

Geochemical Study of Natural Bitumen, Condensate and Gas Seeps from Sousse Area, Central Tunisia

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Abstract—Natural hydrocarbon seepage has helped petroleum exploration as a direct indicator of gas and/or oil subsurface accumulations. Surface macro-seeps are generally an indication of a fault in an active Petroleum Seepage System belonging to a Total Petroleum System. This paper describes a case study in which multiple analytical techniques were used to identify and characterize trace petroleum-related hydrocarbons and other volatile organic compounds in groundwater samples collected from Sousse aquifer (Central Tunisia). The analytical techniques used for analyses of water samples included gas chromatography-mass spectrometry (GC-MS), capillary GC with flame-ionization detection, Compound Specific Isotope Analysis, Rock Eval Pyrolysis. The objective of the study was to confirm the presence of gasoline and other petroleum products or other volatile organic pollutants in those samples in order to assess the respective implication of each of the potentially responsible parties to the contamination of the aquifer. In addition, the degree of contamination at different depths in the aquifer was also of interest. The oil and gas seeps have been investigated using biomarker and stable carbon isotope analyses to perform oil-oil and oil-source rock correlations. The seepage gases are characterized by high CH₄ content, very low $\delta^{13}\text{C}_{\text{CH}_4}$ values (-71,9 ‰) and high C₁/C₁₋₅ ratios (0,95-1,0), light deuterium-hydrogen isotope ratios (-198 ‰) and light $\delta^{13}\text{C}_{\text{C}_2}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values (-23,8‰ and -23,8‰ respectively) indicating a thermogenic origin with the contribution of the biogenic gas. An organic geochemistry study was carried out on the more ten oil seep samples. This study includes light hydrocarbon and biomarkers analyses (hopanes, steranes, n-alkanes, acyclic isoprenoids, and aromatic steroids) using GC and GC-MS. The studied samples show at least two distinct families, suggesting two different types of crude oil origins: the first oil seeps appears to be highly mature, showing evidence of chemical and/or biological degradation and was derived from a clay-rich source rock deposited in suboxic conditions. It has been sourced mainly by the lower Fahdene (Albian) source rocks. The second oil seeps was derived from a carbonate-rich source rock deposited in anoxic conditions, well correlated with the Bahloul (Cenomanian-Turonian) source rock.

Keywords—Biomarkers, oil and gas seeps, organic geochemistry, source rock.

I. INTRODUCTION

SINCE decades, natural hydrocarbon seepage, either offshore or onshore, has helped petroleum exploration as a direct indicator of gas and/or oil subsurface [1], [2]. Seeps are then indicators of tectonic discontinuities (faults) and fractured

rocks. Seeps are effective indicators of tectonic discontinuities and rock formations with enhanced secondary permeability, providing information on the location and depth of gas-bearing faults [3], [4].

This study shows the results of a continuous investigation, carried out between year 2011 and 2014, of one of the most important onshore gas and oil seepage areas in Tunisia, located in Sousse City in the Sahel Basin (Figs. 1 and 2).

II. GEOLOGICAL OVERVIEW

A. Geological Overview

The study area belongs to the Central Eastern onshore portion of Tunisia (Fig. 1). This region was stable platform during the Mesozoic and Palaeogene times, shallow marine carbonates dominated to the South, grading to open marine shaly facies to the North. During Neogene times, an inversion occurred with active subsidence in most of the area. This subsidence is probably related to the active presence of the N-S Axis to the West and the anti-clockwise rotation of the Sicilian-Tunisian block. The lithostratigraphic chart of this zone ranges from Late Triassic to recent and represented by shallow to relatively deep marine deposits mainly made of sequences of shale, carbonates and sandstones [5] (Fig. 1). Three major source rock intervals were deposited in the study area, one during Lower Eocene (Bou Dabbous formation) and two during Cretaceous (Bahloul formation and Fahdene formation) (Fig. 2).

B. Petroleum Source Rocks

Geochemical and geological studies show three main stratigraphic levels in the area that correspond to Lower Fahdene formation (Albian), Bahloul formation (Cenomanian-Turonian) and Bou Dabbous formation (Ypresian) [6]-[10].

The Lower Fahdene formation is composed of black platy limestones, black limestones, and black to gray marl and light gray to dark gray, non laminated nodular limestone. This Formation shows fair to good petroleum potential fossilizing predominantly type II (oil and gas prone) kerogen with some type III contribution. It exhibits a total organic carbon (TOC) around 4%. The average of the total organic carbon values are just about 1.5% and are generating potential of 15 kg of hydrocarbon/ton of rock (exceptionally 75 kg of HC/t of rock). The thermal maturity is relatively low, corresponding to the beginning of the oil window in the paleohigh facies; however, in the basinal facies, it may reach gas window. The Fahdene samples are characterized by a pristane/phytane ratio ranging between 1 and 3 suggesting an important contribution of terrestrial material, moderate to high C₂₈/C₂₉sterane ratio

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(0.69–0.76), abundant C27 regular steranes, C35/C34 homohopane ratios less than 1 and low tricyclic terpane content. The presence of C30diahopane indicates again the contribution of terrigenous material and carbon isotope composition ranging between -28.5 and -29‰.

The Late Cenomanian-Early Turonian laminated, black, organic-rich limestones were described in Central Tunisia and attributed to the Bahloul Formation which is considered as one of the main source rocks in Tunisia and is composed of outer-shelf to slope-laminated and dark-gray to black-colored limestones and marls. This Formation had been deposited in a relatively deep-marine, calm, and anoxic environment. The Bahloul type-II organic matter (marine origin) exhibits high total organic carbon contents (8% in MGR-1 well), with an average value of 2% and a good to excellent petroleum potential, ranging between 2 and 40 kg of hydrocarbon/ton of rock suggest that this unit has probably generated hydrocarbons within the kitchen area. The extracts from the Bahloul Formation are characterized by Pr/Ph ratios ranging between 1.5 and 3, a moderate diasterane content, C27 and C29 sterane have almost the same value, a high C28/C29 ratio (0.82–0.99), a C35/C34 homohopane ratio less than 1, a moderate tricyclic terpane, and carbon isotope compositions between -24 and -24.5‰.

The Bou Dabbous formation covers the entire north and northeastern part of Tunisia, including the Pelagian Sea. This formation is composed by dark-gray to black, micritic limestone, very rich in Globigerina tests, alternating with marl. In the studied area, this formation appears to be a good source rock formation, showing good petroleum potential (as much as 18 kg of hydrocarbon/ton of rock in KRN-1 well) and high total organic carbon contents (as much as 3%). The organic matter is particularly well preserved and of type II origin composed of very sapropelic amorphous material. However, some lateral variations in the organic richness and maturity are observed. The BouDabbous samples are thermally immature to mature and have reached the peak oil-window maturity within the kitchen area. The extracts are characterized by a low Pr/Ph ratio, a very low diasterane content, C27/C29 sterane ratios approximately equal to 1, a high C28/C29 ratio (0.81-1.0), a C35/C34 homohopane ratio greater than 1, and a carbon isotope composition between -27.5 and -28‰.

III. SAMPLES AND METHODS

Oil/gas seeps and crude oils have been characterized by a variety of organic geochemical techniques (Rock Eval, GC, GC-MS, IRMS) (Fig. 7). For the study, the geochemical survey is based on the analysis of oil and gas seeps collected from different wells in the area (Figs. 3, 5 and 6).

Gas chromatography was carried out with Varian 3800 equipped by FID detector and split/splitless injector (split ratio 25:1) and DB-1 fused silica column (100m*0.25mm*0.25µm). Helium was used as carrier gas with a constant flow (5ml/min). Temperature program starts by 35°C to 300°C at 2°C/mn held (15mn) with 3°C/min rate.

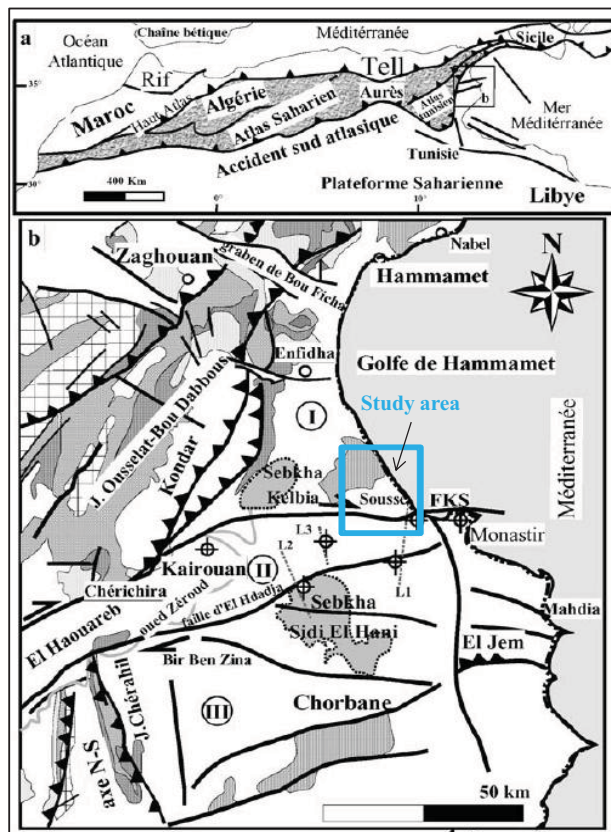


Fig. 1 Tectonic summary map of Central Eastern Tunisia compiled from outcrop and subsurface data [5]

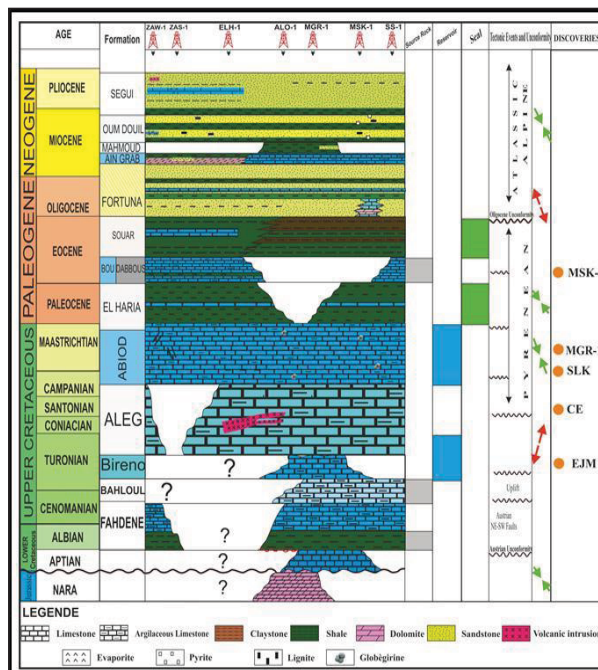


Fig. 2 Stratigraphic section and the major tectonic phases and Total Petroleum System of the Sahel basin [10]

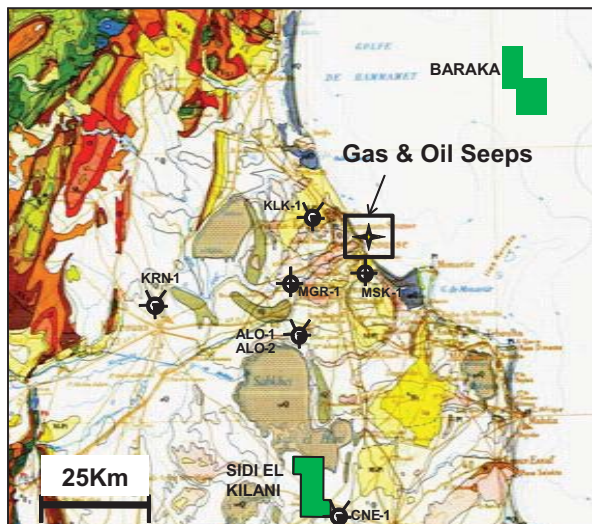


Fig. 3 Geological Map showing location of the selected wells and the oil seeps samples (Location see Fig. 1) [10]

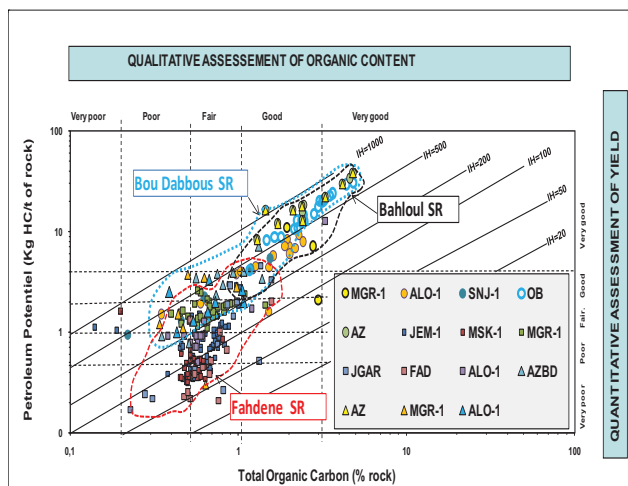


Fig. 4 Quantitative and qualitative assessment source rock characteristics of Lower Fahdene, Bahloul and BouDabbous Formations (dots: Bahloul, triangle: Fahdene and square: BouDabbous) [10]

Saturate and aromatic biomarkers were determined using Agilent 7890A gas chromatograph interfaced to an Agilent 5975 quadrupole mass spectrometer. The GC was equipped with split/splitless injection system, operated in split mode, and DB-1MS fused silica capillary column of 30m length, 0.25mm inner diameter and 0.25 μ m film thickness. Helium was used as a carrier gas with a flow rate of 1ml/min. The oven temperature used to analyse saturates was programmed from 50°C (hold 2min) to 170°C (5min) to 300°C at 1.5°C/min. The mass spectrometer was operated in the electron impact (EI) mode at electron energy of 70eV and a source temperature of 230°C. Aromatics biomarkers were analyzed with the same column but with different oven temperature program starting from 80°C (hold 2min) to 300°C at 3°C/min rate in splitless mode.

Organic extraction was made by soxhlet apparatus using dichloromethane for 18 hours. After extraction the solvent in surplus is removed by means of rotary evaporator. Extracts were separated into their saturate aromatic and polar fractions using the standard method developed by the IFP and called mini-column chromatography [9] (Fig. 7).

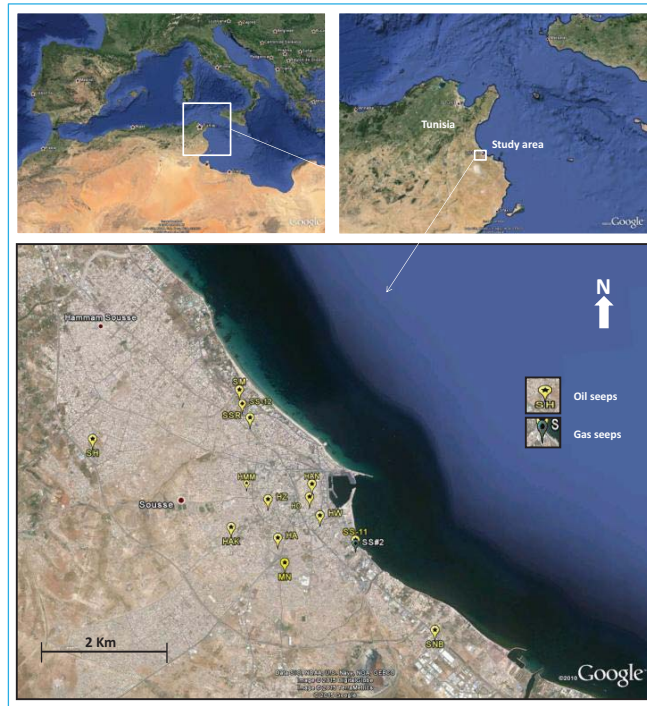


Fig. 5 Map showing the location of the gas and the oil seep samples in Sousse area

IV. RESULTS AND DISCUSSION

A. Geochemistry of Gas Seep

The gas seep sample (SS#2) (Fig. 6) has analyzed at Isotech Labs Inc to evaluate the following components: C1–C6 hydrocarbons, H₂, O₂, CO₂, N₂, and isotopic compositions $\delta^{13}C_{CH_4}$, $\delta^{13}C_{C_2H_6}$, $\delta^2H_{CH_4}$ and $\delta^{13}C_{CO_2}$. Geochemistry results (Table 1) show that the composition of the sample is dominated by Methane, with minor Ethane, CO₂ and O₂. The observed high N₂ values are due to air contamination during sampling. The seepage gases are characterized by high CH₄ content, very low $\delta^{13}C_C$ values (-71,9 ‰) and high C1/C1–5 ratios (0.95–1.0), light deuterium–hydrogen isotope ratios (-198 ‰) and light $\delta^{13}C_{C_2}$ and $\delta^{13}C_{CO_2}$ values (-23,8‰ and -23,8‰ respectively) indicating a thermogenic origin without the contribution of the biogenic gas (Figs. 8 and 9). Based on the above geochemical data and discussion, the seepage gases were likely sourced from the matured source rocks in the area and/or from reservoir oil. The fluids migrate predominantly along faults, fractures and stratigraphic surfaces.



Fig. 6 Photos of SS#2, SS-11, SS-12 and Sonobois (SNB) oil and gas seeps in Sousse area

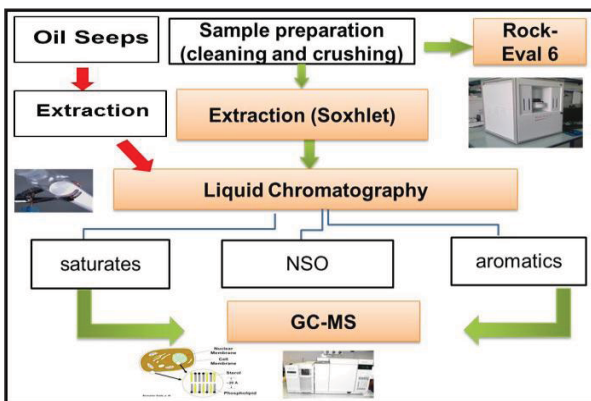


Fig. 7 Scheme summarizes the geochemical analytical procedures performed for this study

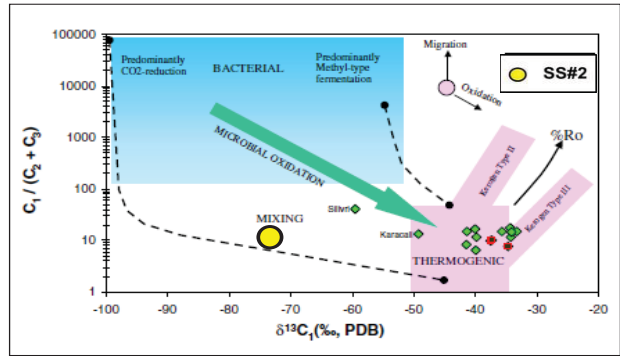


Fig. 8 Cross plot of $\delta^{13}C_1$ values versus $C_1/C_2 + C_3$ for the gas seep sample (SS#2) collected from the SS-11 well showing that gas seep is mixing in origin (thermogenic and biogenic). The boundary lines were taken from [11]

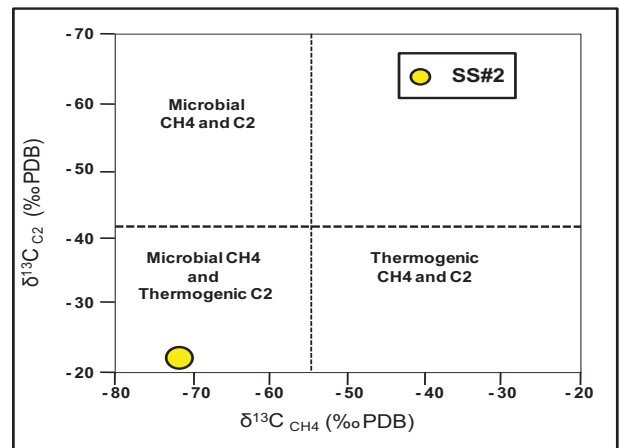


Fig. 9 Genetic zonation diagrams of methane and ethane. $\delta^{13}C_{C_2}$ vs $\delta^{13}C_{CH_4}$ plot [12]-[14]

TABLE I
GAS COMPOSITION AND ISOTOPIC DATA OF SS#2 GAS SEEP SAMPLES

Gas Composition	Quantity	Units
H2	0	ppm
O2+Ar	25800	ppm
CO2	900	ppm
N2	640100	ppm
CO	0	ppm
C1	321000	ppm
C2	12100	ppm
C2H4	5	ppm
C3	4	ppm
C3H6	0	ppm
iC4	57	ppm
nC4	0	ppm
iC5	1	ppm
nC5	0	ppm
C6+	41	ppm
δC_1	-71.9	‰
δC_2	-23.8	‰
δDC_1	-198	‰
δCO_2	-24.8	‰

Chemical analyses are originally in ppm normalized to 1000000ppm

B. Geochemistry of Oil Seeps

The total soluble extract oil seep samples from the Sousse seep sites were low. Only, SS-12 and SS-11 oil samples (Fig.

6) represent high quantity of crude oil.

An organic geochemistry study was carried out on the 10 oil seep samples (location see Fig. 5). This study includes light hydrocarbon and biomarkers analyses (hopanes, steranes, n-alkanes, acyclic isoprenoids, and aromatic steroids) using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The GC traces of the whole oil sample from SS-12 show full n-alkanes distribution ranging from iC4 to n-C20 that is dominated by the light fraction typical of mature light crude oil (Figs. 10-12).

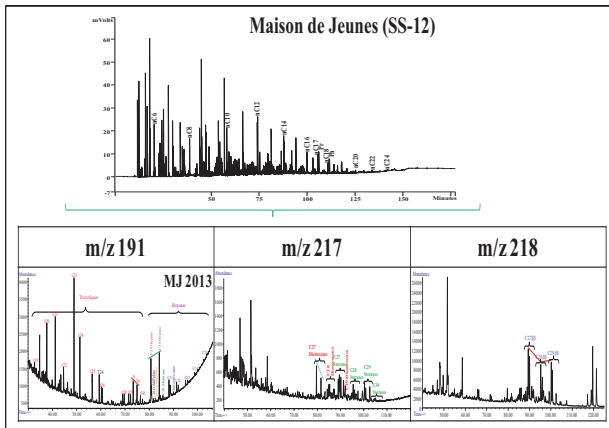


Fig. 10 Gas chromatograms of alkane fractions, Mass chromatograms m/z 191 showing the distribution of tricyclic terpanes, Mass chromatograms m/z 217 & m/z 218 showing the distribution of steranes of the SS-12 oil seeps

matter.

SNB, SA, HAN, SSR, SM, HAS, HAK, HZ, HM, HW and HN oil samples show n-alkanes distribution ranging from n-C15 to n-C36+ (Fig. 14), and moderate high proportions of unresolved branched and/or cyclic alkanes for most of the studied oil samples. These chromatograms are characterised by unimodal n-alkanes distribution ranging from n-C13 to n-C36+, maximizing at, n-C26 and n-C29. These distributions are typical of hydrocarbon sourced from mixed organic matter (Type II/III) with marine source predominance.

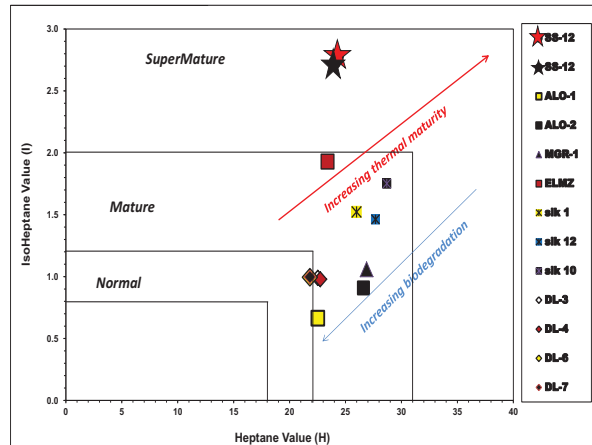


Fig. 12 Thompson's plot of isoheptane versus heptane values [15] for SS-12 oil seep samples from Sousse area showing high mature crude oils (The other samples are crude oils produced in the area)

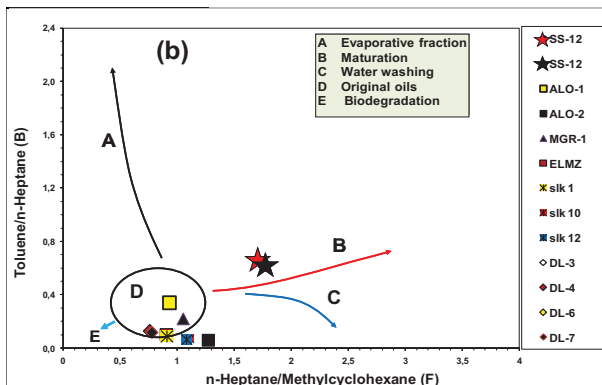


Fig. 11 Paraffinicity F versus aromaticity B plot [15] shows that oil seeps have high F and B ratios suggesting high maturity caused by evaporative fractionation (gas stripping), water washing, biodegradation, or high mature source rocks. (The other samples are crude oils produced in the area)

GC analysis of the saturate hydrocarbon fractions from the SS-12 oil samples (Fig. 13) show a very similar overall distribution of normal alkanes and very high proportions of unresolved branched and/or cyclic alkanes suggesting biodegradation effect. These chromatograms are characterised by an unimodal n-alkanes distribution ranging from n-C11 to n-C20+, maximizing at n-C12. This distribution is typical of marine crude oils sourced from algal/bacterial rich organic

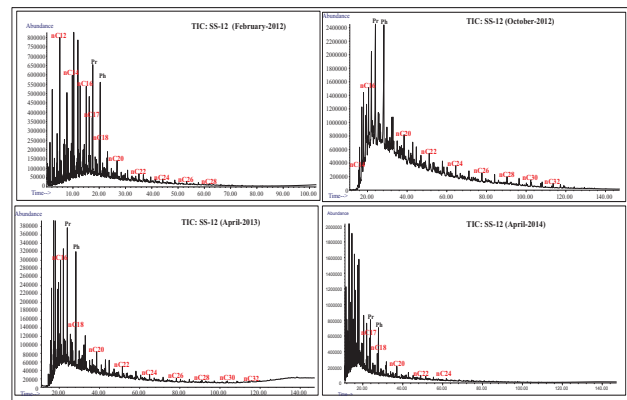


Fig. 13 Gas chromatograms of alkane fractions (TIC) of the SS-12 oil seeps collected in different times

The studied samples show at least two distinct families, suggesting two different origins (Fig. 16). The condensate oil seeps SS-12 appears to be mature, showing evidence of chemical and/or biological degradation (Figs. 11, 12). Biomarker fingerprints of the saturate fraction (Fig. 15) obtained by GC-MS and other characteristic ratios indicate the high level of thermal maturation of the oil and suggest that SS-12 was derived from a clay-rich source rock rich in bacterial-derived organic matter deposited in oxic to suboxic conditions (Fig. 15).

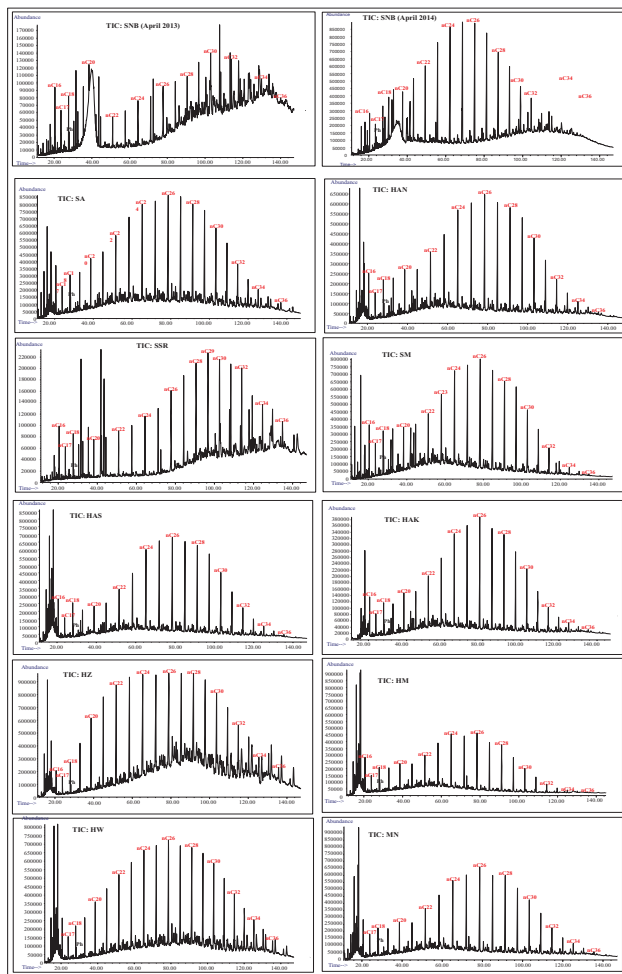


Fig. 14 Gas chromatogram of saturated hydrocarbons for the oil seeps extracts from the water samples showing the light biodegradation of the seepage hydrocarbons

The SS-11, SNB, SA, HAN, SSR, SM, HAS, HAK, HZ, HM, HW and HN oil samples are characterized by low to medium diasterane content, C27/C29 sterane ratios about 1.40 and C35/C34 homohopane ratio greater than 1 (SS-11 sample). The biomarker (saturate and aromatic) fingerprints, suggest that the oil seep samples were derived from a carbonate-rich source rock deposited in suboxic to anoxic conditions (Fig. 15).

C. Oil-Source Rock Correlation and Migration Phenomena

The assessment of the origin and flux of the seeping gas and oil is therefore a key task for understanding, without drilling, the subsurface hydrocarbon potential, genesis, and quality.

Based on biomarker parameters and carbon isotope composition of the analysed oil seeps from Sousse area show: (1) The SS-11, SNB, SA, HAN, SSR, SM, HAS, HAK, HZ, HM, HW and HN oil samples was generated from a mature marly to limy source rock, rich in dominantly marine organic mature rock that was under reducing conditions. Moreover, it was likely derived from the Late Cenomanian- Early Turonian Bahloul formation that reached the peak oil generation in the

study area (Figs. 16, 17). (2) The SS-12 condensate oil seeps have been mainly sourced by the Albian Lower Fahdene formation (Figs. 16, 17).

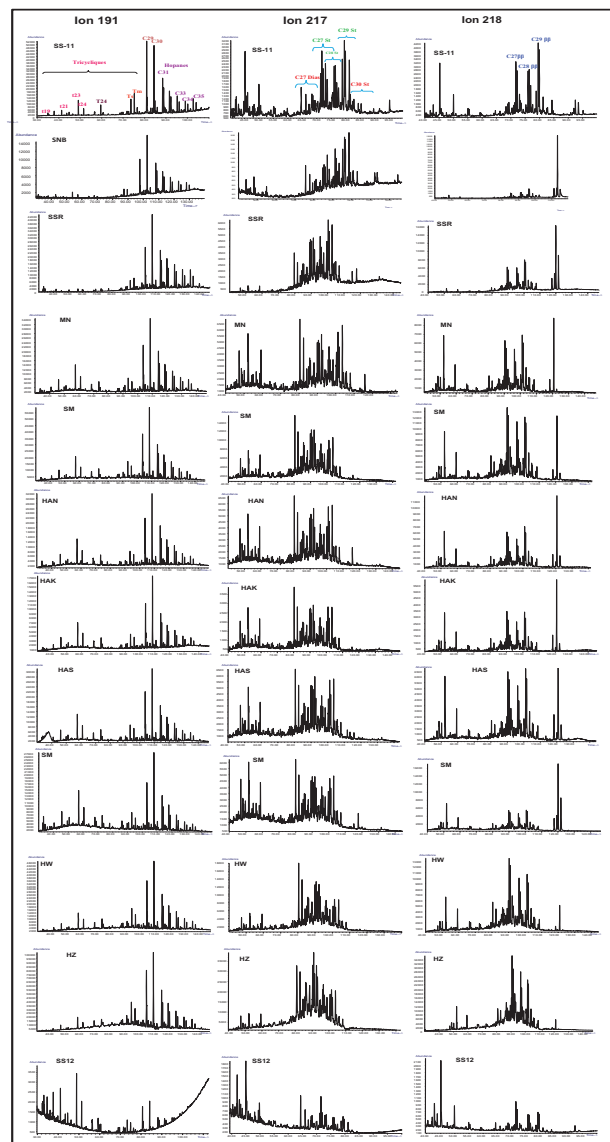


Fig. 15 Gas chromatograms of alkane fractions, Mass chromatograms m/z 191 showing the distribution of tricyclic terpanes, Mass chromatograms m/z 217 & m/z 218 showing the distribution of steranes and Diasteranes of the oil seep samples

The nature of the studied oil seeps, together with the oil generation models reported for this rock unit in the study area, suggests that these oils are a mixture of an initially heavy, altered oil and a second migrated light crude oil resulting from different generation pulses from the source rocks. Evidence for the presence of light oil trapped in the study area should prompt exploration in the area in shallow reservoirs. These macro-oil seeps were related to fault-controlled petroleum migration [10]. This explains the heterogeneous petroleum distribution across the fault. Application of this type of studies

to the structurally complex situation and multi migration history of the Sahel Basin will result in improved exploration models. Nevertheless, how petroleum migrates along the fault still needs more study in order to precisely predict potential exploration targets.

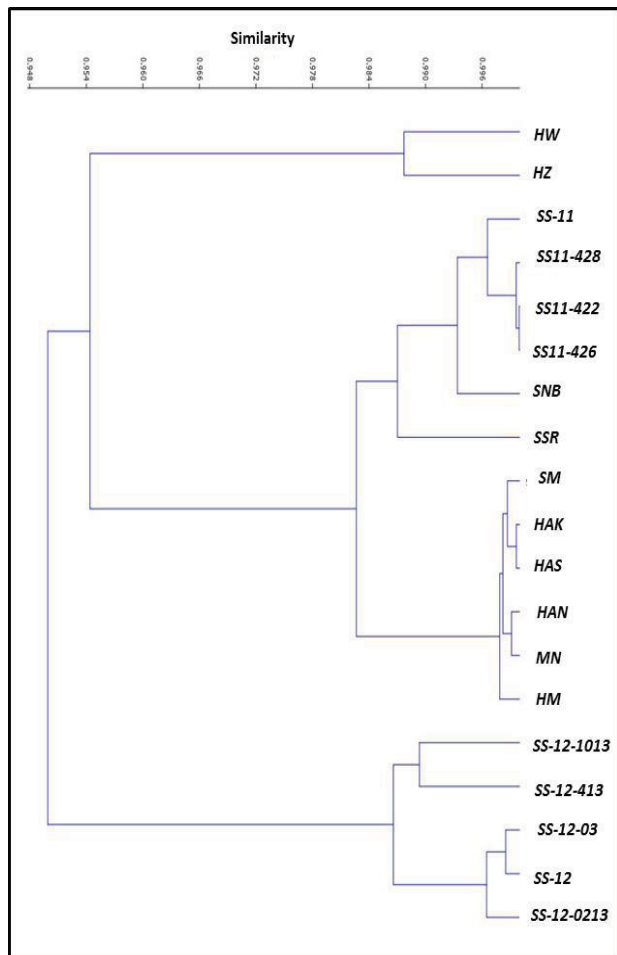


Fig. 16 Dendrogram of hierarchical cluster analysis (HCA) of variables biomarker ratios. The source variables used for calculation of Correlation distance (autoscale preprocessing, incremental linkage) showing two distinct oil families. The first family can be divided into three groups

V. CONCLUSION

Molecular, isotopic and elemental data for the macro-seep samples taken from the Sousse area (Central Eastern of Tunisia) have been investigated. The depositional environment and organic matter characteristics of the possible source for these seeps and oil samples taken from the studied area have been predicted. The gas seep sample, composed of Methane, Ethane and CO₂ appears to be of mixed origin (thermogenic and microbial). This study indicates that the studied oil seeps samples fall into at least two distinct families, suggesting two or more independent hydrocarbon source rocks in this basin. The molecular characteristics of the SS-11, SNB, SA, HAN, SSR, SM, HAS, HAK, HZ, HM, HW and HN oil samples

suggest that the oils were derived from a marly to limy rich source rock deposited in suboxic to anoxic conditions is more probably sourced from the Late Cenomanian-Early Turonian Bahloul formation and the Albian Fahdene formation. The second oil sample (SS-12) appears to be highly mature, showing evidence of chemical and/or biological degradation. Biomarker fingerprints indicate the high level of thermal maturation of the SS-12 oil sample and suggest that it may be derived from a clay-rich source rock rich in bacterial-derived organic matter that was deposited in suboxic conditions. The results suggest the Albian Fahdene formation as possible candidate. Mixture and two types of crude oil and their properties indicate distinct oil characteristics and multi-periods of migration and accumulation in this area.

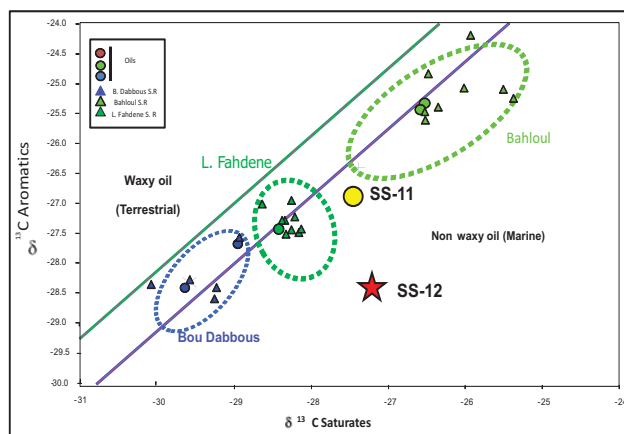


Fig. 17 Plot showing the carbon isotope composition of the analysed oil seeps (SS-11 and SS-12) and source rocks

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