

## **Geochemical Characterization of the Oil in the Tertiary Reservoir in Bai-Hassan Oil Field / Northern Iraq**

*Dler H. Baban*

*College of Science -University of Sulaimani*

### **Abstract**

An oil sample from the Tertiary reservoir in the well BH-22 in Bai –Hassan Oil Field, Northern Iraq has been analyzed by the means of GC and GC/MS. The identified biomarkers and the stable carbon isotopes indicated a low salinity marine carbonate depositional environment for the precursor organic matters of the oil. CPI, 20S/ (20S+20R) C<sub>29</sub>ST,  $\beta\beta$ S/ ( $\beta\beta$ S+ $\alpha\alpha$ R) C<sub>29</sub>ST and other maturity biomarkers showed a moderately mature oil. Non effect of biodegradation has been found out from the ratios of P<sub>1</sub>, P<sub>2</sub>, and P<sub>3</sub> and from the absence of 25-Norhopane biomarker. A Star diagram has been drawn for the analyzed oil sample as a finger print using C<sub>9</sub> – C<sub>20</sub> alkanes.

### **Introduction**

The minor giant oil field of Bai-Hassan is locates near Kirkuk in North Iraq. The field has been discovered in 1953 by the Iraqi Oil Company (IPC) and having come on production in 1960. The structure of the field is about 40km long and about 3.5 km wide and consists of a longitudinal, sinusoidal, asymmetrical anticline. The southern limb of the structure is steeper(37°-65°) than the north eastern limb (22°-35°). The structure of Bai-Hassan consists of two main domes of Kithka at the southern east and Daoud at the western north. The two domes are separated by Shahal saddle which its base is about 90m deeper than Daoud dome's crest. The crest of Kithka Dome is 335m higher than Daoud dome's crest.

### **The studied oil sample and the research methods**

The studied oil sample has been taken from the well BH-22 from the Tertiary Main Limestone reservoir. The well locates at the coordinate 43° 57' 41.8" E and 35° 38' 25 8" N (fig.1).The whole oil sample analyzed by GC, while the GC/MS analysis done for the saturate compounds and that in Baseline Resolution, Inc. (Analytical Laboratories) in Houston, USA. Tens of peaks have been measured through the two analyses reflecting the

properties of the analyzed oil sample. Saturate and aromatic  $C^{13}$  isotopes and the API for the oil sample also have been measured. A number of relationships between different peaks have been plotted to obtain information about the source and depositional environment of the initial organic matters (precursors), maturity stage, biodegradation effect, in addition to draw the star diagram finger print for the analyzed oil sample. Table (1) contains the ratios and values of the majority of the used biomarkers in this study.

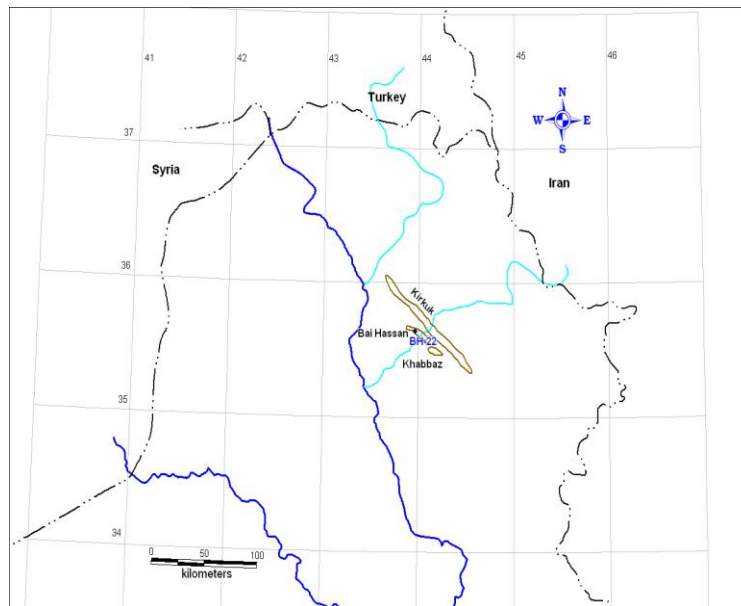


Fig.(1): Location map of the studied BH-22 well.

Table (1): The ratios and values of the majority of the used biomarkers in this study.

Pr/Ph	Pr/(Pr+Ph)	Pr/nC17	Ph/nC18	C27Dia/ (Dia+Reg.Ster) (217m/z)	Dias./Ster. (217m/z)	%C27 (217m/z)	%C28 (217m/z)	%C29 (217m/z)
0.89	0.47	0.26	0.34	0.25	0.23	40.5	23.8	35.7
C29H/C30 H (191 m/z)	C35H/C34H (191 m/z)	$\delta^{13}C$ saturate	$\delta^{13}C$ aromatic	C29 $\beta\beta S$ / ( $\beta\beta S$ + $\alpha\alpha R$ ) (217m/z)	20S/(20S+ 20R) C29ST (217m/z)	%P1	%P2	%P3
1.43	1.16	-27.1	-27.1	0.45	0.36	31.89	16.05	4.48

### **Source and paleodepositional environment of the precursor organic matters**

Brooks et al. (1969) in Philp,(2004) noted the presence of the regular isoprenoids pristane (Pr) and phytane (Ph) in crude oils and coal extracts. This led Powell and Mickidy,(1973) in Philp,(2004) to propose a mechanism for the production of relatively high concentrations of pristane in oxic type environments and high concentration of phytane in reducing type environments. Thus, the Pr/Ph ratio evolved as an indicator of the oxidity of the initial organic matter's depositional environment. The Pr/Ph ratios are very helpful in determining the paleodepositional environment and source of the precursor organic matters of the reservoir oils. It is well known that Pr/Ph ratios more than 3.0 indicates predominantly non marine source from terrestrial organic matter,(terrigenous plant input) deposited under oxic to suboxic conditions (Peters et al.,2005). An oil accumulation have Pr/Ph ratio less than 0.8 indicates saline to hypersaline conditions associated with evaporate and carbonate deposition, while marine organic matters usually have Pr/Ph less than 1.5 (Peters et al.,2005). As the Pr/Ph ratio for the analyzed oil sample is 0.89, therefore a marine influence on the type of the source organic matters can be detected. The plot of the Pr/nC17 and Ph/nC18 values for the analyzed sample on the cross plot in the figure-2 indicated a mature marine source of organic matter (mostly type II kerogen) deposited in a reduced condition with less effect of biodegradation.

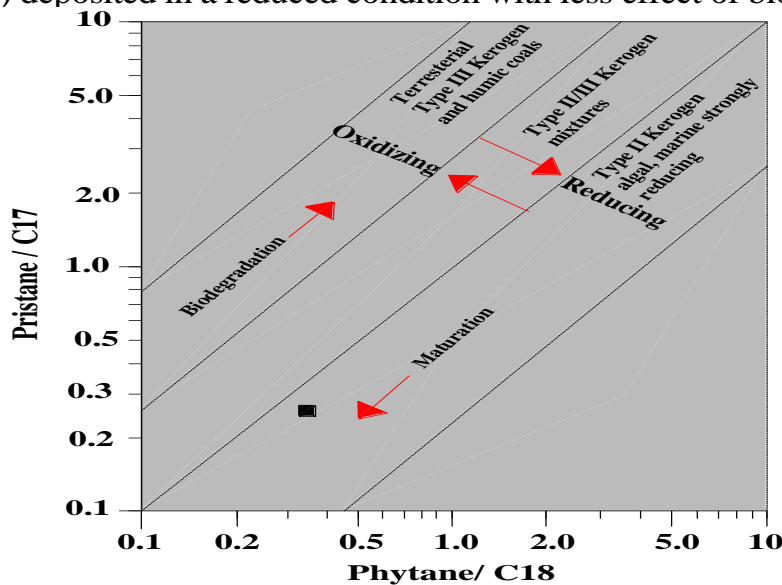


Fig (2): Pristane/C17 versus Phytane/C18 cross plot for the studied oil sample.

Hypersaline lakes and ponds often develop anoxic conditions if saline deep water is covered with water of lower density. Sedimentary rocks that were deposited under these conditions often contain high relative concentrations of gammacerane, which is a biomarker generally associated with water column stratification (Sinninghe Damste et al., 1995 in Brooks and Summons,2004). The measured gammacerane Index (gammacerane/hopane)(191m/z) for the analyzed oil sample was so little(0.13) indicating deposition in a low salinity marine environment. Because some biomarkers pointed to specific taxa, they can also act as indicators of specific habitats. Fresh water environments are often indicated by the presence of biomarkers of typical fresh water organisms such as *Botryococcus braunii*. Lacustrine conditions are often indicated by the predominance of algal steroids (Chen and Summons,2002 in Brooks & Summons,2004). Rearranged steranes (diasteranes) are relatively more abundant in clastic sediments than in carbonates (van Kaam-Peters et al.,1998 in Brooks & Summons,2004). However increase in thermal maturity is also a key factor in the conversion of biomarkers to their rearranged forms. The cross plot of Pr/Pr+Ph and C27/(C27Dias.+Reg.Ster.) (fig.3) indicates mostly anoxic carbonate environment of deposition. The relative abundance of C27,C28, and C29 also supported the marine carbonate environment of deposition for the precursor organic matters of Bai-Hassan oil as it appears from the ternary of C27,C28,and C29 in the figure (4).

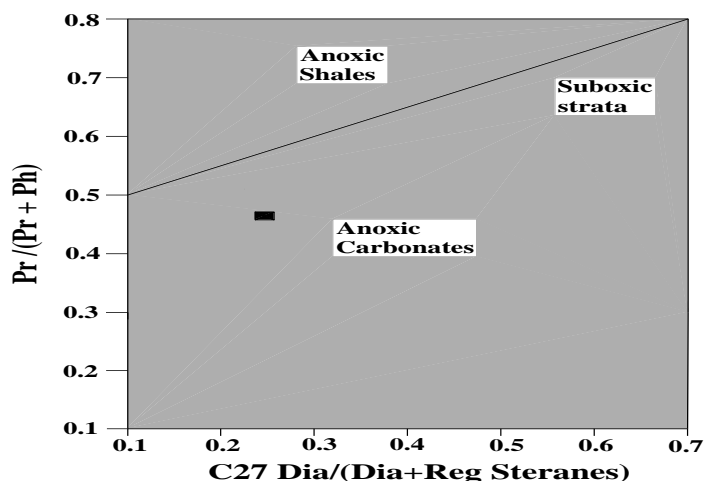


Fig (3): The cross plot of Pr/(Pr+Ph) versus C27 Dia/(Dia+Reg.Sterane), from which anoxic carbonate source of organic matters is clear for the analyzed sample

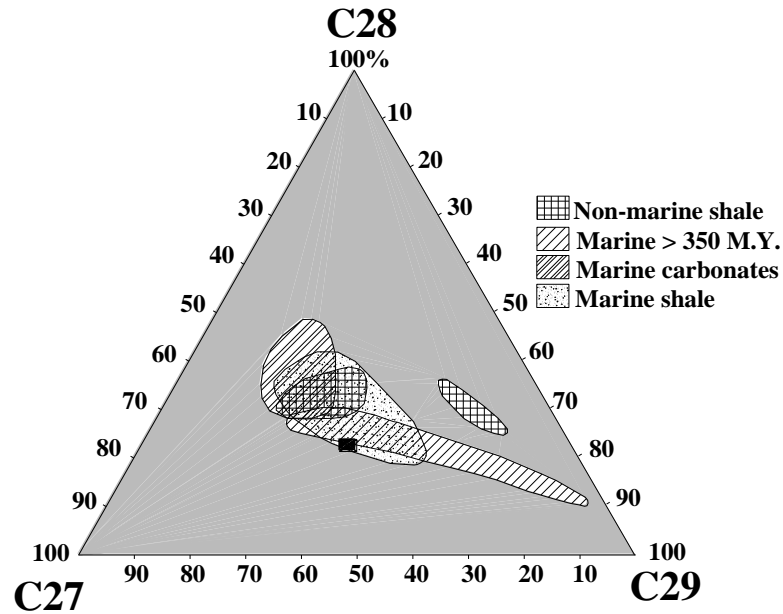


Fig (4): Ternary diagram of C27, C28, and C29 Sterane.

Anoxic, carbonate condition of deposition has also detected from the relationship between the ratios of Diasterane / Sterane with C29H / C30H (fig.5) and C29H / C30H with C35H / C34H (fig.6).

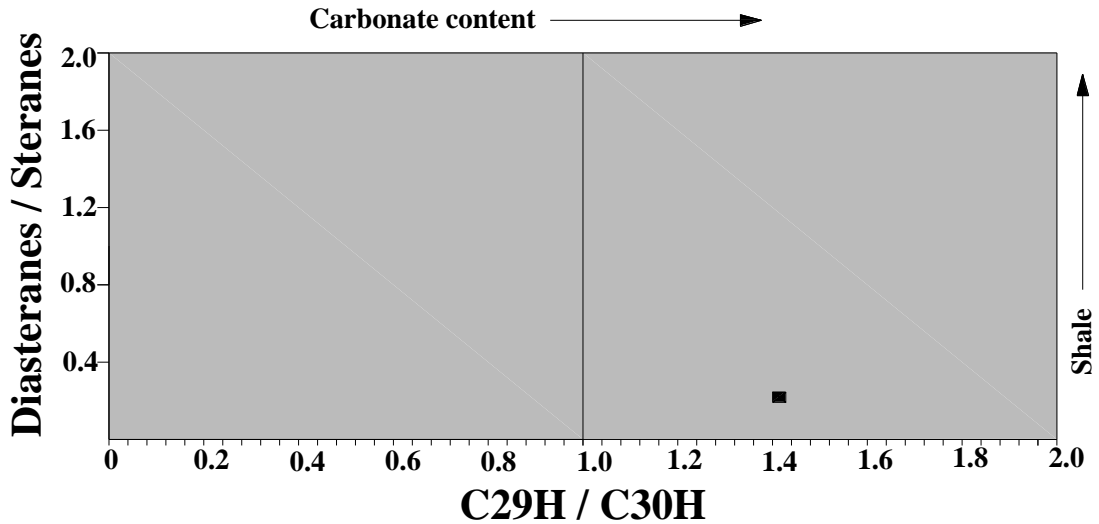


Fig (5): Diasterane/Sterane versus C29H/C30H cross plot showing the influence of Carbonate on the sources of the organic matters.

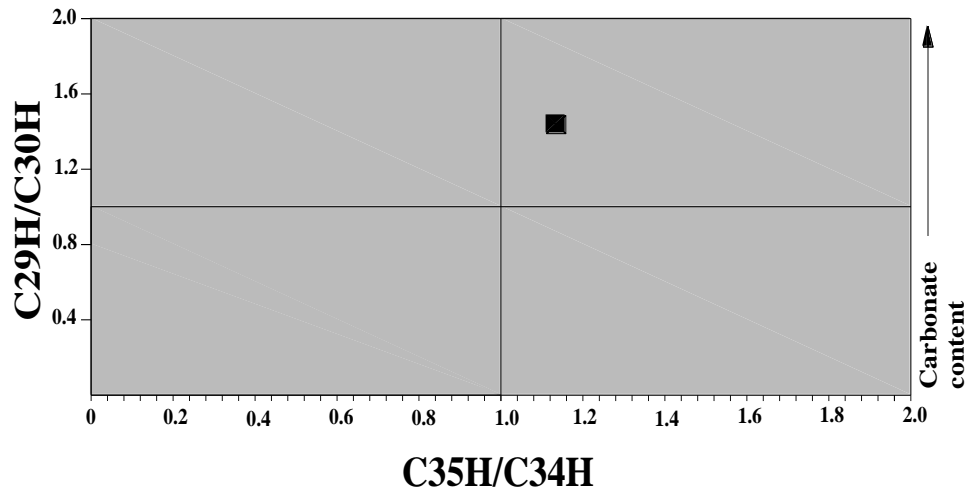
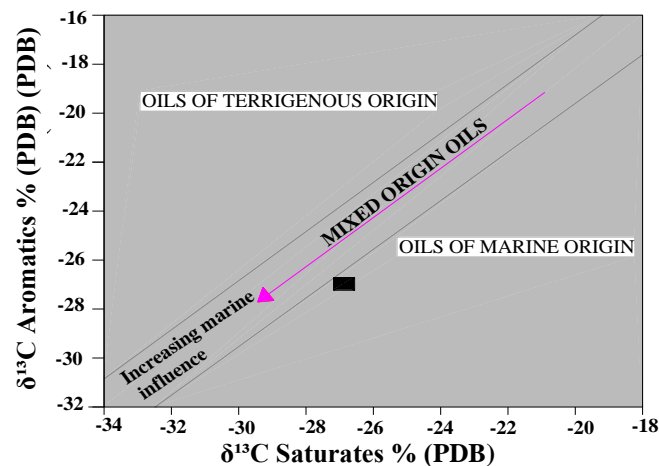


Fig (6): The cross plot of C<sub>29</sub>H / C<sub>30</sub>H versus C<sub>35</sub>H / C<sub>34</sub>H

### **Stable Carbon Isotope**

The stable carbon isotopic composition of organic matter is an important tool with which to differentiate algal and land plant source materials and marine from continental depositional environments (Meyers, 2003 in Youns and Philp 2005). Zein El-Din and Shaltout(1987)in Youns and Philp(2005) concluded that the stable carbon isotope values of crude oils are dependent mainly on the depositional environment of the source rock and the degree of thermal maturity at which the oil was expelled. The carbon isotopic signature of bitumen is relatively heavy for predominantly higher plant sourced oil (Killops et al.,1997). From the plot of  $\delta^{13}\text{C}$  saturate versus  $\delta^{13}\text{C}$  aromatic ratio (fig.7) a marine or slightly mixed origin oils has been detected.



Fig(7): Cross plot of  $\delta^{13}\text{C}$  saturate versus  $\delta^{13}\text{C}$  aromatic for the analyzed oil sample.

## **Maturation**

The gas chromatogram of the saturated hydrocarbon fractions shows a shift in the normal alkane distribution to lower carbon numbers (fig.8), reflecting relatively a moderate level of thermal maturity , The analyzed oil sample is isotopically light sample (saturate fractions is -27.1‰ and aromatic fractions is also -27.1‰PDB);this can be interpreted according to Cooper et al.,(1993) in Justwan, et al.,(2005) in terms of increased type II kerogen contribution. The Carbon Preference Index(CPI) which generally is presented by the following equation:

$$CPI = \frac{1}{2} \left[ \frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{24} + C_{26} + C_{28} + C_{30} + C_{32})} + \frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})} \right]$$

can offer valuable information on the maturation of source rocks and reservoir oil. High CPI values(above 1.5) always refer to relatively immature samples. Low CPI values, however, do not necessarily mean higher maturity; they can also mean a lack of higher n- alkanes stemming from terrestrial input. The measured CPI value for the studied oil sample was equal to 0.98 which means that it is moderately mature oil. The cross plot of the two maturity indicator biomarkers  $20S/(20S+20R)$   $C_{29}ST$  versus  $\beta\beta S/(\beta\beta S+\alpha\alpha R)C_{29}ST$ , (fig.9) shows a moderately mature oil. According to Hunt (1996) the Thermal Equilibrium Value (The end point of the reaction in the oil generation zone (Brooks et al., 1992 in Othman, 2003) for  $S/(S+R)$   $C_{29}ST$  ( $\alpha\alpha\alpha$ ) biomarker is 0.5 (approximately comparable to 0.9%Ro), and for  $\beta\beta S/(\beta\beta+\alpha\alpha R)C_{29}ST$  biomarker is 0.70 (approximately comparable to 0.9%Ro). Accordingly, the estimated maturities as comparable Vitrinite Reflectance for the studied oil have been calculated and appeared to be 0.65 %Ro using  $S/(S+R)$   $C_{29}ST$  ( $\alpha\alpha\alpha$ ) biomarker and 0.58 %Ro using  $\beta\beta S/(\beta\beta+\alpha\alpha R)C_{29}ST$  biomarker, indicating a moderate stage of maturity. The measured API gravity for the studied oil sample (23.9°) may support the moderate maturity of the oil.

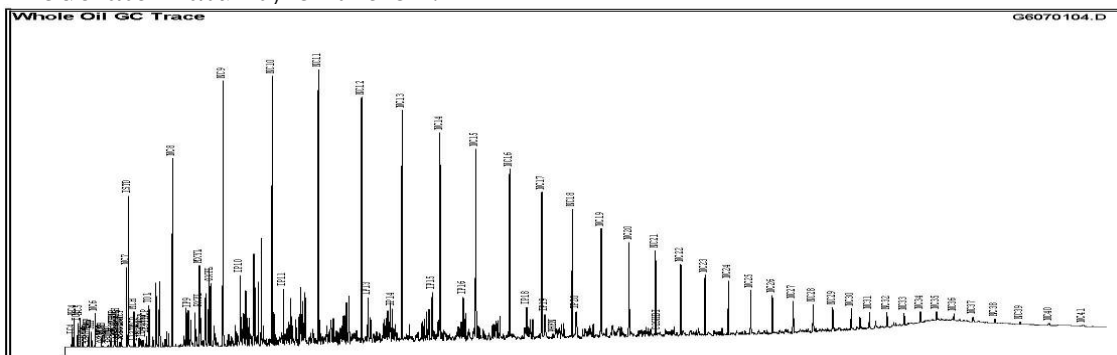


Fig.(8): The GC chromatogram for the analyzed oil sample.

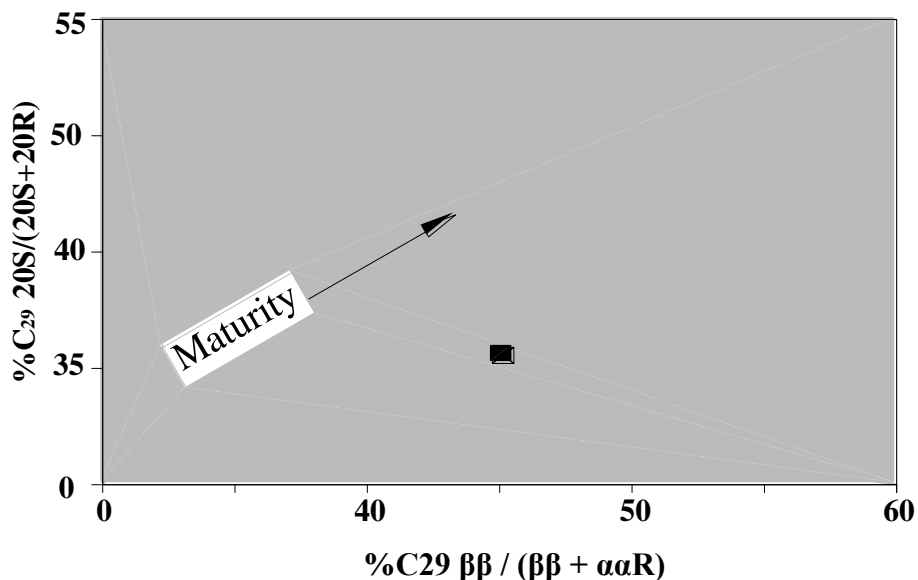


Fig.(9): 20S/(20S+20R) C<sub>29</sub>ST versus ββS/(ββS+ααR) C<sub>29</sub>ST cross plot shows a moderately mature oil.

### **Biodegradation**

The biodegradation of petroleum and other hydrocarbons in the environment is a complex process, whose quantitative and qualitative aspects depend on the type, the nature, and amount of the oil or hydrocarbon present; in addition to the seasonal environmental conditions (such as temperature, oxygen, nutrient, water activity, salinity, and acidity (pH)), and the composition of the allochthonous microbial community (Wang et al., 2006). In general, the degradation of hydrocarbons is ranked in the following order of decreasing susceptibility: normal-alkanes more than branched alkanes more than low molecular weight aromatics more than high molecular weight aromatics and cyclic alkanes (Garrett et al., 1998 in Wang et al., 2006). Mango (1994) established a P1, P2, P3 diagram based on C<sub>7</sub> data to show the effect of biodegradation on the oils or extracts. In the diagram; P1 represents the straight chain C<sub>7</sub> n-alkane; P2 represents mono-branched C<sub>7</sub>s while P3 includes the poly-branched C<sub>7</sub>s, according to Mango; this plot seems to be very sensitive measure of biodegradation. Using Mango's ternary diagram of P1, P2, and P3 for determining the effect of biodegradation on the studied oil sample (fig10), a non effect of biodegradation has been noticed. According to Peters et al., (2005), 25-norhopanes occur in oils where the hopanes were preferentially removed, but are absent where the hopanes show greater bioresistance than the steranes.



Many biodegraded oil contain abundant 25-norhopanes, and high abundance is evidence for severe biodegradation(rank more than or equal to 6) (Trendel et al., 1990 in Peters et al., 2005). As the analyzed oil sample of BH-22 contain no 25-norhopanes, therefore no sever biodegradation activity can be suggested.

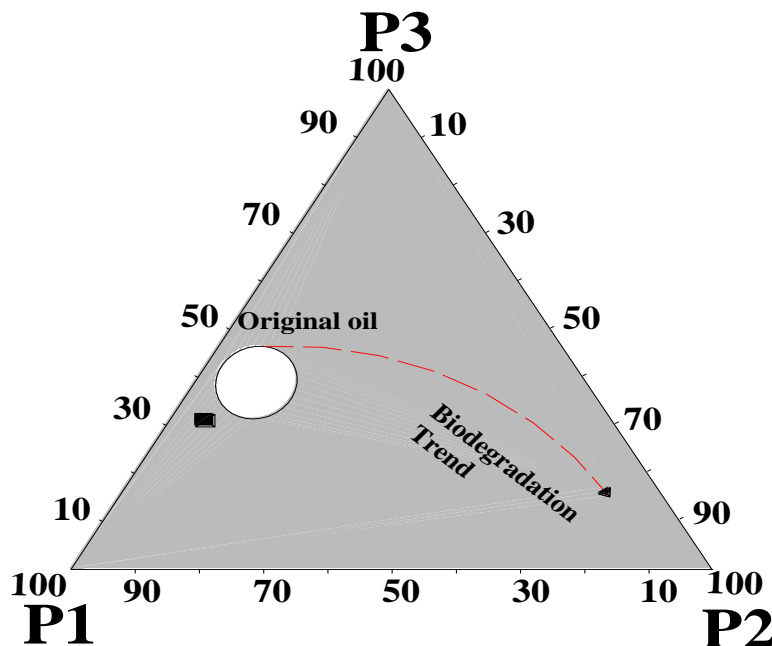


Fig.(10): P1. P2 and P3 ternary diagram shows a non biodegraded oil of BH-22.

### **Star Diagram**

Kaufman et al. (1990) developed a sensitive method, called Reservoir Oil Fingerprinting (ROF), for recognizing differences in the gas chromatograms of oils. Kaufman et al's ROF procedure consists of first numbering all small measurable peaks sequentially through n-C20. Then they visually select fewer than 25 pairs of peaks (usually 12 or so) and calculate the ratios of their peak heights or areas. Peaks are mainly selected in the C9 – C20 range where there is a good distribution of naphthenes and aromatics without too much overlap. The next step is to construct a star diagram (polygon plot) by plotting each peak ratio on a different axis of a polar plot. The figure (11) shows the star diagram or the fingerprint of the analyzed oil sample depending on it's containing of C9-C20 normal paraffin (Table 2). This diagram and the chromatograms of the GC/MS analysis (fig.12) will mark the oil of the Tertairy reservoir in Bai-Hassan oil field.

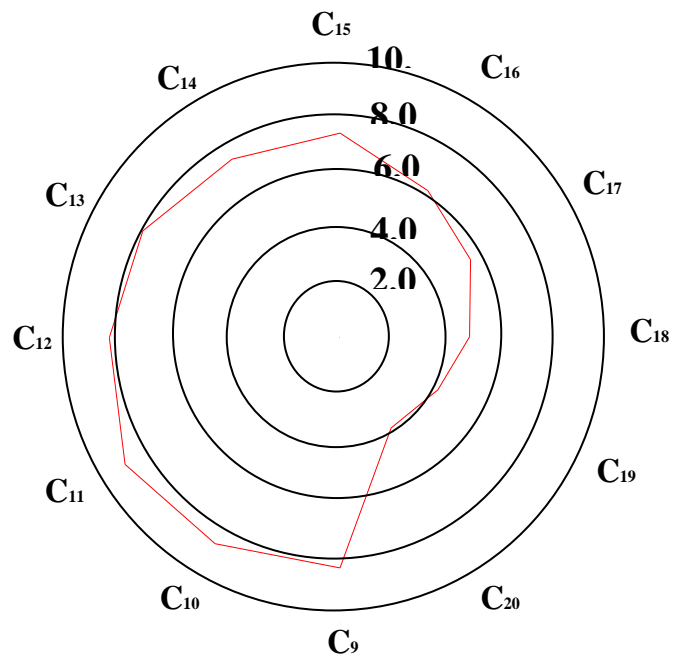
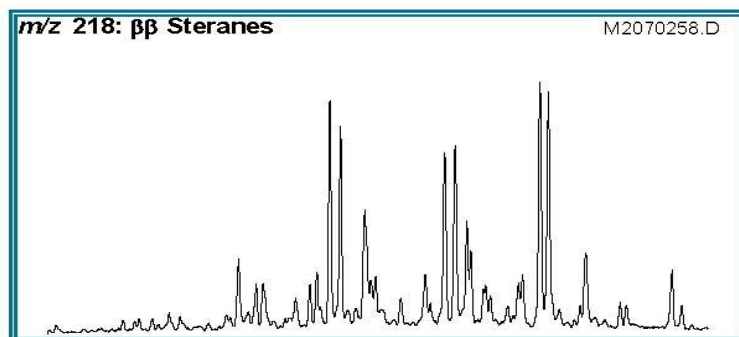
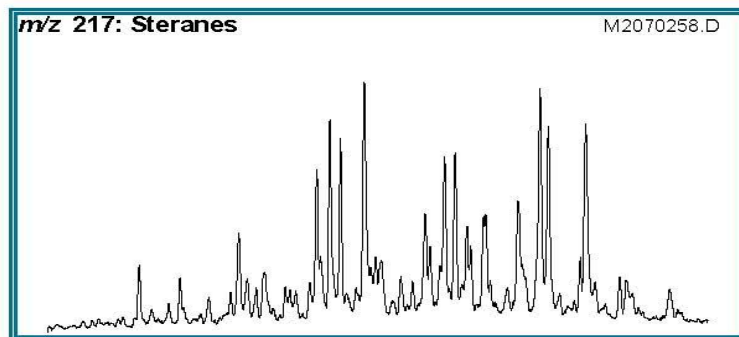
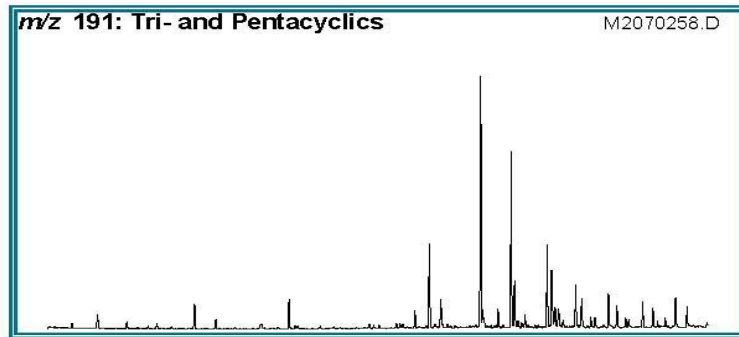


Figure (11): Star diagram for the analyzed oil sample using C9 – C20 peak values.

**Table (2): The ratios of the normal paraffins from C9 to C20 used in drawing the star Diagram for the analyzed oil sample.**

C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
8.12	8.63	9.03	8.36	8.07	7.34	7.19	6.08	5.44	4.75	4.11	3.79



## Conclusions

- The precursor well are from environment
- The study on sample is necessary, right and appears to be mostly of type II kerogen origin.
- The oil is moderately mature.
- No biodegradation activities affected the analyzed oil sample.

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**التمثيل الجيوكيميائي للنفط الموجود في مستودع العصر الثلاثي  
في حقل باى حسن النفطي/ شمال العراق**

**دلير حسين بابان  
قسم الجيولوجي/ جامعة السليمانية**

**المستخلص**

أجريت تحاليل كروماتوكراف الغاز (GC) و كروماتوكراف الغاز/طيف الكتلي

(GC/MS) لنموذج من النفط الموجود في مستودع العصر الثلاثي في حقل باي حسن النفطي في شمال العراق. أظهرت قيم الدالات الحياتية و نسب نظائر الكربون المستقر بأن المواد العضوية الأولية للنموذج النفطي المدروس قد ترسبت في بيئة بحرية كاربوناتية قليلة الملوحة. أما الدالات الحياتية الخاصة بتحديد النضوج الحراري و المتمثلة بعامل التفاضل الكربوني (CPI) و  $\beta/\beta + \alpha$  C29ST و 20S/ (20S+20R) C29ST فقد أكدت بأن النموذج النفطي المحلل هو ناضج حرارياً بصورة معتدلة. أما نسب P1، P2 و P3 لبعضها البعض و غياب C25-Norhopane ضمن نتائج التحليل فقد دلت على عدم تأثر النفط المحلل بالتكسر الحياتي أو النشاط البكتيري. من ناحية أخرى، فقد تم رسم الشكل النجمي كبصمة إبهام خاصة بـ النفط العصر الثلاثي في حقل باي حسن و ذلك اعتماداً على نسب الكربونات من (C9) إلى (C20).