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# **Organic geochemical study of Permian series from the Jeffara and Dahar areas (Southern Tunisia): Identification and characterization of a Tunisian Permian source rock**

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## **ABSTRACT**

Permian rock samples from four wells drilled in the Jeffara (J1 and J2) and Dahar (D1 and D2) areas of southern Tunisia were evaluated using the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method. Quantification of most liquid hydrocarbon compound families released at specific temperature range for the Sh0 and Sh1 as well as Sh2 and S3 parameters was achieved with subsequent calculations of appropriate indices. In addition, stable carbon isotopes evaluation of Permian samples was carried out in order to estimate the origin of their fossilized organic matter. Biomarker analyses were also undertaken on Permian samples and other proven Paleozoic source rocks samples of the study area (Ordovician Azzel and Upper Silurian Fegaguira formations) for comparison purposes.

The results show that the Permian series encompass highly-rich organic matter intervals which may exceed 5%. The organic matter is of type II2-III, proven either by the Rock-Eval<sup>®</sup>, carbon isotopes and biomarker data. Permian samples from three wells (D1, D2, and J2) are found mostly at an early mature stage. Contrary, Permian samples from the J1 Well show abnormal  $T_{max}$  temperatures testifying an overmature stage which could be related to abnormal heat flow around the Jeffara area. The depositional environment of the organic matter-rich Permian intervals is mainly suboxic of normal salinity, similar to the other Paleozoic investigated source rocks in the study area. Overall, this research comes to validate

the occurrence within the Dahar and Jeffara areas of an active Permian oil/gas prone source rock, competitive to the other proven Paleozoic source rocks.

### ***Keywords***

Permian, Southern Tunisia, Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method, stable carbon isotope, biomarker, source rock.

## **1. Introduction**

In Tunisia, the subsurface Paleozoic series have been targeted, for decades long, for petroleum exploration and exploitation, either for source rock or for reservoir rocks characterization and identification. Ordovician, Silurian and Devonian series, as well as the Mesozoic Triassic series have been scrutinized in order to identify prolific petroleum systems in southern Tunisia (Mejri al., 2006); however, Permian series were frequently underestimated and were the least inspected.

Furthermore, previous geological and geochemical studies have mostly focused on three main stratigraphic levels, the Silurian Tannezuft and Fegaguira formations and the Devonian Aouinet Ouenine Formation, considered fairly to highly-rich in organic matter (OM) and measured as pivotal potential source rocks of hydrocarbons in the region (e.g. Underdown and Redfern, 2008.); nevertheless, these source rock have a limited geographic distribution (Ben Ferjani et al, 1990). Consequently, more interest is currently given to other geological horizons such as the Middle Ordovician Azzel Formation or the Permian series, long overlooked, to identify potential functioning petroleum systems. Within this context, Permian series are suspected to bear significant petroleum potential. Indeed, and in some boreholes of southern Tunisia where Permian series were encountered, total organic carbon

(TOC) contents may reach 2.7% with a residual oil potential varying between 0.8 and 5.5 kg / ton of rock (Duvernoy, 1994).

The Permian series were also previously studied by various authors from a sedimentological, petrophysical and petroleum point of view since early thirties ( Berkaloff, 1932; Douvillé et al.1933; Solignac; Berkaloff, 1933 and Douvillé,1934; Matthiew, 1949; Termier,1955, 1957, 1958, 1974; Termier et al, 1977; Glintzboeckel; Rabaté,1964 and Baird,1967; Newell et al.,1976; Razgallah and Vechard,1986; Chaouachi et al.,1987; MRabet et al.,1987; Chaouchi, 1988; Razgallah et al.,1989; Duvernoy and H 'Midi, 1994; Bouaziz , 1995). It is worth noting that Paleozoic series do not outcrop in Tunisia and are overall crossed through boreholes, except for the Permian series, which besides being encountered in subsurface, do also outcrop in Jebel Tebaga of southern Tunisia (Governorate of Medenine; Chaouachi, 1988). This outcrop constitutes the unique Paleozoic land-section of the entire country. However, in the Ghadames Basin and in the Chotts area of southern Tunisia, Permian series are exclusively encountered in boreholes. Furthermore, and according to borehole reports provided by ETAP (Entreprise Tunisienne d'Activités Pétrolière), the Permian series include frequent oil shows and dark black intervals which may include high amounts of organic matter.

On another level, classical organic geochemical techniques are widely used to characterize shale oil and gas play systems (e.gs, Espitalié et al., 1977; Espitalié et al., 1985; Lafargue et al., 1998; Jarvie, 2012; Song et al., 2017; Romero-Sarmiento et al., 2017). More recently, this technology has been also applied to characterize organic matter in recently discovered sediments (younger than 120ky) (e.g., Baudin et al., 2015) and soils (e.g. Soucémariadin et al., 2018). Futhermore, a characterization program for unconventional shale resource systems was developed by IFPEN (France): the Rock-Eval<sup>®</sup> Shale Play method<sup>TM</sup> (Romero-Sarmiento et al., 2014, 2016; Pillot et al., 2014), allowing a better estimate quantification of

hydrocarbons (peaks Sh0 and Sh1) and a more precise determination of the thermal maturity parameter ( $T_{max}$ ). Nonetheless and despite the overall reliability of the technique, the organic matter type and its origin, the mineralogy and the grain types of the hosting rock may sometimes bias the Rock Eval released parameters (Hunt, 1991; Spiro, 1991; Vu et al., 2013; Hazra et al., 2017; Carvajal; Ortiz & Gentzis, 2018; Abarghani et al., 2019; Hazra et al., 2019; Scheeder et al., 2020; Yang and Horsfield, 2020; Hazra et al., 2021; Karayigit et al., 2021). Data checking and the confrontation with results obtained for example from organic matter petrography, GC/MS analyses on source rocks extracts or from carbon isotopic results, can readjust such uncertainties.

Stable carbon isotope ( $\delta^{13}C$ ) analysis is one of the useful indices used to determine the types of organic matter in source rocks (Pancost et al., 1999; Qu et al., 2019). The organic isotopic values of kerogen are controlled by the types of source organic matter. For instance, the values of carbon isotopes of the advanced land plants are generally relative to lower aquatic plankton (Whiticar 1996; Mccarren et al. 2008). Therefore, the carbon isotopic values of kerogen can be used to distinguish the different types of organic matter from source rocks.

Added to these techniques, the analysis of biomarkers by gas chromatography coupled with mass spectrometry (GC-MS) is of great significance in the determination of origin and maturity of organic matter. These biomarkers exist within a complex mixture of organic matter recording all the stages of accumulation, preservation and hydrocarbons migration. In addition, they are "*molecular fingerprints*" capable of highlighting the entire chemical or biological assessment processes and provide information about depositional environments (e.g. Peters & Moldowan, 1993; Peters, et al., 2005; Waples & Curiale, 1999; Cesar and Grice 2018; Luo et al. 2019).

Based on all the above, and aiming to evaluate the Permian series petroleum potentiality, the work herein presents a geochemical study of dark layers encompassed within the Permian series in four drilled boreholes located in the Jeffara Basin and Dahar areas of Southern Tunisia (Fig.1). This is focal as, up to date, no previous geochemical studies have been published on the Permian petroleum potential of southern Tunisia except of internal reports or oral communications. The present study uses specific organic geochemical techniques for the evaluation and characterization of source rocks. More specifically, the study assesses the organic matter present in Permian intervals trying to evaluate its richness, nature, thermal maturity, depositional environment, through the use of a combination of several analytical techniques: Rock-Eval<sup>®</sup> Shale Play<sup>™</sup>, the GC-MS technique (biomarkers) and stable carbon isotopes analyses in order to estimate potentially producible oil intervals.

## **2. Geological setting**

The study area is the Northern edge of the Saharan platform (Fig.1). It is limited to the northeast by the central Mediterranean Sea, to the Northwest by the Chotts area, and to the south by the Tunisian-Libyan border. From a geological point of view, the Saharan platform remained stable since the late Paleozoic, but to the north, a strong subsidence created the Jeffara basin (Fig.1). After the Carboniferous-Permian Hercynian phase, a generalized NE-SW Permian extension took place splitting the Pangea (Arthaud and Matte, 1977), together with the Eurasian/African dextral sliding, responsible for the opening of the Neotethys (Bouaziz et al., 1999). This extensive movement led to the compartmentalization of the Jeffara into horsts, grabens and tilted blocks, delimited by EW major faults separating a carbonate platform in the South from a subsiding basin in the north (Raba,1988; Ben Ferjeni et al.,1990 et Mejri et al., 2006). It was followed by a significant subsidence leading to marine Permian deposits in the Tebaga basin (Touati and Rodgers, 1998) with thicknesses reaching 3000 m. This extensive regime continued until the middle Triassic allowing the final shaping

of the Jeffara basin (Busson, 1967; Newell et al., 1976; Khessibi, 1985; Ben Ayed, 1986; Toomey, 1991; Bouaziz, 1986, 1995). The Hercynian orogeny led to a major regional erosion of hundreds of meters of Carboniferous and early Permian sediments (Bouaziz, 1995). This was followed by Mesozoic subsidence changing to tectonic inversion with prevailing compressional movements of the Alpine orogeny during the Cenozoic (Bouaziz et al., 1999). Although the Saharan platform remained stable since the Late Paleozoic, the Permian basin was crossed by a major shear fault system (Ben Ayed, 1986; Bouaziz, 1986; M'rabet et al., 1987) corresponding to the Gafsa-Jeffara fault zone that extends from the southern Atlas in the northwest to the Nefusa uplift in the southeast (Ben Ayed, 1986; Ben Hassan et al., 2014; Bouaziz, 1986; M'rabet et al., 1987) (Fig. 2). Of note, the only outcropping Permian marine sediments of North Africa occurs within this fault zone at the Jebel Tebaga near Medenine (Newell et al., 1976; Driggs, 1977; Toomey, 1991). Overall, the Permian series could only be recognized by cores of exploration wells (Ben Ismail, 1991; Bouaziz, 1995) and outcrop (Chaouachi, 1988; Ben Ismail, 1991; Bouaziz, 1995) occur uniquely to the North of the Telemzane Arch (Fig. 2). Therefore, the study area is located within this domain which shows various facies ranging from siliciclastic shallow deposits, reefal constructions to deeper marine carbonate deposits (Zaafouri et al., 2017).

### **3. Material and methods**

#### ***3.1 Sampling***

74 investigated rock samples derive from four exploration wells, two drilled in the Jeffara basin (J1 and J2; Figs 1,3) and two of them in the Dahar area (D1 and D2; Figs 1, 3). The studied Samples, which are mainly shaly carbonates in facies, were chosen within the Permian series on the basis of their richness in organic matter and their blackest color. Sample's selection was performed as follow (Table 1):

- Nine samples from the D1 Well ;

- Nineteen samples from the D2 Well;
- Sixteen samples from the J1 Well;
- Thirty samples from the J2 Well.

In addition, five cuttings samples were selected for GC/MS analyses (Table 2): Three cuttings samples from the Permian series of the D1 and D2 wells and two other samples from known source rock of the area, one from the Silurian Fegaguira source rock and one from the Ordovician Azzel source rock (Table 2). It is worth clarifying that the choice of only three samples from the studied wells was based on their richness in TOC and their free hydrocarbon issued by the Rock Eval pyrolysis. They were considered as representative of all studied Permian samples to be scrutinized from a biomarker point of view. The other two samples (Ordovician and Silurian) were selected for organic matter biomarkers comparison with the organic matter biomarkers of the studied Permian samples.

Carefully grinded and powdered samples to around 63  $\mu\text{m}$ , were used for Rock-Eval<sup>®</sup> Shale Play<sup>™</sup>, stable carbon isotopes and biomarkers analyses.

### ***3.2 Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method***

The crushed samples were first characterized by open-system pyrolysis using a Rock-Eval<sup>®</sup> 6 (e.g., Espitalié et al., 1985; Lafargue et al., 1998; Behar et al., 2001) device operated at IFP Energies nouvelles (IFPEN - France). This technique was used here to determine the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> parameters (e.g. Sh0, Sh1, HC content, HQI, PIShale) as well as a more accurate thermal maturity of the investigated samples. This method was also used to estimate the TOC content and the kerogen type of the selected rock samples, the source rock quality and the thermal maturity of organic matter. For these purposes, the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method was tested on 40 mg of powdered samples following the procedure described in Romero-Sarmiento et al. (2015; 2016; 2017). The Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method is characterized by a starting thermal vaporization step at low temperature (100°C). Then, the

oven temperature increases from 100°C to 200°C, and following this rise, it is raised again from 200°C to 350°C and finally the pyrolysis temperature increases from 350°C to 650°C at 25°C/min. Two plateaus of 3 minutes are imposed at 200 and 350°C (Romero-Sarmiento et al. 2014; 2016 a,b). The quantity of hydrocarbon compounds released during the thermal vaporization step from 100°C to 200°C corresponds to the Sh0 parameter. The Sh1 parameter provides the quantity of hydrocarbon compounds released during the thermal vaporization step from 200°C to 350°C and the Sh2 parameter provides the quantity of hydrocarbon compounds released during the final pyrolysis step from 350°C to 650°C (Romero-Sarmiento et al. 2014; 2016a,b).

### ***3.3 Decarbonation***

Based on Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> results, a total of twenty samples were selected (5 per well) to obtain the corresponding isolated OM (OM concentrate). These 20 samples do not include the five samples which were analyzed by GC/MS. The mineral matrix of the bulk rock sample is destroyed using non-oxidant acid (HCl) to remove carbonates, sulphides, sulphates, clay minerals, quartz and silicates. It is widely known that certain minerals remain after acid attacks, in particular pyrite. Finally, the obtained OM concentrates were analyzed by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> to estimate the hydrocarbon content index of the OM concentrates ( $\text{HCcont (OM)} = \text{Sh0 (OM)} + \text{Sh1 (OM)}$ ), in milligrams of HC per gram of OM concentrate.

### ***3.4 Stable carbon isotope analysis***

In this study, stable carbon isotope ( $\delta^{13}\text{C}$ ) analyses were only performed on 20 isolated organic matter concentrates, as five rock samples showing high TOC values were selected for each investigated well (four samples per well), and obtained by destroying the carbonate matrix with HCl acid treatment.. The stable carbon isotope analyses were carried out using a ThermoFischer Scientific EA - Isolink II-MAT253 spectrometer operated at IFPEN (France).

The stable carbon isotope data are presented in the  $\delta$  notation relative to V-PDB standard with the analytical precision estimated to be  $\pm 0.2$  ‰.

### ***3.5 Biomarkers***

A total of selected five Permian cuttings samples were analyzed in this study, for GC-MS analysis, in which three of them are from the D1 and D2 wells and two from known source rocks of the area (Fegaguira and Azel formations)

The organic extraction was carried out by a Soxhlet apparatus using dichloromethane. Afterwards, the solvent was removed by means of a rotary evaporator. The extracts were separated into their saturated fractions employing the standard mini-column chromatography (e.g., Behar et al, 1984). The saturate and aromatic biomarkers were determined using Agilent 7890A gas chromatograph coupled to an Agilent 5973 Series Mass Selective Detector (Peters et al., 2005). The separation was carried out using a DB-1MS fused silica capillary column of 30m length, 0.25mm inner diameter and 0.25 $\mu$ m film thickness. Helium was used as a carrier gas with a flow rate of 1 ml/min. The oven temperature used to analyse saturates was programmed from 50°C (2 min) to 170°C at 5°C/min and to 300°C at 1.5°C/min. The ion source was operated in electronic impact (EI) mode at 70 eV at 280°C. The MS was operated in selective ion monitoring (SIM) for the following ions: alkanes (m/z 57), steranes (m/z 217), and terpanes (m/z 191). Biomarker identification was performed using published data and laboratory records.

## **4. Results and Discussion**

### ***4.1 Source rock quality, organic matter type and thermal maturity***

Free and sorbed liquid hydrocarbons (Sh0 and Sh1 peaks), that could be present in studied samples (e.g., Romero-Sarmiento et al., 2015; 2016; Fig.4; Table1), were quantified using the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method.

Figure 5 shows free and/or sorbed liquid hydrocarbon content (HCcont = Sh0 + Sh1; Table 1) versus TOC content. A positive correlation between the total quantity of hydrocarbons (Sh0 + Sh1 in mg HC / g of rock) and TOC values is observed for Permian samples of the different wells. However, most of the studied samples show low to medium oil saturation, the oil crossing the effect and potential productive intervals were identified in three samples from well J2 (samples J2-S<sub>21</sub>, J2-S<sub>23</sub> and J2-S<sub>24</sub>). Sample J2-S<sub>26</sub> shows also good oil potential. The Permian specimen of the J1 Well (Table 1); however, reveal relatively low TOC contents, which rarely exceed 0.50%, recorded in the majority of samples. Nevertheless, intervals preserved high amounts of organic matter with TOC contents that can reach up to 7.76% in well D1 (Table 1, Fig.6), 7.69 in J2 (Table 1, Fig.7), 1.32% in J1 (Table 1, Fig.8) and 5.54% in D2 (Table1, Fig.9).

Overall, the Permian series are generally rich in organic matter (OM) and the obtained TOC values varied between 0.5% and 7.76% with an average of 4.13 % (Table 1). The results demonstrate that the J1 samples are characterized by low residual oil potentials that did not exceed 0.40% mg HC/g.rock due to either to a very advanced thermal maturity or a poor quality of the oil. The organic matter could have been poorly preserved during its deposition (Hunt, 1996; Vecoli, et al., 2009). Conversely, the other wells D1, D2 and J2 have a high oil potential that can reach 31.46 mg HC/g rock, for the well D1, 21.08 mg HC/g rock, for D2, and 12.69 mg HC/g rock for J2.

The HI (HI = Sh2 100/TOC) / TOC and (SH2/S3) /TOC diagram (Fig. 10 and Table 1) is classically used to provide information on the type of generated hydrocarbon (Espitalié et

al., 1986) by the analyzed rocks. The diagram presented in the Fig. 11 reveals that the source rocks of J2 and D2 generated an average quantity of oil.

$T_{max}$  is a widely used parameter for evaluating the thermal maturity (Espitalié et al., 1977), but may also be influenced by kerogen type (Hunt, 1996; Vecoli, et al., 2009, Vu et al., 2013, Yang and Horsfeld, 2020 and Karayigit et al. 2021). Indeed, the Hydrogen Index (HI) and/or the Oxygen Index (OI) when correlated to  $T_{max}$  ( $HI = Sh_2 * 100 / TOC$ ) /  $T_{max}$  ( $Sh_2$  peak maximum temperature; Fig. 10 and Table 1) may possibly imply the organic matter origin in the analyzed samples (Espitalié et al., 1986). Based on thermal maturity, the  $T_{max}$  ( $Sh_2$  peak maximum temperature) Rock-Eval® Shale Play™ values, recorded in the Permian age samples taken from Well D1, depending on depth and oscillate from 435 to 439 ° C in the interval (2144 -2393m), corresponding to the early stage of the oil window.

The values of  $T_{max}$  recorded at the lower parts of D2 and J2 wells ranged from 431°C to 450°C, and these samples are early mature to mature. On the other hand, the studied samples from J1 display very high values which are exceeding 500 °C, demonstrating an over-mature organic matter. This can be explained by the NW-SE crustal lithospheric anomaly, which could have caused a high mantle heat flux located within the Jeffara basin (Gabtani, 2006). A crustal thinning would have created a significant burial of sedimentary layers associated to the manifested rifting (McKenzie 1978; Wernicke, 1981; Barbier et al., 1986; Doglioni, 1994 in Gabtani., 2006). This burial started during the Late Carboniferous and may have lasted up to the early Permian (Memmi et al., 1986 in Gabtani., 2006; Fig. 12). This was confirmed through the variation of geothermal flux, identified in the region compared to the average geothermal gradient. In fact, the distribution of the geothermal flux in terms of "heat-flow density" (HFD) at the level of the Mediterranean basin and, in particular, at the southern segment of the Geotraverse (EGT-S) campaign, shows a heat flux anomaly superior than 100 MW/m<sup>2</sup> in the Jeffara region (Bouaziz et al., 2015; Gabtani., 2006; Mraidi et al.; 2021; Fig. 12 (C)).

The analyzed samples show relatively low values of HI in all studied wells (D1, D2, J1, and J2) varying between 18 and 300 mg HC / g TOC, typical of mixed organic matter between type III of continental origin and type II of marine planktonic origin. The HI/OI diagrams (Fig.13 (A)), HI / T<sub>max</sub> (Fig. 11) and Sh2 / TOC (Fig.13 (B)) made it possible to determine the type of organic matter (Hunt, 1996; Vecoli, et al., 2009) in the different studied samples (Fig. 13 A-B). The location of the representative points of the analyzed samples on the HI/OI and HI/T<sub>max</sub> diagram indicates that their organic matter is of mixed origin between terrestrial origin and marine origin, especially for samples from D1, D2, and J2 W well. We may note, that the poor preservation of Permian organic matter in the J1 well may have resulted in its oxidation, hence its leaning to the type III-IV organic matter as presented in the diagram (Fig. 13).

#### ***4.2. Bulk carbon isotope interpretations***

After de-carbonation, TOC contents, as expected, became very high reaching a maximum equal to 15.26% for the de-carbonated sample J-S26, while the Minc % percentages became very low of the order of 0.61 against 9.14 for the sample D1-S4, which shows that the de-carbonation process was effectively carried out (Fig. 14 ; Table 3).

Figure 14 illustrates the bulk carbon isotope ( $\delta^{13}\text{C}$ ) results obtained from investigated samples. The stable carbon isotope signature was determined to establish the type of OM present in source rocks and the relationship of this OM with the depositional environment (Meyers, 1994; Calvert et al., 1996). Indeed, the organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) contents of the source rocks are presented below:

For the D1 well, the  $\delta^{13}\text{C}_{\text{org}}$  values were -22.65 ‰, -18.95 ‰, -25.21 ‰, -24.01 ‰ and -23.90 ‰, with an average value of -22.9 ‰. For the D2 well, they were -19.18 ‰, -21.45 ‰, -21.80 ‰, -20.72 ‰ and -21.36 ‰, with an average value of 20.9 ‰. For well J1, these values were -22.12 ‰, -23.69 ‰, -21.95 ‰, -24.23 ‰ and -24.53, with an average value

equal to -23.3 ‰. For well J2, they reached -21.83 ‰ -23.72 ‰, -23.24 ‰, -26.28 ‰ and -22.62 ‰, with an average value of -23.5 ‰.

The  $\delta^{13}\text{C}$  contents of studied Permian samples reflects no major difference among the studied wells. Furthermore, this data can be efficiently used for the determination of the types of OM in source rocks (Pancost et al. 1999). The OMs in the sedimentary rocks are generally classified into three types according to the difference in the micro-components of kerogen defined as insoluble organic matter: type (I), type (II) and type (III), (Strauss and Peters-Kottig, 2003; Thomas et al., 2004; Hermann et al., 2010). Besides, the  $\delta^{13}\text{C}$  isotope content of kerogen remains the same as that of the organism source material (Forsman and Hunt 1958). The  $\delta^{13}\text{C}$  isotopic values of kerogen are controlled by the types of parent OM (Whiticar 1996; Mccarren et al. 2008). Therefore, kerogen  $\delta^{13}\text{C}$  isotopic values can be employed to distinguish organic material types from source rocks (Grasby and Beauchamp, 2008; Luo et al., 2014). The division of kerogen types of organic matter according to carbon isotope ratio values (Meyers, 1997) is presented in Figs 15-17.

Previous studies indicated that the  $\delta^{13}\text{C}$  isotope values of terrestrial plants are generally equal to -21.60 and -26.70 ‰, while the  $\delta^{13}\text{C}$  isotopic values of aquatic plankton vary between -27.60 and -32.60 ‰, (Ehleringer 1991; Angradi 1994; Qin 2005; Yang et al. 2014). In this study, the  $\delta^{13}\text{C}$  isotopic values of Permian age source rocks extracted from the different wells are in the kerogen range of type II2 / III (Table 3). The  $\delta^{13}\text{C}$  isotopes values coupled to the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> results confirms a terrestrial origin of organic matter deposited in a marine setting.

The comparison of the %C after elemental analysis and TOC obtained by the Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> analysis after de-carbonation shows a strong correlation between % C and the TOC (Fig. 18) which is confirmed by the recorded quantity of TOC available in each sample (Fig. 19). In order to demonstrate that the values of  $\delta^{13}\text{C}_{\text{org}}$  do not respond

exclusively to the amount of organic carbon present in the sample, we describe the relationship between  $\delta^{13}\text{C}_{\text{Org}}$  and TOC (Fig. 19), the calculated  $R^2$  value for their relation is ( $R^2 = 0.1729$  for J1;  $R^2 = 0.1321$  for D2;  $R^2 = 0.3995$  for D1; and  $R^2 = 0.4162$  for J2), which highlights the fact that  $\delta^{13}\text{C}_{\text{Org}}$  is not dependent on the TOC (Hartke et al., 2021).

#### ***4.3 Source-rock hydrocarbon potential from Tunisian Permian series***

Based on Rock-Eval<sup>®</sup> pyrolysis results, some analyzed intervals of the Permian series in the different studied wells hold a moderate source rock potential. Indeed, the interval 1549m - 2282m (Fig.6) for the D1 well, the interval 986m - 1560m (Fig. 7) for the D2 well and the interval 1175 – 1296 (Fig. 8) for the J2 well are moderately rich in organic matter of "Oil- and Gas- prone" quality and which can be retained as petroleum source rocks. The common kerogen type in these samples is type II/III, of terrestrial origin, which was transported into marine setting; however, the analyzed Permian series of the J1 Well (Fig. 9) are lacking any source rock potential coupled to the fact that samples are over-mature, probably due to an anomaly in the heat flow in the region.

#### ***4.4. Biomarker distributions and palaeoenvironmental conditions***

##### **4.4.1 Alkanes fingerprinting**

Saturated hydrocarbons chromatograms of the Azzel and Fegaguira samples show slightly developed UCM (Unresolved Complex Mixture), testifying that the extracts were partially biodegraded (Gough and Al., 1990). The total ion chromatogram (TIC) represents the distribution of *n*-alkanes and *iso*-alkanes. Based on Eglinton and Hamilton, 1967; Meyers, 1997; Tissot and Welte, 1984; Peters et al., 2005; the abundance of short-chain *n*-alkanes indicates an algal derived organic matter. Nonetheless, The TIC of the saturated hydrocarbon fraction (Fig.20) displays a unimodal distribution of *n*alkanes going from *n*-C<sub>15</sub> to *n*-C<sub>35</sub> centered with low molecular weight (C<sub>17</sub>) regular decrease beyond *n*-C<sub>17</sub>; therefore, a marine setting is inferred based on Blanchart, 2011 ; Hu et al., 2013.

Both source rock samples show in general a predominance of 2,6,10,14- tetramethyl hexadecane (phytane), compared to 2,6,10,14- tetramethyl pentadecane (pristane) (Fig. 20). Samples, D1-S4, D1-S5 and D2-S16, show a unimodal distribution of n-alkanes ranging from  $n\text{-C}_{13}$  to  $n\text{-C}_{34}$  and a UCM of low intensity (Fig.20).

Otherwise, these samples were characterized with a weak relation between  $\text{Pr}/n\text{-C}_{17}$  and  $\text{Ph}/n\text{-C}_{18}$  that did not exceed 0.53 and 0.73 (Fig.20; Table4).

#### **4.4.2. Terpanes and Steranes**

The mass fragmentograms  $m/z=191$  related to the distribution of terpanes of the studied samples show a predominance of tricyclic terpanes over pentacyclic terpanes (hopanes) in the Azzel and Fegaguira Paleozoic samples as shown by the high values of the  $\text{C}_{23\text{tr}}/\text{H}_{30}$  ratio ( $>4$ ) in contrast to the Permian sample (D1-S4, D1-S5 and D2-S16; Fig.21).

Pentacyclic hopanes are characterized by an abundance of  $17\alpha(\text{H}),21\beta(\text{H})$ -trisorhopane ( $\text{H}_{30}$ ) compared to  $\text{C}_{29}$ - $17\alpha(\text{H}),21\beta(\text{H})$ -trisorhopane ( $\text{H}_{29}$ ) indicating a clayey lithology of the studied rocks (Peters et al.,2005). A low concentration of Gammacerane was observed in all samples indicating that the organic matter was deposited and preserved in a marine environment of normal salinity (Venkatesan, 1989). The studied samples show low  $\text{C}_{35}$  homohopane/ $\text{C}_{34}$  homohopane ( $\text{C}_{35}/\text{C}_{34}\text{H}$ ) ratios ( $<1$ ) for Azzel, Fegaguira, D1-S4, D1-S5 and D2-S16, therefore indicating an oxic to suboxic depositional environment (Peters and Moldowan, 1993; Jiang and George, 2018).

The studied Azzel and Fegaguira samples show a predominance of  $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$ -20R steranes ( $\text{C}_{27}$  steranes) compared to  $\text{C}_{28}$  and  $\text{C}_{29}$  steranes. The predominance of  $\text{C}_{27}$  steranes in these Ordovician (Azzel) and Silurian (Fegaguira) is indicative of an organic matter of marine origin (Volkman et al., 2003) that could have generated the free hydrocarbons (Fig.21). Conversely, the analyzed D1-S4, D1-S5, and D2-S16 Permian samples show an abundance of  $\text{C}_{27}$  and  $\text{C}_{29}$  compared to  $\text{C}_{28}$ . This abundance is significant of

a mixed organic matter of the type II/III (marine dominated with terrestrial organic matter input) which is responsible of the extracted free hydrocarbons.

#### **4.4.4. Salinity**

Gammacerane is a C<sub>30</sub> triterpane, a biomarker that plays an important role in discriminating the salinity of sedimentary water. (Jiafmo et al., 1986; Sinninghe Damsté et al., 1995). When samples show a low concentration of gammacerane, this reflects a normal salinity of their source rocks depositional environment. An abundance of gammacerane was well determined and associated with a hypersaline environment (Niu et al., 2018).

The gammacerane/hopane ratios of the different samples are low in the order of 0.05 for samples D1-S4, D1-S5, and D2-S16; and equal to 0.13 and 0.24 for Azzel and Fegaguira source rocks, respectively. Thus, it would appear that the depositional environment of the Azzel and Fegaguira source rocks is relatively more saline than that of the D1-S4, D1-S5 and D2-S16 samples.

#### **4.4.5. Organic matter origin**

Different parameters were used to analyze terpanes and steranes and provide information on the terrestrial or marine nature of the organic matter.

As demonstrated in the previous section, the variation of the C<sub>19</sub> tricyclic terpene / (C<sub>19</sub> tricyclic terpene + C<sub>23</sub> tricyclic terpene) ratio as a function of C<sub>24</sub> tetracyclic terpene / (C<sub>24</sub> tetracyclic terpene + C<sub>23</sub> tricyclic terpene) (C<sub>19</sub>tr / (C<sub>19</sub>tr + C<sub>23</sub>tr)) allowed differentiating the terrestrial origin from the marine origin of the OM in the Azzel, Fegaguira, and Permian source rocks (Table 4). The analyzed samples were characterized by very low to low C<sub>19</sub>tr / (C<sub>19</sub>tr + C<sub>23</sub>tr) ratios and C<sub>24</sub>Tet / (C<sub>24</sub>Tet + C<sub>23</sub>tr) ratios. These values did not exceed 0.19 and 0.10 for the Azzel and Fegaguira source rocks, respectively. They were moderately high for samples D2-S<sub>16</sub> from (0.3) to high for samples (D1-S<sub>4</sub>, D1-S<sub>5</sub>) of the order of 0.4 and 0.5. The plotting of the representative points of the different analyzed samples, shown in the Fig. 22,

testifies the OM marine setting with a major terrestrial contribution in samples D1-S<sub>4</sub>- D1-S<sub>5</sub>, and D2-S16. On the other hand, D1-S<sub>4</sub> and D1-S<sub>5</sub> samples are also distinguished by relatively higher C<sub>24</sub>Tet / C<sub>26</sub>tr ratios (4.59), compared to the other two source rocks and D2-S16 sample, which confirms the input of terrestrial OM. Samples of the Azzel (Ordovician) and Fegaguira (Silurian) formations seem to be of almost exclusively marine origin. Overall, the ternary diagram (Fig. 22) confirms the previous result and indicates that the Azzel and Fegaguira source rocks were generated by essentially marine OM. The OM contained in Permian samples (D2-S16, D1-S<sub>4</sub>, and D1-S<sub>5</sub>) mainly has a terrestrial origin.

#### **4.4.6. Redox condition**

The ratios Pr / Ph, Pr / nC<sub>17</sub> and Ph / nC<sub>18</sub> were used to specify the nature of the depositional environment and to determine the lithology of source rocks (Peters and Moldowan, 1993; Peters et al., 2005). The studied samples are characterized by Pr / Ph ratios varying between 1.08 and 1.18 and by relatively low Pr / nC<sub>17</sub> and Ph / nC<sub>18</sub> ratios ranging between 0.33 - 0.50 and between 0.38 - 0.50, respectively. The plotting data of the examined samples on the Pr / n-C<sub>17</sub> versus Ph / n-C<sub>18</sub> diagram (Fig. 23) demonstrates that the OM in these samples was deposited in a dysoxic to anoxic environment.

The values of the C<sub>26</sub> tricyclic / C<sub>25</sub> tricyclic ratio and those of the C<sub>31</sub>R (17 $\alpha$ , 21  $\beta$  (H)-homohopane (22R)) / C<sub>30</sub> Hopanes ratio, in the Permian samples, indicate an essentially clay lithology of these rocks. The clay fraction was higher in the Azzel and Fegaguira source rocks than in the D2-S<sub>16</sub>, D1-S<sub>4</sub> and D1-S<sub>5</sub> source rocks (Table 4). These hypotheses were confirmed by the position of representative samples points on the C<sub>27</sub> $\beta\alpha$  20R diasterane /C<sub>27</sub> $\beta\beta$  20S Steranes diagram as a function of C<sub>29</sub>/C<sub>30</sub> hopanes Homohopanes (Fig.24 (B)).

#### **4.4.7. Maturity**

The Ts / Tm ratio is often used to measure the degree of maturity (Peters and Moldowan, 1991.) with mature stage represented by a ratio higher than 1 (Ts / Tm > 1). The Azzel and

Fegaguira source rocks show high  $T_s / T_m$  values ( $> 1$ ), while Permian samples (D2-S<sub>16</sub>, D1-S<sub>4</sub> and D1-S<sub>5</sub>) have a predominance of  $T_m$  over  $T_s$  ( $T_s / T_m < 1$ ), which testifies that they are in an early mature stage, unlike the other two samples. The location of samples on the  $C_{27}\beta\alpha$  20R diasterane /  $C_{27}\beta\beta$  20S Steranes versus  $18\alpha$  (H), 22, 29, 30-trisnorneohopane ( $T_s$ ) /  $C_{27}17\alpha$ -22, 29, 30-trisnorhopane ( $T_m$ ) diagram (Fig.25) confirms the difference in thermal maturity between the investigated samples. Fegaguira and Azzel samples showed ratios greater than 0.4, indicating that they are mature for hydrocarbon generation. Nevertheless, one Permian sample (D2-S<sub>16</sub>), appears to be the least mature compared to all analyzed samples with values of  $C_{29}\alpha\alpha S$  (5alpha, 14alpha, 17alpha, 24-ethylcholestane 20S)/ $C_{29}(S+R)$  and  $C_{29}\beta\beta$  (5alpha, 14beta, 17beta, 24-ethylcholestane)/ $(\alpha\alpha+\beta\beta)$  ratios below 0.4 (Fig.25).

## 5. Conclusions

Based on the Rock\_Eval<sup>®</sup> Shale Play<sup>™</sup> analyses results of analyzed samples from Permian series in the southern Tunisia, it is found that the Permian series encompass moderate to good source rock potential in three of the four studied wells (D1, D2, and J2). The OM of Permian samples from these three wells is qualified as type II2 / III with a major terrestrial contribution, and seems to be in the early oil window stage. The identified OM in the Permian sediments of well J1 is oxidized in the depositional environment, and furthermore it has been affected by an abnormal heat testified by high  $T_{max}$  temperatures. This could be related to crustal thinning in the study area.

Carbon isotopes results ( $\delta^{13}C$ ) concurs with some of the Rock-Eval<sup>®</sup> results and indicate that the organic matter within the Permian sediments is of type II2 / III.

High TOC selected Permian samples (D2-S<sub>16</sub>, D1-S<sub>4</sub>, and D1-S<sub>5</sub>) were subjected to further analyses via GC/MS analyses of their free oil extracts. All studied Paleozoic samples were found to belong to source rocks of marly-clayey lithology, in agreement with samples lithology. The OM deposition took place in a marine setting with relatively normal salinity,

and under dyoxic-anoxic conditions. The OM in the studied Permian series seems to have a mixed origin, and majority is derived from high terrestrial plant matter inputs into marine environment. Nonetheless, future palynological and palynofacies analyses should be undertaken in the future for better understanding of the OM origin in the studied Permian series.

The main outcome of this geochemical study is that it contributes to verify the petroleum potential of the Permian series of southern Tunisia as a moderate to good oil/gas prone source rock either in the Dahar or the Jeffara area. It is worth noting that studied samples herein belong to drilled wells on relatively high structures and laterally, where the Permian is more deeply buried, maturity could be more enhanced and hydrocarbon generation/expulsion could have occurred.

Lastly, further investigations combining geochemical results with geophysical interpretations and basin modeling are now needed to be able to achieve a volumetric assessment of the Permian source rock generated/expelled hydrocarbon amounts.

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### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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<b>D</b>	1	M-	0.63	19.8	10.9	13.	20.5	3.0	406	7.	141	31.46	0.
<b>1-</b>	5	C		8	5	92	1	7		76			79
<b>S<sub>1</sub></b>	4												
	9												
<b>D</b>	2	M-	0.56	1.21	10.6	2.0	1.77	31.	435	4.	220	12.45	5.
<b>1-</b>	1	C			8	5		64		85			21
<b>S<sub>2</sub></b>	4												
	4												
<b>D</b>	2	M-	0.08	0.36	2.38	1.7	0.44	18.	437	1.	129	2.82	1.
<b>1-</b>	1	C				9		18		84			33
<b>S<sub>3</sub></b>	5												
	9												
<b>D</b>	2	M	0.06	0.43	2.05	2.3	0.49	12.	439	1.	175	2.54	0.
<b>1-</b>	2					1		24		17			89
<b>S<sub>4</sub></b>	8												
	2												
<b>D</b>	2	M	0.02	0.29	1.03	1.3	0.31	6.4	436	1.	92	1.34	0.
<b>1-</b>	3					6		5		12			76
<b>S<sub>5</sub></b>	9												
	3												
<b>D</b>	3	M	0.06	0.50	1.74	3.0	0.56	10.	431	1.	90	2.30	0.
<b>1-</b>	6					6		71		93			57
<b>S<sub>6</sub></b>	3												
	9												
<b>D</b>	3	M	0.02	0.17	0.53	1.5	0.19	10.	424	1.	46	0.72	0.
<b>1-</b>	9					8		53		14			34
<b>S<sub>7</sub></b>	3												
	2												
<b>D</b>	3	M	0.01	0.05	0.22	1.2	0.06	16.	429	0.	39	0.28	0.
<b>1-</b>	9					5		67		57			18
<b>S<sub>8</sub></b>	5												
	0												
<b>D</b>	4	M	0.02	0.13	0.34	1.1	0.15	13.	424	0.	49	0.49	0.
<b>1-</b>	0					8		33		69			29
<b>S<sub>9</sub></b>	5												
	2												
<b>D</b>	1	C	0.01	0.09	0.35	0.7	0.10	10.	428	0.	70	0.45	0.
<b>2-</b>	0					8		00		50			45
<b>S<sub>1</sub></b>	8												
	3												
<b>D</b>	1	C	0.04	0.64	11.8	2.0	0.68	5.8	416	5.	213	12.50	5.
<b>2-</b>	1				2	2		8		54			85
<b>S<sub>2</sub></b>	7												
	5												
<b>D</b>	1	C	0.09	0.75	6.42	1.4	0.84	10.	426	3.	213	7.26	4.
<b>2-</b>	2					4		71		01			46
<b>S<sub>3</sub></b>	4												
	0												
<b>D</b>	1	C	0.34	1.28	11.0	1.0	1.62	20.	421	4.	276	12.69	10
<b>2-</b>	2				7	8		99		01			.2



<b>D</b>	2	M	0.05	0.18	0.78	0.5	0.23	21.	449	0.	122	1.01	1.
<b>2-</b>	4					8		74		64			34
<b>S<sub>1</sub></b>	1												
7	2												
<b>D</b>	2	M	0.04	0.19	0.54	0.6	0.23	17.	457	0.	68	0.77	0.
<b>2-</b>	5					0		39		79			90
<b>S<sub>1</sub></b>	4												
8	2												
<b>D</b>	2	M-	0.02	0.11	0.46	0.5	0.13	15.	454	0.	81	0.59	0.
<b>2-</b>	5	C				0		38		57			92
<b>S<sub>1</sub></b>	8												
9	8												
<b>J</b>	2	M-	0.01	0.02	0.05	0.7	0.03	33.	382	0.	50	0.08	0.
<b>1-</b>	2	C				6		33		10			07
<b>S<sub>1</sub></b>	6												
2	2												
<b>J</b>	2	M-	0.00	0.01	0.04	0.6	0.01	0.0	457	0.	36	0.05	0.
<b>1-</b>	2	C				5		0		11			06
<b>S<sub>2</sub></b>	6												
3	2												
<b>J</b>	2	M	0.01	0.06	0.34	0.6	0.07	14.	555	1.	26	0.41	0.
<b>1-</b>	2					6		29		32			52
<b>S<sub>3</sub></b>	6												
9	2												
<b>J</b>	2	M	0.01	0.02	0.09	0.5	0.03	33.	562	0.	20	0.12	0.
<b>1-</b>	2					8		33		44			16
<b>S<sub>4</sub></b>	7												
0	2												
<b>J</b>	2	M	0.01	0.03	0.12	0.8	0.04	25.	550	0.	23	0.16	0.
<b>1-</b>	2					3		00		52			14
<b>S<sub>5</sub></b>	7												
3	2												
<b>J</b>	2	M	0.01	0.05	0.10	0.7	0.06	16.	567	0.	19	0.16	0.
<b>1-</b>	2					3		67		54			14
<b>S<sub>6</sub></b>	7												
4	2												
<b>J</b>	2	M	0.01	0.04	0.11	0.6	0.05	20.	538	0.	34	0.16	0.
<b>1-</b>	2					0		00		32			18
<b>S<sub>7</sub></b>	9												
7	2												
<b>J</b>	2	M	0.01	0.03	0.09	0.7	0.04	25.	556	0.	19	0.13	0.
<b>1-</b>	3					4		00		48			12
<b>S<sub>8</sub></b>	0												
5	2												
<b>J</b>	2	M	0.01	0.04	0.15	0.8	0.05	20.	548	0.	17	0.20	0.
<b>1-</b>	3					0		00		86			19
<b>S<sub>9</sub></b>	0												
6	2												
<b>J</b>	2	M-	0.00	0.02	0.05	0.6	0.02	0.0	499	0.	16	0.07	0.
<b>1-</b>	4	C				5		0		31			08

<b>S<sub>1</sub></b>	1												
0	5												
<b>J</b>	2	M-	0.00	0.03	0.04	0.6	0.03	0.0	416	0.	36	0.07	0.
<b>1-</b>	5	C				8		0		11			06
<b>S<sub>1</sub></b>	2												
1	5												
<b>J</b>	2	M-	0.01	0.02	0.05	0.5	0.03	33.	409	0.	29	0.08	0.
<b>1-</b>	6	C				6		33		17			09
<b>S<sub>1</sub></b>	1												
2	4												
<b>J</b>	2	C	0.01	0.03	0.06	0.5	0.04	25.	404	0.	29	0.10	0.
<b>1-</b>	7					3		00		21			11
<b>S<sub>1</sub></b>	3												
3	8												
<b>J</b>	3	C	0.00	0.03	0.05	0.6	0.03	0.0	383	0.	28	0.08	0.
<b>1-</b>	2					3		0		18			08
<b>S<sub>1</sub></b>	1												
4	0												
<b>J</b>	3	C	0.02	0.04	0.10	0.9	0.06	33.	578	0.	18	0.16	0.
<b>1-</b>	3					2		33		57			11
<b>S<sub>1</sub></b>	6												
5	6												
<b>J</b>	3	C	0.01	0.04	0.13	0.8	0.05	20.	412	0.	43	0.18	0.
<b>1-</b>	4					3		00		30			16
<b>S<sub>1</sub></b>	0												
6	0												
<b>J</b>	9	C	0.02	0.20	4.44	1.7	0.22	9.0	432	3.	137	4.66	2.
<b>2-</b>	8					6		9		24			52
<b>S<sub>1</sub></b>	6												
<b>J</b>	1	C	0.02	0.11	1.26	1.7	0.13	15.	431	1.	85	1.39	0.
<b>2-</b>	0					1		38		49			74
<b>S<sub>2</sub></b>	0												
0	0												
<b>J</b>	1	C	0.07	0.39	3.82	1.4	0.46	15.	435	4.	93	4.28	2.
<b>2-</b>	0					0		22		12			73
<b>S<sub>3</sub></b>	1												
8	1												
<b>J</b>	1	C	0.16	1.00	9.30	1.9	1.16	13.	431	7.	121	10.46	4.
<b>2-</b>	0					7		79		69			72
<b>S<sub>4</sub></b>	3												
8	8												
<b>J</b>	1	M-	0.01	0.12	0.64	1.1	0.13	7.6	433	1.	47	0.77	0.
<b>2-</b>	0	C				0		9		37			58
<b>S<sub>5</sub></b>	6												
0	0												
<b>J</b>	1	C	0.06	0.46	6.21	0.9	0.52	11.	431	3.	203	6.73	6.
<b>2-</b>	1					9		54		06			27
<b>S<sub>6</sub></b>	2												
2	2												
<b>J</b>	1	C	0.04	0.36	3.66	0.8	0.40	10.	433	2.	169	4.06	4.

2- S <sub>7</sub>	1 3 6					2		00		17			46
J 2- S <sub>8</sub>	1 1 3 8	C	0.07	0.50	5.70	1.2 3	0.57	12. 28	431	2. 79	204	6.27	4. 63
J 2- S <sub>9</sub>	1 2 0 6	C	0.12	0.63	5.72	1.1 2	0.75	16. 00	437	2. 61	219	6.47	5. 11
J 2- S <sub>1</sub>	1 2 1 4	C	0.05	0.26	2.51	1.1 5	0.31	16. 13	438	1. 47	171	2.82	2. 18
J 2- S <sub>1</sub>	1 2 2 0	C	0.12	0.73	7.80	1.4 2	0.85	14. 12	437	4. 17	187	8.65	5. 49
J 2- S <sub>1</sub>	1 2 2 4	C	0.05	0.36	3.16	1.2 2	0.41	12. 20	436	2. 31	137	3.57	2. 59
J 2- S <sub>1</sub>	1 2 2 6	C	0.09	0.57	4.16	1.3 2	0.66	13. 64	436	2. 81	148	4.82	3. 15
J 2- S <sub>1</sub>	1 2 2 6	C	0.18	0.57	5.72	1.0 0	0.75	24. 00	433	2. 03	282	6.47	5. 72
J 2- S <sub>1</sub>	1 2 2 4	C	0.09	0.47	3.51	1.1 5	0.56	16. 07	434	1. 72	204	4.07	3. 05
J 2- S <sub>1</sub>	1 2 2 8	M- C	0.12	0.59	4.21	0.9 8	0.71	16. 90	433	2. 06	204	4.92	4. 30
J 2- S <sub>1</sub>	1 2 2 8	C	0.14	0.75	6.22	1.0 7	0.89	15. 73	434	2. 98	209	7.11	5. 81
J 2- S <sub>1</sub>	1 2 2 4	C	0.08	0.51	5.44	1.1 8	0.59	13. 56	436	2. 95	184	6.03	4. 61
J 2- S <sub>1</sub>	1 3 0	M- C	0.02	0.13	1.30	1.1 8	0.15	13. 33	439	1. 65	79	1.45	1. 10

9	4												
<b>J</b>	1	C	0.39	1.41	9.75	1.1	1.80	21.	432	4.	219	11.55	8.
<b>2-</b>	3					4		67		46			55
<b>S<sub>2</sub></b>	9												
0	5												
<b>J</b>	1	C	0.91	2.44	17.0	1.3	3.35	27.	431	6.	245	20.38	12
<b>2-</b>	4				3	2		16		95			.9
<b>S<sub>2</sub></b>	1												0
1	0												
<b>J</b>	1	C	0.07	0.29	2.64	0.9	0.36	19.	440	1.	161	3.00	2.
<b>2-</b>	4					7		44		64			72
<b>S<sub>2</sub></b>	2												
2	5												
<b>J</b>	1	C	0.56	1.81	13.7	1.0	2.37	23.	436	4.	294	16.16	12
<b>2-</b>	4				9	7		63		69			.8
<b>S<sub>2</sub></b>	3												9
3	0												
<b>J</b>	1	C	0.42	1.20	7.07	0.8	1.62	25.	438	2.	260	8.69	8.
<b>2-</b>	4					6		93		72			22
<b>S<sub>2</sub></b>	5												
4	0												
<b>J</b>	1	C	0.22	1.24	10.3	1.0	1.46	15.	441	3.	271	11.76	10
<b>2-</b>	4				0	1		07		80			.2
<b>S<sub>2</sub></b>	8												0
5	8												
<b>J</b>	1	C	0.20	1.93	18.9	1.0	2.13	9.3	434	6.	283	21.08	17
<b>2-</b>	4				5	8		9		69			.5
<b>S<sub>2</sub></b>	9												5
6	0												
<b>J</b>	1	C	0.19	1.37	13.0	1.0	1.56	12.	436	5.	261	14.60	12
<b>2-</b>	4				4	7		18		00			.1
<b>S<sub>2</sub></b>	9												9
7	5												
<b>J</b>	1	C	0.05	0.48	4.90	0.9	0.53	9.4	450	3.	140	5.43	5.
<b>2-</b>	5					7		3		51			05
<b>S<sub>2</sub></b>	6												
8	0												
<b>J</b>	1	M-	0.06	0.31	3.21	1.1	0.37	16.	442	2.	117	3.58	2.
<b>2-</b>	5	C				5		22		75			79
<b>S<sub>2</sub></b>	7												
9	6												
<b>J</b>	1	M	0.05	0.30	2.44	0.8	0.35	14.	441	1.	168	2.79	2.
<b>2-</b>	6					7		29		45			80
<b>S<sub>3</sub></b>	4												
0	3												

**Abbreviations:** **HCcont** = hydrocarbon content index. **TOC:** total organic carbon (%). **Tmax:** S2 maximum peak temperature (°C). **PP:** Petroleum potential ((SH0+SH1+SH2) mg HC.g/rock). **IH:** Hydrogen Index..

**M=Marl, C=clay**

Table 2

Samples	Lithology	Age	Depth(m)
D1-S4	M	Permian	2282
D1-S5	M	Permian	2393
D2-S16	M-C	Permian	2404
Fegaguira	C	Upper Silurian-	3838
Azzel	C	Ordovician	3913

Abbreviations: M=Marl, C=clay

Table 3

Well	Depth (m)	Age	Before acid attack		After acid attack		C(%)	$\delta^{13}\text{C}$ (‰)	$\sigma$
			TOC(%)	MINC(%)	TOC(%)	MINC(%)			
D1-S <sub>2</sub>	214 4	Permian	4.85	8.77	14.88	0.50	15.17	-22.65	0.02
D1-S <sub>3</sub>	215 9	Permian	1.84	8.47	15.16	0.87	15.59	-18.95	0.016971
D1-S <sub>4</sub>	228 2	Permian	1.17	9.14	9.78	0.61	9.64	-25.21	0.019092
D1-S <sub>5</sub>	239 3	Permian	1.12	8.04	3.75	0.45	3.52	-24.01	0.243245
D1-S <sub>6</sub>	363 9	Permian	1.93	8.48	2.54	0.42	2.29	-23.90	0.147078
D2-S <sub>2</sub>	117 5	Permian	5.54	7.25	9.74	0.66	9.97	-21.83	0.021213
D2-S <sub>3</sub>	124 0	Permian	3.01	7.66	7.39	0.50	6.57	-23.72	0.03677
D2-S <sub>4</sub>	129 2	Permian	4.01	8.08	12.39	0.65	13.74	-23.24	0.104652
D2-S <sub>10</sub>	194 8	Permian	3.35	7.83	6.93	0.33	7.19	-26.28	0.02545584
D2-S <sub>13</sub>	209 6	Permian	1.57	8.18	11.83	0.29	12.12	-22.62	0.062933
J1-S <sub>3</sub>	226 9	Permian	1.32	7.36	2.13	0.47	1.85	-22.12	0.017678
J1-S <sub>5</sub>	227 3	Permian	0.52	3.43	0.67	0.41	0.58	-23.69	0.136472

<b>J1-S<sub>6</sub></b>	227 4	Permi an	0.54	7.63	1.95	0.39	2.22	-21.95	0.20647 5
<b>J1-S<sub>9</sub></b>	230 6	Permi an	0.86	6.48	1.58	0.35	1.39	-24.23	0.558614 36
<b>J1-S<sub>15</sub></b>	336 6	Permi an	0.57	7.29	1.87	0.26	1.60	-24.53	0.09758 1
<b>J2-S<sub>1</sub></b>	986	Permi an	3.24	6.67	0.92	0.39	1.09	-19.18	0.15556 3
<b>J2-S<sub>4</sub></b>	103 8	Permi an	7.69	5.68	2.78	0.35	3.02	-21.45	0.25668
<b>J2-S<sub>11</sub></b>	122 0	Permi an	4.17	7.14	5.44	0.27	5.40	-21.80	0.08343 9
<b>J2-S<sub>21</sub></b>	141 0	Permi an	6.95	8.27	12.75	0.38	13.1 6	-20.72	0.10677 3
<b>J2-S<sub>26</sub></b>	149 0	Permi an	6.69	7.91	15.26	0.31	15.8 9	-21.36	0.06788 2

. **TOC**: total organic carbon (%). **MINC** =Mineral carbon (%)

Table 4

Parameters	Fegaguira	Azzel	D2-S <sub>16</sub>	D1-S <sub>4</sub>	D1-S <sub>5</sub>
% C27	45	43	30	34	38
% C28	23	28	21	10	8
% C29	31	29	30	55	53
C19 tr/(C19 tr+C23 tr)	0.06	0.19	0.28	0.25	0.4
C22tr/C21tr	0.23	0.27	0.62	0.24	0.24
C23 tr/H30	4.06	1.99	0.5	0.14	0.1
C24Tet/ (C24 Tet+C23 tr)	0.16	0.1	0.28	0.46	0.47
C24Tet/ C26tr	0.38	0.25	0.86	3.29	2.81
C24tr/C23tr	0.61	0.61	0.48	0.51	0.55
C26tr/C25tr	0.09	1.05	0.91	0.49	0.66
C27β <sub>α</sub> Dia/C27β <sub>β</sub> S Stéranes	1.34	1.44	0.49	0.5	0.68
C29/C30HH	0.7	0.79	0.82	0.52	0.53
C29S/(S+R) stéranes	0.59	0.6	0.39	0.49	0.5
C29β <sub>β</sub> /C29 (αα+ββ) stéranes	0.59	0.6	0.39	0.53	0.55
C31R/H	0.24	0.25	0.38	0.34	0.46
C35/C34	0.56	0.5	0.88	0.47	0.69
C35HH/C34HH	0.5	0.56	0.88	0.47	0.69
Gammacérane/hopane	0.13	0.24	0.05	0.05	0.03
Ph/nC18	0.4	0.59	0.35	0.28	1.03
Pr/nC17	0.37	0.5	0.43	0.43	0.69
Pr/Ph	1.08	1.15	1.51	0.74	1.07
Ts/Tm	2.68	1.94	0.67	0.52	0.7

$\%C27=100 \cdot C27\beta\beta(R+S) / (C27\beta\beta(R+S) + C28\beta\beta(R+S) + C29\beta\beta(R+S))$ : m/z 218

$\%C28=100 \cdot C28\beta\beta(R+S) / (C27\beta\beta(R+S) + C28\beta\beta(R+S) + C29\beta\beta(R+S))$ : m/z 218

$\%C29=100 \cdot C29\beta\beta(R+S) / (C27\beta\beta(R+S) + C28\beta\beta(R+S) + C29\beta\beta(R+S))$ : m/z 218

## Figures captions

Fig. 1 (A) Digital Elevation Model (DEM) of Mediterranean Sea domain. Boxed area indicates location of the Tunisia region (Alyahyaoui, et al 2015) and (B) Digital elevation model of the south-eastern of Tunisia indicating the location study area (1: Mediterranean Sea, 2: SE Jeffara Basin, 3: Dahar, 4: Jebel Tebaga, 5: Chotts area of the North Range (modified from Bouaziz., et al 1995 ).

Fig. 2 Late Hercynian unconformity subcrop map of southern Tunisia (Modified from Memmi et al., 1986).

Fig. 3 Location map of studied wells.

Fig.4 Pyrograms obtained by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> method for one selected sample (J2-S<sub>26</sub>), illustrating that this method provide a good assessment of free and/or retained hydrocarbons in rock sample.

Fig.5 Free and/or sorbed liquid hydrocarbon content [HCcont] versus TOC content from D1-S5 source rock samples (modified from Romero-Sarmiento et al., 2016a).

Fig. 6 Parameters obtained by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> and for D1 studied samples.

Fig.7 Parameters obtained by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> and for J2 studied samples.

Fig.8 Parameters obtained by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> and for J1 studied samples.

Fig.9 Parameters obtained by Rock-Eval<sup>®</sup> Shale Play<sup>™</sup> and for D1 studied samples.

Fig.10 (A)-HI/ TOC, (B)-SH<sub>2</sub>/S<sub>3</sub> / TOC shows potential generation of the” D1, J2, J1 and D2 of the Permian.

Fig.11 HI / T<sub>max</sub>, showing the type of showing stages of maturity and organic matter contained in the Permian source rocks of the wells.

Fig.12 (A)-3D block diagram of the crustal thinning of the crust on glove-finger form on the Jeffara, (B)-a synthetic model of a collapse at the sedimentary weft after a significant rifting associated to a mantle rise (Gabtni.,2006) and (C)-Map of geothermal flux changes (Della Vedova et al., 1995in Gabtni,2006) (above) and average geothermal gradient (expressed in °c/100m) (in the bottom) in the Jeffara region.

Fig.13 (A)-HI / IO and SH<sub>2</sub> / Toc showing the type of organic matter contained in the Permian source rocks.

Fig.14 Rock samples studied from different wells D1, J2, J1 and D1 from the Jeffara area showing the percentages of MINC (A) and the percentages of organic carbon content (B) before and after isolation of organic matter (OM) obtained by conventional acid attack following IFPEN procedures (Durand and Nicaise, 1980).

Fig.15 Relationship between TOC and δ<sup>13</sup>C (‰) of organic matter between different Permian wells.

Fig.16 HI (kerogen and maturity dependent) plot versus carbon isotope ratios of organic matter in Permian source rocks from wells D1, J2, J1 and D1. (Raja et al., 2015).

Fig.17 Comparison δ<sup>13</sup>C (‰) of organic matter values between the kerogen of potential source rock (liu et al., 2012).

Fig.18 Relationship between TOC from Elemental Analysis (%) and TOC from Rock-Eval® Shale Play™ (%) of organic matter of different D1-S5 wells.

Fig.19 Relationship between TOC and  $\delta^{13}\text{C}$  (‰) of organic matter.

Fig.20 GC/MS TIC distribution characteristics of samples Azzel, Fegaguira (D1-S4-D1-S5) and D2-S16.

Fig.21 Partial mass fragmentograms of aliphatic hydrocarbon fraction showing the distribution of terpanes/hopanes (m/z 191) and steranes (m/z 217) of selected samples from the Permian.

Fig.22 Ternary diagram based on the composition of  $\text{C}_{27}\%$ ,  $\text{C}_{28}\%$ ,  $\text{C}_{29}\%$  steranes showing the origin and the deposition medium of the organic matter of the samples Azzel, Fegaguira, (D1-S4-D1-S5) and D2-S16 .

Fig.23 Diagram of the Pristane / n- $\text{C}_{17}$  ratio versus the Phytane / n- $\text{C}_{18}$  ratio showing the deposition medium of the organic matter contained in the samples Azzel, Fegaguira sources of Dahare area and D1 of Jeffara.

Fig.24 (A)  $\text{C}_{26}\text{tr} / \text{C}_{25}\text{tr}$  diagram versus  $\text{C}_{31}\text{R} / \text{C}_{30}$  Hopanes of samples Azzel, Fegaguira, D2-S16, D1-S4 and D1-S5. (B) Diagram  $\text{C}_{27}\beta\alpha$  dia /  $\text{C}_{27}\beta\beta$  s steranes as a function of  $\text{C}_{29} / \text{C}_{30}$  hopanes relating to samples Azzel, Fegaguira, D2-S16 and (D1-S4, D1-S5).

Fig.25 Diagram  $\text{C}_{29}\beta\beta / \text{C}_{29} (\alpha\alpha + \beta\beta)$  steranes as a function of  $\text{C}_{29} \alpha\alpha 20\text{s} / (20\text{s} + 20\text{r})$  steranes of Azzel, Fegaguira And Permian samples D2-S16, D1-S4 and D1-S5.

### **Table captions**

Table 1 Bulk parameters obtained by the Rock-Eval® Shale Play™ method for studied D1-S5 samples in well D1, J2, J1 and D1.

Table 2 sources rocks samples investigated from southern Tunisia in the Azzel, Fegaguira, and Permian source rocks

Table 3 TOC and MINC before and after acid attack, organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) and elemental composition (C %) of the 20 selected samples of D1-S5.

Table 4 Biomarkers parameters based on GC-MS results of the source rock Azzel, Fegaguira, D2-S16, D1-S<sub>4</sub> and D1-S<sub>5</sub>.

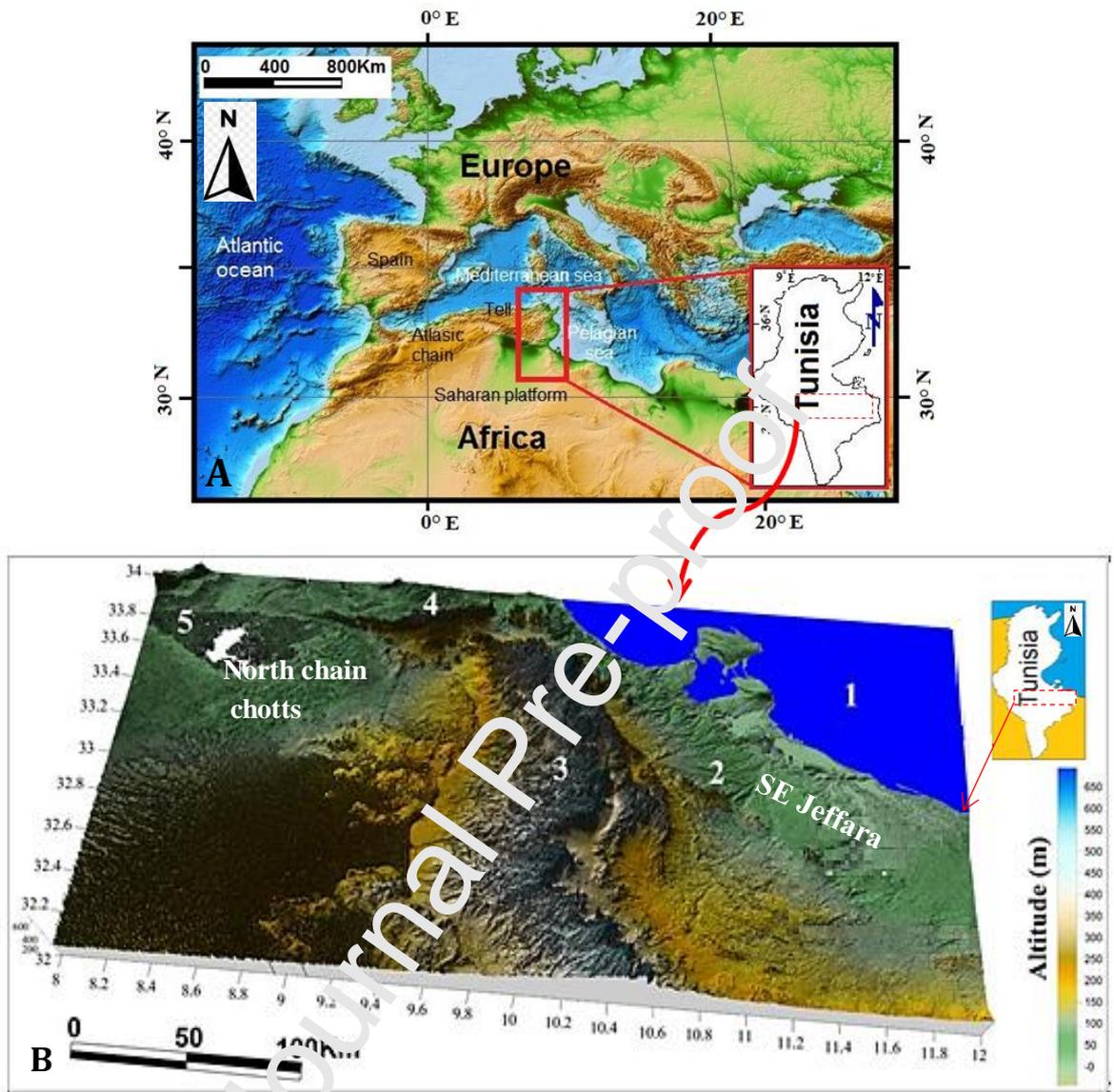


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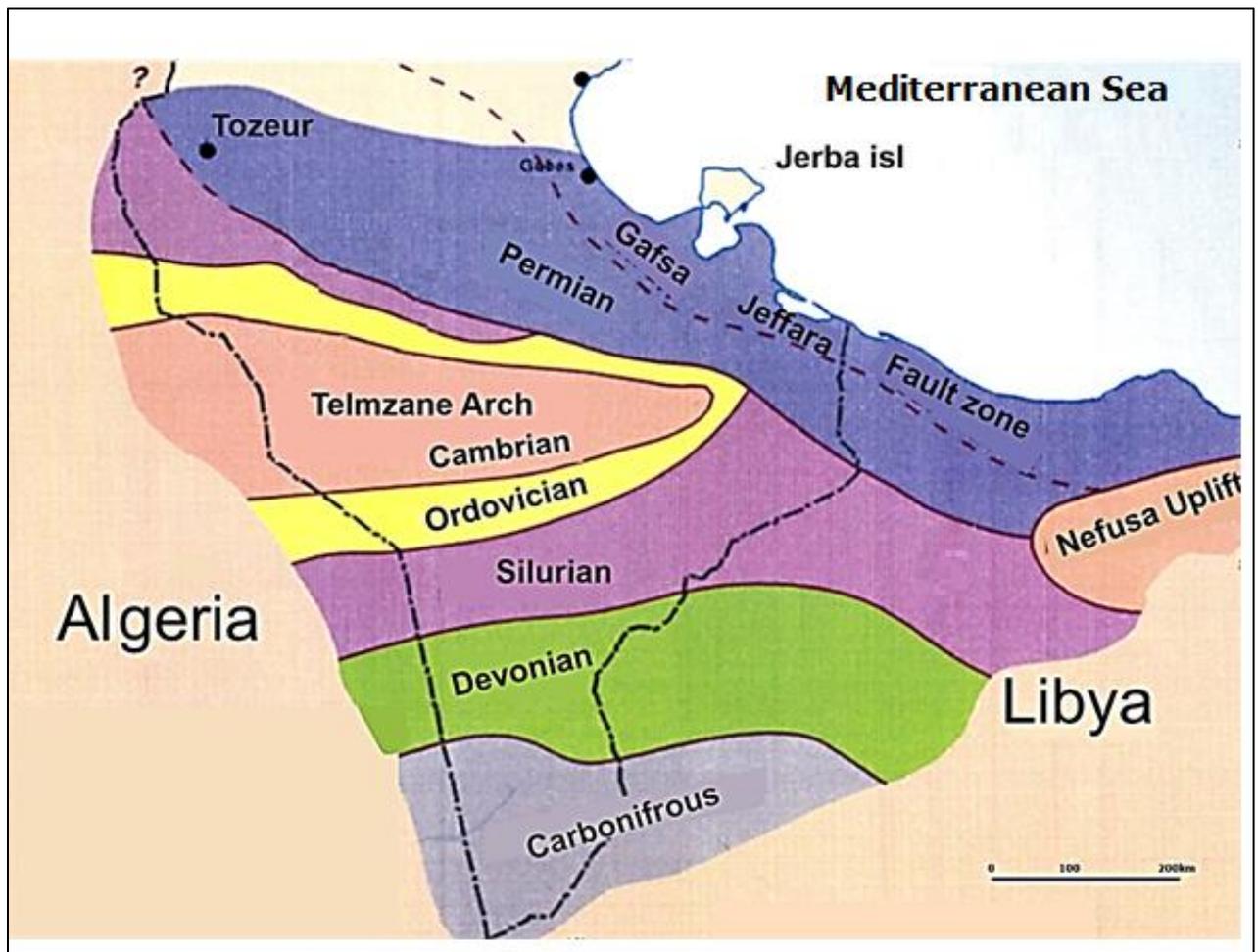


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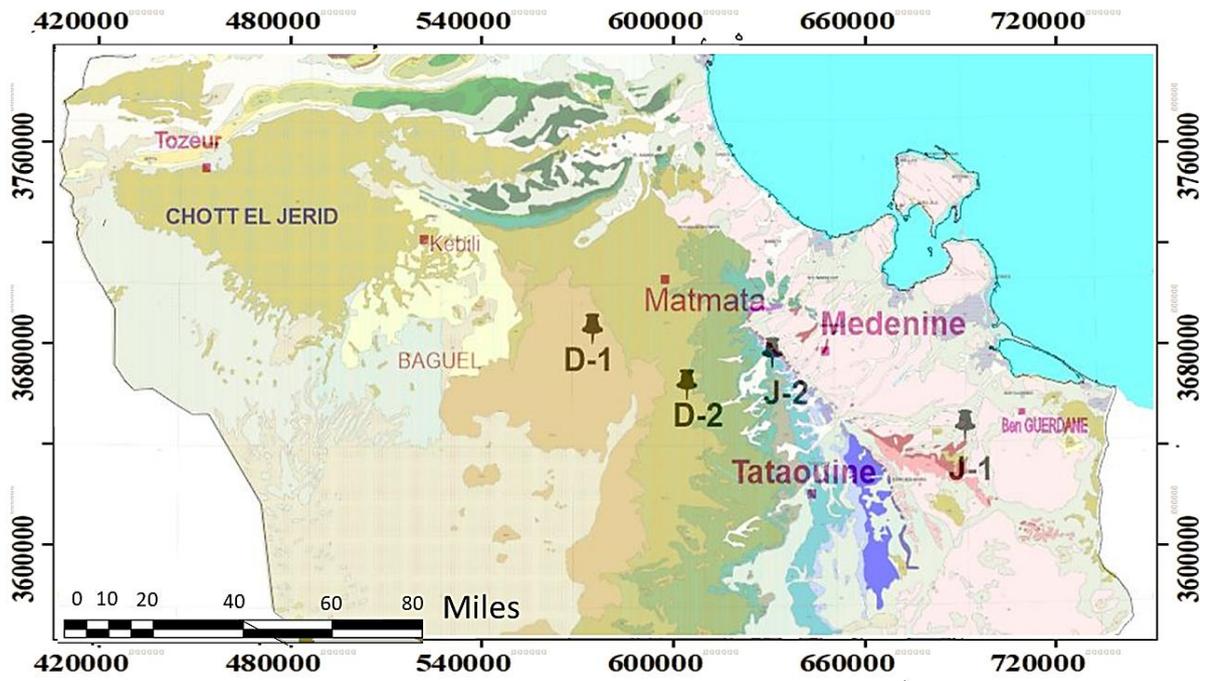


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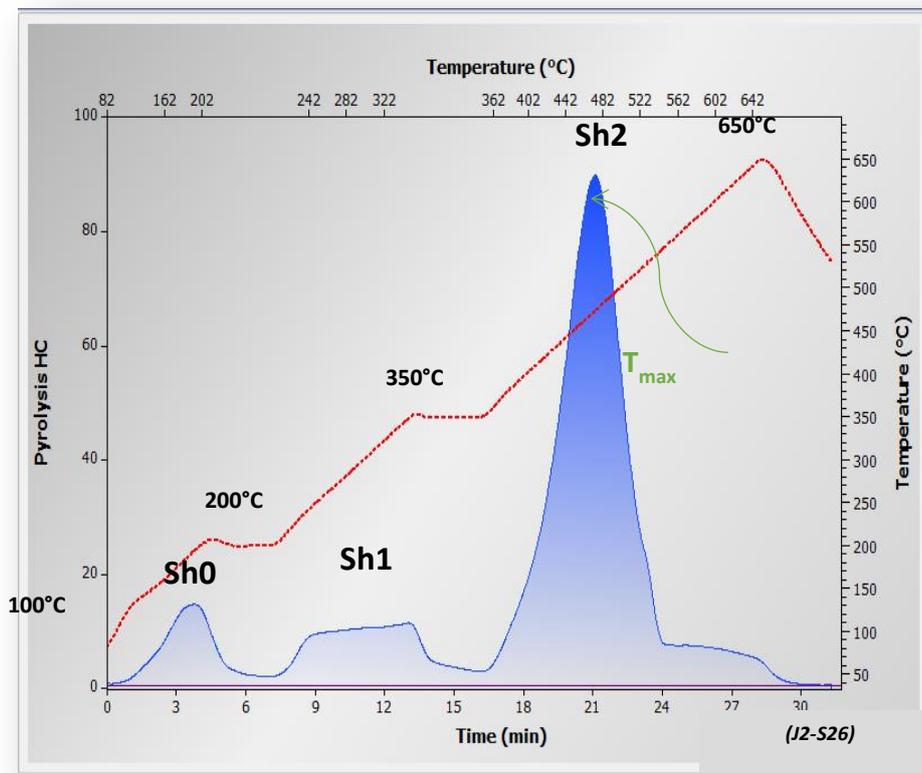


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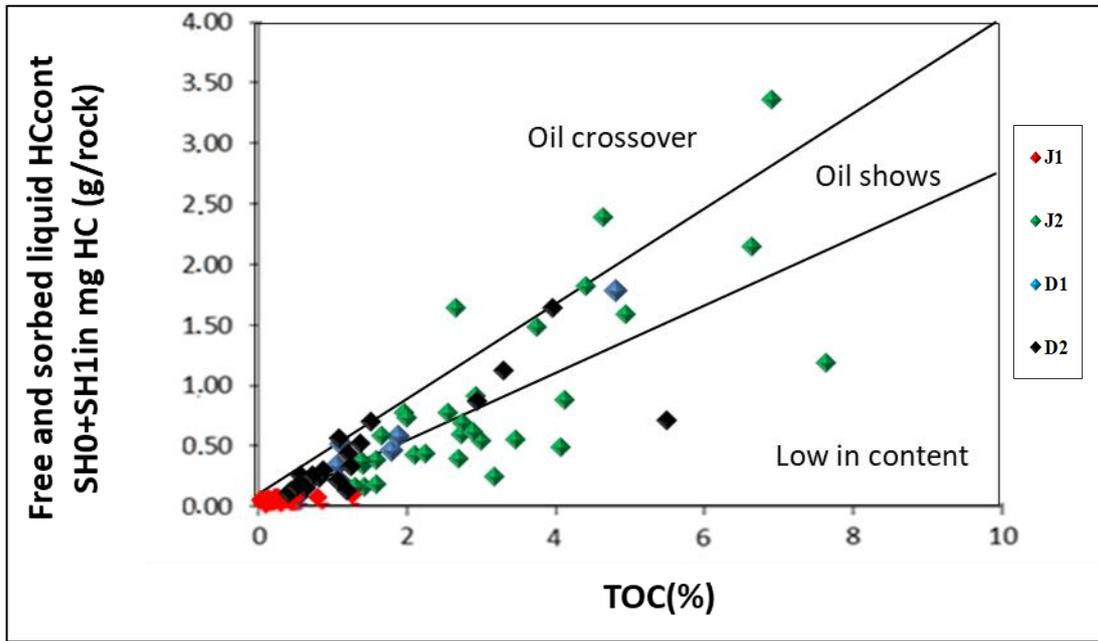


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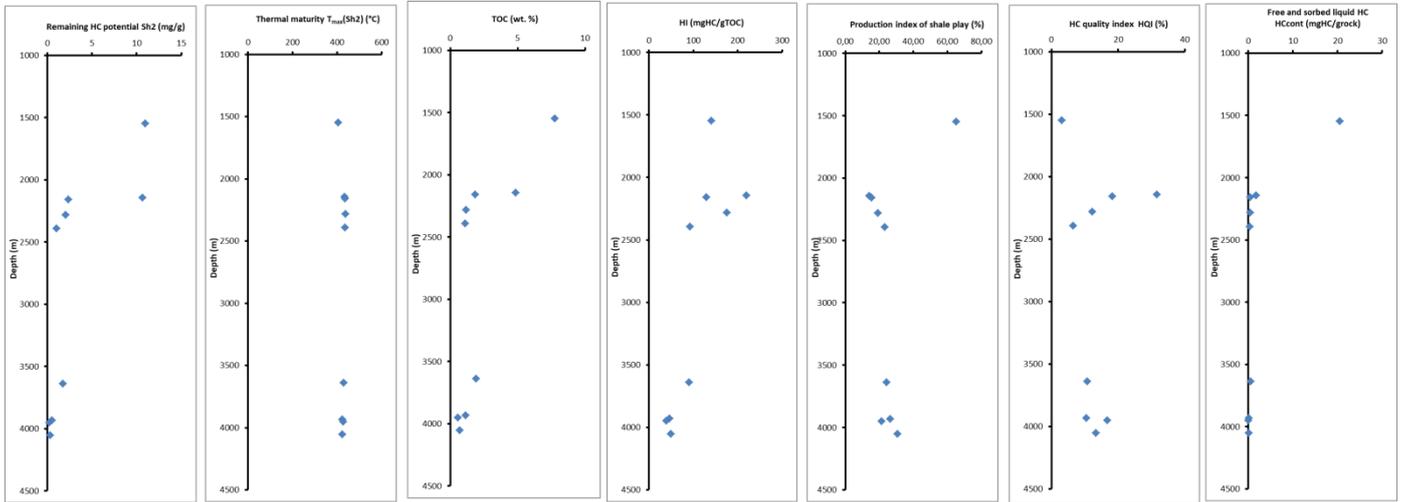


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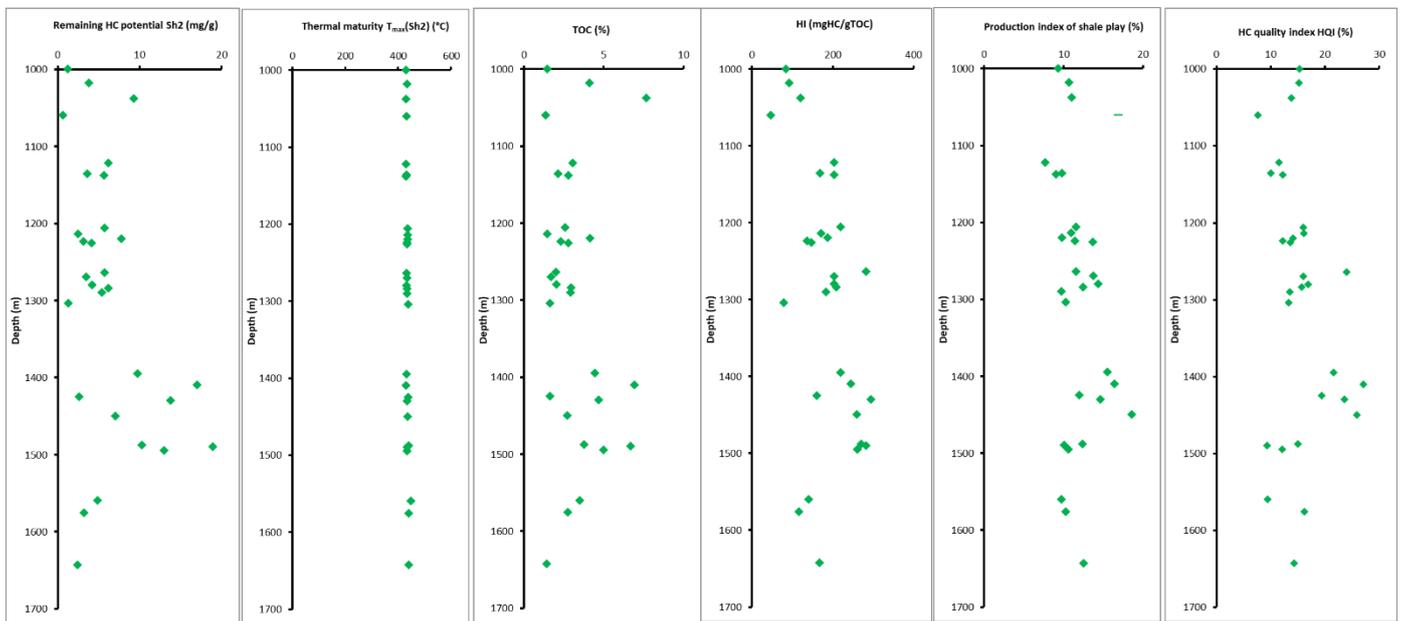


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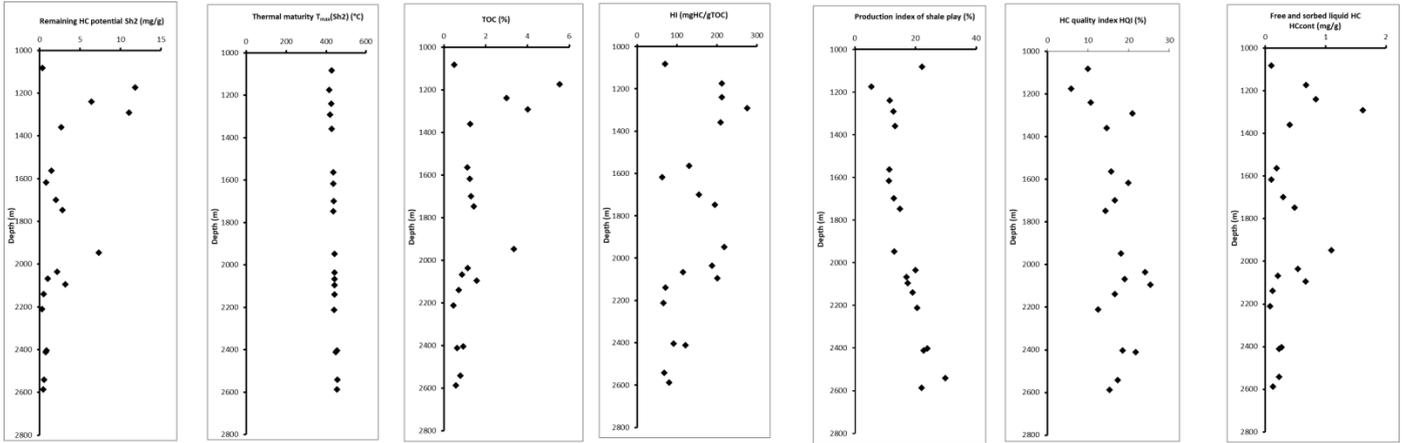


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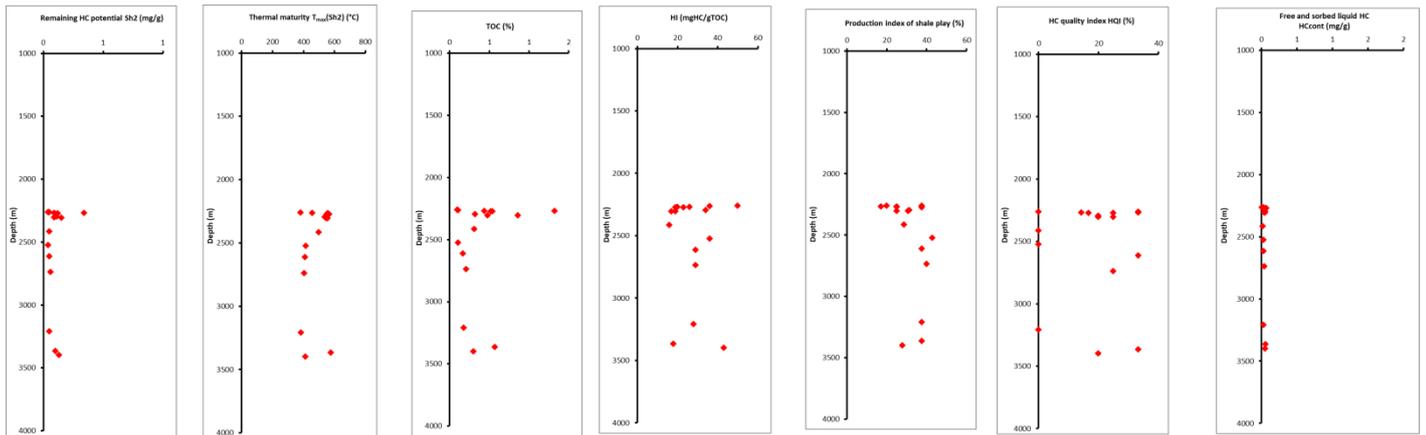


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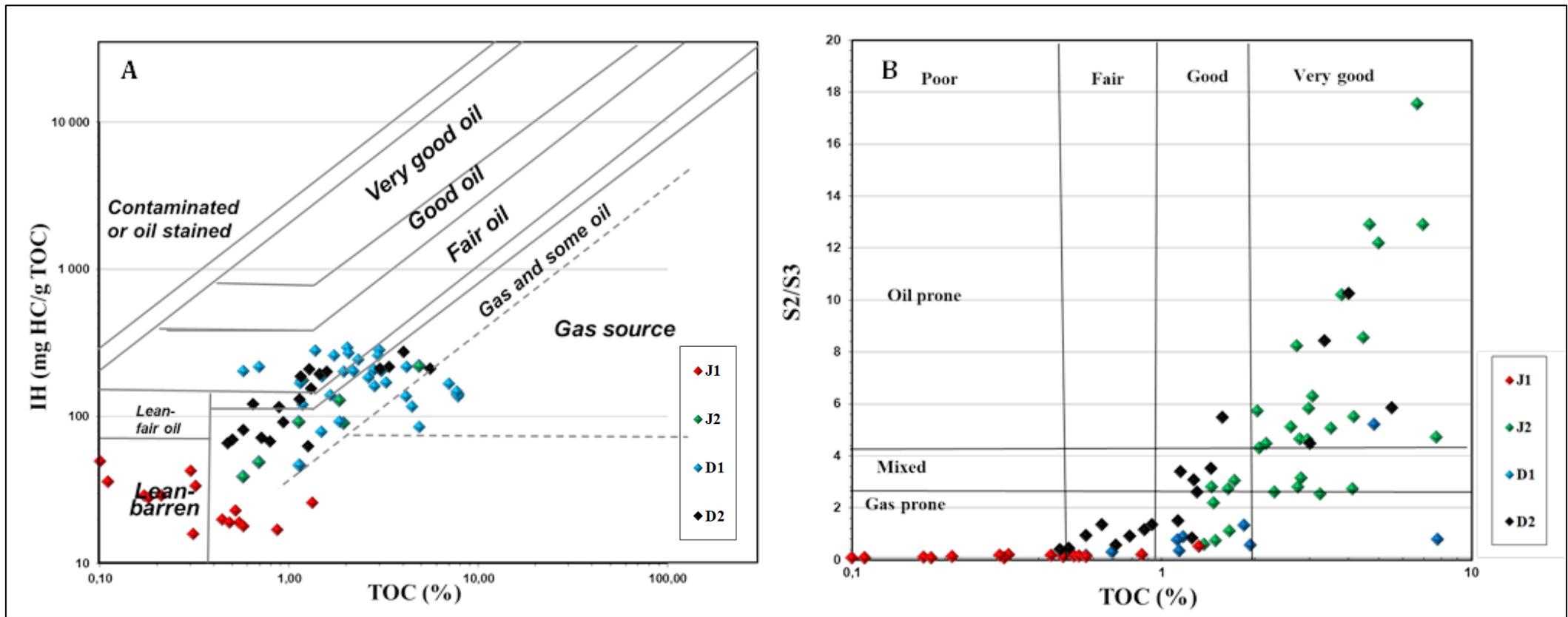


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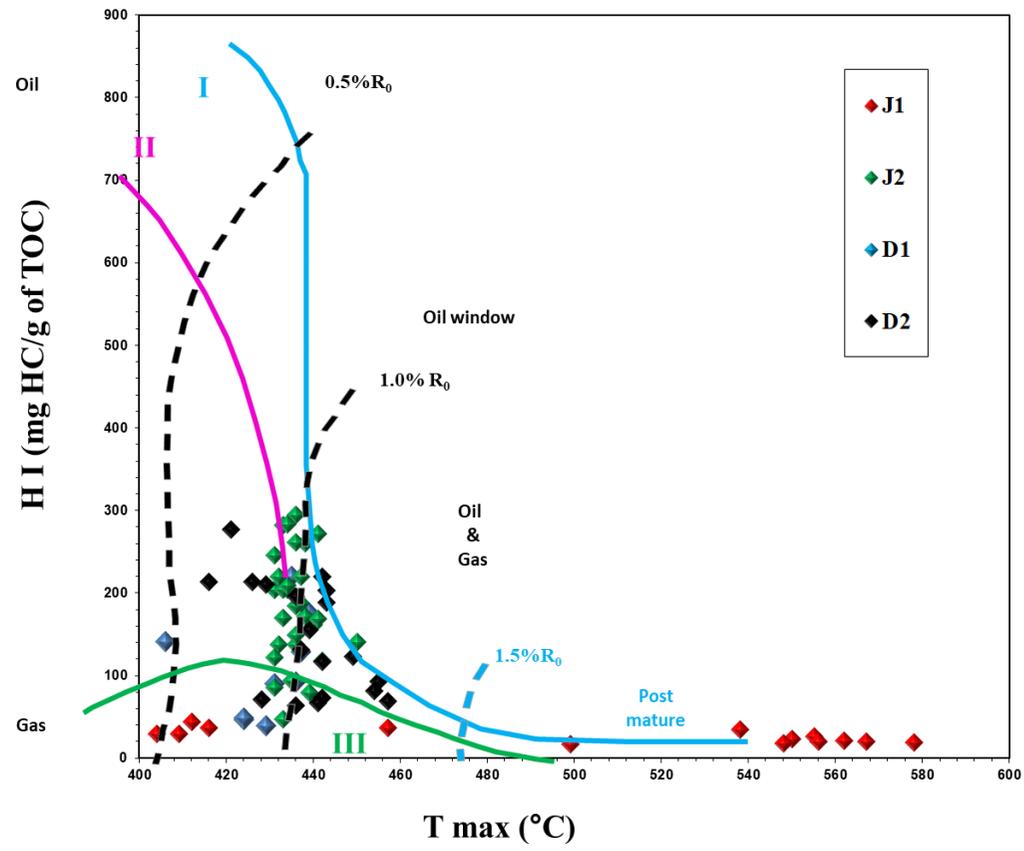


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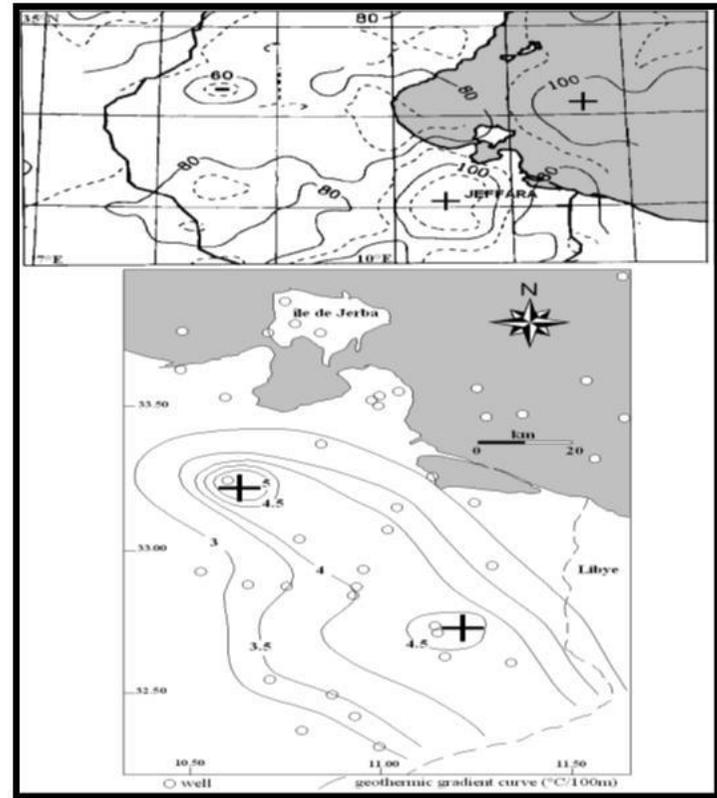
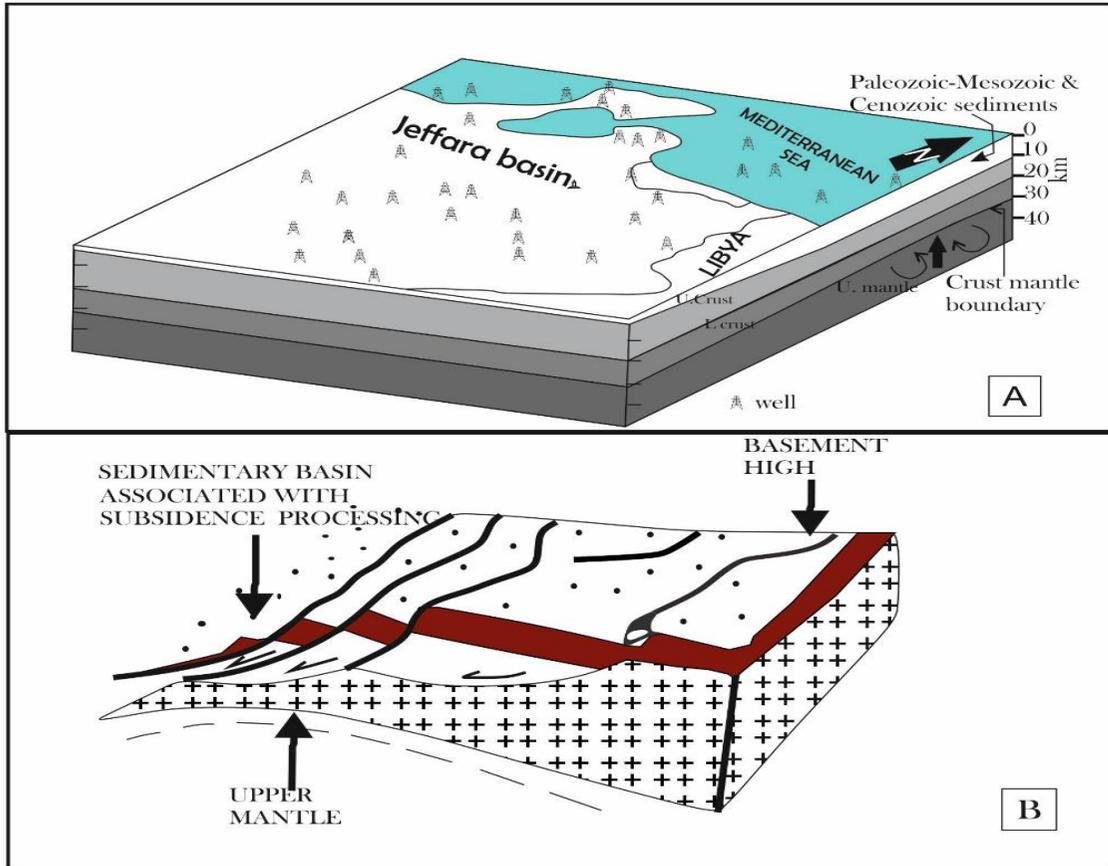


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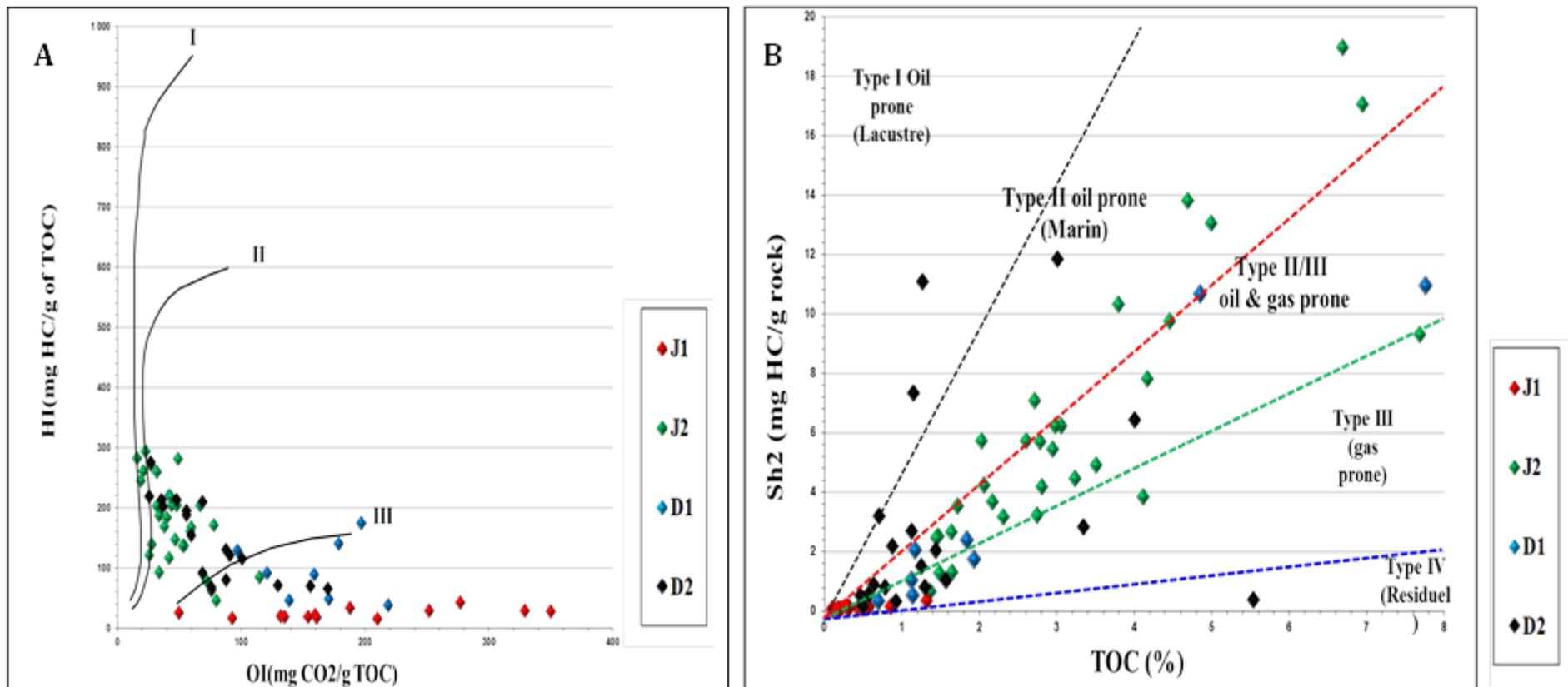


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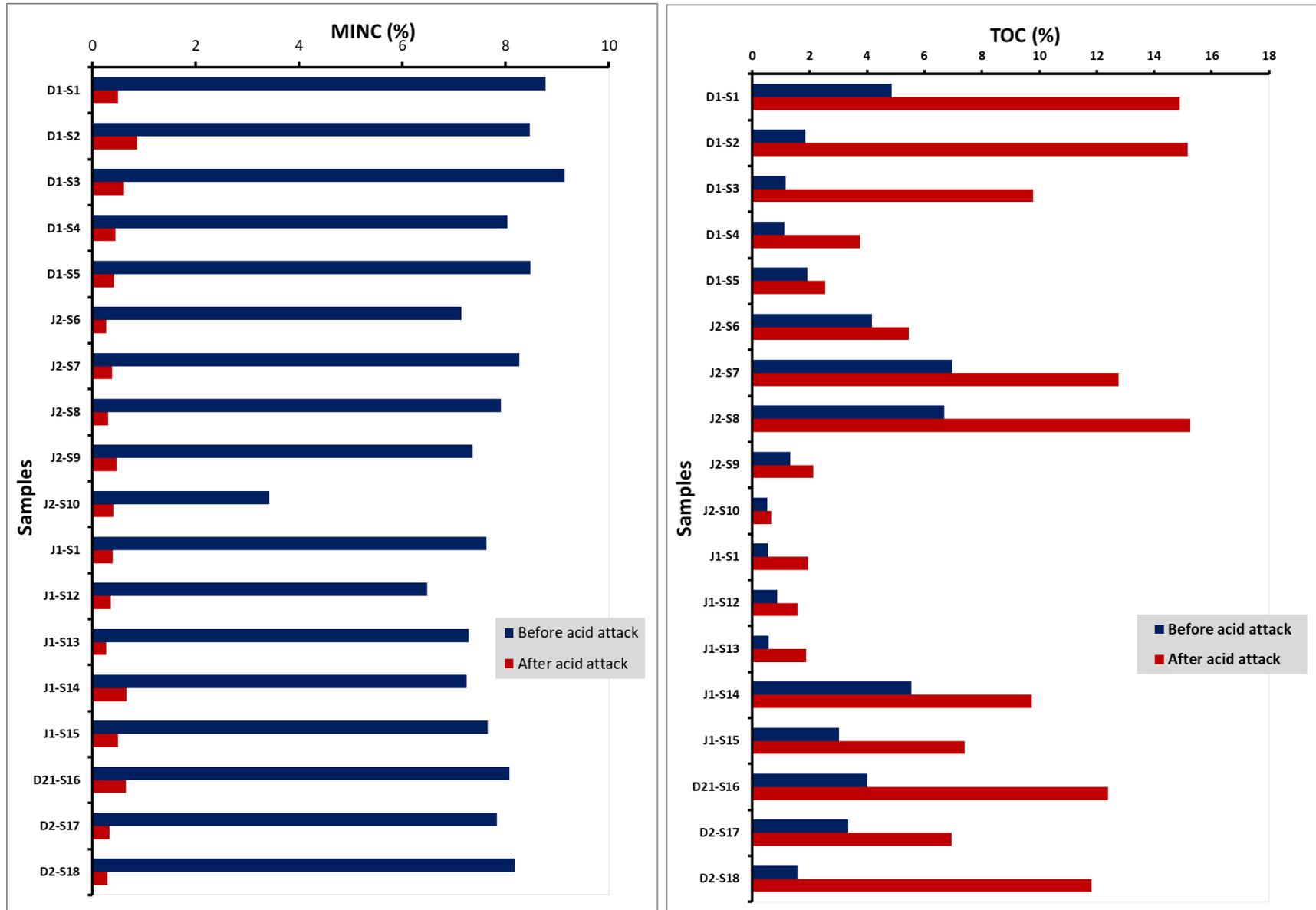


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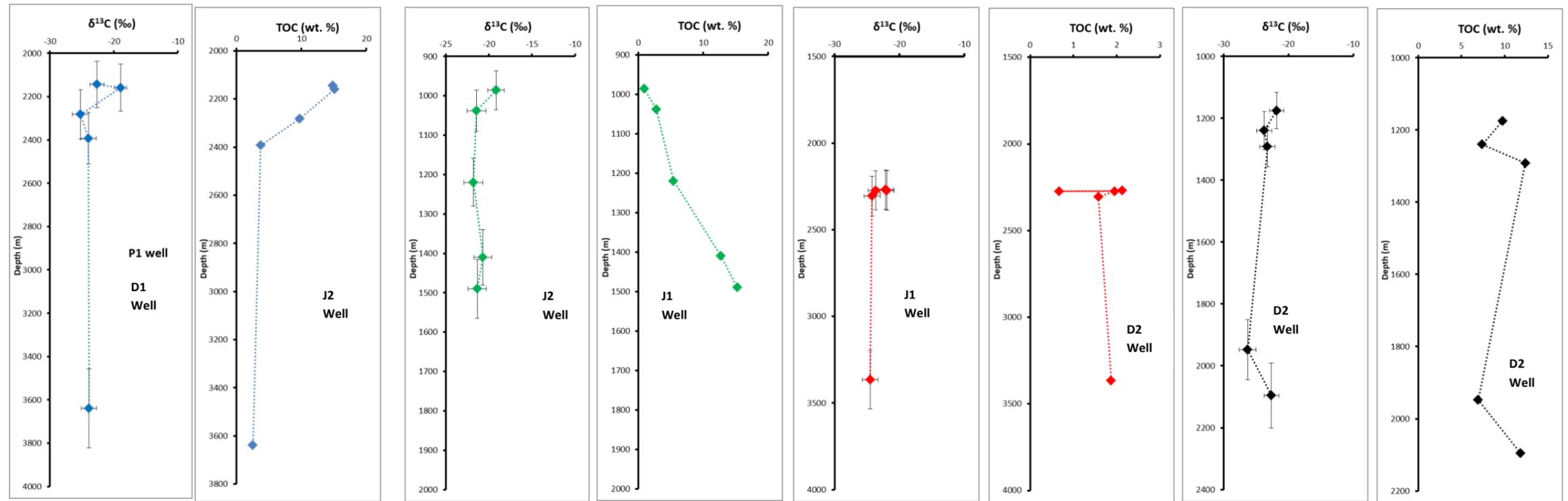


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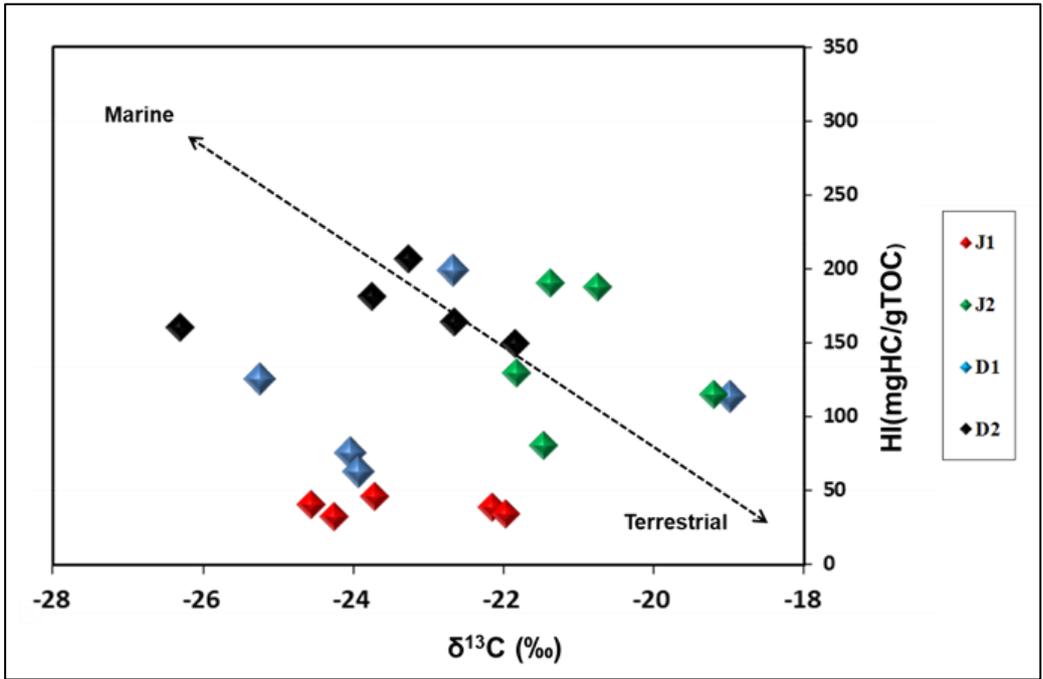


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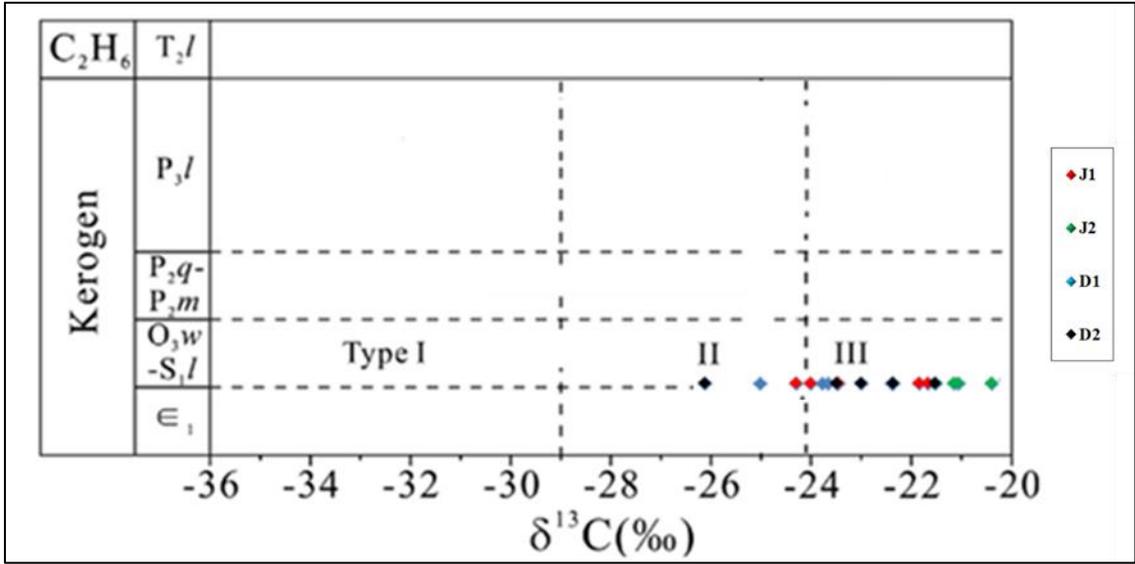


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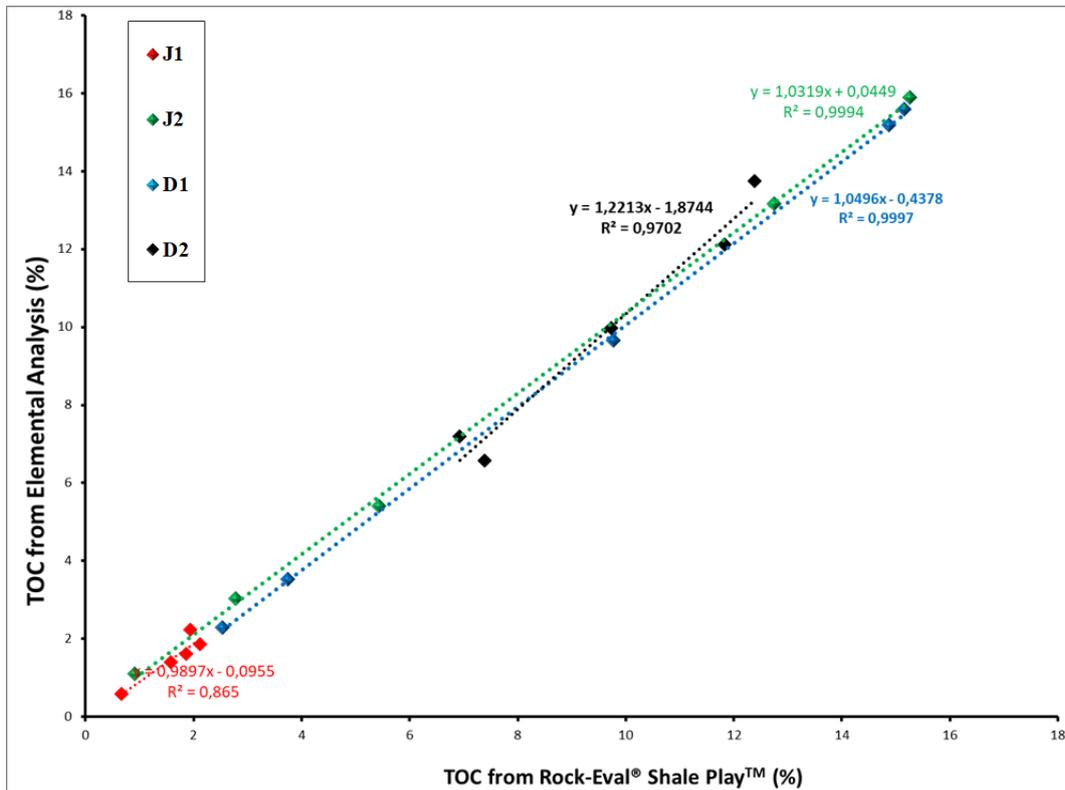


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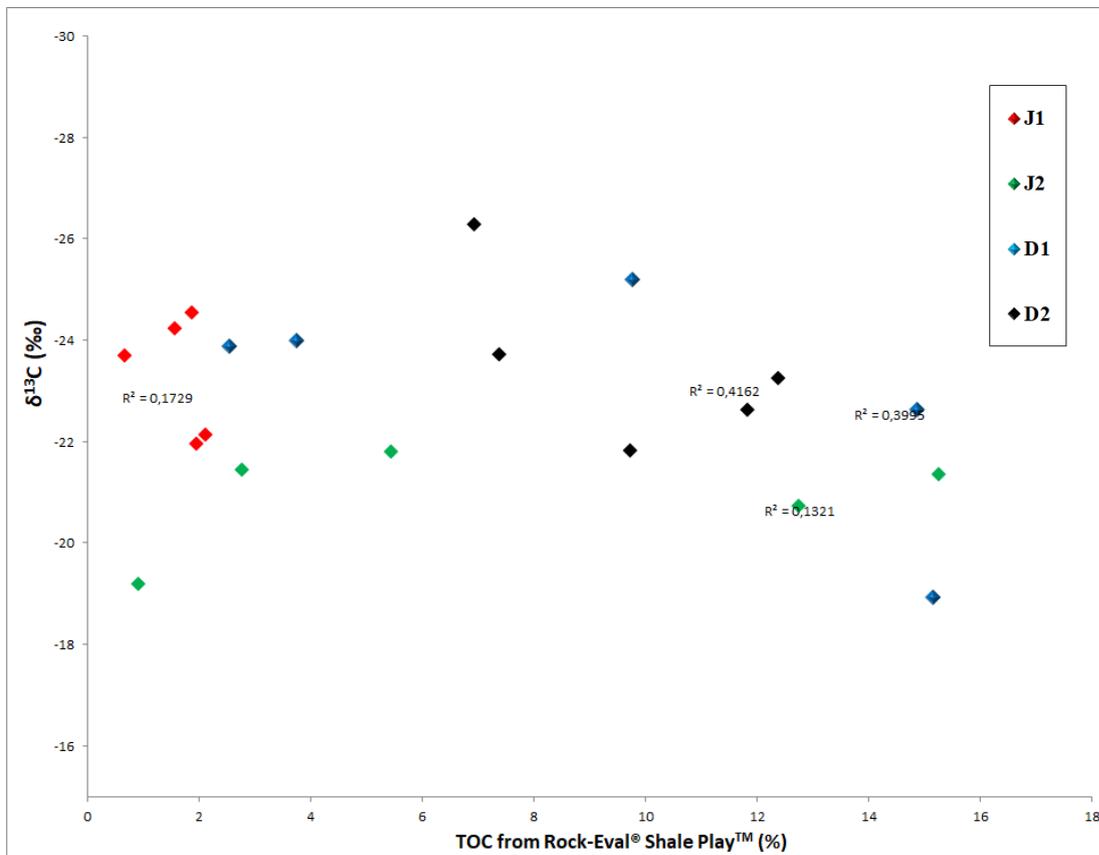


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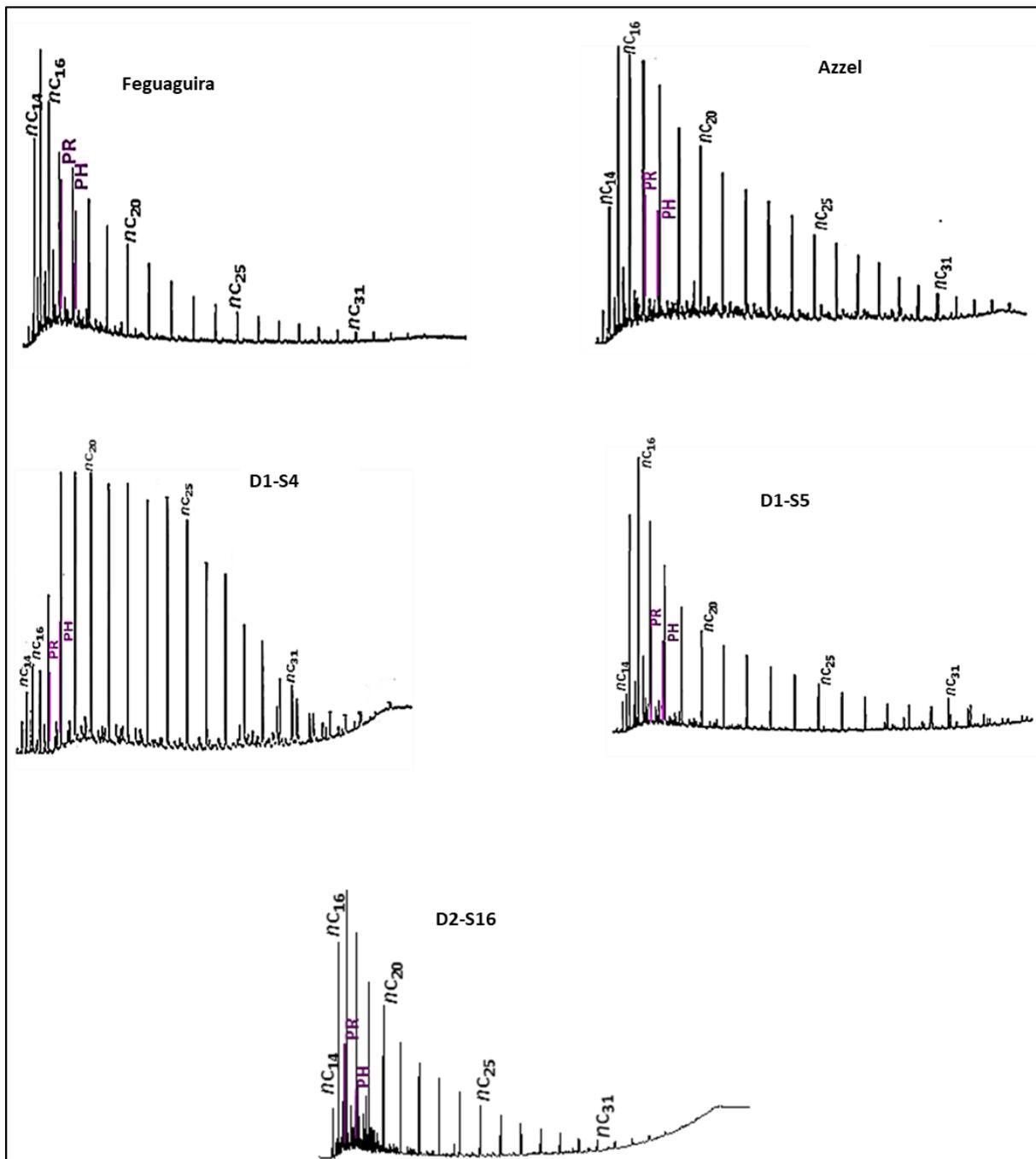


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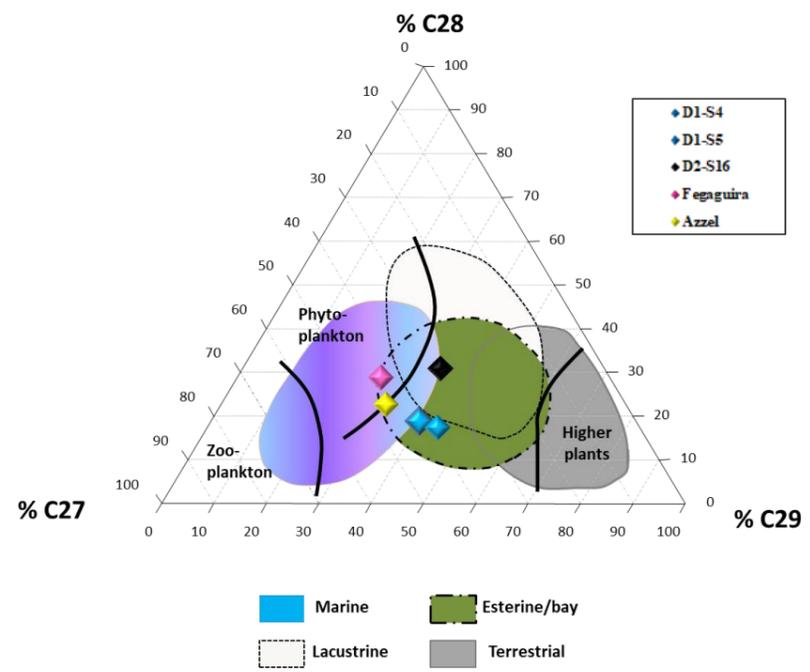


Figure 22

Figure 22

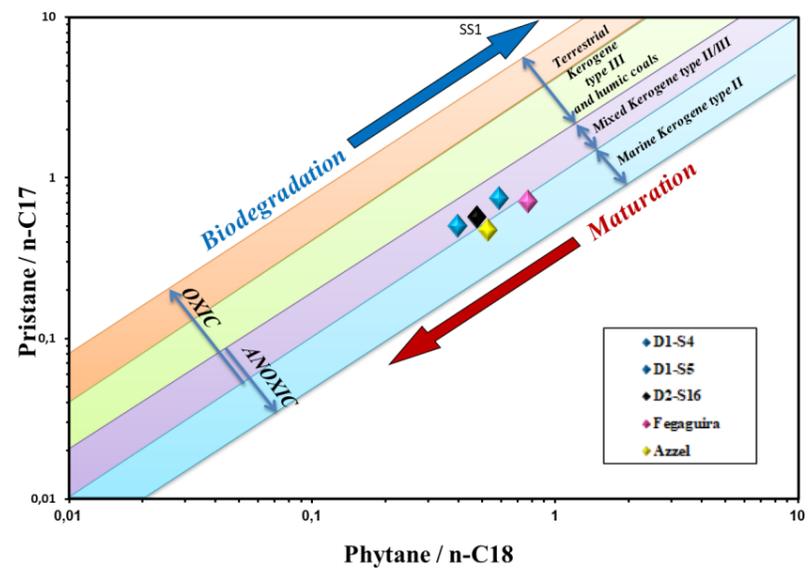


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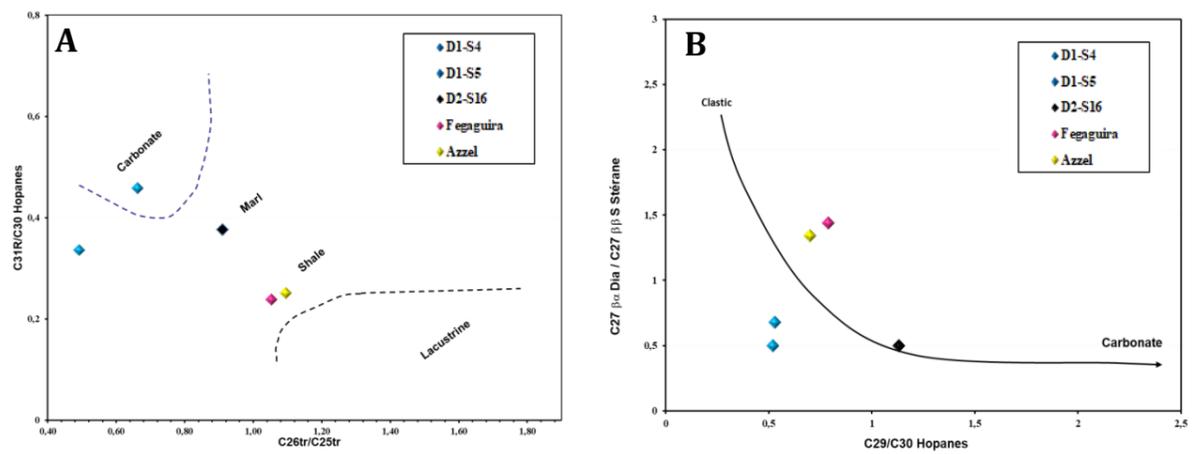


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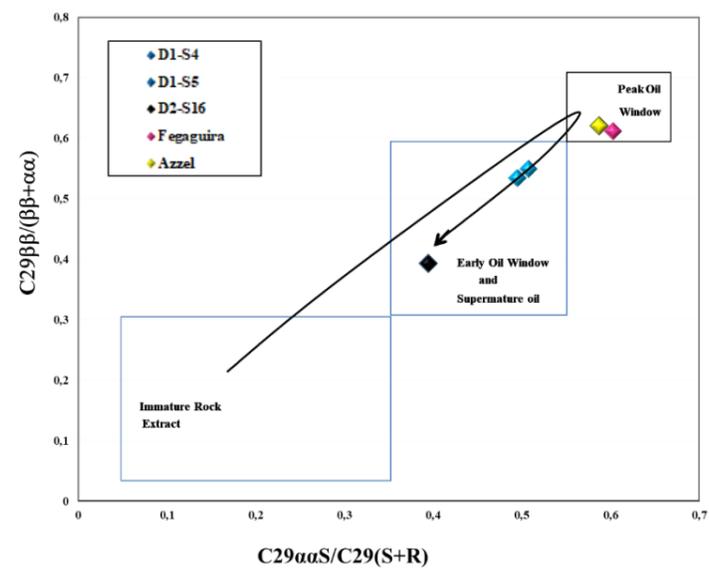


Figure 25