

## Geochemistry of a crude oil from a shallow well in Bazian Area, Sulaimani, Kurdistan Region, NE Iraq



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### Abstract:

A crude oil sample from a shallow well in Bazian area, Sulaimani Governorate, Kurdistan Region was analyzed physically and geochemically in terms of source and its biomarker content. Physical properties of the sample indicate that this crude oil have high boiling point which mean absence of light ends, and middle distillate (i.e. gases, naphtha, kerosene, diesel fuel, etc.) with specific gravity of 0.9572, and API equals to 16.32. Chemical analysis show the sulfur content about 1.7% as well as rich in Fe and Ca. GC/MS analysis indicate to absence of n-alkanes, this supported by the mass chromatogram of  $m/z$ 85 which show no biomarkers related to n-alkanes in the sample. Only a small portion of tricyclic terpanes (Cheilanthanes) are present. Mass chromatogram of  $m/z$  217 shows some diasteranes, while other steranes are totally absent. No clear aromatic compounds were found in the studied sample. Severe biodegradation was indicated by the shape of chromatogram, absence of n-alkanes, partial degradation of steranes, remaining of diasteranes. The process of water washing may be accompanied with biodegradation as the aromatic components are removed. The presence of tricyclic terpanes usually related to non-terrestrial source material, which possibly the Kolosh Formation and/or older rock units are the source of this heavy oil.

**Keywords:** Biodegradation, Biomarkers, Kurdistan Region, Kolosh Formation.

### 1. Introduction

Petroleum geochemistry is one of the essential subjects to evaluate the type of oils (Tissot and Welte, 1978, Blanc and Connan, 1993; Hunt, 1996, Hegazi and El-Gayar, 2009). Peters et al. (2005) discussed the biodegradation and water washing processes on the organic matter within oils and source rocks. They summarized changes in properties of crude oils due to biodegradation. One of the most important processes which affect crude oils in reservoirs, especially shallow reservoirs, is biodegradation (Hegazi and El-Gayar, 2009). Palmer (1984) considered

aerobic bacteria as principal agent in the subsurface degradation of petroleum. It has been conclusively demonstrated that the anaerobic biodegradation of alkanes is possible with a strain of sulfur-reducing bacteria; however, this form of biodegradation has very limited effects on oil properties (Blanc and Connan, 1993). A general sequence of increasing resistance to biodegradation is n-alkanes, isoalkanes, isoprenoids, steranes, hopanes/diasteranes, aromatic steroids and porphyrins (Peters and Moldowan, 1993 in Hegazi and El-Gayar, 2009). The detection of subsurface biodegradation has relied on the observed decrease in the

relative abundances of readily utilized components (Hegazi and El-Gayar, 2009).

In this study, an oil sample in one of the boreholes within Sulaimani Governorate, Bazian area, was subjected to different analyses in order to understand the origin and evaluate this kind of oil. Recently the area surveyed by different oil companies seismically but until now there is no published data!

## 2. Sample and methods

The studied area is locating within the High Folded Zone (HFZ) of Kurdistan Region, NE Iraq (Fig. 1). This area studied by several researchers from the geophysical, hydrogeological and structural point of view (Aziz, 2005, Hamamin, 2011, Al-Hakari, 2011). The studied well reached to Kolosh Formation and drilled nearly 45m from this rock unit.

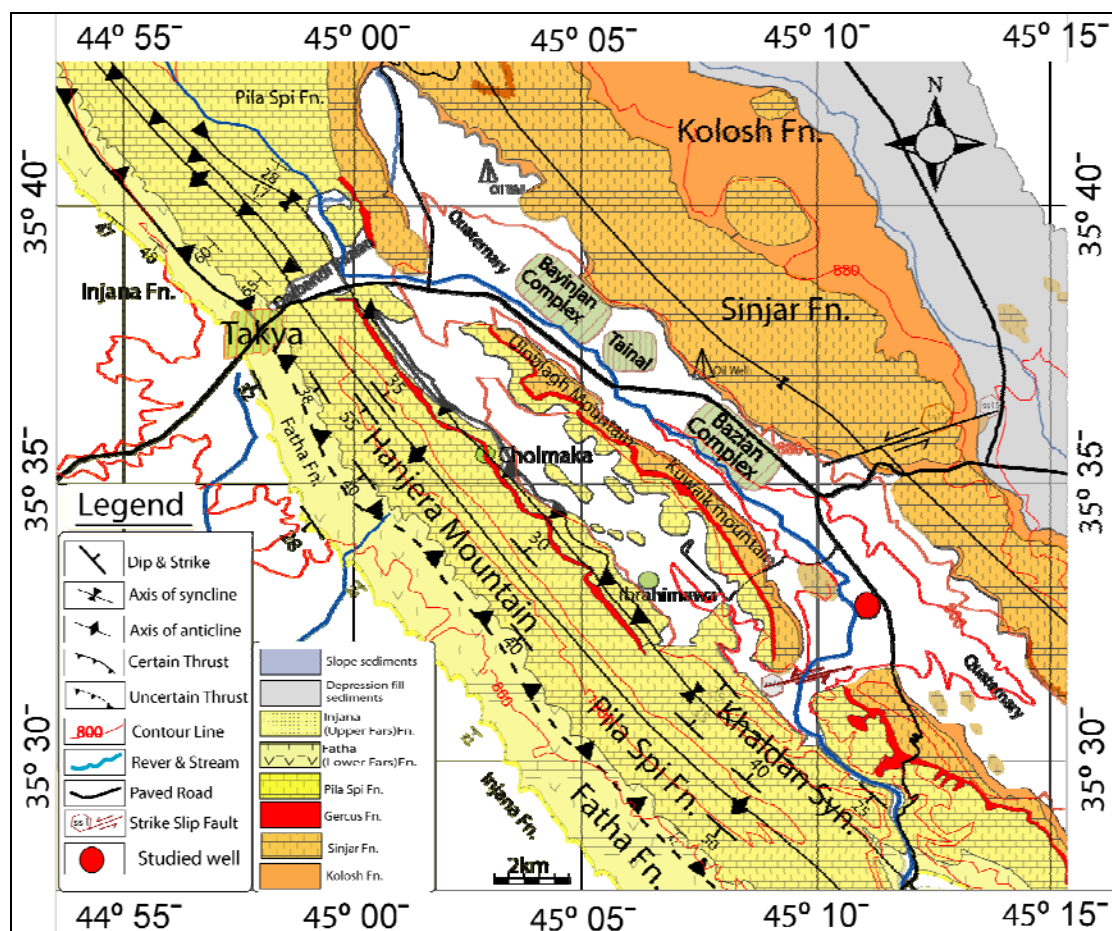


Fig .1. Geologic al map of the studied area (after Al-Hakari, 2011) and location of the studied well. The area locating northeast of Hanjera Mountain is representing High Folded Zone (HFZ).

The oil sample obtained from a well drilled in 1990 with a depth of 135m. The borehole with elevation 792m above sea level and has Lat. N 35° 32.906' and Longit. E 045° 11.1', basically drilled for water but instead of water oil found!

Geologically the studied area covered by recent sediments (Fig.1) of a thick nearly 90-100m. (Aziz, 2005, Hamamin, 2011). The underlain rock unit is Kolosh Formation (Al-Hakari, 2011). The Kolosh Formation (Palaeocene-Eocene) in the

type section is composed of 777.4m of mudstone, silty shales, marlstones, and marly limestones, blue coloured, with purple pigmentation, and green sands in places (Bellen et al., 1959). An intergradational (120m thick) occurs on the top, and is taken as intertonguing with Sinjar Limestone and Khurmala Formations (Buday, 1980, Jassim and Goff, 2006; Al-Hakari, 2011). The Kolosh Formation is also studied by Lawa (2004) and Jaff (2008) around the study area, they concluded that the age is Early to Middle Paleocene and generally consists of thick sequence of grayish green to dark grey calcareous shale, mostly alternated with thick beds of greenish grey to brownish grey calcareous sandstone, rich in chert and carbonate fragments. They also indicate that the sequence changed from siliciclastic-turbidite to siliciclastic-carbonate in late Paleocene. The depositional environment of the Kolosh Formation appears to vary from deep-to shallow marine. The lower part of the formation contains sandstone; these are overlain by carbonate shelf deposits in the upper part (Aqrabi et al., 2010).

### 2.1 Sample preparation

About five liters of the oil obtained from the well, and preserved in the lab. Part of it subjected to chemical analysis, and other part for Inductive Coupled Plasma (ICP) analysis and the third part for extraction of bitumen to be analysed by GC-MS technique.

### 2.2 Chemical analysis

The chemical analysis done at the department of Chemistry of the School of Science, University of Sulaimani. The physical and chemical analyses for the crude oil sample are done according to the American Specification Test Method (ASTM) tests for petroleum products. The sulfur content determined by X-Ray fluorescence.

### 2.3 ICP analysis

There are many elements which have good relations with organic matter; there percentages in the samples can be determined using Inductive Coupled Plasma (ICP). Inductive coupled plasma (ICP- Spectrometer) (Perkin Elmer-Optima 2100- DV-Spectrometer) used to determine the metal ions concentration. Sixteen elements were analyzed using ICP of the department of Chemistry.

### 2.4 GC-MS analysis

There are different methods in extraction of bitumen, depending on the aims. The used procedure is outlined in Mohialdeen (2008.) The method carried out at the Department of Organic Geochemistry, Institute for Geology and Mineralogy, University of Cologne, Germany. Later on, the aliphatic and aromatic fractions injected into GC/MS instrument for analyses and studying the biomarkers, first as Total Ion Chromatogram (TIC) and second as Selected Ion Monitoring (SIM).

GC/MS analysis was performed using a Single-Quadrupole-Instrument (HP 5890/5989A MS Engine) at 70 eV ionization energy, equipped with a HP5-column(50 m length, 0.2mm ID, 0.33  $\mu$ m FT) coated with 5% phenylsiloxane. Sample was injected in splitless mode under constant pressure of carrier gas flow at a rate of 30cm s<sup>-1</sup>. The GC temperature program started at 70°C held isothermally for 2min, then heated at 10°C/min to 160°C/min and 3°C/min to 330°C. The HPCHEMESTATION software used for determining the biomarkers. Computer matching of mass spectra with those in the Wiley 138 mass spectral database was used for initial identification of a compound.

### 3. Results and discussion

#### 3.1 Elemental analysis

The results of physical and chemical analyses of the studied sample shown in table 1, as well as the elemental compositions of the studied oil sample using ICP is explained in table 2.

Based on the tests used for determining the physical and chemical properties, the studied crude oil sample is heavy, because its API-gravity is very low (16.32) and this like for heavy crude oil (Hunt, 1996). Flash and pour points are high (Table 1) which indicates the absence of light hydrocarbons (Tissot and Welte, 1978). Although similar crude oil samples with low API unit have high percentage of sulfur (Mello et al., 1988), the studied sample has sulfur content about 1.7%.

Sulfur % and V/Ni ratio generally used in construction of the depositional environment (Mello et al., 1988; Mohialdeen and Raza, 2012). The high ratio of V/Ni (4.64) is good indicator for marine and carbonate depositional environment of the source rocks of this oil. The high V/Ni ratio indicates to oils originated from a reducing, carbonate-rich source-rock facies that receive more marine organic matter (Mello et al., 1988, Peters et al., 2005). Possibly the source rock of this heavy oil is the Kolosh Formation (Palaeocene-Early Eocene) which is composing of a sequence of clastic sediments and some carbonate shelf deposits. Other older rock units, such as Shiranish Formation (Late Cretaceous) also can be considered as a source of this heavy oil. Rising up of oils through fractures to reach near earth's surface, which light components escape and heavy components remain.

**Table 1.** Physical and chemical analyses of the studied sample with standard methods used.

Test	Method	Results
Sp.Gr. at 15.6 ° C	ASTM D-1298	0.9572
API	ASTM D-1298	16.32
Flash point (C.O.C.) ° C	ASTM D-92	162
Pour Point ° C	ASTM D-97	-3
Water content (v/v%)	ASTM D-95	5-2
Distillation (v/v%)	ASTM D-86	0.0
Naphtha		0.0
Kerosene		0.0
Gas oil		0.0
Sulfur content (w/w)%	X-Ray fluorescence	1.7

**Table 2.** Elemental compositions of the studied oil sample using ICP.

Metal analysis (mg/kg)	
V	1.95
Ni	0.42
Co	0.015
Cr	0.49
Cu	60
Mg	19.5
Mo	0.008
Fe	44.4
Zn	6.5
Al	1.0
Cd	0.0
Ca	665
Pb	0.095
Na	0.05
As	0.0
Sb	0.0

#### 3.2 Biomarkers

Biomarkers are geolipids which derived from biolipids either without any transformation or with minor rearrangements which do not significantly affect the carbon skeleton (Connan, 1993). Biomarkers identified from total ion chromatograms (TIC) and typically

measured using selected ion monitoring (SIM/GCMS), and their distributions calculated using areas under the peaks. The SIM approach allows a rapid, general assessment of thermal maturity of samples (Peters et al., 2005).

### 3.2.1 Aliphatic fractions

The gas chromatograms clearly indicate to absence of n-alkane biomarkers (Fig.2), as well as the mass chromatogram of m/z85 indicates to removing all n-alkanes in the sample (Fig.3).

### 3.2.1.1 Hopanes:

Hopanes are C27- C35 pentacyclic triterpanes that originate from bactriohopanoids in bacterial membranes and generally dominate the triterpanes in petroleum (Connan, 1993, Peters et al., 2005). Hopanes are typical biomarkers for prokaryotic cyanophytes (Schwark and Empt, 2006).

In the chromatogram of the studied sample (Fig. 4) it is clear that there is no hopanes are present, only a small portion of tricyclic terpanes (Cheilanthanes) are present.

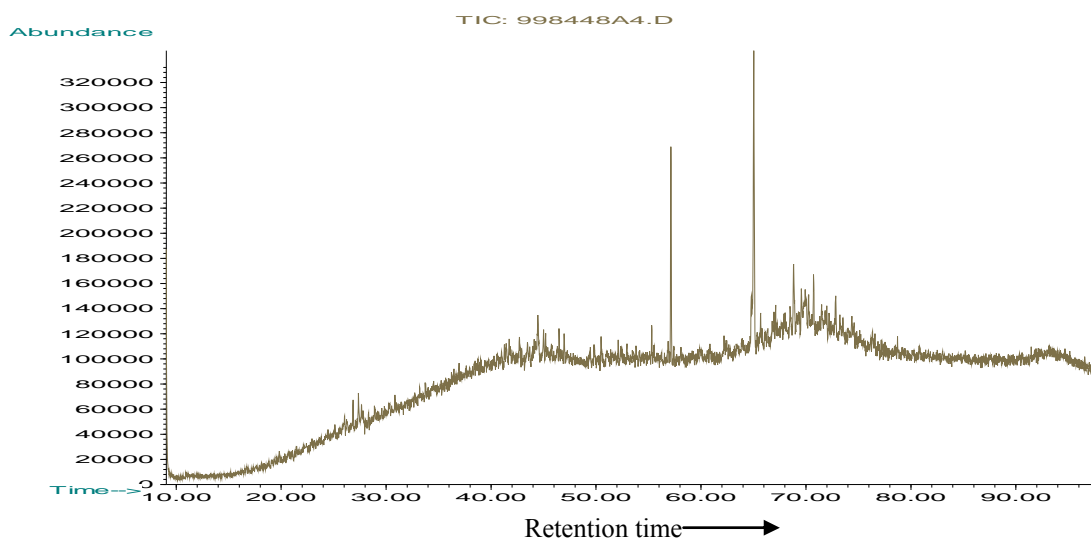


Fig.2. Total Ion Chromatogram ( $C_{15+}$ ) of the studied sample, Bazian, Sulaimani, Kurdistan Region, NE Iraq.

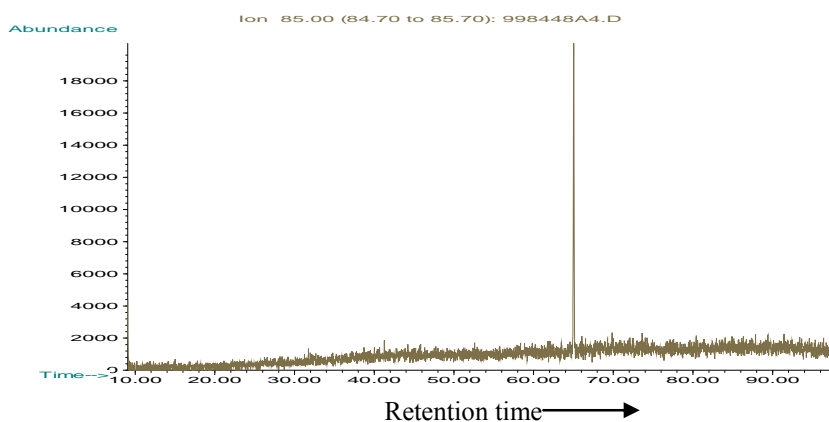


Fig.3. Mass chromatogram (m/z 85) of Oil sample, Bazian, Sulaimani, Kurdistan Region, NE Iraq.

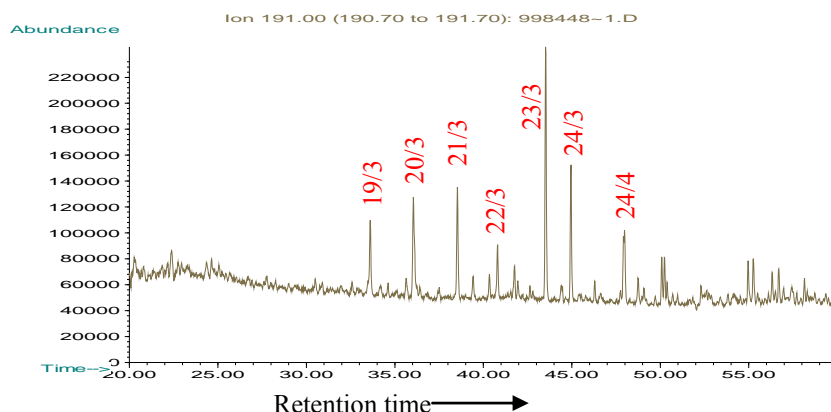


Fig.4 . Mass chromatogram (SIM/GCMS mode) for hopanes,  $m/z$  191, of the studied sample, Bazian, Sulaimani, Kurdistan Region, NE Iraq. Tricyclic terpanes are the major components present.

### 3.2.1.2 Steranes:

Steranes are a class of tetracyclic, saturated biomarkers constructed from six isoprene subunits ( $\approx C_{30}$ ). Steranes originate from sterols, which are important membrane and hormone components in eukaryotic organisms (Peters et al., 2005).

Steroids represent biomarkers for algal eukaryotes (Schwark and Empt, 2006). Most commonly used steranes are in the range  $C_{26}$  -  $C_{30}$  and are detected using  $m/z$  217 mass chromatograms. Using of SIM/GCMS ( $m/z$  217) the chromatogram indicates to some diasteranes in the sample, while other steranes are totally absent (Fig.5). Removing of the tetracyclic steranes usually cause by severe degradation (Tissot and Welta, 1978, Wang, et al., 2013).

### 3.2.2 Aromatic fractions

Aromatics are organic compounds with one or more benzene rings in their structure, including pure aromatics, such as benzene and polycyclic aromatic hydrocarbons, plus cycloalkanoaromatics, such as monoaromatic steroids, some cyclic sulfur compounds such as benzothiophenes, and porphyrins (Peters et al., 2005). Aromatic biomarkers can provide valuable information on organic matter input, biodegradation, maturity, etc.

The aromatic hydrocarbons in the studied sample, as studied from TIC, is generally associated with an elevated baseline, especially in the relatively heavier components, due to the unresolved complex mixture (UCM) (Fig.6).

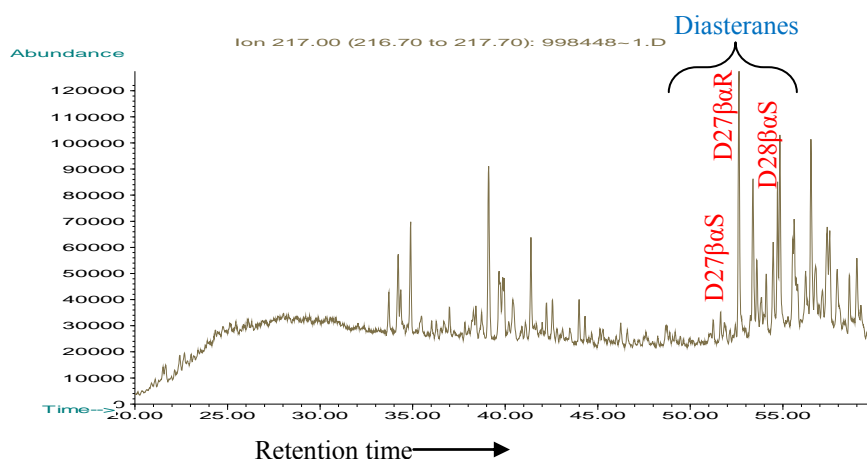


Fig.5. Mass chromatogram (SIM/GCMS mode) for steranes,  $m/z$  217, of the studied sample, Bazian, Sulaimani, Kurdistan Region, NE Iraq. Diasteranes are the most abundant biomarkers.

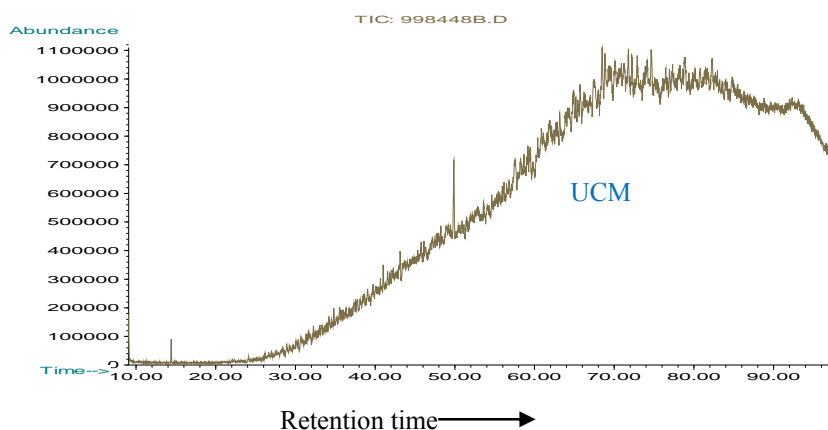


Fig.6. Total Ion chromatogram (TIC) of aromatic fraction with unresolved complex mixture (UCM), Oil sample, Bazian, Sulaimani, Kurdistan Region. No clear aromatic components can be identified.

No clear aromatic compounds were found in the studied sample.

The shape of chromatogram's envelope with elevation of the baseline usually indicates to biodegradation (Cooper, 1990). The studied sample has this type (elevated baseline) of chromatogram (Fig.2). The n-alkanes have been attacked significantly which no one of alkanes is remaining (Fig.3). Severe biodegradation is relatively easy to recognize as aromatics and alkanes are in general strongly altered (Blanc and Connan, 1993). The steranes

are still present with partial degradation (Fig.5), the same for hopanes is correct (Fig.4). Diasteranes are known to be more bacterially resistant than regular steranes (Blanc and Connan, 1993, Wang, et al., 2013).

As biodegradation progresses and the major resolved components are removed, the characteristic broad hump of the UCM becomes apparent in chromatogram. This is clearly appeared in the aromatic chromatogram (Fig.6).

According to Peters and Moldowan (1993 in Peters et al., 2005) the biodegradation stage could be determined as heavy biodegradation (6) while on the scale of Wenger et al. (2002) mostly is severe biodegraded oil. The process of water washing may be accompanied with biodegradation as the aromatic components are not present and removed. Water washing results in a removal of more soluble hydrocarbons from crude oils.

The presence of tricyclic terpanes usually related to non-terrestrial source material (Philip and Gilbert, 1986), which possibly the Kolosh Formation is the source of this heavy oil which is marine deposits. Ranyay (2009) concluded from his study of Kolosh Formation in NE Iraq, that the amorphous organic matter is the major type and possibly deposited in anoxic, reduced marine carbonate environments. He also concluded that the lower part of Kolosh Formation is in early mature stage in the nearby area (TaqTaq Oil Field) to this study area.

The absence of other biomarkers and the occurrence of tricyclic terpanes indicate to heavy biodegradation process because it is less subjected to microbial alteration than any other biomarkers (Behar and Albrecht, 1984).

#### 4. Conclusions

The studied crude oil sample from Bazian area, Sulaimani, Kurdistan Region shows high boiling point which mean absence of light ends, middle distillate (i.e. gases, naphtha, kerosene, diesel fuel, etc.), specific gravity of 0.9572 and API equals to 16.32. The high V/Ni ratio indicates to oils originated from reducing marine carbonate-rich source-rock sediments.

The absence of main groups of biomarkers, except of tricyclic terpanes and some diasteranes, indicate to heavy biodegradation process. The process of water washing may be accompanied with biodegradation, as the aromatic components also removed. The presence of tricyclic terpanes usually related to non-terrestrial source material, which possibly the Kolosh Formation and/or older rock units are the source of this heavy oil.

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