carbonates, are obviously explaining the wide range of  $\delta^{13}C$  values recorded by Schwartz et al.<sup>15</sup> in their archaeological samples of Hacinebi, Choga Mish, Ur, Farrukhabad, Gawra, Nuzi, Jerablus Tahtani, etc.

To get rid of any subsequent controversy regarding our statement, dedicated experiences were conducted to collect required demonstrative proofs. 9 samples of bituminous mixtures from Mari in which the mineral composition was determined by X-Ray diffraction were selected as test series. By chance X-Ray analyses reveal a great variety of mineralogical composition among samples with bituminous mixtures almost devoid of carbonates or carbonate-rich. On each sample we have measured the  $\delta^{13}C$  of the raw material as carried out by Schwartz et al.<sup>15</sup> and the  $\delta^{13}C$  of asphaltenes as processed in our approach. The obtained data, gathered in Table 5, are presented in Figure 7. The results fully confirm what was expected. First of all the  $\delta^{13}C$  values measured on raw samples are directly related to the amount of carbonates and especially of calcite in the present case (Figure 7A). Occurrence of large amount of calcite ( $\delta^{13}C$  around 0) should be shifting the bulk values towards heavier ones. This trend

is indeed observed herein for values move from  $-29$  to  $-21$  ‰ / PDB when the % of carbonates or calcite (not shown) increases. Secondly  $\delta^{13}\text{C}$  values of asphaltenes (Figure 7B) are independent of the mineral composition and cluster in a very narrow range which clearly indicates that the bitumen of Mari is originating from Hit. This assumption has been confirmed by molecular data on biomarkers.<sup>13</sup> In conclusion the assessment of the origin of bitumen, carried out by Schwartz et al.<sup>15</sup> is not substantiated by their geochemical data in particular by their isotope ones for the utilization of  $\delta^{13}\text{C}$  values measured on raw samples is not permitting to gather a genetic characteristic of the bitumen, necessary to find its source. By the way we must emphasized that the assessment of bitumen origin in the Near East is a difficult task for the geochemical contrasts registered among samples are falling within a narrow range as shown in Figure 5. This really implies that the geochemical techniques applied should be very reproducible and accurate to draw conclusions on the basis of very limited variations. Clustering of data, obtained on 10 samples of Mari (Table 5) (Figure 7B) illustrates the required accuracy needed to approach the truth.

### Origin of bitumen based on biomarkers, isotope data on asphaltenes and biomarkers

“Saturates” have been analysed by GC-MS in order to examine sterane (m/z 217) and terpane (m/z 191) patterns which are currently used to sort out some specific genetic parameters which enable to differentiate various bitumen origins. As usual in such a type of samples, biomarker fingerprints display various degrees of alteration from unaltered (state 1) to the most highly affected which is rank state 16 in our alteration scale. In the present series, 3 samples only bears very low degree of alteration (state 0 and 1) and most of them are belonging to the 3 to 6 state of alteration (Table 6). This result means that the  $\text{C}_{27}$ - $\text{C}_{29}$  steranes are generally biodegraded and show a preferential removal of  $\text{C}_{27}$  steranes as reported by Peters and Moldowan<sup>22</sup> for level 6 of biodegradation in their alteration scale. As a consequence, sterane ratios cannot be used as genetic parameters to trace the source of the bitumen. Due to the fact that terpanes do not show obvious alteration features they may be used to provide genetic parameters.

Figure 8 reproduce sterane and terpane patterns of two unaltered samples: one originates from the famous natural asphalt deposit of Hit (n° 231), in present day Iraq (Figure 6), the other (n° 1128) was chosen among the Tell Brak archaeological samples. At a first glance both samples display quite similar patterns. This property is a general feature of Near East bitumens and asphalt which do not show striking differences within their molecular chemistry. To solve the enigma and try to differentiate samples, one should rely on details which are accessible by quantitative measurements of molecular ratios. Among the 65 molecular ratios which are systematically acquired, one particular ratio has been selected as fairly discriminant. It refers to Tm ( $17\alpha(\text{H})$ -22,29,30-trisnorhopane) and Ts ( $18\alpha(\text{H})$ -22,29,30-tisnorhopane) structures which occurs with different ratios in Hit and Brak as seen in Figure 8. Due to the presumed unaltered character of most terpane patterns, this ratio may be considered as a good genetic parameter. In order to set up a classification of sample in terms of source area, a cross plot of  $\delta^{13}\text{C}$  of asphaltenes has been carried out with Tm/Ts ratios (Figure 9). Figure 9 presents the data splitted into two diagrams: 9a refers to a suite of reference samples (see Fig.6 for location) in which we have gathered samples of crude oils from

subsurface reservoirs (Kirkuk, Fallujah, Damir Dagh, Kilf), natural asphalt (Hit, Sari Sati, Fattah, Kifri, Zakho), bitumen veins (Harbol, Aman Hassan) as well as archaeological bitumens (Khorsabad, Niniveh, Assur, Tell es Sawwan, Telul eth Telathat, Khirbet Derak); 9b presents data from Brak.

Comparison of Figures 9A & 9B confirms the two major source areas already defined and furnish some suggestions to delineate more precise area of provenances for the bitumen in Northern Irak. The bitumen of the Hit area is well defined by oil seeps of Hit-Abu Jir and the crude oil of Fallujah 1 well at depth. Samples n° 1123, 1124 and 1025 of Brak belong to this genetic family. As by-product of the study, one should notice that the bitumen analysed in Khorsabad, dated from the Assyrian period, seems to be imported from Hit. This feature is consistent with the historical record. Bitumen veins of Aman Hassam (Figure 6) in Iran have not been found in the sample set. The bitumen oil seepage from the Zakho town has apparently been used in Khirbet Derak which is located at 40 km to the North West of Mossoul, i.e. in its neighbourhood (Table 7).

Other bitumens from Brak seems to have various origins in northern Irak, n°1125, 1122, 1128 and 1026 may be coming from Kirkuk-Kifri oil seeps,<sup>23</sup> n°1175,1176,1177 and 1224, closely related to the archaeological bitumens from Telul eth Telathat, may have the same origin which is not determined yet, n°1126 has an unknown origin. In addition to analyses carried out on asphaltenes,  $\delta^{13}\text{C}$  of specific compounds in “saturates” were also measured using the so-called GC-C-IRMS device (Gas Chromatography-Combustion-Isotope Ratio-Mass Spectrometry). In the present cases  $\delta^{13}\text{C}$  values of individual biomarkers may not be systematically used as genetic parameters for the recorded values may be the result of several phenomena: source, partial biodegradation of the molecule, effect of an abundant unresolved complex mixture in case of rather low concentrations. In order to select the most representative data the biomarker fingerprint were carefully examined. As a consequence we have focused on  $\delta^{13}\text{C}$  values of two important biomarkers, Tm ( $17\alpha(\text{H})$ -22,29,30-trisnorhopane, Figure 8) and  $17\alpha,21\beta(\text{H})$ -29-homohopane22S ( $\text{C}_{31}\alpha\beta$ HopaneS, Figure 8), which are well preserved and rather abundant in all samples. The samples compared using this type of geochemical data comprise 6 samples of Brak (n° 1128, 1126, 1122, 1124, 1025, 1123), 3 samples of Mari (n°96, 94 and 90 which was already referred as particular),<sup>13</sup> 2 samples of Mashnaqa (n° 563 and 554) thought to have different origins and 3 samples of Hit (n° 231, 233, 235). The basic information on samples and the  $\delta^{13}\text{C}$  values on asphaltenes and biomarkers are listed in Table 8.

Plot of  $\delta^{13}\text{C}$  values (in ‰ /PDB) of Tm and  $\text{C}_{31}\alpha\beta$ HopaneS as a function of Tm to Ts ratios are presented in Figure 10A & B. Inside the Hit reference set up with samples n° 231, 233 and 235, are found two samples of Mari (n°96 and 94) one sample of Mashnaqa (n°563) and two samples of Brak (1025 and 1123). Other samples are dispersed in other area which suggests other sources. In that respect sample 1124 of Brak is not falling within the Hit area but occurs in its vicinity. One should in particular notice the location of sample n° 90 from Mari which display a particular behaviour and therefore is not originating from Hit as others. This sample was previously<sup>13</sup> identified as unique in Mari for it was the only one to contain significant amount of n-alkanes. Such a characteristic has never been seen in all natural asphalt from Hit analysed so far.

**Table 2** Rock-Eval data

Archaeological number	Date		S1	S2	S3	COT	Tmax	HI	IP	OI
	Max	Min								
1128	-3500		27.5	102.25	6.25	23.55	427	434	0.21	27
1126	-3400		29.74	251.28	10.89	42.99	429	585	0.11	25
1127	-3400									
1124	-3200		17.24	114.42	5.16	22.04	428	519	0.13	23
1125	-3200		16.89	147.96	6.4	27.7	430	534	0.1	23
1025	-3100	-3000	15.86	115.57	4.57	24.02	427	481	0.12	19
1026	-3000	-2900	8.94	95.84	4.54	21.7	431	442	0.09	21
1123	-3000	-2900	18.8	115.84	6	22.77	425	509	0.14	26
1122	-3000	-2900	25.96	194.78	10.16	36.51	427	533	0.12	28
1175	-2300	-2200								
1176	-2300	-2300								
1224	-1950									
1177	-1280									

**Table 3** Gross composition of extracts and isotopic data

Archaeological number	Date		EO %/sample	Gross composition of EO				Asphaltene isotopes	
	Max	Min		sat100	aro100	res100	asp100	$\delta^{13}\text{C}$	$\delta\text{D}$
1128	-3500		34.93	3.32	3.4	14.08	79.2	-27.6	-54
1126	-3400		60.7	1.34	3.29	20.44	74.93	-27.7	-54
1127	-3200								
1124	-3200		28.51	2.16	4.64	20.32	72.88	-28.2	-63
1125	-3200		28.11	2.18	4.84	18.56	74.42	-27.9	-65
1025	-3000	-2900	29.25	1.45	3.22	16.78	78.55	-28	-59
1026	-2900		18.35	0.91	2.96	18.41	77.72	-27.4	-63
1123	-2900		31.52	1.95	4.13	16.79	77.13	-28.1	-60
1122	-2900		39.13	2.38	3.81	18.41	75.4	-27.7	-57
1175	-2300	-2200	59.46	2.22	5.3	23.89	68.59	-27.7	-77
1176	-2300	-2300	60.38	1.56	5.45	25.78	67.21	-27.6	-72
1224	-1950			16.57	21.71	46.28	15.44	-27.5	-59
1177	-1280		50.48	3.65	4.94	16.12	75.29	-27.6	-62

**Table 4** Carbon isotope values of asphaltenes

Sample number	Crude oil (subsurface)	Asphalt (surface)	Name of the oil field or oil seep	$\delta^{13}\text{C}$	Average value	Standard deviation	Average value	Standard deviation
1356		Oil seep	Zakho	-27.1				
1482		Oil seep	Zhako	-26.9				
1483		Oil seep	Zhako	-26.9				
1357		Oil seep	Sari Sati	-27.6				
1358		Oil seep	Quantil Bridge	-27.8				

Table Continued...

Sample number	Crude oil (subsurface)	Asphalt (surface)	Name of the oil field or oil seep	$\delta^{13}\text{C}$	Average value	Standard deviation	Average value	Standard deviation
					-27.3	0.4		
185		Oil seep	Fattah 1	-27.8				
186		Oil seep	Fattah 2	-27.8				
187		Oil seep	Fattah 3	-27.5				
188		Oil seep	Fattah 3B	-28				
209		Oil seep	Kifri	-27.7				
210		Oil seep	Kifri	-27.5				
211		Oil seep	Kifri	-27.6				
					-27.5	0.3		
							-27.5	0.4
690	Oil field		Damir Dagh	-27.4				
614	Oil field		Jambur-Bai Hassan	-27.5				
688	Oil field		Bai Hassan	-27.1				
1353	Oil field		Bai Hassan 13	-27.8				
687	Oil field		Kirkuk 130	-27.7				
1355	Oil field		Kirkuk 131	-27.7				
					-27.7	0.2		

Table 5 Isotopic data on whole sample, asphaltene and mineralogical composition of samples from Mari

Archaeological number	Archaeological Campaign	Average date	Asphaltenes		Whole sample		Mineralogical composition (X-Ray diffraction analysis)				
			$\delta^{13}\text{C}$	$\delta\text{D}$	%carbon	$\delta^{13}\text{C}$	quartz %	calcite %	dolomite %	gypsum %	felspars %
92	Mari 87	-2400	-28.3	-62	38	-27.2	8	38	2	1	2
97	Mari 87	-2330	-28.3	-56	25	-22.5	11	46	10	1	5
102	Mari 87	-2330	-28.2	-49	32	-23.9	5	57	3	1	1
89	Mari 87	-2100	-28	-60	24	-22.5	6	60	7	1	1
90	Mari 87	-2100	-28.3	-67	20	-28.3	96	0	0	0	1
99	Mari 87	-2100	-28	-71	27	-23.2	9	44	8	1	1
100	Mari 87	-2050	-28.2	-78	44	-27.8	7	35	1	4	1
94	Mari 87	-1750	-28.2	-59	23	-26.5	56	11	1	0	3
96	Mari 87	-1750	-28	-69	40	-25.4	9	41	5	1	1
98	Mari 87	-1750	-28.1	-47	25	-23.6	6	36	4	0	3

Table 6 Steranes and terpanes : state of alteration

Archaeological number	Date		Degree of alteration	Steranes			Diasteranes	Terpanes	
	Max	Min		C21- C22	C27- C29	C29 $\alpha\alpha\text{R}$		Tricyclo-polyterpanes	C27- C35 hopanes
1128	-3500		3	present	no alteration		absent	present	no alteration
1126	-3400		12	present	altered -no C27	$\alpha\alpha\text{R}$ altered	absent	present	no alteration
1127	-3200		1	present	no alteration		present	present	no alteration
1124	-3200		11	present	altered -no C27		absent	low-present	no alteration

Table Continued...

Archaeological number	Date	Degree of alteration	Steranes		Diasteranes	Terpanes	
I125	-3200	13	present-alter?	altered-almost no C27		absent	low-altered no alteration
I025	-3000 -2900	7	present	altered-less C27		absent	low-present no alteration
I026	-2900	14	absent	altered-less C27	αααR altered	traces	absent no alteration
I123	-2900	7	present	altered-almost no C27		absent	low-present no alteration
I122	-2900	11	present	altered-less C27		absent	present no alteration
I175	-2300 -2200	13	altered-present	altered-no C27		absent	traces no alteration
I176	-2300 -2300	13	altered-present	altered-no C27		absent	traces no alteration
I224	-1950	7	no alteration	altered-less C27		present	low-present no alteration
I177	-1280	3	no alteration	no alteration		present	low-present no alteration

**Table 7** δ<sup>13</sup>C and δD of asphaltenes, Ts/Tm ratio of various samples : natural asphalts, crude oils and archaeological samples.

Sample Type	Archaeological		Date for archaeological samples			Steranes and terpanes	Asphaltenes		TpI
	Number	Location	Maxi	Average	Mini	Alteration type	δ <sup>13</sup> C	δD	Ts/Tm
Natural	16	Hit				I	-28.2	-73	0.18
	135-1	Abu Jir				I	-28.3	-87	0.11
	135-2	Abu Jir				I	-28.3	-87	0.13
Asphalt	231	Hit				I	-28.3	-93	0.1
	232	Hit				I	-28.3	-90	0.13
Crude oil	695	Kilf				I	-28	-85	0.42
	1352	Kilf				I	-28		0.41
	694	Fallujah				I	-28.2	-76	0.14
Natural asphalts and bitumen veins	1351	Fallujah				I	-28.2		0.13
	1356	Zakho				I	-27.1		0.63
	1357	Sara Sati				I	-27.6		0.12
	443	Harbol				I	-27.5	-79	0.06
	185	Fattah1				I	-27.8	-102	0.16
	186	Fattah2				II	-27.8	-99	0.17
	188	Fattah 4				I	-28	-103	0.09
Archaeological samples	209	Kifri				I	-27.7	-83	0.27
	1388	Telul Eth-Thalathat	-4500	-4350	-4200	7	-27.6	-71	0.18
	1389	Telul Eth-Thalathat	-4500	-4350	-4200	9			0.16
	1390	Telul Eth-Thalathat	-4500	-4350	-4200	13	-27.5	-71	0.18
	66	Khorsabad	-800	-750	-700		-28.3	-58	0.1
	513	Khirbet Derak		-4500		13-15	-27.1	-65	0.63
	174	Tell es Sawwan	-5500	-4750	-5000	13	-27.7	-56	0.32
	175	Tell es Sawwan	-5500	-4750	-5000	14	-27.9	-58	0.3
	225	Niniveh		?		14	-27.7	-64	0.28
	226	Assur		?		13	-27.7	-55	0.27
	1454	Harbol				I			0.05



Table Continued...

natural Asphalts and bitumen veins	1482	Zhako				1	-26.9	-86	0.66
	1483	Zhako				1	-26.9	-92	0.66
	1099	Aman Hassan				1	-28.5	-101	0.17
	687	Kirkuk 117				1	-27.3	-65	0.43
	1348	Kirkuk 117				1	-27.3		0.4
Crude	1354	Kirkuk 130				1	-27.7	-82	0.31
	1355	Kirkuk 131				1	-27.7	-77	0.29
oils (oil fields)	690	Damir Dagħ				1	-27.4	-77	0.29
	1349	Damir Dagħ				1	-27.4		0.26
	1350	Bai Hassan				1	-27.1		0.2
	1353	Bai Hassan 13				1	-27.8		0.17
	1128			-3500		3	-27.6	-54	0.36
Archhjaeological samples	1126			-3400		12	-27.7	-54	0.54
	1127			-3200		1			0.27
	1124	Tell		-3200		11	-28.2	-63	0.14
	1125			-3200		13	-27.9	-65	0.24
	1025	Brak	-3000	-2950	-2900	7	-28	-59	0.15
	1026			-2900		14	-27.4	-63	0.31
	1123			-2900		7	-28.1	-60	0.14
	1122			-2900		11	-27.7	-57	0.32
	1175		-2300	-2250	-2200	13	-27.7	-77	0.16
	1176			-2300		13	-27.6	-72	0.17
	1224			-1950		7	-27.5	-59	0.17
	1177			-1280		3	-27.6	-62	0.16

Table 8  $\delta^{13}\text{C}$  of asphaltenes and some terpanes of Tell Brak, Mari, Mashnaqa and Hit.

Archaeological number	Sample location	Sample type	Bitumen origin	Date			Alteration of steranes and terpanes	$\delta^{13}\text{C}$ of terpanes				
				Max	Average	Min		$\delta^{13}\text{C}$ asp	Ts/Tm	31 $\alpha$ $\beta$ Ho-paneS	Tm	29 $\alpha$ $\beta$ Ho-pane
1128	Brak	Archeol			-3500		4	-27.6	0.36	-31.9	-28.2	-30
1126	Brak	Archeol			-3400		12	-27.7	0.54	-31.3	-29.5	-31.1
1124	Brak	Archeol			-3200		11	-28.2	0.14	-32.9	-30.2	-31.6
1025	Brak	Archeol		-3000	-2950	-2900	7	-28.2	0.15	-31.9	-29.7	-31.3
1122	Brak	Archeol			-2900		11	-27.7	0.32	-32.3	-30	-31.2
1123	Brak	Archeol			-2900		7	-28.1	0.14	-31.4	-28.9	-30.4
96	Mari	Archeol	Hit	-1800	-1750	-1700	11	-28	0.12	-30.8	-28.6	-30.5
94	Mari	Archeol	Hit	-1800	-1750	-1700	1	-28.2	0.12	-31.2	-29.2	-30.1
90	Mari	Archeol	unknown	-2200	-2100	-2000	11	-28.3	0.37	-29.9	-31	-31.9
563	Mashnaqa	Archeol			-4000		3	-27.9	0.15	-30.1	-29.7	-29.9
554	Mashnaqa	Archeol		-3700	-3650	-3400	10	-27.6	0.23	-30.7		-30.3
231	Hit	Natural asphalt					1	-28.3	0.1	-30.6	-29.2	-30.6

Table Continued...

Archaeological number	Sample location	Sample type	Bitumen origin	Date	Alteration of steranes and terpanes			$\delta^{13}\text{C}$ of terpanes		
233	Hit	Natural asphalt			15	-28.2	0.14	-30.9	-28.9	-31.1
235	Hit	Natural asphalt			1	-28.2	0.12	-31.6	-29.2	-31.1

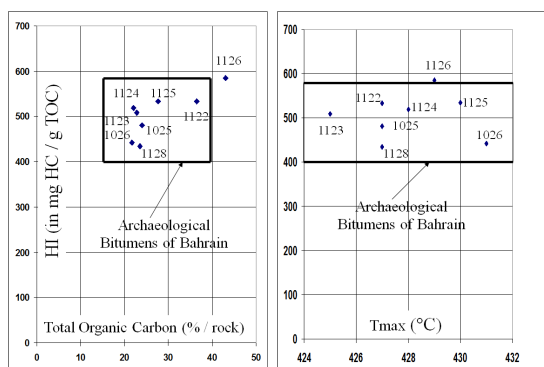


Figure 2 Plot of HI vs. TOC and  $T_{max}$

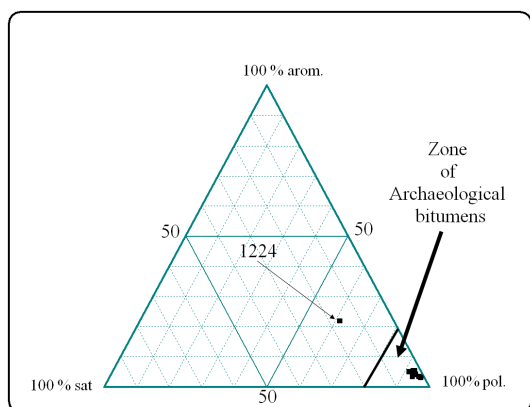


Figure 3 Plot of extract composition in the ternary diagram: % aromatiques, % saturates, % polar.

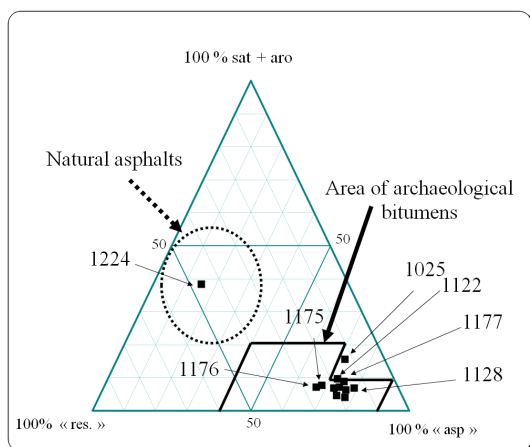


Figure 4 Plot of extract composition in the ternary diagram: % sat + aro, % resins, % asphaltenes.

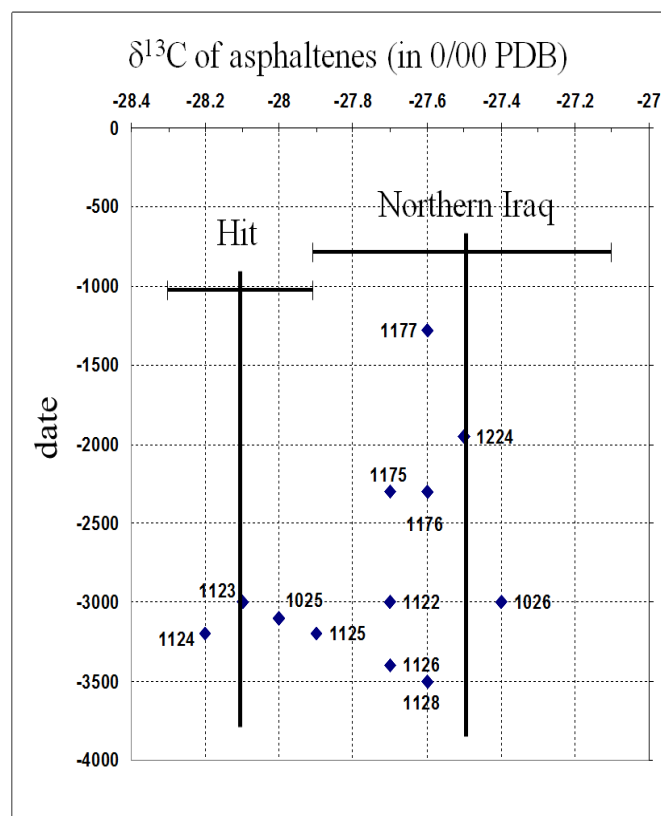


Figure 5  $\delta^{13}\text{C}$  of asphaltenes as a function of sample age.

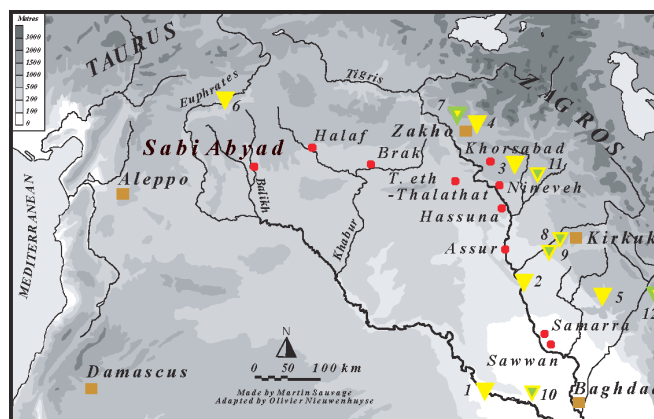


Figure 6 Location of samples used in the study. Significance of numbers: 1, Hit; 2, Fattah; 3, Sara, Sati-Qandil Bridge; 4, Zakho; 5, Kifri; 6, Samsat; 7, Kilf oil; 8-9, Kirkuk-Bai Hassan; 10, Fallujah; 11, Damir Dagh; 12, Amam Hassan.

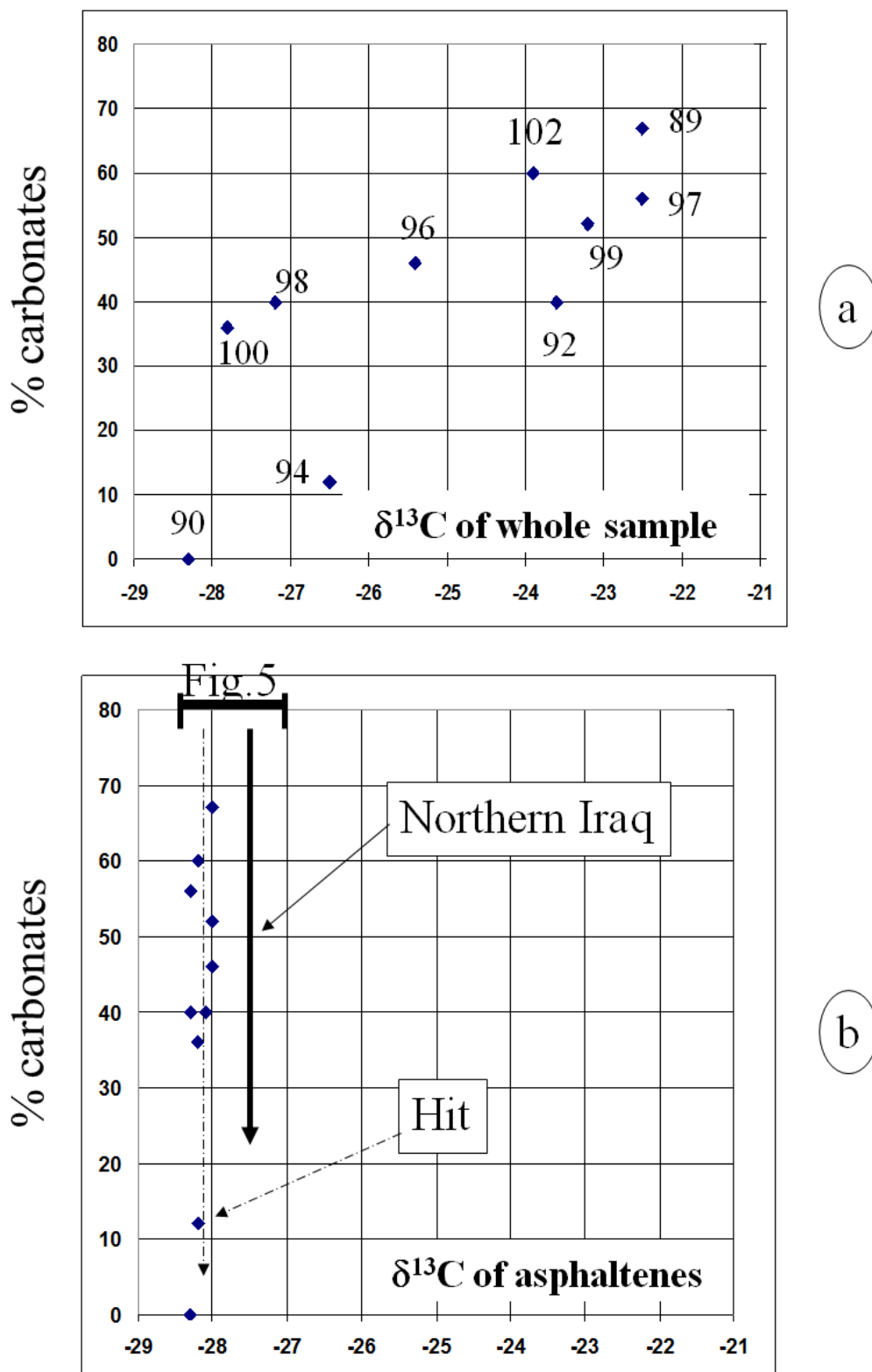


Figure 7 Carbon isotope values of asphaltenes and whole sample as a function of the carbonate content.

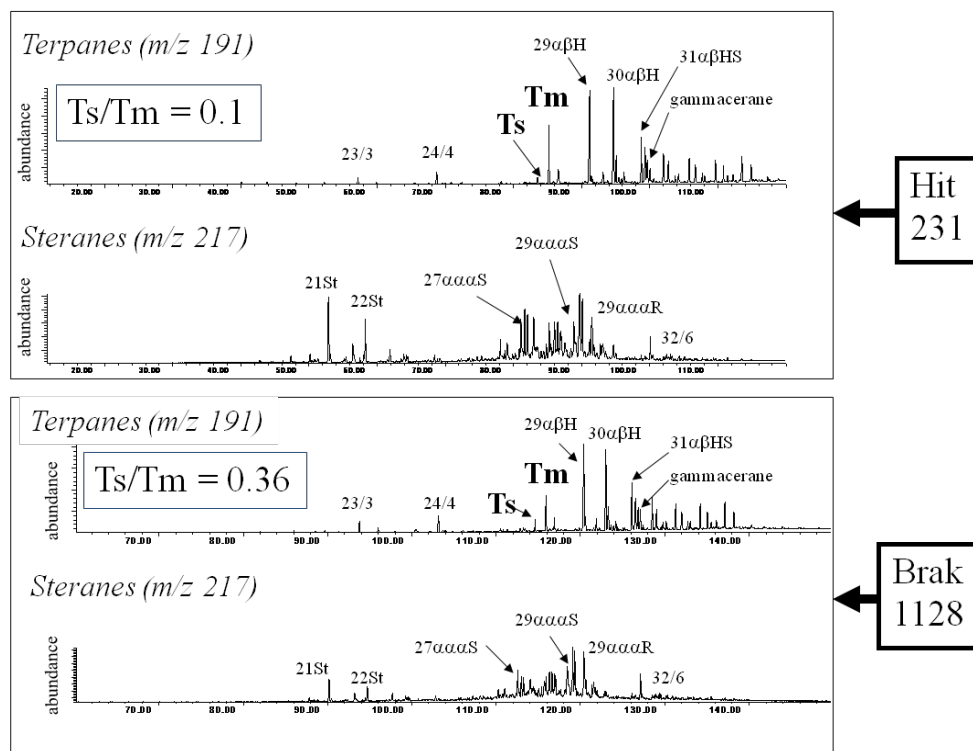


Figure 8 Examples of sterane ( $m/z217$ ) and terpene ( $m/z191$ ).

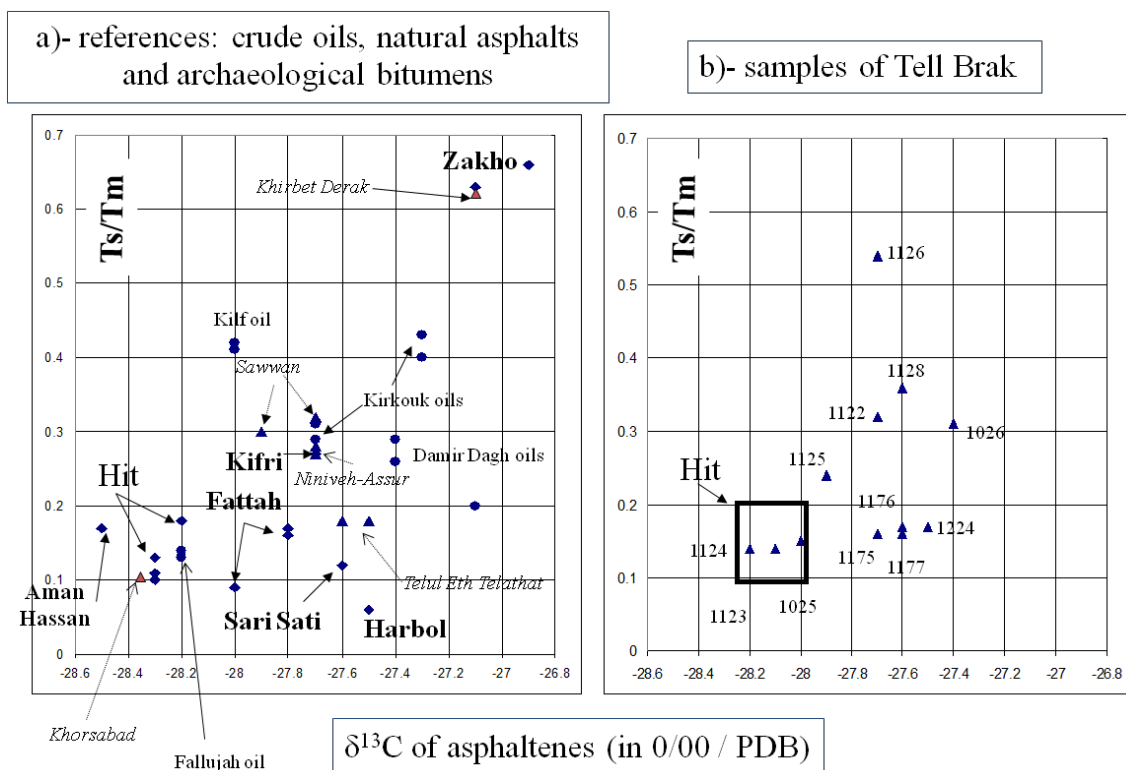


Figure 9 Ts/Tm vs.  $\delta^{13}C$  of asphaltenes. A. references: crude oils (circle), natural asphalts (diamond) and archaeological bitumens (triangle). B. Samples of Tell Brak.

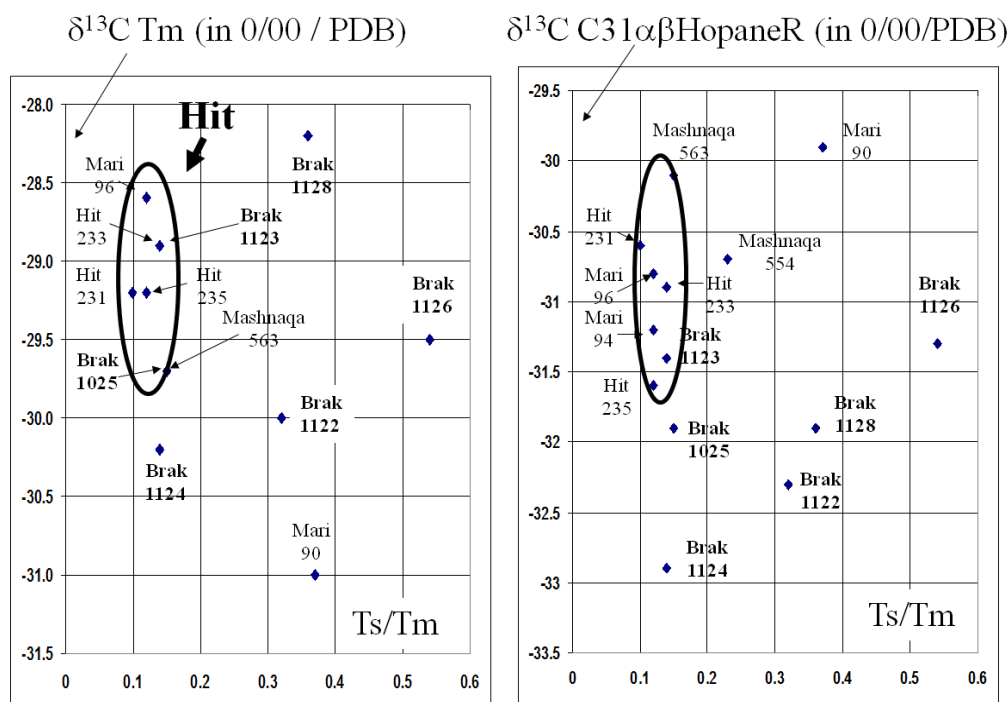


Figure 10  $\delta^{13}\text{C}$  of Tm and  $\text{C}_{31}\alpha\beta\text{HopaneR}$  vs. Ts/Tm.

## Conclusion

The geochemical study of 13 archaeological samples from tell Brak has shown that all the samples analysed are true archaeological bitumens as defined previously; i.e. mixtures of natural asphalts or bitumen with various mineral and organic debris. None of them are raw pristine geological bitumens from storages as thought at the beginning of the study. Contents of bitumen, used to prepare archaeological mixtures fall within classical ranges currently used in the Near East and the Gulf. The bitumen import in Tell Brak has been diversified with two main areas: Hit along the Euphrates and Northern Iraq. According to present state of the study and the present knowledge of either archaeological bitumens or oil seeps, bitumen seems to have been brought from the Kirkuk-Kifri area and from other places. In particular the same source of bitumen has been used apparently in Telul eth Telathat and Brak. As far as changes through time, we have observed utilisation of bitumen from northern Iraq between 3500 and 3400 BC, from Hit and northern Iraq between 3200 and 3000 BC and solely from northern Iraq between 2300-1280 BC. These information are however deduced from a low number of samples, restricted to 13 samples, and is obviously too restricted to draw general conclusion about trade patterns through time. It only indicates that Brak was at a commercial crossroads receiving raw material from the south along the Rhabour but also from the East through several trade routes to the Mossul-Baghdad areas.<sup>24</sup>

## Acknowledgments

The authors are grateful to all archaeologists who have provided samples for references and to Elf Aquitaine Production for their technical support and the access to a data bank on crude oils. We

are indebted to the technical staff from the CSTJF of Elf Aquitaine production in Pau who has carried out most of the analyses. In that respect we want to thank Daniel Dessort, Jean-Bernard Berrut, Béatrice Ruiz, Dominique Duclerc et Yannick Poirier for their efficient technical assistance.

## Conflicts of interest

Author declares that there is no conflicts of interest.

## References

- Boëda E, Connan J, Dessort D, et al. Bitumen as a hafting material on Middle Palaeolithic artefacts. *Nature*. 1996;380:336–338.
- Boëda E, Bonilauri S, Connan J, et al. Middle Palaeolithic bitumen use at Umm el Tlel around 70000 BP. *Antiquity*. 2008;82(318):853–861.
- Boëda E, Bonilauri S, Connan J, et al. New evidence for significant use of bitumen in Middle Palaeolithic technical systems at Umm el Tlel (Syria) around 70,000 BP. *Paléorient*. 2009;34(2) :67–83.
- Forbes RJ. Bitumen and petroleum in Antiquity. Studies in ancient technology. 2nd edn. Volume 1, Leiden: EJ Brill; 1964. p. 1–123.
- Marschner RF, Wright HY. Asphalts from Middle Eastern archaeological sites. *Archaeological Chemistry 2*, Chicago: Advanced Chemical series; 1978. p. 150–171.
- Marchner RF, Dufy LJ, Wright HT. Asphalts from ancient town sites in Southern Iran. *Paléorient*. 1978;4:97–112.
- Connan J. Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations. *Phil Trans R Soc Lond*. 1999;354(1379):33–50.

8. Connan J. Technical Report on the Comparative, Compositional and Isotopic Analysis of the H3 Bitumen. In: Carter R, Crawford H, editors. Maritime interactions in the Arabian Neolithic: Evidence from H3, As-Sabiayh, an Ubaid-remated site in Kuwait. Brill, Boston and Leiden: American School of Prehistoric Research Monograph Series, Appendix II; 2010. p. 261–287.
9. Connan J, Deschesne O. *Le bitume à Suse-Collection du Musée du Louvre*. Paris et Pau: Coédition Elf Aquitaine-Réunion des Musées Nationaux-Collection Monographie; 1996.
10. Connan J, Lombard P, Killick R, et al. The archaeological bitumens of Bahrain from the Early Dilmun period (c.2200 BC) to the sixteen century AD: a problem of sources and trade. *Arabian archaeology and epigraphy*. 1998;9:141–181.
11. Connan J. Les mélanges bitumineux du Tell d'Akkaz (Koweït). The bituminous mixtures from Tell Akkaz (Kuwait). In: Gachet-Bizollon J, editor, Lyon: Le Tell d'Akkaz au Koweït/Tell Akkaz in Kuwait, TMO 57, Chapitre XV; 2011. p. 339–412.
12. Connan J, Carter R. A geochemical study of bituminous mixtures from Failaka and Umm an-Namel (Kuwait), from the Early Dilmun to the Early Islamic period. *Arab arch epig*. 2007;18:139–181.
13. Connan J, Deschesne O. Le bitume à Mari. In: Akh Purattim, Margueron JC, Rouault O, Lombard P. editors, Série "Akh Purattim-Les Rives De L'euphrate. Mémoires d'archéologie et d'histoire interdisciplinaires, Maison de L'Orient et de la Méditerranée-Ministère des affaires étrangères, 2007. p. 165–206.
14. Connan J, Carter R, Crawford H, et al. A comparative geochemical study of bituminous boat remains from H3, As-Sabiayh (Kuwait) and RJ-2, Ra's al-Jinz (Oman). *Arab arch epig*. 2005;16:21–66.
15. Schwartz M, Hollander D, Stein G. Reconstructing Mesopotamian exchange networks in the 4th millenium BC: geochemical and archaeological analyses of bitumen artefacts from Hacinebi Tepe, Turkey. *Paléorient* 2000;25(1):67–82.
16. Schwartz M, Hollander D. The Uruk expansion as dynamic process: a reconstruction of Middle to Late Uruk exchange patterns from bulk stable isotope analyses of archaeological bitumen. *Journal of Archeological Science Reports*. 2016;7:884–899.
17. Connan J, Breniquet C, Huot JL. Les objets bituminés de Tell el 'Oueili : des témoins de la diversité des réseaux d'échanges commerciaux de l'Obeid 0 à l'Uruk récent, in *Oueili*. Paris: Travaux de 1987 et 1989, ERC; 1996. p. 413–453.
18. Connan J. L'archéologie moléculaire et isotopique: étude géochimique des bitumes, brais et goudrons de bois. In: Miskovsky JC, editor. *Géologie de la Préhistoire: Méthodes, Techniques, Applications*. Paris: Association pour l'étude de l'environnement géologique de la préhistoire; 2002. p. 1045–1066.
19. Connan J. Quelques secrets des bitumes archéologiques de Mésopotamie révélés par les analyses de géochimie organique pétrolière. *Bull Centres Recherches Exploration-Production, Elf Aquitaine*. 1988;12(2):759–787.
20. Karhu J. Carbon isotope. In: Marshall CP, Fairbridge RW, editors. *Encyclopedia of Geochemistry*. Kluwer Academic Publishers; 1999. p. 67–73.
21. Clark ID. Stable isotopes. In: Marshall CP, Fairbridge RW. *Encyclopedia of Geochemistry*, Kluwer Academic Publishers; 1999. p. 588–592.
22. Peters KE, Moldowan JM. *The biomarker guide*. New Jersey: Englewood cliffs, Prentice-Hall; 1993.
23. Pascoe EH. Geological notes on Mesopotamia with special reference to occurrences of petroleum. *Memoir of the Geological Survey of India*. 1922;48:1–90.
24. Connan J, Van de Velde T. An overview of bitumen trade in the Near East from the Neolithic (around 8000 BC) to the Early Islamic period. *Arb arch epig*. 2010;21:1–19.