Occurrence and Geochemical Significance of Carbazoles and Xanthones in Crude Oil from the Western Desert, Egypt

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Abstract. This paper describes an approach that involves the evaluation of the occurrence and distributions of nitrogen- and oxygen-containing aromatic compounds in Egyptian crude oils and source rocks. Carbazoles and xanthones represent nitrogen- and oxygen-containing aromatic compounds, respectively.

Alkylcarbazoles and benzocarbazoles were quantitatively studied in crude oils taken from the Abu Gharadig and Shushan basins in north Western Desert of Egypt in order to investigate their occurrence, concentrations and distributions. The abundances of carbazole, methylcarbazoles and dimethylcarbazoles in the marine Abu Gharadig oils are much higher than that of the terrestrial Shushan oils. The results presented here indicate that thermal maturation can be ruled out as a major factor in controlling the changes in the carbazole ratios in the crude oils. Most likely, source characteristics of the studied samples play a significant role in controlling the distribution of carbazole compounds in reservoired oils. The alkylcarbazoles 1MC/1MC+1EC, 3MC/4MC and 18DMC/18DMC+1EC when correlated with specific biomarker signatures provide background information discriminating between two main types of depositional setting: 1) Terrestrial dominated source deposited in oxidizing conditions for the Shushan oils and, 2) marine shale dominated sourced oils deposited in suboxic environments for the Abu Gharadig samples. Similarly, benzocarbazole distributions were found to be independent of maturity, but influenced by organic facies and depositional environments. Therefore, in this study, alkylcarbazole and benzocarbazoles compounds are well suited for the differentiation of Abu Gharadig and Shushan crude oils with respect to origin and variations of facies and depositional environment.

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Using various kinds of Egyptian crude oils derived from marine carbonates, marine clastics and terrestrial sources, the current study indicates that xanthones and its alkylated homologues are abundant only in source extracts and crude oils that have terrestrial organic matter input. This is the second description of xanthones in crude oils, and the first in Egyptian petroleum systems. Overall, based on the data of this study, xanthones signatures show great promise as terrestrial source markers in a given petroleum system.

Introduction

Many molecular markers based on aliphatic and aromatic hydrocarbons are proven to be well suited for the characterization of oil families and assignment of source facies, thermal maturity level, degree of preservation, and migration. On the other hand, heterocompounds (nitrogen, oxygen, and sulphur, NSO compounds) that make up a small portion of most crude oils (Tissot and Welte, 1984) have significant implications in petroleum exploration, because their greater structural diversity results in greater variations of their physico-chemical properties. Consequently, heterocompounds can provide useful geochemical clues that trace petroleum molecules back to their biological precursors.

Organic nitrogen compounds occur in crude oils in small amounts, with an average content of 0.1% by weight (Baxby *et al*., 1994). Most nitrogen compounds in crude oil are in heterocyclic aromatic structures and are concentrated in the high molecular weight and high boiling point fractions (Ball *et al*., 1951; Tissot and Welte, 1984; and Baxby *et al*., 1994). There are two classes of nitrogen compounds; basic (pyridinic-type), and non-basic (pyrrolic-type structures), and in most cases, non-basic predominates over basic nitrogen (Richter *et al*., 1952; Dorbon *et al*., 1984; Wilhelms *et al*., 1992; and Baxby *et al*., 1994). The pyrrolic nitrogen compounds, particularly the carbazole derivatives, exist in source rocks and crude oils, and have been reported to show great promise as potent geochemical parameters that might play a significant role in exploration and production for crude oil.

The concentrations and the ratio of two benzocarbazole isomers, benzo[a] and benzo[c]carbazole, may be used as an indicator of oil secondary migration distance, with the benzo[a] isomer being removed preferentially (by sorption on to mineral and organic surfaces) during migration (Larter *et al*., 1996). Such approaches have been confirmed by

laboratory and field studies (Celgg *et al*., 1998a-b; Harrison *et al*., 1997; Li *et al*., 1997; Wilhelms *et al*., 1997; Zhu *et al*., 1997; Horsfield *et al*., 1998; Li *et al*., 1999; Larter *et al*., 2000; Terken and Frewin, 2000).

Based on data from a series of marine carbonate source rocks from a natural maturity sequence [vitrinite reflectance (R_o) 0.45-1.30%] from the Duvernay Formation of the western Canada Basin, Li *et al.* (1997) noted that the concentrations of carbazoles in the extracts increased with maturation, and a similar trend was observed for benzocarbazoles and the ratio of benzo[a]carbazole / (benzo[a]carbazole + benzo[c]carbazole) (a/a+c for simplicity). Horsfield *et al*. (1998) presented the first report linking carbazole distributions to crude oil maturity, and subsequent discussion has been extended by Clegg *et al*. (1998a), who provided convincing evidence of source maturity control on alkylcarbazole and benzocarbazole concentrations and distributions in petroleums from the Sonda de Campeche area, Gulf of Mexico.

Despite the common occurrence of organic nitrogen compounds in crude oil, very little work was observed for the influence of source characteristics on the pyrrolic compounds. In a study by Li *et al*. (1995) several crude oils from marine, freshwater and brackish-brine lacustrine to swampy lake environments revealed no characteristic pyrrolic nitrogen compound distributions that could be assigned to any given depositional conditions. In crude oils of the Rainbow Shekilie-Zamma subbasins of NW Alberta (Canada), the saturated and aromatic hydrocarbon distributions responded to variations in thermal maturity and depositional conditions, whereas pyrrolic nitrogen compounds did not respond to the same extent (Li *et al*., 1999). Similarly, in the Permian derived Phosphoria oils of Wyoming, molecular parameters based on the saturated hydrocarbons (*e.g.* Pr / Ph and *Ts* / (*Ts* + *Tm*)) responded to source organic input, depositional environment and thermal maturity, whereas the pyrrolic nitrogen compounds did not appear to respond to these geological factors (Silliman *et al*., 2002). On the other hand, there are situations where it is clear that nitrogen compounds respond to changes in depositional environment. For example, Clegg *et al*. (1997) compared the pyrrolic nitrogen compound distributions in bitumens from two carbonates of the Keg River Formation (Elk Point Group, Middle Devonian, western Canada) representing two different source facies. In crude oils from the Gulf of Suez, a positive correlation between the benzocarbazole [a] / ([a] + [c]) ratio and Pr/Ph and *Ts* / (*Ts* + *Tm*)

parameters suggested that facies and depositional environment of the relevant source rocks influenced the benzocarbazole distributions in this setting (Bakr and Wilkes, 2002).

The first detailed investigation of oxygen compounds in crude oil was described by Snyder *et al*. (1968). Xanthones are aromatic oxygen-containing compounds synthesized by fungi, lichens, lower vascular plants, and higher plants (Berti and Bottari, 1968; Culberson, 1969; Chexal *et al*., 1975; Devon and Scott, 1975; and Peres *et al*., 2000). Highly substituted xanthones (with hydroxy-, methoxy- and alkylgroups) occur in many different terrestrial plants (Tomasek and Crawford, 1986; and Peres and Nagem, 1997) especially those that prefer tropical or subtropical climates. Many shrubs and herbs, which occur widely in temperate regions of the world, contain xanthones (Wu *et al*., 1998). Only one recognition of xanthones in crude oil was reported by Oldenburg *et al*. (2002).

Considering these observations, it appears that our knowledge of the oxygen heterocompounds (xanthones) is only at the very beginning, while the nitrogen heterocompounds (carbazoles and benzocarbazoles) and their behavior in petroleum systems need to be justified for crude oils from various petroleum systems. As far as Egyptian petroleum systems are concerned, and to the best of the author knowledge, carbazoles and benzocarbazoles (nitrogen heterocompounds) have been only reported in the Gulf of Suez crude oils (Bakr and Wilkes, 2002), while xanthones (oxygen heterocompounds) have not yet been reported as constituents of any Egyptian crude oils.

With this background, the present paper deals with the characterization, distributions and consequence geochemical significance of nitrogen (carbazoles and benzocarbazoles) and oxygen (xanthones) heterocompounds in crude oils produced from fields located in the north Western Desert of Egypt. This is the first recognition and description of xanthones compounds in Egyptian crude oils, and is considered as the second reports of these compounds in fossil organic mater. Further, this communication represents the second report describing the occurrence and distributions of carbazoles and benzocarbazoles compounds in Egyptian crude oils. The behavior of nitrogen compounds are then compared with the biomarker parameters in order to ascertain whether nitrogen compounds also inherit compositional variations that could be

attributed to source rock characteristics. They may therefore be considered ideal for the investigation of how organofacies and depositional environment affect the distribution of heterocompounds in crude oils.

Materials and Methods

Samples

Eight crude oil samples from north Western Desert have been utilized in this study. These samples include four oils from Abu Gharadig Basin and four oils from Shushan Basin (Fig. 1 and Table 1). Additionally, other crude oils from the Gulf of Suez and source rock extracts from Khatatba Formation were also analyzed for the characterization of xanthones compounds. Description of these latter samples is not included in this article.
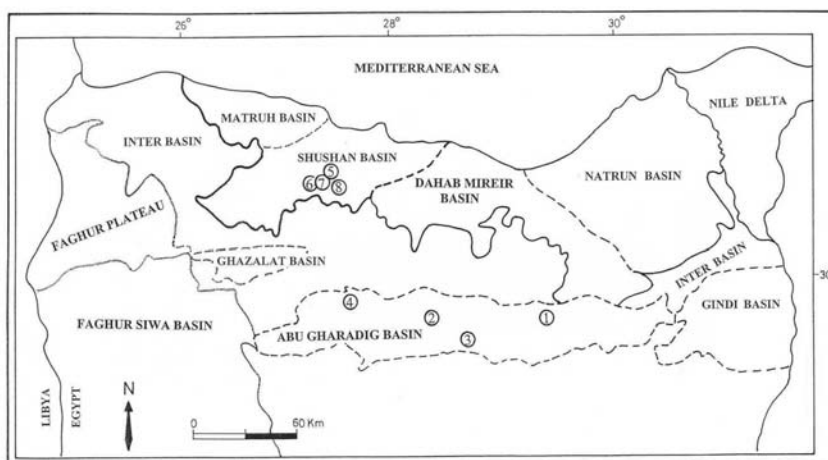

Fig. 1. Map showing the location of the studied oil samples. Numbers of samples refer to Table 1 (after EGPC, 1992 and Petroconsultant, 1997).

Analysis of Pyrrolic Nitrogen and Xanthones Compounds

Crude oil samples were separated into aliphatic hydrocarbons, aromatic hydrocarbons and NSO compounds by medium pressure liquid chromatography according to the method of Radke *et al*. (1980). The pyrrolic nitrogen compounds, as well as the xanthones compounds which are constituents of the NSO compound fraction, were then analyzed by gas chromatography-mass spectrometry using a Finnigan MAT 95S mass

spectrometer coupled with Hewlett Packard 5890B gas chromatograph. The gas chromatograph is equipped with a temperature-programmable injection system (Gerstel KAS 3) and a BPX5 fused silica capillary column (SGE) of 50 m length, 0.22 mm i.d. and 0.25 μm film thicknesses. Helium was used as the carrier gas. The oven temperature was programmed from 60 to 340°C (final hold time 8 min) at 3°C/min. The mass spectrometer was operated in the electron impact (EI) mode at an electron energy of 70 eV and a source temperature of 260°C.

Table 1. Selected geochemical ratios in the investigated oil samples.

Sample no.	Oil well	Wax[a]	Pr/Ph[b]	DBT/PH[c]	C_{35}/C_{34}[d]	C_{39}/C_{27}[e]	C_{29} Dia[f]	% 20S[g]	C_{29}/C_{30}[h]	Ts/Ts+Tm[i]	α/α+c[j]
1	WD-33	0.98	1.50	0.54	0.63	1.32	0.48	0.49	0.38	0.71	0.61
2	BED-4	0.41	1.48	0.65	0.64	1.29	0.29	0.49	0.35	0.53	0.60
3	GPT-SW	0.69	1.30	0.74	0.66	1.48	0.40	0.43	0.41	0.56	0.59
4	Ram1	0.75	1.40	0.70	0.82	1.54	0.18	0.39	0.43	0.47	0.61
5	A-11	1.54	3.91	0.19	0.40	2.96	1.47	0.31	0.10	0.33	0.44
6	M. NE-15	1.51	3.61	0.16	0.37	2.78	1.79	0.35	0.09	0.31	0.41
7	M-16	1.55	3.51	0.17	0.42	3.30	1.50	0.33	0.09	0.31	0.49
8	M-25	1.52	3.52	0.12	0.33	3.39	1.40	0.38	0.17	0.37	0.39

Wax.[a]: $\Sigma(n\text{-}C_{21}\text{-}n\text{-}C_{31})/\Sigma\ (n\text{-}C_{15}\text{-}n\text{-}C_{20})$

Pr/Ph[b] Pristane/Phytane

DBT/PH[c] : Dibenzothiophene/Phenanthrene

C_{35}/C_{34}[d] : C_{35}/C_{34} hopanes (m/z 191)

C_{29}/C_{27}[e] : C_{29} ααα 20R sterane/C_{27} ααα 20R sterane (m/z 217)

C_{29} Dia[f] : C_{29} diasterane/sterane (m/z 217)

% 20S[g]: C_{29} ααα sterane 20S/(20S + 20R) (m/z 217)

C_{29}/C_{30}[h]: C_{29} ααα sterane-R/ C_{30} hope (m/z 217, m/191)

Ts/(Ts+Tm)[i] : 18α(H)-22,29,30-trisnorneohopane / (18α(H)-22,29,30-trisnorneohopane + 17α(H)-22,29,30-trisnorhopane) (m/z 217)

α/α+*c*[j] : benzo[α]carbazole / (benzo[α]carbazole + benzo[*c*]carbazole)

Full scan mass spectra were recorded over the mass range of 150 to 300 Da at a scan rate of 1 s per decade, an inter scan time of 0.2 s and a scan cycle time of 0.5 s. Identification of individual carbazoles and benzocarbazoles was based on comparison with authentic standards and literature data (Bowler *et al.,* 1997). Quantification was performed using *N*-phenylcarbazole as an internal standard taking into account all significant fragment ions of the target compounds.

Results and Discussions

General Characteristics

A complete characterization of bulk properties (API and sulphur contents), *n*-alkanes, pristane, phytane, biomarkers steranes and hopanes, and aromatics (phenanthrenes, dibenzothiophenes) of the Abu Gharadig and Shushan crude oil samples have been reported in details elsewhere (Bakr, this issue). In this study, the molecular parameters used in relation to the variability of the pyrrolic nitrogen compounds, will be briefly discussed. As given in Table 1, typically, nonwaxy characters, enhanced C_{35} homohopanes, low diasterane content, high sterane/hopane values, low Pr/Ph, in combination with relatively high values of DBT/PHEN and *Ts*/*Ts+Tm* were observed for the Abu Gharadig crude oil samples. These geochemical parameters indicate that Abu Gharadig oils were sourced from marine shale of Type II deposited in suboxic environment. Compared with the Abu Gharadig, the Shushan oil samples are waxy in nature and showed some significantly different characteristics. These differences are represented by lower C_{35} homohopanes, lower sterane/hopane values, and a strong dominance of C_{29} over C_{27} steranes, higher Pr/Ph, and lower DBT/PHEN (Table 1). All these features are considered typical of oil generated from clay-rich terrigenous source rocks that received greater higher plant input, and are likely generated from type III-II sources deposited under oxic conditions.

Occurrence and Distribution of Carbazoles

Concentrations of Carbazoles (C_0-C_2)

Carbazole is a tricyclic aromatic nitrogen compound which may be alkylated and annelated to form two main series of derivatives, namely alkylated carbazoles and alkylated benzo- and dibenzocarbazoles. The concentrations of carbazole, individual alkyl- carbazoles and the benzo[a]- and benzo [c] carbazoles in the studied oil samples are given in Table 2. The codes used for the assignment of carbazoles and benzocarbazoles are presented in Table 3.

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Table 2. Concentrations of carbazoles and benzocarbazoles for the investigated oil samples (µg/g oil) (see Table 3 for description of codes).

Sample no.	Oil well	C	1	3	2	4	18	1E	13	16	17	14+4E	15+3E	26	27	12	24	25	BaC	BcC
1	WD-33	2.00	4.61	1.93	2.22	2.98	2.54	0.41	1.59	1.73	2.45	1.92	2.87	0.94	0.45	0.27	0.94	0.86	1.05	0.67
2	BED-4	0.82	2.39	1.14	1.18	1.17	1.82	0.16	1.35	1.47	1.92	1.40	1.75	0.78	0.38	0.25	0.63	0.59	0.36	0.24
3	GPT-SW	0.76	2.70	1.04	1.29	1.49	2.92	0.25	1.83	1.95	2.95	2.06	2.53	1.07	0.45	0.38	0.94	0.86	0.49	0.34
4	Raml	0.41	0.74	0.26	0.49	0.52	2.44	0.05	1.16	0.42	0.58	0.41	0.52	0.24	0.40	0.08	0.20	0.19	0.08	0.05
5	A-11	0.15	0.28	0.15	0.16	0.59	0.24	0.07	0.21	0.16	0.24	0.23	0.25	0.13	0.02	0.02	0.10	0.07	0.15	0.18
6	M.NE-15	0.13	0.40	0.19	0.20	0.86	0.47	0.21	0.43	0.39	0.47	0.46	0.45	0.23	0.09	0.09	0.19	0.17	0.17	0.24
7	M-16	0.16	0.49	0.20	0.24	1.01	0.35	0.22	0.51	0.35	0.57	0.41	0.52	0.23	0.07	0.07	0.17	0.19	0.16	0.16
8	M-25	0.14	0.40	0.15	0.23	0.79	0.40	0.28	0.59	0.39	0.56	0.56	0.56	0.26	0.11	0.16	0.23	0.15	0.13	0.39

**Table 3. The codes used for the assignment of carbazoles and
benzocarbazoles in Table 2.**

Code	Compound
C	carbazole
1	1-methylcarbazole
3	3-methylcarbazole
2	2-methylcarbazole
4	4-methylcarbazole
18	1,8-dimethylcarbazole
1E	1-ethylcarbazole
13	1,3-dimethlycarbazole
16	1,6-dimethylcarbazole
17	1,7-dimethylcarbazole
14	1,4-dimethylcarbazole
4E	4-ethylcarbazole
15	1,5-dimethylcarbazole
3E	3-ethylcarbazole
26	2,6-dimethylcarbazole
27	2,7-dimethylcarbazole
12	1,2-dimethylcarbazole
24	2,4-dimethylcarbazole
25	2,5-dimethylcarbazole
BaC	benzo[a]carbazole
BcC	benzo[*c*]carbazole

An extracted ion chromatogram displaying the distribution of the C_0-C_2 carbazoles in a representative crude oil sample is displayed in Fig. 2. The present study shows that the concentration of individual pyrrolic nitrogen compounds (homologues C_0-C_2) is significantly different in the Abu Gharadig and Shushan oils, and it is suitable for differentiating the samples related to the two basins. Figure 3 displays in µg/g oil, the different concentration ranges of C_0-C_2 carbazoles for the studied crude oil samples. Overall, the highest yields of carbazole, methylcarbazoles and dimethylcarbazoles were recognized in the Abu Gharadig oils, whereas Shushan oils exhibit lowest concentrations of C_0-C_2 carbazoles. In Abu Gharadig crude oils, carbazole, summed methyl carbazole and
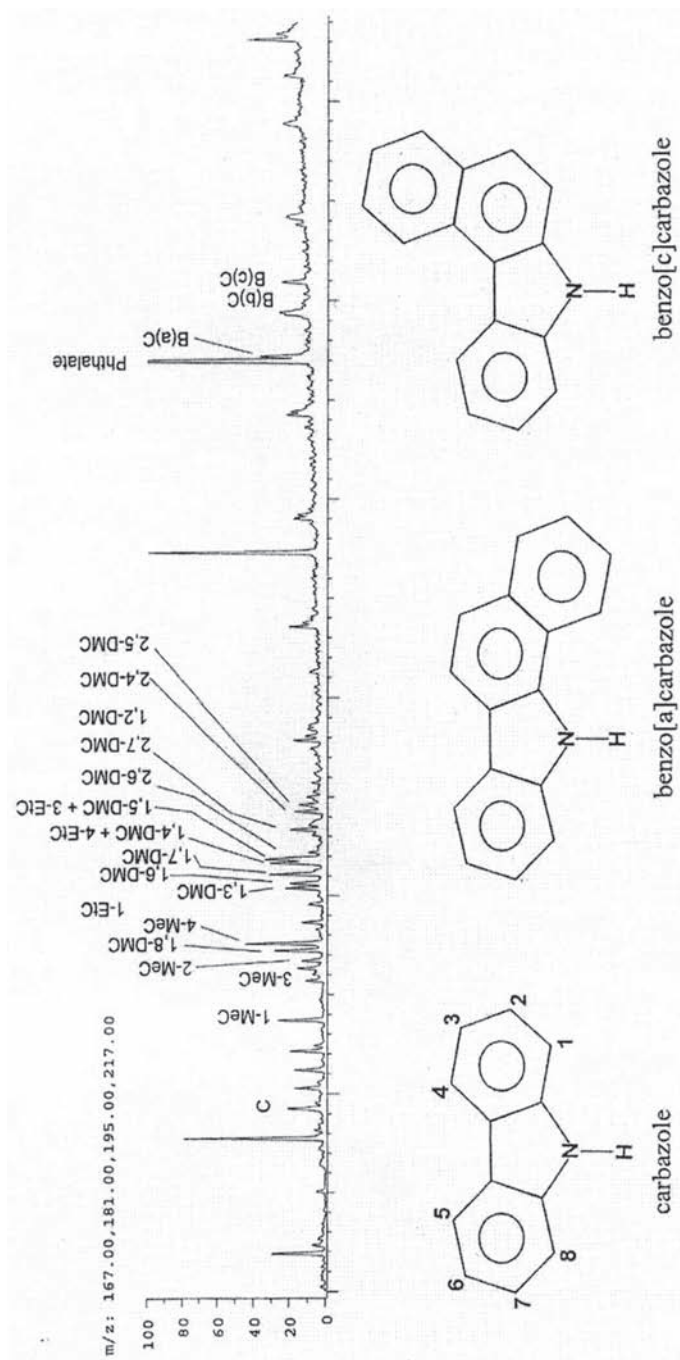
Fig. 2. Carbazoles distribution as revealed by extracted ion chromatrograms from full scan GC-MS measurements for a representative crude oil sample.
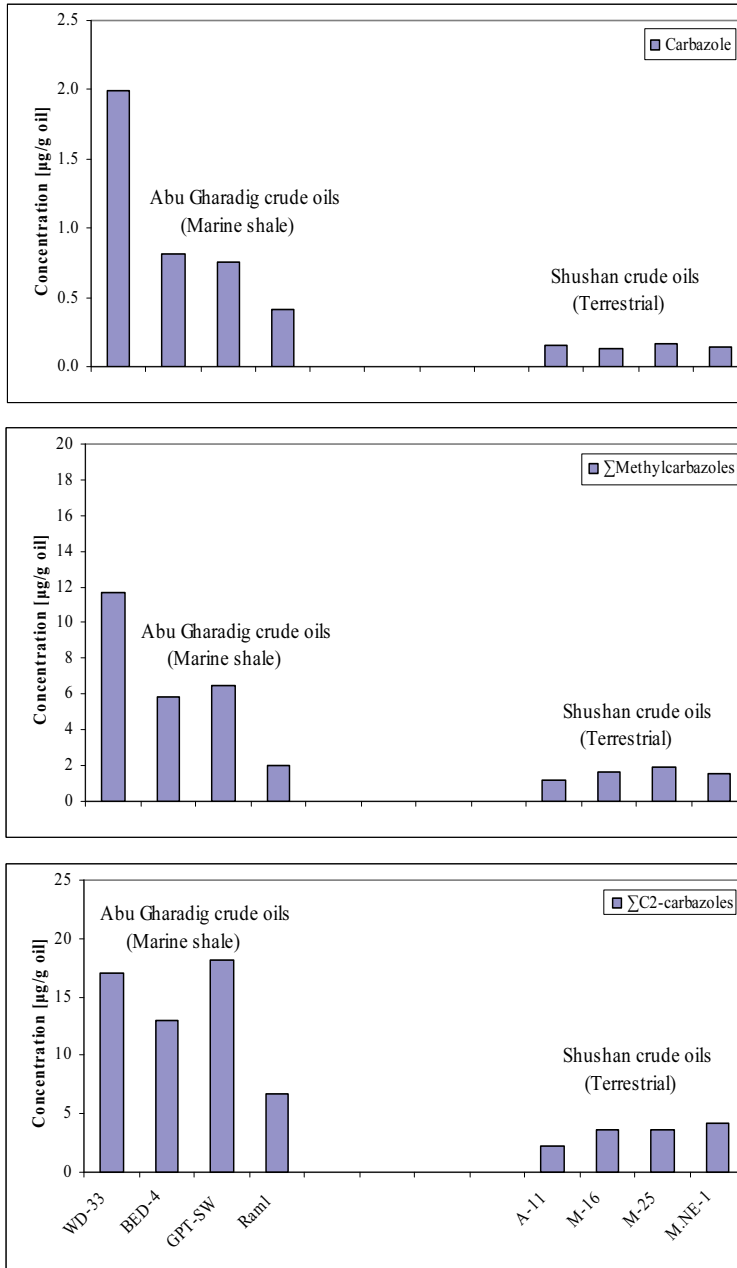
Fig. 3. Concentrations of carbazoles in crude oil samples from the Abu Gharadig and Shushan basins.

summed C_2-carbazole concentrations range from 0.41 to 2.0, 2.01 to 11.73 and 6.68 to 18.19 µg/g oil, respectively. Whereas in Shushan oils, carbazole, summed methyl carbazole and summed C_2-carbazole concentrations range from 0.13 to 0.16, 1.17 to 1.94 and 2.20 to 4.24 µg/g oil, respectively.

These findings provide evidence that the occurrence and distributions of pyrrolic nitrogen compounds is controlled by source characteristics of the studied samples. It is noteworthy that the yields determined here for the Abu Gharadig (marine shale) and Shushan (terrestrial) crude oils are significantly lower than those of the crude oils from Gulf of Suez (marine carbonate) (Bakr and Wilkes, 2002).

Compositions of Carbazoles

C_1-Carbazoles

All four methylcarbazole isomers 1-, 3-, 2-, and 4-methylcarbazoles are present in the studied oil samples (Table 2). For the Abu Gharadig oils, 1-methylcarbazole is the most abundant methylcarbazole and 3-methylcarbazole is the least abundant (Table 2). As for the Shushan oils, 4-methylcarbazole is the most abundant and 3-methylcarbazole is the least abundant methylcarbazole. In the work of Dorbon *et al*. (1984) on crude oils and Li *et al*. (1995) for source rocks, it was reported that 4-methylcarbazole is the most abundant and 1-methylcarbazole is the least abundant methylcarbazole.

Triangular diagrams have been used previously to evaluate variations of the alkylcarbazoles (Li *et al*., 1995; Clegg *et al*., 1997, 1998a,b; Horsfield *et al*., 1998). The distributions of the methylcarbazoles, 1-, 3+2-, and 4- are shown in a ternary plot after Li *et al*. (1995) (Fig. 4A). This figure demonstrates that the two oil families Abu Gharadig and Shushan are well differentiated on the basis of the methylcarbazole distribution. Abu Gharadig oils have higher values of 1-methylcarbazole and 3+2-methylcarbazoles than Shushan oils. On the other hand, significantly higher relative amounts of 4-methylcarbazole (~ 50%) were found in the Shushan oil samples. In Abu Gharadig oil samples, 1-methylcarbazole, 3+2-methylcarbazoles and 4-methyl-carbazole range from 37 to 41, 35 to 39 and 20 to 26% of the total

methylcarbazoles, respectively. As for Shushan oil samples, 1-methylcarbazole, 3+2-methylcarbazoles and 4-methylcarbazole range from 24 to 26, 23 to 26 and 50 to 52% of the total methylcarbazoles, respectively. Previously it was reported that immature (~ 0.5% R_o) and mature (~ 0.8% R_o) Lower Keg River carbonates as well as Posidonia Shale samples of different maturity (0.48-1.45% R_o) could be discriminated in this plot (Clegg *et al.*, 1997, 1998b). Furthermore, Li *et al*. (1995) had earlier shown that even stronger variations of the methylcarbazoles occurred in a data set based on a much broader selection of crude oil and source rock samples. It may be concluded that the methylcarbazoles are well suited for the differentiation of Abu Gharadig and Shushan crude oils with respect to geographical origin and variations of facies and depositional environment. Most likely, source rock type of the two oil families appears to play an important role in controlling carbazole distributions. This is probably being indicative of differences in kerogen type and mechanisms of primary migration.

C_2-Carbazoles

Dimethylcarbazoles are abundant in all the studied oil samples. Partially shielded carbazoles, *i.e.* one alkyl group present at the 1-position (Li *et al.*, 1995) are dominant. This includes dominance of carbazoles containing isomers with methyl groups at the 1,8-positions and 1-position, *e.g.* 1,8-dimethylcarbazole, 1,3-dimethylcarbazole, 1,6-dimethylcarbazole, 1,7- dimethylcarbazole, 1,4-dimethylcarbazole and 1,5- dimethylcarbazole (for simplicity, the 1,4- and 1,5-dimethyl-carbazoles are referred to the corresponding peaks in Fig. 2, despite their co-elution with 4-ethylcarbazole and 3-ethylcarbazole, respectively). A ternary plot of the relative abundances of 1,8-, 2,7- and 1,3-dimethylcarbazoles representing so called shielded, exposed and partially shielded carbazoles is illustrated in Fig. 4B. As can been observed, the relative abundance of 1,8- dimethylcarbazoe ranges from 36 to 62%, with relatively high values (ca. > 51%) in all Abu Gharadig oil samples and low values (ca. < 51%) in all Shushan samples. The relative amount of 1,3-dimethylcarbazole ranges from 30 to 55%, with relatively high values (ca. > 43%) in all Shushan oil samples and low values (ca. < 43%) in all Abu Gharadig samples. All oil samples from the two basins are characterized by low relative amounts of 2,7-dimethylcarbazole with an
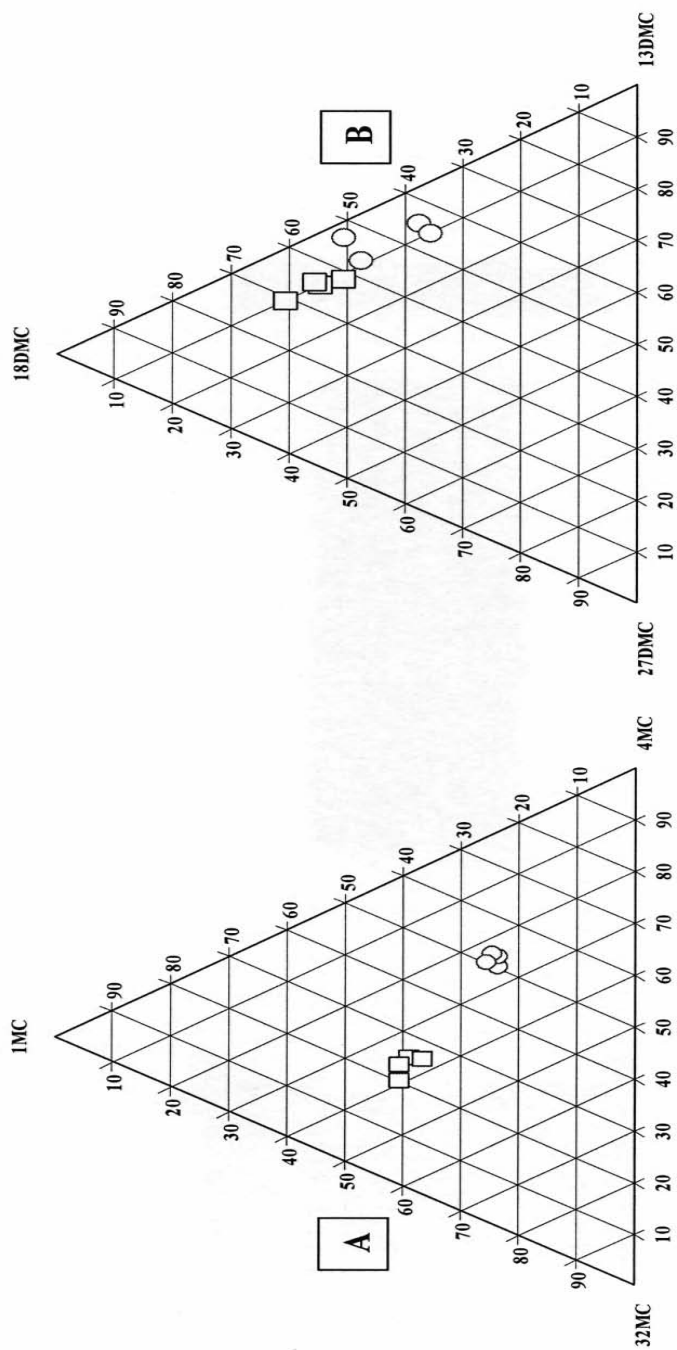
Fig. 4. Triangular diagrams showing the distribution of (A) methylcarbazoles and (B) selected C$_2$-carbazoles for the investigated samples (squares, Abu Gharadig oils; circles, Shushan oils).

average value of 7% of the total dimethylcarbazoles. Most likely, the most significant differences between the oil samples of the two basins seem to be the relative amounts of 1,3- dimethylcarbazole and 1,8-dimethylcarbazole instead of 2,7-dimethylcarbazole. As compared to the 1-, 3+2, and 4-methylcarbazoles plotted in the ternary diagram shown in Fig. 4A, the variations in the relative amounts of 1,8-, 1,3- and 2,7-dimethylcarbazoles could also differentiate between crude oils of the two basins (Fig. 4B).

Carbazole Distribution and Maturity

Maturation effects on carbazole distributions in crude oils and source rocks have been noted previously (Clegg *et al*., 1998b; Harrison *et al*., 1997; Li *et al*., 1997; and Horsfield *et al*., 1998), where maturity covered a considerable span. Clegg *et al*. (1997) compared the immature Lower Keg River Member wackestones with the immature Upper Keg River Member marlstones from the La Crete sub-basin in western Canada in order to investigate the possible lithofacies dependency of pyrrolic nitrogen compound distributions. These authors considered the source of the pyrrolic nitrogen compounds to be facies dependent, although they did not exclude primary expulsion at very early stages of thermal maturation as another possible alternative explanation to the observed pyrrolic nitrogen compound distributions. In contrast, Li *et al*. (1999) in their studies on samples from the same area could not detect clear differences in the distributions of alkylcarbazoles and benzocarbazoles among the end member oils.

In this study, the maturation parameter based on the isomerization at C-20 in the C_{29} ααα steranes (20S/20S+20R) indicates a high maturity level biased towards Abu Gharadig oils (Table 1). Several alkylcarbazole parameters previously thought to be maturity related (*e.g.*, Clegg *et al*., 1998b; Li *et al*., 1997) are plotted against the biomarker maturity parameter C_{29} ααα steranes (20S/20S+20R) in Fig. 5. These alkylcarbazole parameters include 1MC/1MC+1EC, 3MC/4MC and 18DMC/18DMC+1EC.

Although a slight increase or decrease in some of these parameters with increasing biomarker maturity C_{29} ααα steranes (20S/20S+20R)
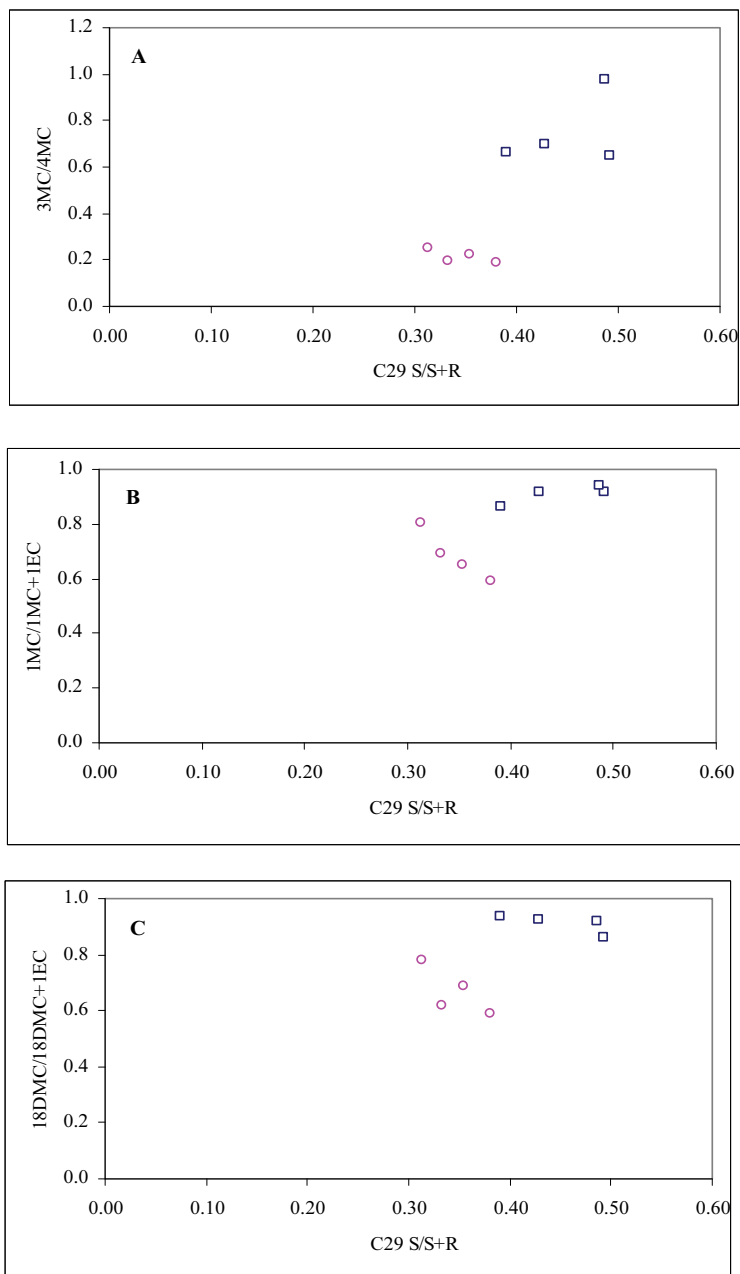
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Fig. 5. Cross plots of C29 *ααα* sterane 20S/(20S+20R) and carbazole ratios for the investigated samples (squares, Abu Gharadig crude oils; circles, Shushan crude oils).

ratio may be present, the differences of carbazole ratios between the two basins do not show a direct maturity-dependence despite a considerable maturation span. Therefore, these observations may indicate that thermal maturation can be ruled out as a major factor in controlling the changes in the carbazole ratios in the crude oil samples of the Abu Gharadig and Shushan basins.

As the chemical structures of alkylcarbazoles are similar to those of the alkyl dibenzothiophenes, Clegg *et al*. (1998b) suggested that alkylcarbazoles may be formed through alkylation of the parent compound and interconversion of isomers in similar ways to those proposed for dibenzothiophenes (Radke *et al*., 1982), phenanthrenes (Alexander *et al*., 1995) and phenols (Ioppolo- Armanios *et al*., 1994). This suggestion may be quite plausible if potential source rocks across a wide range of thermal maturity are concerned, *e.g.* in the Gulf of Mexico (Clegg *et al*., 1998b). However, the effects of thermal maturation on the alkylcarbazole distribution in the reservoired oil (which are normally generated within a relatively narrow maturity window for any given source rock) are clearly less pronounced than those on the distributions of saturated hydrocarbon biomarkers, aromatic hydrocarbons and sulphur-heterocyclic aromatics. Similar observations have been made previously from various crude oils in a relatively closed petroleum system in Alberta (Li *et al*., 1999).

Carbazole Distributions and Environments, and Source-Dependency

The different depositional environments were clearly indicated from biomarker signatures, such as Pr/Ph, C_{35}/C_{34} homohopanes and sterane/hopane ratios (Table 1). Cross plots of the alkylcarbazoles 1MC/1MC+1EC, 3MC/4MC and 18DMC/18DMC+1EC versus Pr/Ph (Fig. 6), waxiness (Fig. 7) and C_{29}/C_{27} steranes (Fig. 8) when applied to the studied crude oil samples serve to distinguish two main types of depositional setting; terrestrial dominated source deposited in oxidizing conditions for the Shushan oils and marine shale dominated sourced oil deposited in suboxic environments for the Abu Gharadig samples. Shushan oil samples are dominated by C_{29}/C_{27} sterane ratios, and are characterized by higher Pr/Ph, higher waxiness, and lower alkylcarbazoles concentrations than Abu Gharadig oils (Tables 1 and 2).
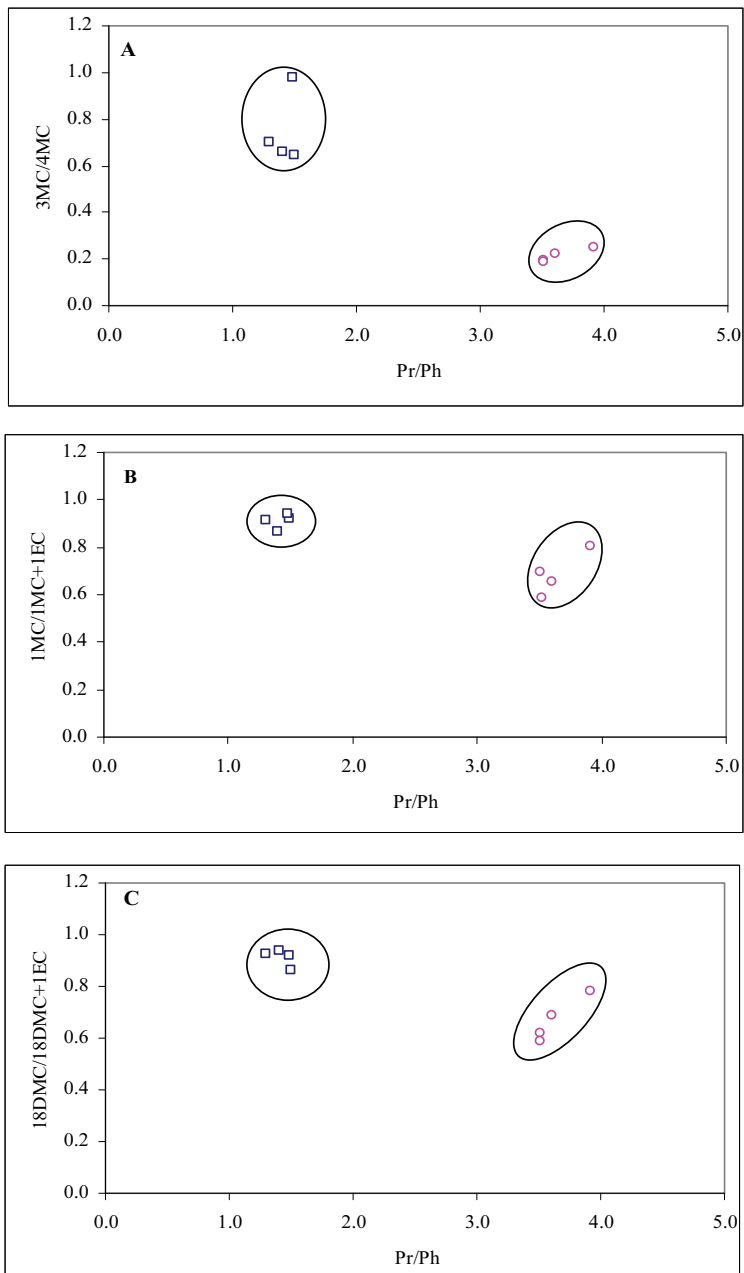
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Fig. 6. Cross plots of Pr/Ph and carbazole ratios for the investigated samples (squares, Abu Gharadig crude oils; circles, Shushan crude oils).
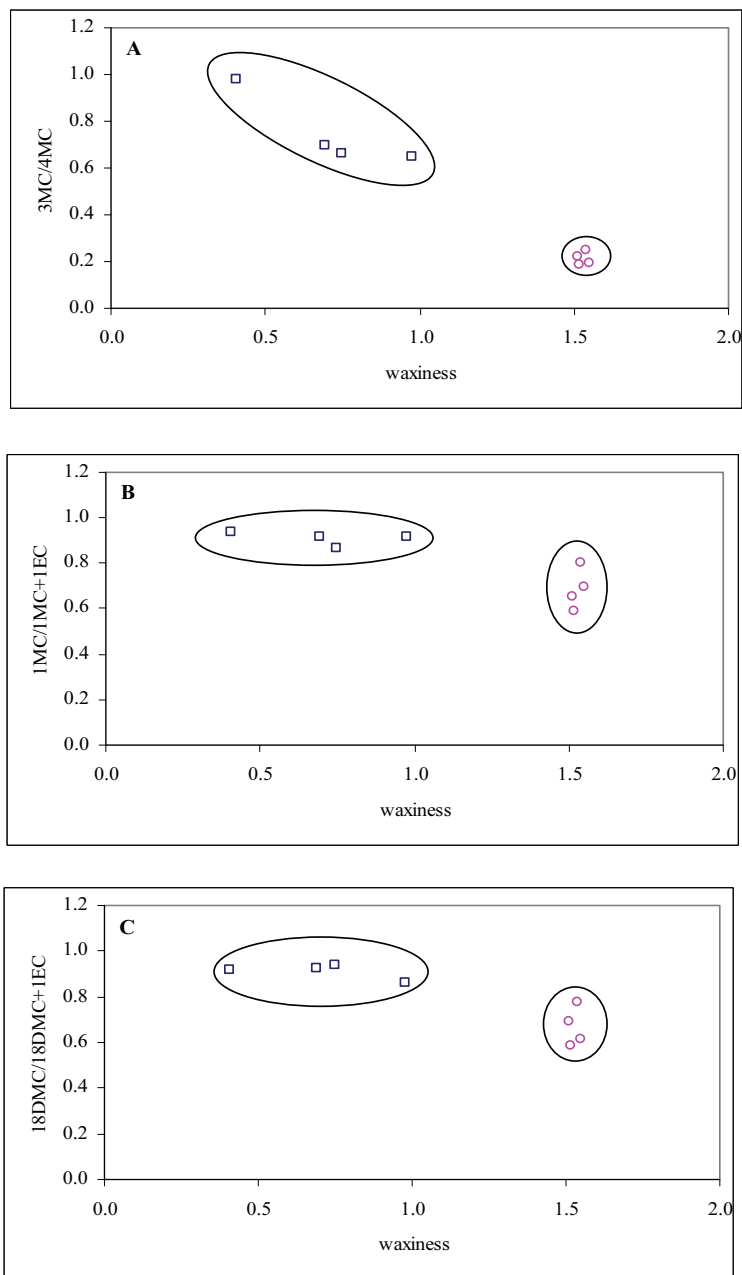
Fig. 7. Cross plots of waxiness $\sum$ (*n*-C$_{21}$-*n*-C$_{31}$)/$\sum$ (*n*-C$_{15}$-*n*-C$_{20}$) and carbazole ratios for the investigated samples (squares, Abu Gharadig crude oils; circles, Shushan crude oils).
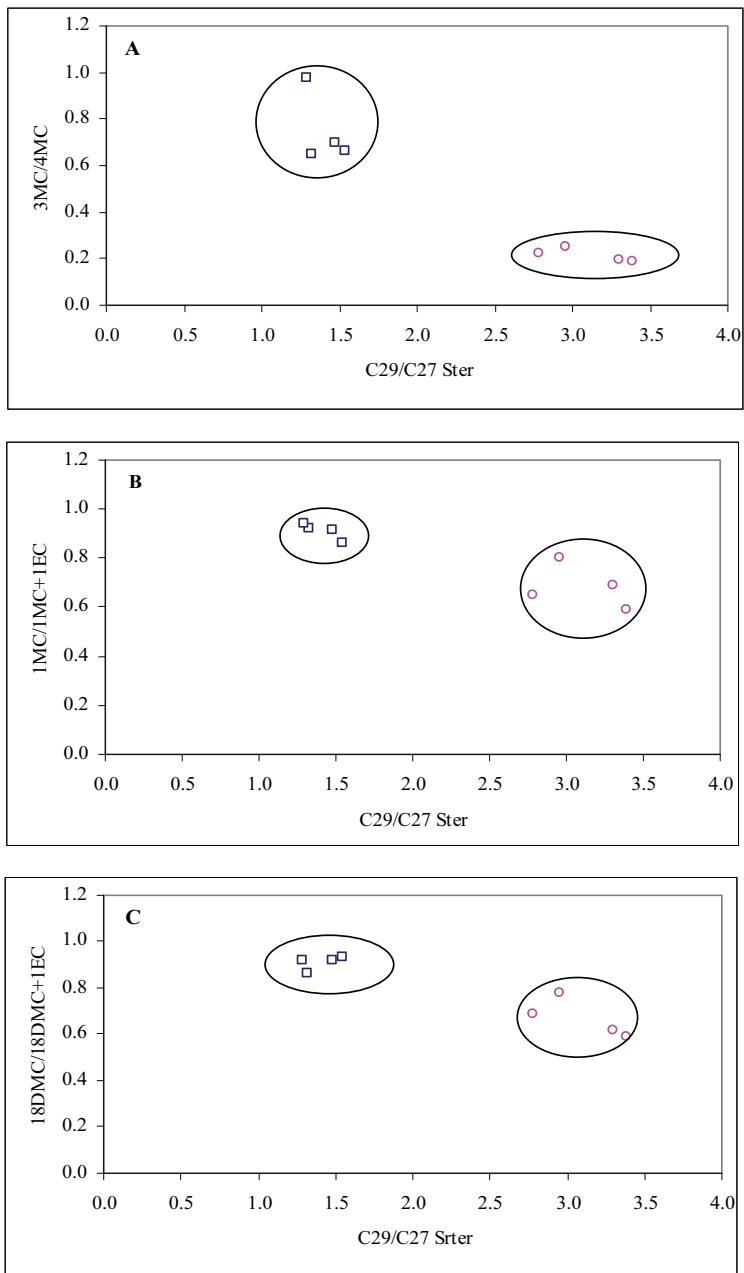
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Fig. 8. **Cross plots of C$_{29}$ ααα 20R sterane/C$_{27}$ ααα 20R sterane and carbazole ratios for the investigated samples (squares, Abu Gharadig crude oils; circles, Shushan crude oils).**

These differences observed between the Abu Gharadig and Shushan oils must be a reflection of the differences in the depositional environment and/or organic input into their source rocks. The Abu Gharadig and Shushan oil groups are also clearly differentiated in Fig. 9. The terrestrially sourced Shushan oils, generally have relatively low values of 1MC/1MC+1EC, 3MC/4MC and 18DMC/18DMC+1EC ratios, as compared to the marine clastic sourced Abu Gharadig crude oils. All these observations may indicate that the alkylcarbazole distributions, with significant variations between 1-, 3-, 4-methylcarbazoles, and 1,8-dimethylcarbazoles, may have strong environment dependence, based on the limited number of samples investigated here from the different depositional conditions in the two basins.

Benzocarbazoles

Occurrence and Distribution af Benzocarbazoles

The concentrations of the benzocarbazole isomers in the studied crude oil samples are low (Table 2). Benzo[*b*]carbazole was near or even below the detection limit in many samples. The ratio benzo[a] to benzo[c] carbazoles [*a*/(*a*+*c*)] covers a range from 0.39 to 0.61 for the studied crude oil samples (Table 1). A noteworthy feature is that the variability of *a*/(*a*+*c*) in this study is less than the range of variability, which has been reported earlier in facies and depositional environment, migration, and maturity related case studies (Larter *et al*., 1996; Clegg *et al*., 1998b; Horsfield *et al*., 1998; Bakr and Wilkes, 2002).

The benzocarbazoles *a*/(*a*+*c*) ratio for the studied samples is plotted relative to source maturity indicator, C_{29} ααα steranes (20S/20S+20R), in Fig. 10A. The scatter among the data points overshadows any control that maturity might have on these oils. Other factors effects may be important contributors in determining benzocarbazole distributions in the Western Desert crude oils. The results from this study suggest that maturity effects may be subordinate to other factors.

The behavior of the benzocarbazole *a*/(*a*+*c*) parameter is considered in terms of palaeoenvironmental conditions, Pr/Ph (Fig. 10B), source and waxiness (Fig. 10C), and C_{29}/C_{27} sterane (Fig. 10D). From Fig. 10B-D, the benzocarbazole *a*/(*a*+*c*) reveals geographical correspondence emerging where the highest and lowest *a*/(*a*+*c)* values are found in Abu
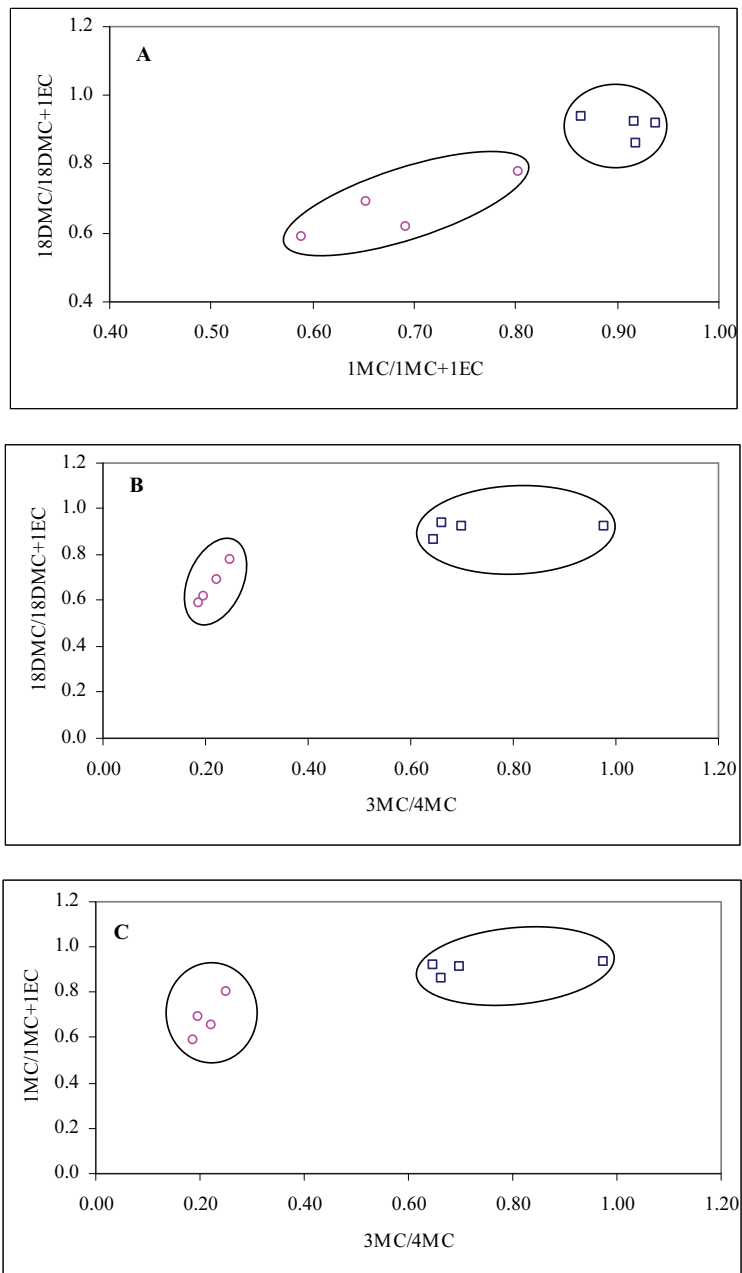
M.M.Y. Bakr

Fig. 9. Cross plots of C_1- and C_2-carbazole ratios for the investigated samples (squares, Abu Gharadig crude oils; circles, Shushan crude oils).
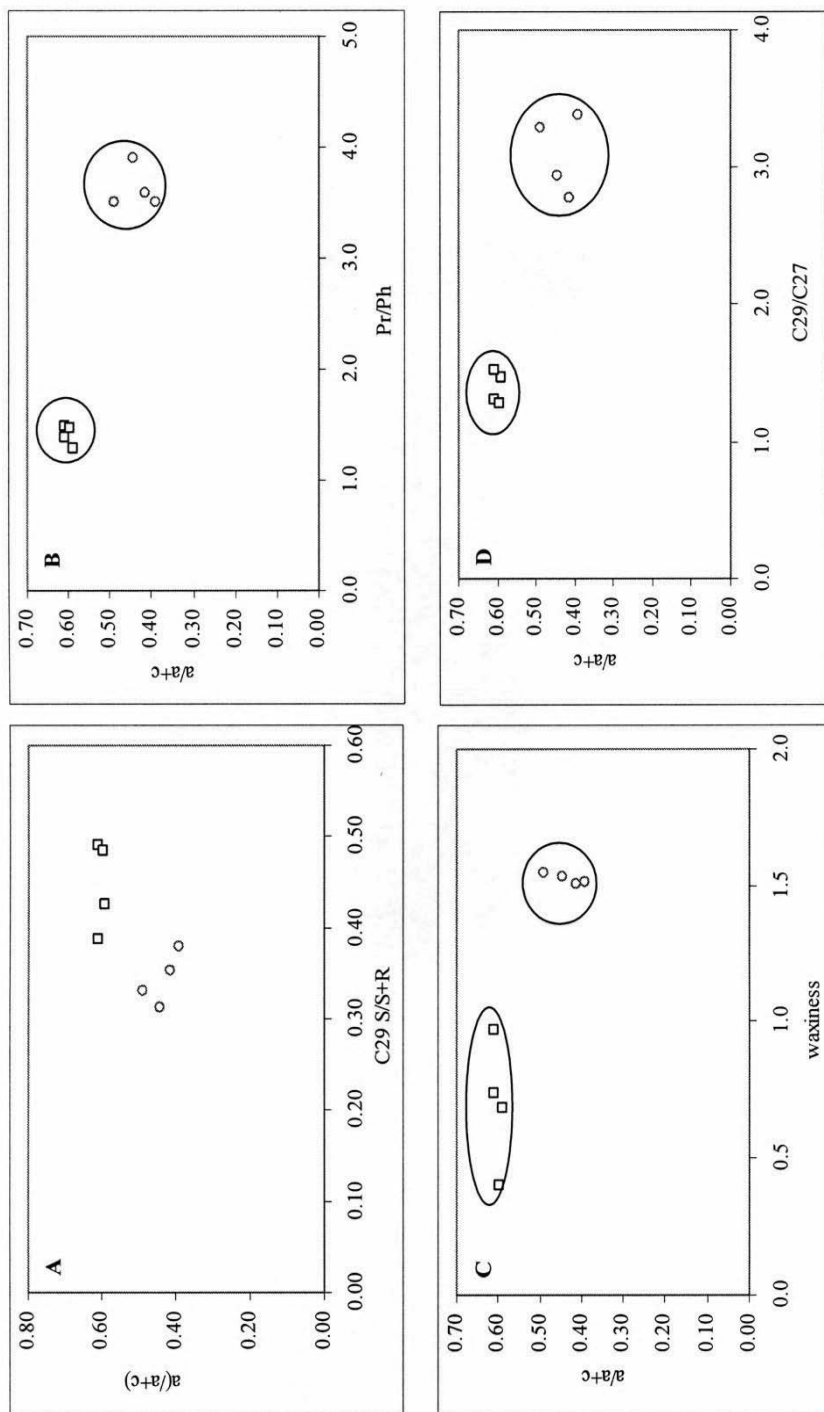
Fig. 10. Cross plots of benzocarbazole $a/a +c$ ratio versus C29 $\alpha\alpha\alpha$ sterane 20S/20S+20R), Pr/Ph, waxiness $\Sigma(n\text{-}C_{21}\text{-}n\text{-}C_{31}) / \Sigma(n\text{-}C_{15}\text{-}n\text{-}C_{20})$, and C_{29} $\alpha\alpha\alpha$ 20R sterane/C$_{27}$ $\alpha\alpha\alpha$ 20R sterane for the investigated samples (squares, Abu Gharadig oils; circles, Shushan oils).

Gharadig and Shushan oil samples, respectively. Generally, crude oil samples from the Abu Gharadig Basin have relatively high $a/a+c$ values (0.59 to 0.61), together with low Pr/Ph, low C_{29}/C_{27} sterane and low waxiness values. On the other hand, crude oil samples from the Shushan Basin have relatively low $a/(a+c)$ values ranging from 0.39 to 0.59, together with relatively high values of Pr/Ph, C_{29}/C_{27} sterane and waxiness. The relation observed between $a/(a+c)$ parameter and Pr/Ph in this study contradict the case reported by Bakr and Wilkes (2002) for oil from the Gulf of Suez, Egypt. It is likely that depositional environments and source retention effects have the dominant influence on the benzocarbazole distributions in the crude oil under investigation.

Occurrence of Xanthones in the Western Desert Oil Fields

Xanthones consist of a tricyclic aromatic structure including an ether and a keto function within the ring system. Xanthone and its alkylated homologues were identified in the Shushan oil samples and source rocks collected from the Jurassic Khatatba Formation. On the other hand, xanthones were absent from the Abu Gharadig oil, and occurred in very low amounts in WD-33 oil sample.

An extracted ion chromatogram displaying the distribution of xanthones in a representative Shushan oil sample is shown in Fig. 11. The concentrations in μg/g oil of xanthone, the sum of methylxanthones and the sum of the C_2 xanthones are illustrated in Fig. 12. All Shushan oils are enriched in xanthones. These oil samples contain all the three compound groups at concentrations ranging from 1.54 to 2.31, 2.30 to 7.41, and 4.57 to 8.02 μg/g oil, for xanthone, C_1-, and C_2-xanthones, respectively. In Abu Gharadig oils, only WD-33 sample contains 0.38, 2.67 and 0.50 μg/g oil of xanthone, C_1-, and C_2-xanthones, respectively. A noteworthy feature in Abu Gharadig oils is that oil sample WD-33 contains higher waxy $\sum(n\text{-}C_{21}\text{-}n\text{-}C_{31})/\sum (n\text{-}C_{15}\text{-}n\text{-}C_{20})$ ratios than other oils of this family, reflecting relatively higher concentrations of land plant input in sample WD-33 than the remaining Abu Gharadig oil samples (Table 1).

The relative abundance of xanthone, the sum of the methylxanthones and the sum of the C_2-xanthones in the studied oil samples together with representative source rock samples from the Jurassic Khatatba Formation is shown in the ternary plot of Fig. 13. From this figure, the data show
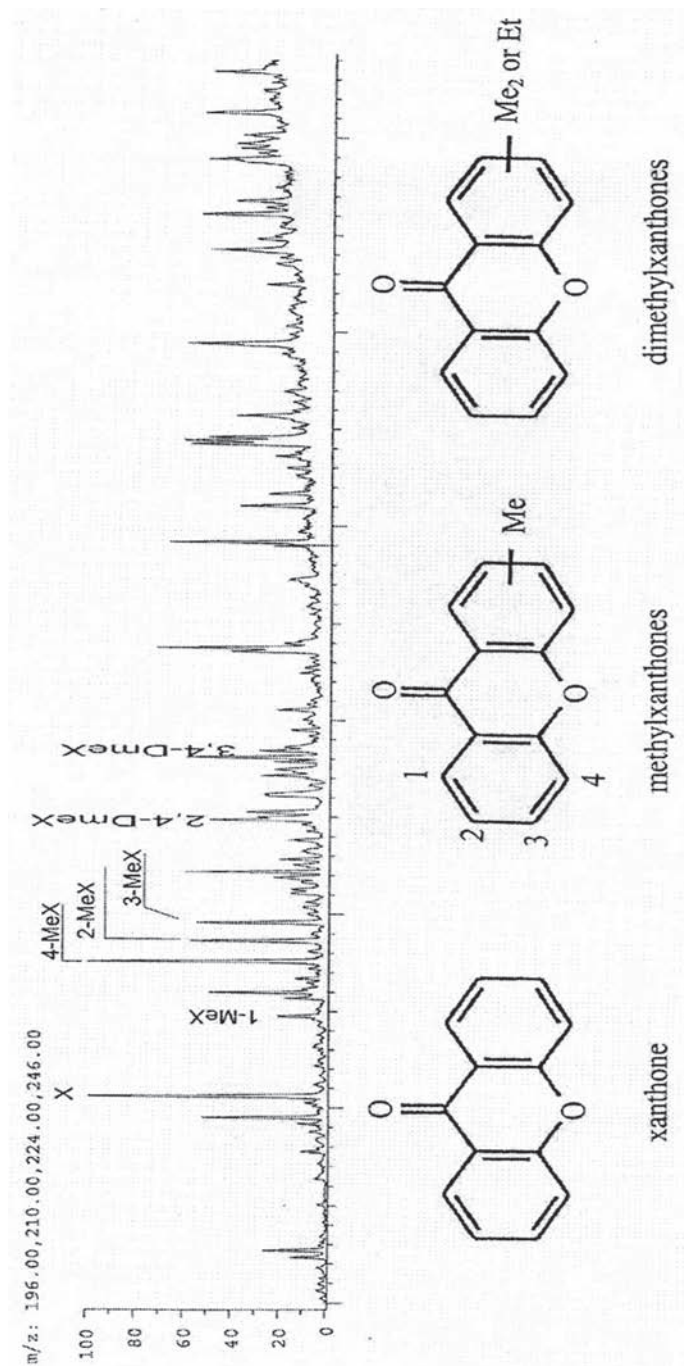
Fig. 11. Xanthones distribution as revealed by extracted ion chromatograms from full scan GC-MS measurements for a representative Shushan oil sample.
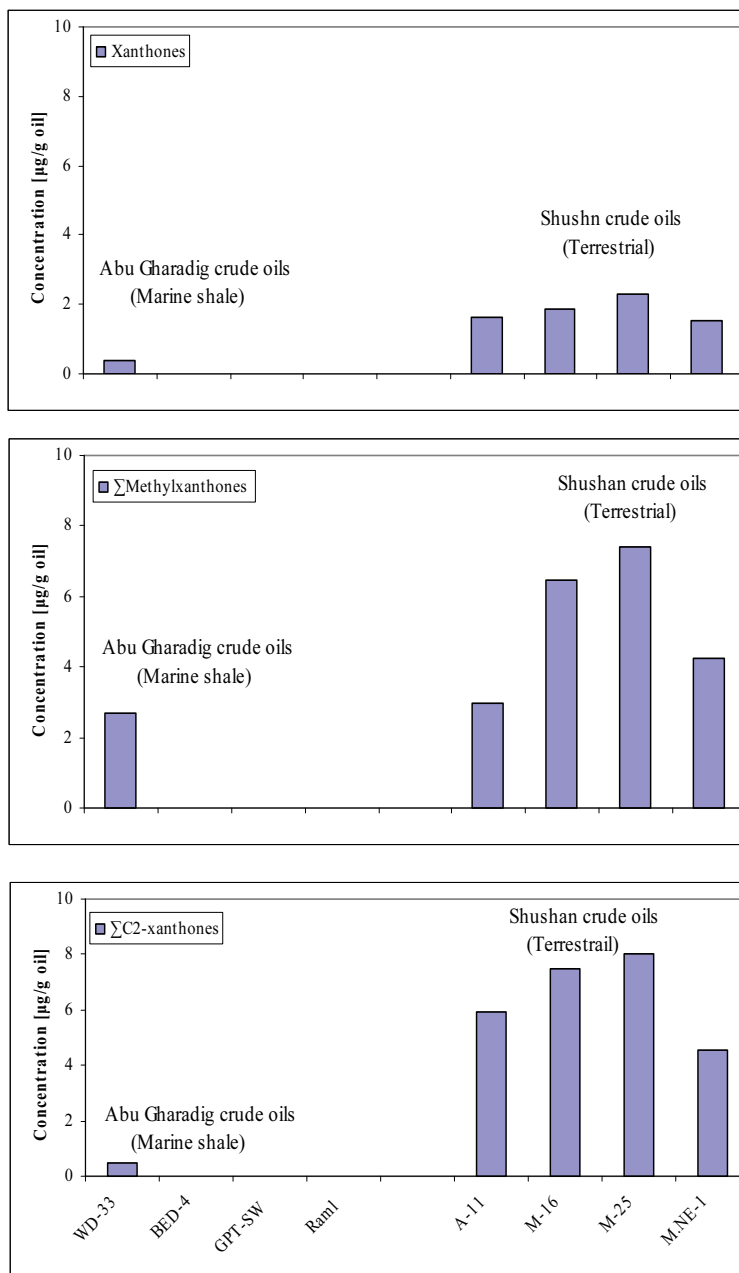
M.M.Y. Bakr

Fig. 12.   Concentrations of xanthones in crude oil samples from the Abu Gharadig and Shushan basins.

that the Khatatba source rocks contain higher proportion of xanthones than do the Shushan oils. Biomarker signatures of the Khatatba Formation extracts and Shushan oils indicate a significant contribution of terrestrial organic matter (Bakr, in press). The xanthones distributions for Shushan oils and Khatatba source rocks plot in a small area in Fig. 13, suggesting a genetic relationship between these samples. These observations clearly indicate that the most probable source of the Shushan oils is the Jurassic Khatatba rocks.
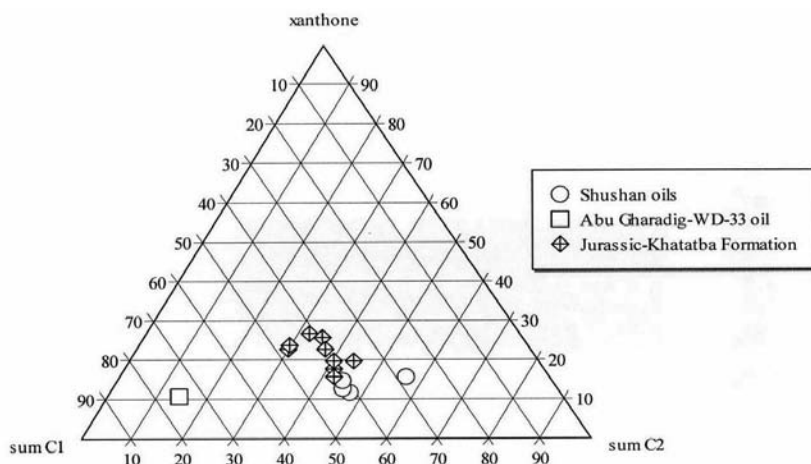

Fig. 13. Ternary diagram showing the C_0-, C_1 and C_2-xanthones distribution in crude oil and source rock samples from the western desert of Egypt (sum Cl = sum C1 = xanthones; sum C2 = sum C2 = xanthones).

Xanthones were not detected in the Gulf of Suez petroleum system that includes both marine carbonate and clastic source rocks. Also, oils sourced from marine shale in Abu Gharadig Basin lack xanthones (except sample WD-33).

The reason behind that is most likely due to the lack of potential terrestrial plants precursors in the clastic and carbonate source rocks of these marine Egyptian petroleum systems. As far as the studied Egyptian samples are concerned, xanthones are abundant only in source extracts and crude oils that have terrestrial organic matter input. Hence, xanthones signatures show great promise as terrestrial source markers in a given petroleum system. The results of this study are preliminary; however, detailed data will be published elsewhere.

Conclusion

The concentrations and molecular distributions of carbazole, methylcarbazoles, dimethylcarbazoles and benzocarbazoles in the Abu Gharadig and Shushan oil samples are largely controlled by source facies and depositional environments rather than reflecting maturation processes. The relative distribution of 2-, 3- and 4-methylcarbazole reveals a strong influence of the source rock. Generally, Abu Gharadig oils show a higher abundance of 1-methylcarbazole and 3+2-methylcarbazoles than Shushan oils. Whereas, significantly high relative amounts of 4-methylcarbazole were found for the Shushan oil samples.

Dimethylcarbazoles are abundant in all the studied oil samples. The most significant differences between the oils of the two basins seem to be the relative amounts of 1,3-dimethylcarbazole and 1,8-dimethylcarbazole rather than the 2,7-dimethylcarbazole.

It may be concluded that the methylcarbazoles and benzocarbazole *a/(a+c)* ratios are considered to be powerful markers for the discrimination of Abu Gharadig oils from the Shushan oils with respect to geographical origin and variations of facies and depositional environment. However, the exact controls for differences need further study.

Xanthones and its alkylated homologues were not recorded in oil samples from marine carbonate or clastic source. Xanthones are abundant in source extracts and crude oils that have terrestrial organic matter input. Based on the data of the current study, xanthones signatures show great promise as terrestrial source markers in a given petroleum system.

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وجود مركبات الكربازول والزانسون ودلالتها الجيوكيميائية في زيت النفط بالصحراء الغربية بمصر

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المستخلص. يناقش البحث وجود وتوزيع مركبات الكربازول والزانسون في عينات من زيت النفط المصري في مناطق حوضي ترسيب أبو الغراديق وشوشان بالصحراء الغربية. توصف مركبات الكربازول بأنها إحدى مشتقات مركبات النيتروجين الأروماتية، بينما تعتبر مركبات الزانسون إحدى مشتقات مركبات الأوكسجين الأروماتية. وقد وجدت اختلافات جوهرية بين زيت النفط المتواجد في حقول حوضي أبو الغراديق وشوشان الترسيبية من حيث صخور المصدر والصفات الجيوكيميائية. وأشارت الدراسة إلى نشأة زيت نفط حوض شوشان من مواد عضوية نباتية وجدت في بيئة قارية، ونشأة زيت نفط حوض أبو الغراديق من مواد عضوية تكونت فى بيئة بحرية غنية بسحنات الطفلة.

وأكدت الدراسة وجود مركبات الكربازول في زيت نفط حوض أبو الغراديق بتركيزات كبيرة عن مثيلاتها في زيت نفط حوض شوشان، وبالتالي أمكن استخدام مركبات الكربازول في التمييز بين زيت نفط حوضي أبو الغراديق وشوشان. وقد دلت الدراسة أيضًا على تحكم كل من السحنة العضوية والبيئة الترسيبية في توزيع مركبات الكربازول في زيت النفط محل الدراسة، بينما اتضح أن درجة نضوج البترول ليس لها تأثير في توزيع مركبات الكربازول.

أما بالنسبة لمركبات الزانسون وهي مركبات ذات صفات نباتية، فقد أكدت الدراسة عدم وجود تلك المركبات في زيت نفط حوض أبو الغراديق التي نشأت في بيئة بحرية غنية بسحنات الطفلة (عدا عينة واحدة)، كما أفادت الدراسة أيضًا إلى عدم وجود مركبات الزانسون في زيوت نفط خليج السويس التي تكونت في بيئة بحرية غنية بسحنات كربونات أو سحنات طفلة، بينما أشارت التحليلات الجيوكيميائية إلى تواجد مركبات الزانسون فقط في زيت نفط حوض شوشان الترسيبي الذي يتميز عن بقية زيوت النفط بصفاته النباتية، كما وجدت مركبات الزانسون أيضًا في صخور مصدر متكون الخطاطبة ذات الصفات النباتية.