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Saturated biomarkers in the estimation of organic geochemical homogeneity of crude oils from four oil fields in Libya

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Abstract: Seven crude oils from four oil fields in the Sirte and Murzuq Basins in Libya were investigated in order to estimate their organic geochemical homogeneity. Saturated biomarkers (*n*-alkanes and isoprenoids) were analyzed using gas chromatography–mass spectrometry (GC–MS). The parameters calculated from the distributions of *n*-alkanes and isoprenoid aliphatic alkanes, pristane and phytane were used to interpret the organic geochemical characteristics of the oils. Based on the high relative concentration of lower *n*-alkane homologues in the C_{11}–C_{16} range and high *API* values, the oils were classified as light oils. These results also implied that the oils were not biodegraded. The parameters calculated from the distributions of saturated biomarkers indicated that all investigated oils were generated from source rocks containing organic matter of a similar marine origin but with a contribution of terrestrial organic matter. The results also demonstrated that these source rocks were deposited in an oxic environment. The same source rock or the same type of source rocks for all seven samples were postulated. It was concluded that, if the crude oils from these distant basins originated from the same source rocks, they must have had different lengths of their migration pathways.

Keywords: oil–oil correlation; Murzuq Basin; Sirte Basin.

INTRODUCTION

In organic geochemical investigations of the sedimentary formations of the lithosphere, correlation studies of crude oils (oil–oil correlations) occupy a special place.[1–4] For this purpose, numerous bulk and specific correlation para-

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meters are used. Bulk correlation parameters refer to the general chemical and physicochemical properties of crude oils (*API* gravity, bulk composition, stable carbon isotope composition and fractions, asphaltene content, sulphur content). Specific correlation parameters are molecular parameters that are calculated from the abundance and distribution of individual biological markers in the saturated and aromatic fractions of oils (*n*-alkanes, isoprenoid aliphatic alkanes, polycyclic alkanes of sterane and terpane types, naphthenoaromatics and polycyclic aromatic hydrocarbons).

The task of these studies was the correlation of oils (from the same or from proximate oil fields or basins) according to the origin and geologic history. The aim was to define the type of precursor biomass of the investigated oils, the redox conditions in the environment during deposition of the precursor biomass, the length of the migration path of the oil from the source to the reservoir rocks, the degree of maturation, geologic age and the intensity of transformations in the reservoir rocks (cracking, deasphalting, water washing, biodegradation). Oil correlation studies can be of great importance in geological and geophysical oil and gas prospecting and explorations.

Bulk and specific correlation parameters are not straightforward. Their values are influenced by a number of geochemical factors. Due to this, a successful oil–oil correlation often requires usage of a large number of parameters, while interpretation of their values is reminiscent of mosaic making, where each cube has to take its proper place in order to obtain the correct image.

In the present paper, seven crude oils from four oil fields in Libya were investigated. Four samples belong to the Murzuq Basin and three samples to the Sirte Basin.

Previous geological explorations of crude oils belonging to the oil fields of Libya indicated their great diversity according to geological history, which has also caused differences in physical, physicochemical and chemical characteristics. Most of these oils were generated during the Mesozoic and Cenozoic. The Hercynian orogeny that encompassed all of Libya during the Late Carboniferous is the main reason for the lack of Paleozoic oil fields in this area.[5]

Organic-geochemical studies have identified six significant source rock formations in Libya. They are Campanian, Turonian and Nubian sediments in the Sirte Basin, followed by Silurian and Middle Devonian sediments in the Muruzq and Gadamis Basins, and finally sediments from the early Eocene in the Sabaratah Basin. However, the geologic history of the area that belongs to present-day Libya was characterized by a large number of tectonic movements that caused very complex migration patterns of the hydrocarbons in the subsurface. A small amount of the oil generated ended up in the effective reservoir rocks. Some hydrocarbons remained trapped in the original source rocks, some were lost during the migration, and some even migrated to the surface. The final outcome is that more than 90 % of the crude oils found in the territory of Libya originate from the Campanian Sirte shale source rocks and the Silurian Tanzuft shale in the Murzuq Basin.[5]

Correlation studies using biological markers of the crude oils from Libya have already been conducted. Numerous bulk and specific biomarker parameters were used for characterization of the crude oils originating from the East Sirte Basin[6] and the Murzuq Basin.[7] In previous correlation studies of the oils from the Sirte Basin, their origin and geological history were explained. This study required a large number of biomarker parameters from the saturated hydrocarbon fraction and naphthalene, phenanthrene and dibenzothiophene maturation parameters from the aromatic fraction to be determined.[8,9]

In the present paper, an attempt was made to estimate the type of the precursor biomass, deposition environment, degree of maturation and intensity of changes in reservoir rocks of the crude oils from the Murzuq and Sirte Basins in Libya. This type of research is particularly significant in oil-source rock and oil–oil correlation studies because similarities in these characteristics are considered as clear and convincing evidence of geochemical and genetic correlation of the investigated samples.[10–12] For this purpose, the parameters determined from the distributions and abundances of *n*-alkanes and isoprenoid aliphatic alkanes pristane and phytane, which are considered to be among the most often used biomarkers in organic geochemical studies, were used.

The distribution of *n*-alkanes in geologic samples is influenced by both, source and maturity. Domination of odd-carbon-numbered *n*-alkanes (and among them particularly n-C_{27}, n-C_{29} and n-C_{31}) is indicative of immature source rocks with significant input of terrestrial organic matter. In marine organic matter, *n*-alkanes are usually found in the n-C_{24}–n-C_{35} range with uniform distribution of even and odd homologues. With increasing maturity, the distribution of even and odd homologues in all samples becomes more uniform while the *n*-alkane maximum is shifted towards lower homologues.[2]

The pristane/phytane ratio is used for the assessment of redox conditions in the environment during deposition of sediments. Values of this ratio < 1 are typical of samples deposited in an anoxic environment while values > 1 indicate an oxic depositional environment. This ratio is also influenced by maturity and precursor organic matter type and hence, it should always be interpreted in comparison with other organic geochemical parameters.[2]

In the present research, the parameters determined from the distributions and abundances of *n*-alkanes and isoprenoid aliphatic alkanes pristane and phytane were used with a general aim to determine the level of the geochemical homogeneity of the investigated oils.

EXPERIMENTAL

Samples

Details related to samples and sampling procedure are given in Supplementary material to this paper.

Separation and instrumental techniques

The *API* gravity was calculated according to Eq. (1):

$$API = \frac{141.5}{d} - 131.5 \tag{1}$$

The specific gravity (d) of the crude oils was determined by the pycnometer method, using 50 cm^3 pycnometers. The asphaltenes were precipitated from the original crude oils by addition of a 40-fold excess of *n*-pentane followed by resuspension in *n*-pentane and centrifugation (3–4 times). The saturated hydrocarbons, aromatic hydrocarbons and polar compounds were isolated from the deasphalted crude oil fraction using medium pressure liquid chromatography. For this purpose, the main chromatographic column Merck Lobar Größe A, 250 mm×10 mm, LiChroprep Si 60 (40–63 μm) was used in connection with an appropriate precolumn: 80 mm×10 mm, LiChroprep Si 60 (40–63 μm). The saturated hydrocarbons analyzed in this research were isolated using *n*-hexane as the mobile phase at 5 ml min^{-1}. The system was equipped with a Knauer Azura P4 pump and a Shimadzu RID-10A detector connected to a Waters Millipore 730 Data Module. A detailed description of the analytical method employed is described in the literature.[1]

An Agilent 7890A gas chromatograph was used for the analyses of the isolated fractions of the saturated hydrocarbons. A HP5-MS capillary column (30 m×0.25 mm, 0.25 μm film; temperature range: 80 °C for 0 min; then 2 °C min^{-1} to 300 °C and held for 20 min) with helium as the carrier gas (flow rate 1 cm^3 min^{-1}) was used. The gas chromatograph was coupled with an Agilent 5975C mass detector, operating at 70 eV, and scanning masses in the 45–550 range. *n*-Alkanes and isoprenoid aliphatic alkanes, pristane and phytane, as dominant individual peaks in total ion currents (*TIC*) were identified according to their elution order and using a full mass spectra library (NIST11).

All analyzes were conducted in duplicate.

RESULTS AND DISCUSSION

The *TIC* chromatograms of the saturated fractions isolated from the Jakhira and Jalu oils (Sirte Basin) are shown in Fig. 1. The *TIC* chromatograms of the saturated fractions isolated from the El Sharara and Elephant oils (Murzuq Basin) are shown in Fig. 2. The *API* gravity, content of asphaltenes and bulk composition of the investigated oils are given in Table I. The parameters calculated from the distributions of *n*-alkanes and isoprenoid aliphatic alkanes, pristane and phytane are given in Table II.

Sirte Basin

A common feature of the investigated crude oils from the Sirte Basin (Fig. S-1 of the Supplementary material), Jak-1, Jak-2 and Jal-1, is a low content, or even absence, of asphaltenes and high content of saturated hydrocarbons relative to the content of aromatic hydrocarbons and compounds that contain N, S and O atoms (NSO compounds; Table I). These oils also contain C_{11}–C_{16} *n*-alkanes in high concentrations (Fig. 1). As a result, they could be classified as light oils. Their high *API* values confirm this conclusion (37–45°, Table I).

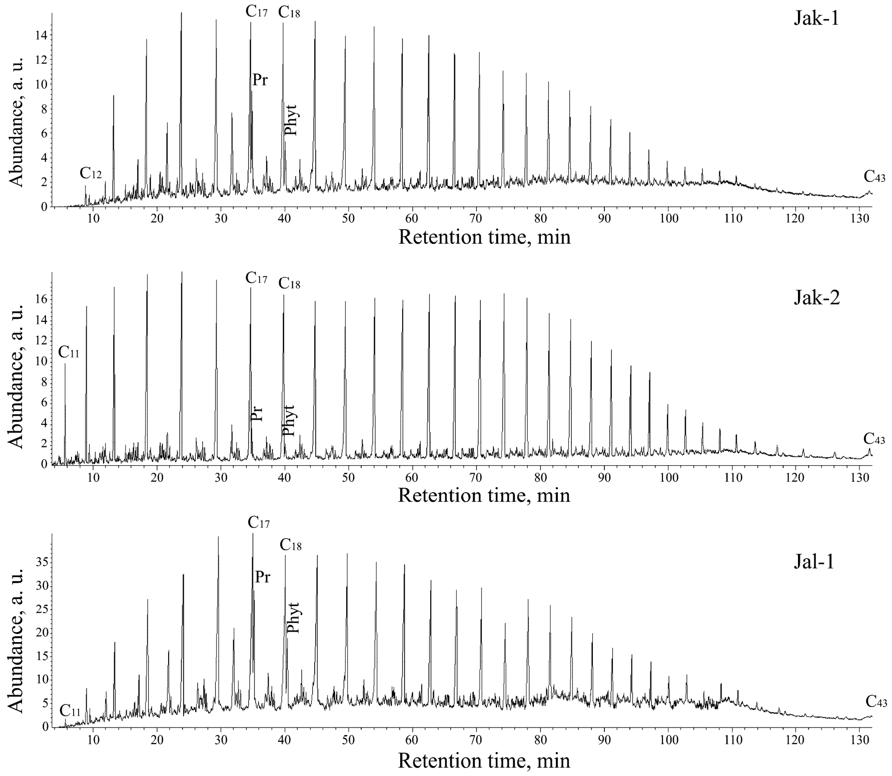

Fig. 1. Total Ion Currents (TIC) of alkane fractions of crude oils from the Jakhira and Jalu oil fields (Sirte Basin).

TABLE I. *API* gravity, content of asphaltenes and bulk composition of the investigated oils

No.	Sample	*API* gravity, °	Content of asphaltenes, %	Bulk composition, %		
				Saturated hydrocarbons	Aromatic hydrocarbons	NSO compounds
1	Jak-1	38	0.60	74.10	15.70	10.20
2	Jak-2	45	0.00	88.70	7.80	3.50
3	Jal-1	37	2.20	63.60	19.10	17.20
4	ELS-1	44	0.40	63.90	23.10	13.00
5	ELS-2	44	0.40	62.80	25.20	12.00
6	ELS-3	43	0.20	67.10	22.30	10.60
7	Eleph-1	38	0.80	55.50	25.40	19.10

This abundance and distribution of *n*-alkanes was enabled by the relatively high temperatures in the reservoir rocks. This particularly applies to the samples from the Jakhira oil field (132 and 135 °C, Table S-I of the Supplementary material). For the sample Jal-1, the reservoir temperature is lower (75 °C), and the reservoir depth is shallower (3003 m) than those in the Jakhira reservoir (Table S-I). However, even this lower temperature in the Jalu reservoir is higher than 66 °C, which is considered the threshold temperature when crude oil biodegradation ceases.[1–4] It could be concluded that due to these high temperatures there were no conditions for microbial degradation of the Jakhira and Jalu crude oils in their reservoirs. As a result, the samples from the Sirte Basin are characterized by the noticeable dominance of *n*-alkanes over the isoprenoids pristane and phytane (Pr/*n*-C_{17} and Phyt/*n*-C_{18} << 1, Table II). On the other hand, high formation temperatures in this area could have stimulated an intense process of cracking of higher *n*-alkanes and formation of lower homologues.

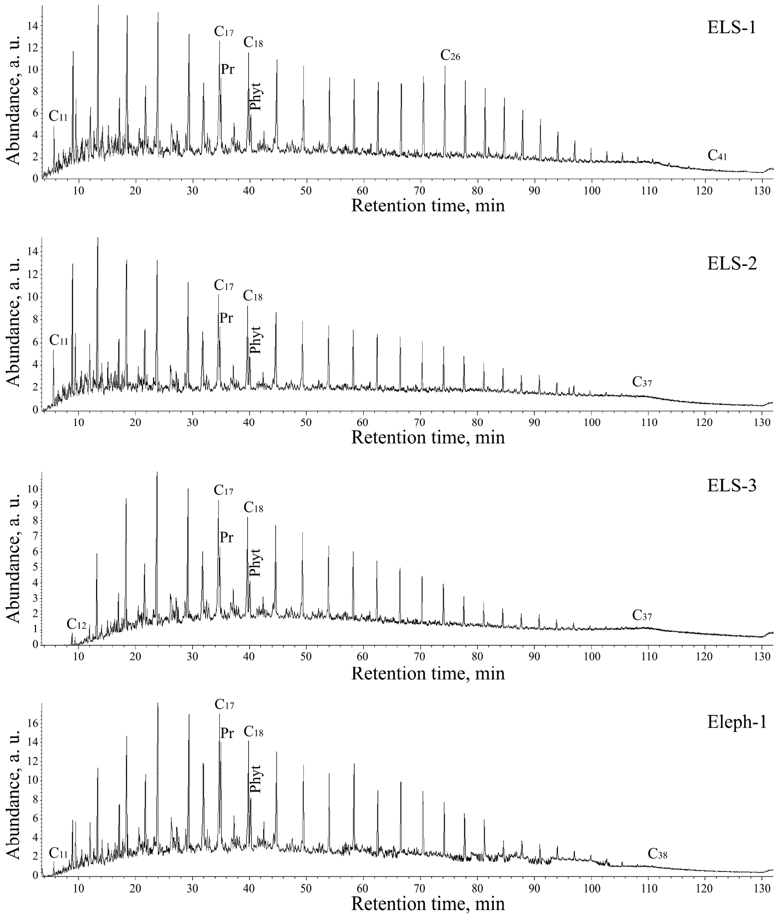

Fig. 2. Total Ion Currents (*TIC*) of alkane fractions isolated from the crude oils from the El Sharara and Elephant oil fields (Murzuq Basin).

TABLE II. Parameters calculated from the distributions of *n*-alkanes and isoprenoid aliphatic alkanes, pristane and phytane; Pr – Pristane; Phyt – Phytane; *CPI* – carbon preference index; Pr/Phyt, Pr/*n*-C17, and Phyt/*n*-C18 – ratios of their respective areas in GC–MS chromatograms

No.	Sample	*CPI*	Pr / Phyt	Pr / *n*-C_{17}	Phyt / *n*-C_{18}
1	Jak-1	1.06	2.60	0.60	0.23
2	Jak-2	1.03	2.20	0.16	0.08
3	Jal-1	1.02	1.67	0.63	0.42
4	ELS-1	0.99	2.06	0.62	0.33
5	ELS-2	1.05	1.78	0.58	0.37
6	ELS-3	1.02	2.14	0.56	0.31
7	Eleph-1	1.04	1.95	0.75	0.49

All three samples have carbon preference index (*CPI*) values higher than one (1.02–1.6, Table II). The sample Jal-1 having *CPI* = 1.02 is also characterized by the lowest abundance of the higher *n*-alkane homologues in the C_{19}–C_{36} range (Fig. 1). All three samples are also characterized by bimodal distribution of *n*-alkanes, with this pattern being the least pronounced in sample Jal-1.

Although crude oil is a form of organic substance of sedimentary formations that is mainly marine in origin,[1–4] these *CPI* values clearly show that a precursor biomass of terrestrial origin also contributed to the formation of oil from the Sirte Basin. The lower abundance of the higher *n*-alkane homologues in the Jal-1 oil, as well as the lower *CPI* values (Fig. 1, Table II), are probably due to the higher maturity of this oil. Its lowest reservoir temperature (Table S-I) may also indicate that maturation processes occurred before accumulation in the reservoir rocks. This could have taken place either in the source rocks or during oil migration to the reservoir. The depth difference between the Jakhira and the Jalu reservoirs is 700 meters. Due to this, if these oils had migrated from the same source rocks, the Jalu oil could have had the longest migration path. In this case, more intensive maturation processes of this oil could have occurred during migration.

The ratio of the relative concentrations of pristane and phytane was higher than 1 in all three samples from the Sirte Basin (Table II). The higher abundance of pristane than phytane clearly indicates oxic conditions in the environment during deposition of the precursor organic material. Simultaneously, these results support the presumption on a terrestrial contribution to the investigated oils.[1–4]

Murzuq Basin

The four samples from the Murzuq Basin investigated in this study (Fig. S-1) are also characterized by a low content of asphaltenes and by a higher content of saturated hydrocarbons relative to the content of aromatic hydrocarbons and NSO compounds (Table I). Similar to the oil samples from the Sirte Basin, the samples ELS-1–ELS-3 and Eleph-1 could be characterized as light oils with high values of the *API* gravities (38–44°, Table I). A high relative concentration of lower *n*-alkane homologues in the C_{11}–C_{16} range (Fig. 2) is also noticeable in these samples.

The high concentration of lower *n*-alkane homologues can be explained with intense maturation processes in deep reservoir rocks at high temperatures: from 81 °C for the oil from the reservoir rock at a depth of 3664 m, up to 142 °C for the oil from the deepest reservoir rock at 4369 m (Table S-I).

Due to the high reservoir temperatures, there were no conditions for microbial degradation of the investigated oils from the Murzuq Basin. Due to this, these oils also show a predominance of *n*-alkanes over the isoprenoids pristane and phytane (Pr/$_n$–C_{17} and Phyt/$_n$–C_{18} $\ll 1$, Table II).

The sample ELS-1 that originates from the deepest reservoir rock (4369 m, Table S-I) is the only one having a *CPI* value a slightly lower than one (*CPI* = = 0.99, Table II). The other samples have the *CPI* values slightly above one (Table II). The *CPI* values for these samples clearly indicate that the organic matter of terrestrial origin contributed to the formation of these oils.[1–4] However, a noticeable biomodal distribution of *n*-alkanes in the sample ELS-1, with high abundance of the higher homologues maximizing at *n*-C_{26}, indicates that terrestrial precursor biomass also contributed to the formation of this oil, and that the distribution of odd and even homologues is a result of the intense maturation processes that could have occurred in the reservoir rock at high temperatures.

The dominance of pristane over phytane (Pr/Phyt > 1, Table II) shows unequivocally that the precursor organic matter of the oils in the Murzuq Basin was deposited under oxic conditions. On the other hand, these values of the Pr/ /Phyt ratio support the statement on the participation of the terrestrial precursor biomass in the formation of these oils.

Geochemical homogeneity

Analysis of *n*-alkane and isoprenoid aliphatic alkane biomarkers leads to very reliable conclusions about the origin and geological history of the petroleum belonging to the Sirte and Murzuq Basins. Regardless of the spatial distance of these basins, all the analyzed oils seem to have a similar marine origin, which is also characterized by the contribution of the terrestrial precursor biomass. Precursor organic matter of these oils was deposited in an oxic environment. Owing to the high temperatures in their reservoir rocks, the oils were not biodegraded, but they were exposed to maturation processes, and to cracking of higher *n*-alkane homologues and the formation of lower ones in the C_{11}–C_{16} range. For only one sample (Jal-1) could it be stated that maturation occurred mainly in the source rock or during migration. Regardless of the observed differences between the analyzed oils, some organic-geochemical correlation parameters indicate their high geochemical homogeneity. Accordingly, the same source rock or the same type of the source rock could be proposed for all seven samples. In the case that this assumption is correct, the lengths of the migration paths of these oils would vary over a wide range.

CONCLUSIONS

In this paper, the specificity of the obtained results allowed an estimation of the type of the precursor organic matter, depositional environment, degree of maturation and intensity of the changes in the reservoir rocks of the Murzuq and Sirte Basins (Libya) only based on the parameters determined from the distribution and abundances of *n*-alkanes and isoprenoid aliphatic alkanes. The obtained results were further used to define the level of the geochemical homogeneity of the investigated samples.

In all of the investigated oil samples, the TIC chromatograms of the alkane fractions were dominated by peaks belonging to the homologous sequence of *n*-alkanes and the isoprenoids pristane and phytane. It was concluded that the oils were not biodegraded.

Based on the high concentration of *n*-alkanes in the C_{11}–C_{16} range in all the investigated oils, it was concluded that they were exposed to cracking processes in the reservoir rocks where lower homologues were formed from the higher hydrocarbons. Only for the sample Jal-1 (Murzuq Basin), was it presumed that the maturation processes occurred in the source rock or during migration. This sample originated from the shallowest reservoir rock (with the lowest temperature) and therefore, it was assumed that this sample had the longest migration route.

Except from one oil (ELS-1, Murzuq Basin), the *CPI* values of all the other samples suggested that the investigated oils had a similar marine origin with contribution of terrestrial organic matter. The values of the Pr/Phyt ratios supported this statement but also indicated that the precursor organic matter of these oils was deposited in an oxic environment.

Bimodal distribution of *n*-alkanes in the sample ELS-1 with relatively high concentration of the higher homologues having maximum at *n*-C_{26}, confirmed terrestrial contribution in the formation of this crude oil as well.

The organic geochemical correlation parameters calculated from the distributions and abundances of *n*-alkanes and isoprenoid aliphatic alkanes, pristane and phytane suggested high geochemical homogeneity of the crude oils from the distant basins Sirte and Murzuq. A very reasonable assumption was made about the same source rock or the same type of the source rock for all seven samples. The same source rock and distant basins might indicate that the investigated oils had different lengths of their migration pathways.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/index, or from the corresponding author on request.

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ИЗВОД

ЗАСИЋЕНИ БИОМАРКЕРИ У ПРОЦЕНИ ОРГАНСКО-ГЕОХЕМИЈСКЕ ХОМОГЕНОСТИ СИРОВИХ НАФТИ ИЗ ЧЕТИРИ НАФТНА ПОЉА У ЛИБИЈИ

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Седам сирових нафти из четири нафтна поља у Басенима Sirte и Murzuq у Либији испитивани су са циљем да се процени њихова органско-геохемијска хомогеност. Засићени биомаркери (*n*-алкани и изопреноиди) анализирани су гасно-хроматографско–масеном спектрометријом (GC–MS). Параметри израчунати на основу расподеле *н*-алкана и изопреноидних алифатичних алкана, пристана и фитана, употребљени су за интерпретацију органско-геохемијских карактеристика нафти. На основу високе релативне концентрације нижих *н*-алканских хомолога у C_{11}–C_{16} опсегу и високих *API* вредности, нафте су класификоване као лаке нафте. Ови резултати су показали да нафте нису биле биодеградоване. Параметри израчунати на основу расподеле засићених биомаркера показали су да су све испитиване нафте настале из изворних стена које су садржале органски материјал сличног маринског порекла или са доприносом сувоземног органског материјала. Резултати су такође показали да су ове изворне стене сталожене у оксичној средини. Претпостављено је да свих седам узорака потичу из исте изворне стене или из изворних стена истог типа. Закључено је да, ако нафте из ових удаљених басена потичу из исте изворне стене, дужине њихових миграционих путева су морале бити различите.

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