

Identification and geochemical significance of polarized macromolecular compounds in lacustrine and marine oils

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Abstract Polarized macromolecular compounds in typical lacustrine and marine shale oils collected from the Ordos Basin and Tarim Basin of China were analyzed by FT-ICR-MS. Maturity was taken into consideration by diagenesis physical simulation experiments on shale oils, which had been collected at various temperature and pressure stages. The results showed that similar components existed in non-hydrocarbon and asphaltenes and the main peak compound classes of N_1 and O_2 were potential parameters for identifying typical marine oil and lacustrine oil in China. Nitrogen compounds/(nitrogen compounds and oxygen compounds), such as $N_1/(O_2+N_1)$, $N_1/(O_3+N_1)$, $N_1/(N_1O_1+N_1O_2)$ are the maturity indicators, which are related with C-N and C-O bond energy. Differences in molecular components and weights between marine and lacustrine oils are the effective index to identify source maturity and sedimentary environment.

Key words polarized macromolecular compound; oil; FT-ICR MS; sedimentary environment; maturity

1 Introduction

Biomarkers are well utilized in oil-source correlation, maturity evaluation and biodegradation recognition (Peters et al., 2011). A practical method for biomarkers separation is column chromatography and saturated hydrocarbons, aromatic hydrocarbons, non-hydrocarbons and asphaltenes were separated (SANA). Saturated and aromatic hydrocarbon fractions were analyzed by GC-MS, but the non-hydrocarbons and asphaltenes could not be analyzed for strong polarity and high molecular weights. Thermal cracking of asphaltenes are often considered to further dig out the underlying geochemical information (Solli and Leplat, 1986; Ganz and Kalkreuth, 1987; Trejo et al., 2007).

Super high resolution was realized on FT ICR-MS to analyze molecular ranges from several Daltons to thousands Daltons and achieve molecular formula composition by considering the element isotopes (Marshall et al., 1998; Qian et al., 2001). Het-

eroatom compounds in petroleum could be selectively ionized in high abundant complex hydrocarbons by ESI, and the combination of ESI to FT-ICR-MS has become one of the crucial methods for the analysis of polar macromolecular compounds, especially in heavy oil (Qian et al., 2001; Shi et al., 2008). Diversities of polarized macromolecular compounds in different regions, maturities and biodegradations have been suggested with the help of ESI-FT-ICR-MS (Hughey et al., 2002; Hughey et al., 2004; Hughey et al., 2007; Kim et al., 2005). However, indicators and parameters are out of expectation because of the absence of geological consideration and biomarkers. Information interpreted from polarized macromolecular compounds is rarely used in sedimentary environments and maturity.

Based on that, three aims are listed in this paper. Firstly, try to figure out distribution variations by comparing macromolecular compositions and high weights of non-hydrocarbons and asphaltenes; secondly, compare the differences in macromolecular

compositions between marine and lacustrine shale oils and to summarize the sedimentary markers; and thirdly, analyze the macromolecular compositions of shale oils from various temperature stages and propose the maturity indicators for macromolecular compositions.

2 Samples and experiment

Oils from marine environments are available in Makit Slope, Southwest Tarim Basin ($56 \times 10^4 \text{ km}^2$). Biomarkers, stable carbon isotopes and geological conditions indicate that the oils from well BK3, Ma4, are derived from marine source rocks and oils from well Qu1 giving some different source information indicate a terrestrial contribution (Cui et al., 2011, 2013a). The Ordos Basin is the second largest lacustrine basin in China ($37 \times 10^4 \text{ km}^2$). Source/oil correla-

tions suggest that lacustrine shales of Chang 7 are the source rocks (Wang et al., 1995; Hanson et al., 2002; Wang et al., 2009; Zhang et al., 2008; Zhang et al., 2011). Locations of the basins and sampling sites are presented in Fig. 1 and information about the oils is list in Table 1. Low maturity ($R_o=0.58$ calculated from 20 reflected points) and high TOC (TOC=13%) shale samples were collected from Well S105. Low maturity samples were ground as fine as 120 meshes for physical simulation. Digenesis physical simulation systems include heating furnace, pressure, liquid supply, products gathering, general controlling platform and supplementary systems. The maximum temperature and pressure are 550°C and 275 MPa, respectively. Shale oils produced at different temperatures and pressures were collected. Polar macromolecular compounds were analyzed under the negative ion mode of ESI FT ICR-MS. Experimental condition for sample simulating is given in Table 2.

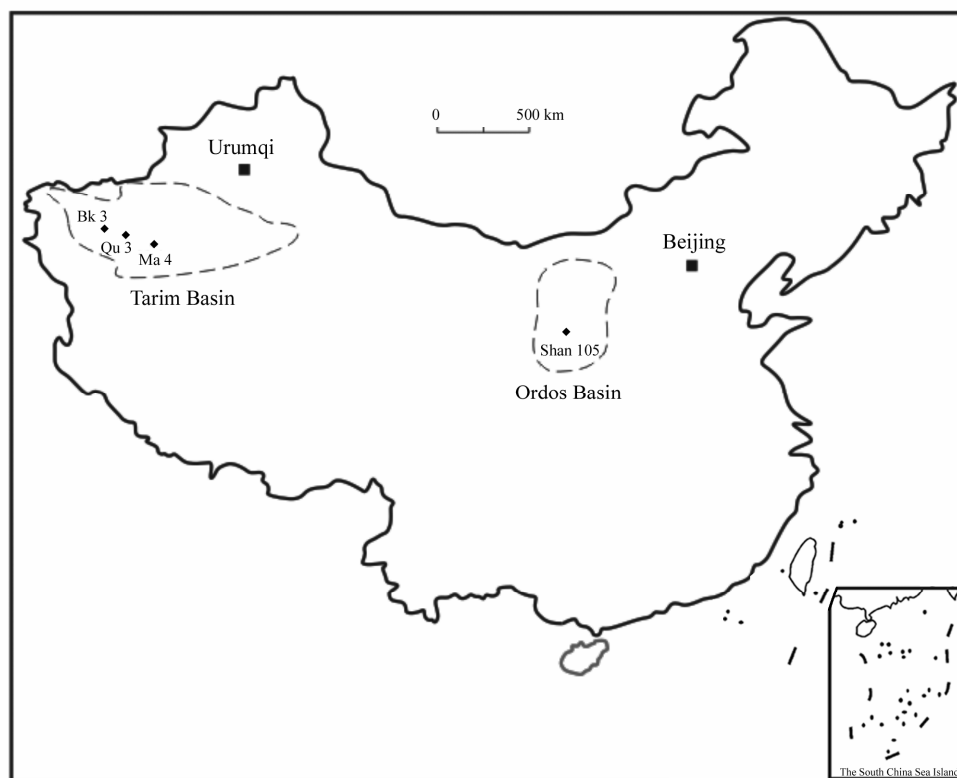


Fig. 1. Locations and sites of the basins and sampling wells.

Table 1 Geographical information on and physical properties of oils

Basin	Well	Depth (m)	Formation	Density (g/cm ³)	Viscosity (mm ² /s) (30°C)	Wax (%)	Sulfur (%)	Freezing point (°C)	Initial boiling point (°C)
Tarim	BK3H	4772–4775	C1b	0.8005	2.10	5.29	0.16	<-34	4.52
	Qu1	4746–4731	C1b	0.8300	—	1.19	0.27	—	—
	Ma4	2044–2140	O1-2y	0.8100	—	0.69	—	-35°	—
Ordos	Shan105	2092–2093	T3y	0.8000	—	—	—	—	—

Table 2 Designing program for diagenesis physical simulation

Furnace No.	1	2	3	4	5	6
Max pressure (MPa)	42.5	45.0	47.5	50.0	62.5	70
Max temp. (°C)	300	325	350	400	450	550
Heating rate (°C/h)	10	10	10	10	10	10
Heating time (h)	28	30.5	33	38	43	53
Pressure adding rate (MPa/h)	1.51	1.47	1.43	1.31	1.45	1.32
Pressure time (h)	28	30.5	33	38	43	53
Hold (h)	72	72	72	72	72	72
Close/open	Semi-close	Semi-close	Semi-close	Semi-close	Semi-close	Semi-close
Total time (h)	98	102.5	105	110	115	125

Analytical conditions for ESI FT ICR-MS are generally described as follows: dichloromethane is used for dissolving oil, preparing c.0.1 mg/mL for the solution. 1 mL of the solution is put into 1 mL ethanol, then 10 μ L 35% (v/v) NH_4OH is added, aiming at accelerating the deprotonation process under ESI of the negative ions. The instrument for this analysis is Apex-ultra FT ICR-MS equipped with Shielded superconducting magnet and field density of 9.4 T. Operating software is XMASS version 6.0 (Bruker Daltonics, USA). Every mass spectrum is composed of and overlain by 64 spectra, which aim at guaranteeing the repeatability. Data analysis 3.4 is provided for analyzing the relative abundance and quality identification.

3 Results and discussion

3.1 Polarized macromolecular compounds in lacustrine oils

Polarized macromolecular compounds are characterized by strong polarity, high molecular weight, and complicated structure. Utilizing FT-ICR-MS, we could precisely define the elemental associations and the isotopic characteristics. The FT-ICR-MS spectra of oils from the Ordos Basin under negative ions are presented in Fig. 2. Resolution of M/z 400 can reach 300000. Partial magnification of M/z 296.1–296.3 and M/z 297.1–297.3 is illustrated in Fig. 2. Accurate molecular weights are referred for compound peak identification. 5 peaks and 9 peaks are recognized, respectively in Fig. 2, and compound classes O_1 , O_2 , O_3 , O_4 , N_1 , N_2 , N_1O_1 and N_2O_1 were determined.

The constituents and relative abundances of polarized macromolecular compounds are similar in non-hydrocarbons and asphaltenes. Class N_1 is the most abundant, and Class N_2 is much higher in asphaltenes. Molecular distributions are somewhat discrete. Class N_1 is generally lower in non-hydrocarbons, and high abundance is among C_{19} – C_{30}

with the highest abundant $\text{C}_{23}\text{H}_{18}\text{N}_1$. Wider distribution in asphaltenes is C_{20} – C_{35} with the highest compound $\text{C}_{25}\text{H}_{18}\text{N}_1$. In non-hydrocarbons, Class O_2 typically includes lipid acids $\text{C}_{16}\text{H}_{32}\text{O}_2$ and $\text{C}_{18}\text{H}_{36}\text{O}_2$, and in asphaltenes $\text{C}_{28}\text{H}_{26}\text{O}_2$ are also included (see Figs. 3 and 4).

3.2 Polarized macromolecular compounds in marine oils

Typical oils from the Basituo Oilfield and Hetianhe River Gasfield have been suggested to be derived from marine source rocks and proved to be mature to highly mature (Cui et al., 2011, 2013). Class O_2 is dominant in abundance, while compound N_1 is relatively low as compared to BK4 and Ma4 oils (Fig. 5).

Oils from Well Qu1 are different from those from BK4 and Ma4. High Pr/Ph, high C_{24} tetracyclic terpane, high C_{29} steranes and high β -carotane are all indicative signs for contributions from territorial source rocks, and the isotopic data provide information about marine contributions. We are inclined to get the mixture source for oils from Qu1 (Cui et al., 2011). FT-ICR MS analysis presents the dominant peak which indicates Class N_1 , and relatively high compound O_2 can also be shown in oils from Qu1. The mixed sources for oils from Qu1 are concurred with the data from biomarkers (Fig. 6).

Nitrogen compounds in marine algae are higher than those in territorial high plants. Proteins of abundant nitrogen compounds are higher in aquatic organisms and animals (Meyers and Ishiwatari, 1993; Meyers, 1994; Dean, 1999). While in the early diagenesis, organic nitrogen compounds are mainly transformed into N_2 and/or NH_3 in the process of microorganism and mineral catalysis. Only a small proportion of nitrogen compounds is saved in kerogens and become stable components (Chen et al., 2002). Marine oils are relatively abundant in nitrogen proteins. But in the typical oil comparison of marine and

territorial sources, compounds of class O₂ are relatively abundant in marine oils and compounds of class N₁ are relatively high in territorial oils. Surely, when lacustrine depositions in territorial layers are dominant, the quality of organic matters also is altered. For in this kind of environment, lipids and proteins from lacustrine organisms have led to the enhancement of organic nitrogen. In addition, a remarkable increase has been approved in biodegradation of class O₂ (Hughes et al., 2007; Kim et al., 2005). In this analysis, no strong biodegradation evidence has ever been developed from these selected oils (UCM lump absent in GC). Under similar maturity and biodegradation, on the FT-ICR MS spectra, marine oils are dominant in class O₂, while territorial oils are dominant in class N₁.

3.3 Maturity effect on polarized macromolecular compounds

The maturity of hydrocarbons generating from source rock is increasingly becoming higher with the thermal evolution. But for most basins, especially in the superimposed basins, multiple-layer sources are developed with similar maturities. The mixed oils are ubiquitous but rare for the collecting and sampling from low mature, mature and high mature oils. Our goal is to recognize the maturity effect on the polarized macromolecular compounds. We selected the

lower mature shales of Bed Chang 7 in the Yangchang Formation of the Ordos Basin. Diagenesis physical simulation experiments were carried out on the samples which have been guaranteed in the same kerogen type and biodegradation level. Shale oils retained in shales with various maturities were detected. The simulation result showed that as the temperature and pressure go up, there exists an alteration trend in these shale oils. One of the apparent trends is the dominant class transformation from N₁ to O₂.

In the lower temperature stage, polar compounds were dominated by N₁ compounds. While when the temperature rose to 450°C, compounds of class O₂ increased and those of class N₁ decreased. Calculating the relative abundances of compounds of class N₁, compounds of class N/(compounds of class N and those of class O), $N_1/(O_2+N_1)$, $N_1/(O_3+N_1)$, $N_1/(N_1O_1+N_1O_2)$, we are coming to hold that these indicators are well related with maturities (temperatures), and can be recognized as an efficient index for maturity evaluation. When the maturity goes up, the value of indicators will come down (Figs. 7 and 8). The N and O elements decreased during the maturity evolution. Molecular compositions of shale oils of different maturities (temperatures) are related with N and O bonding and bond energy. C-O bond energy is about 235–256 kcal/mol and C-N bond energy is about 150–178 kcal/mol, so class N/class O tends to decrease in the process of source rock thermal evolution.

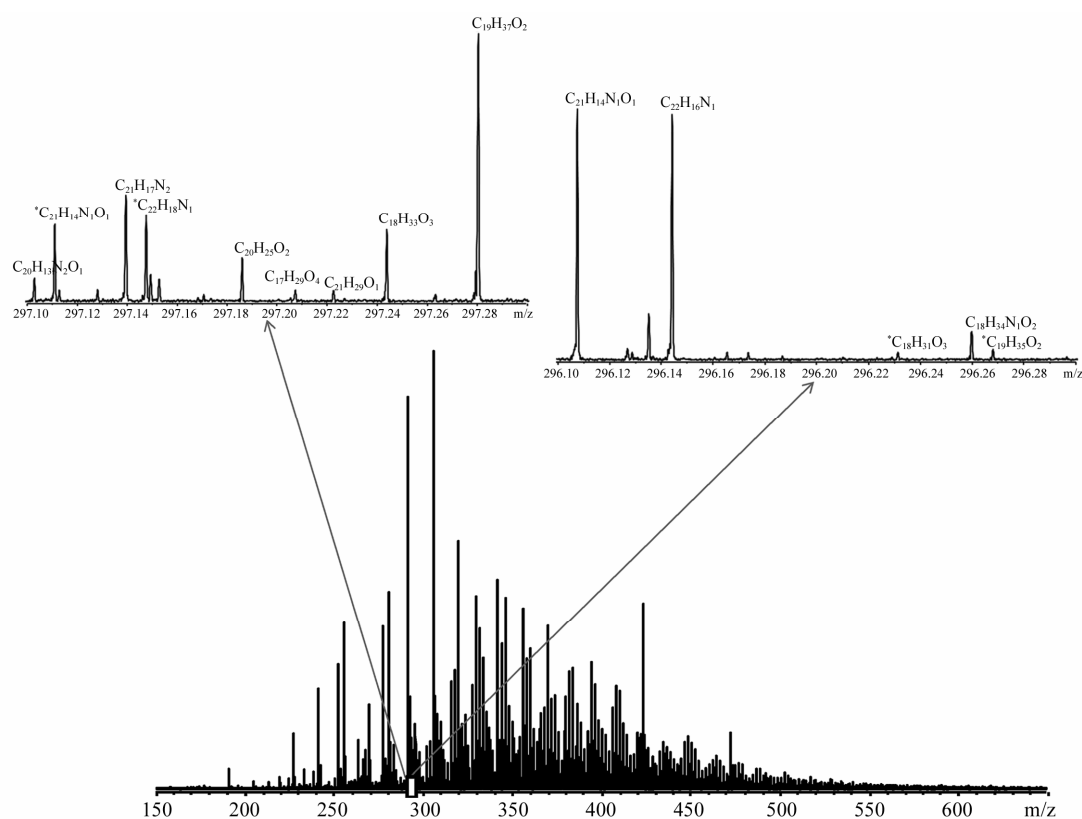


Fig. 2. Mass spectra and compounds identification of negative ion ESI-FT-ICR MS for lacustrine oil from Well S105, Ordos Basin.

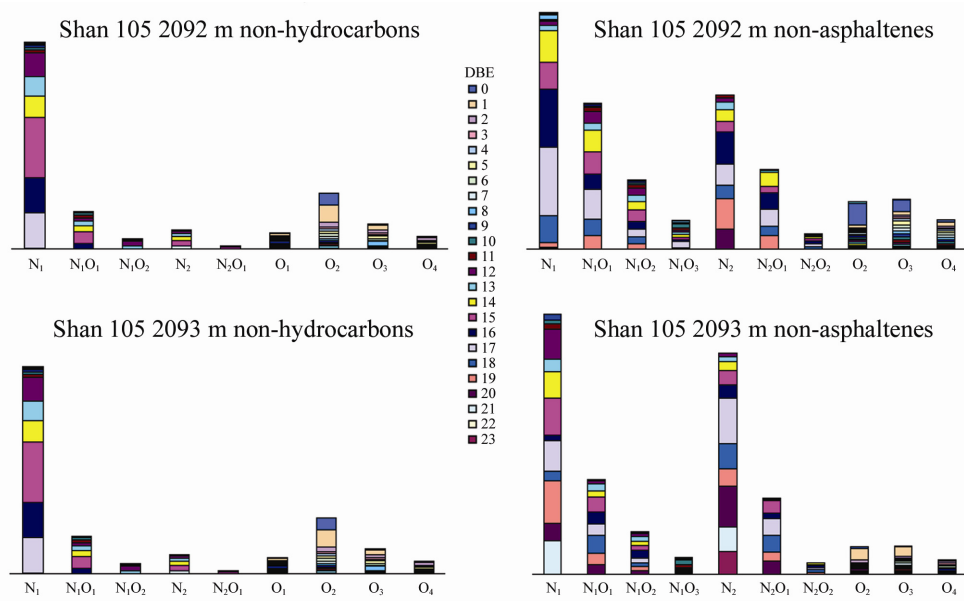


Fig. 3. Comparison of polarized macromolecular compounds between non-hydrocarbons and asphaltenes in territorial oils from different depths of the Ordos Lacustrine Basin.

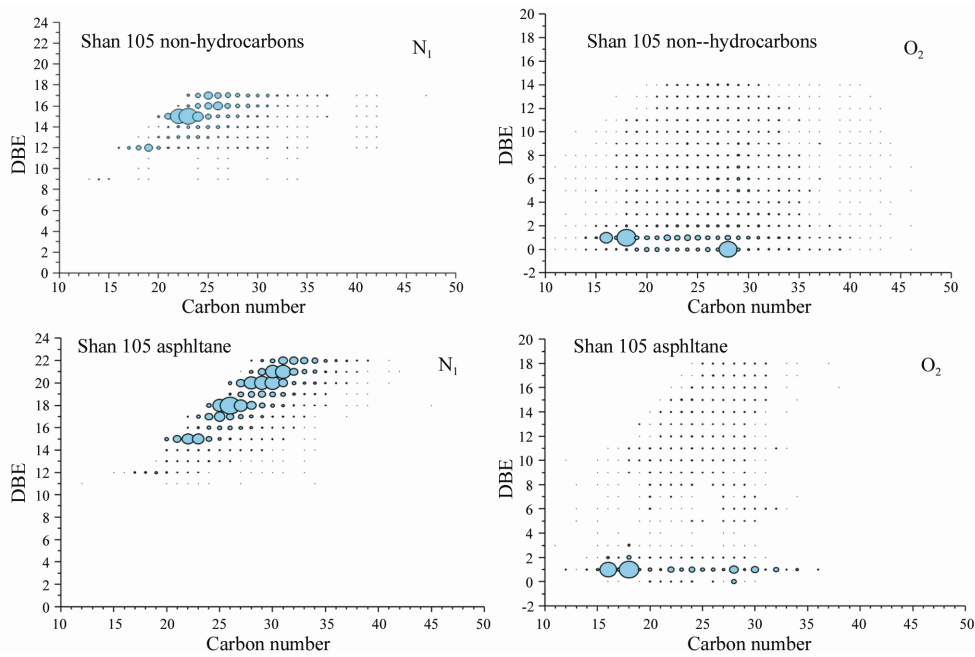


Fig. 4. Correlation plot for DBE and carbon number of main polarized molecular types in non-hydrocarbons and asphaltenes in Ordos oils (PS: Size of the circle for relative abundance).

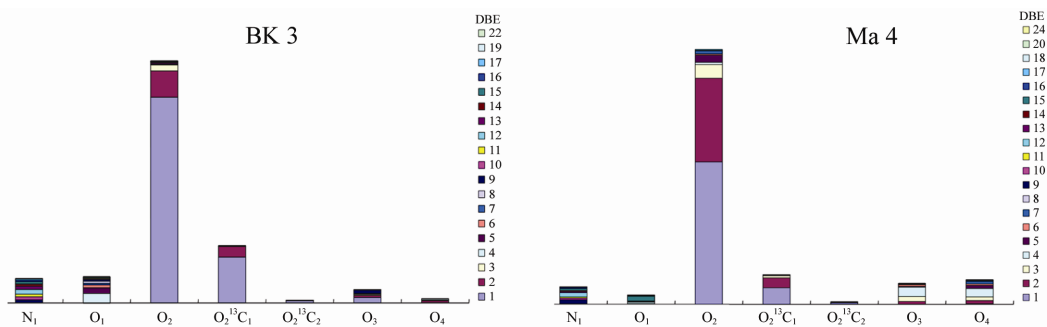


Fig. 5. Comparison of the classes of polarized macromolecular compounds in marine oils from the Tarim Basin.

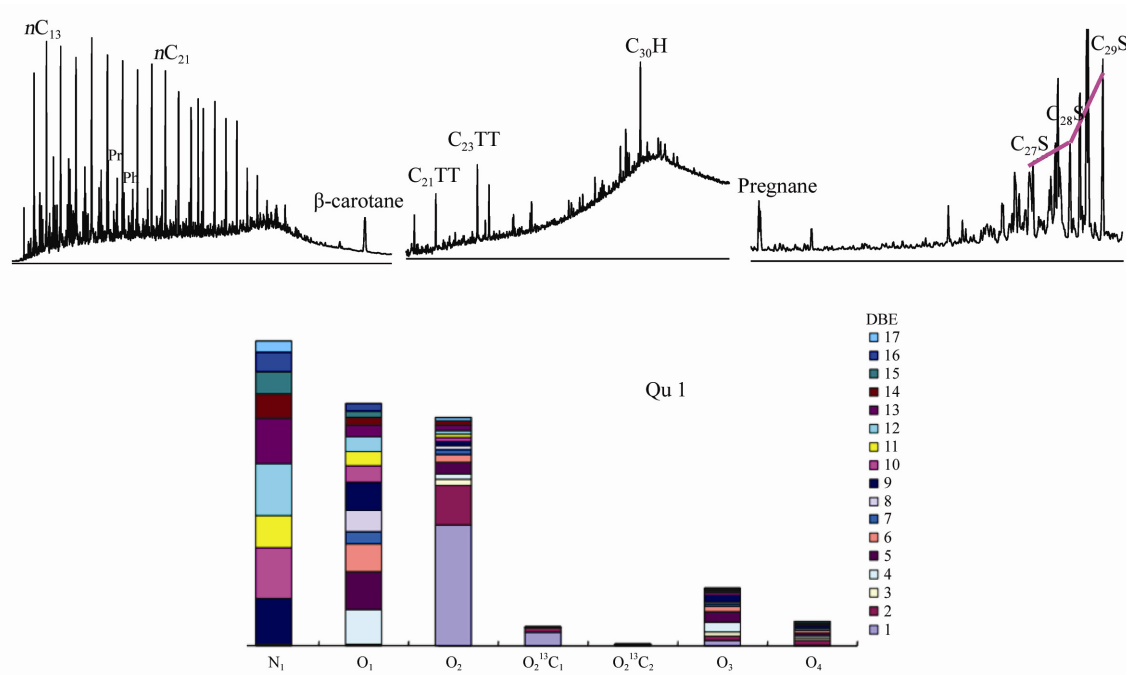


Fig. 6. TIC, typical m/z 217, m/z 191 in the saturated fraction and polarized macromolecular compounds in crude oils from Well Qu 1 in the Tarim Basin.

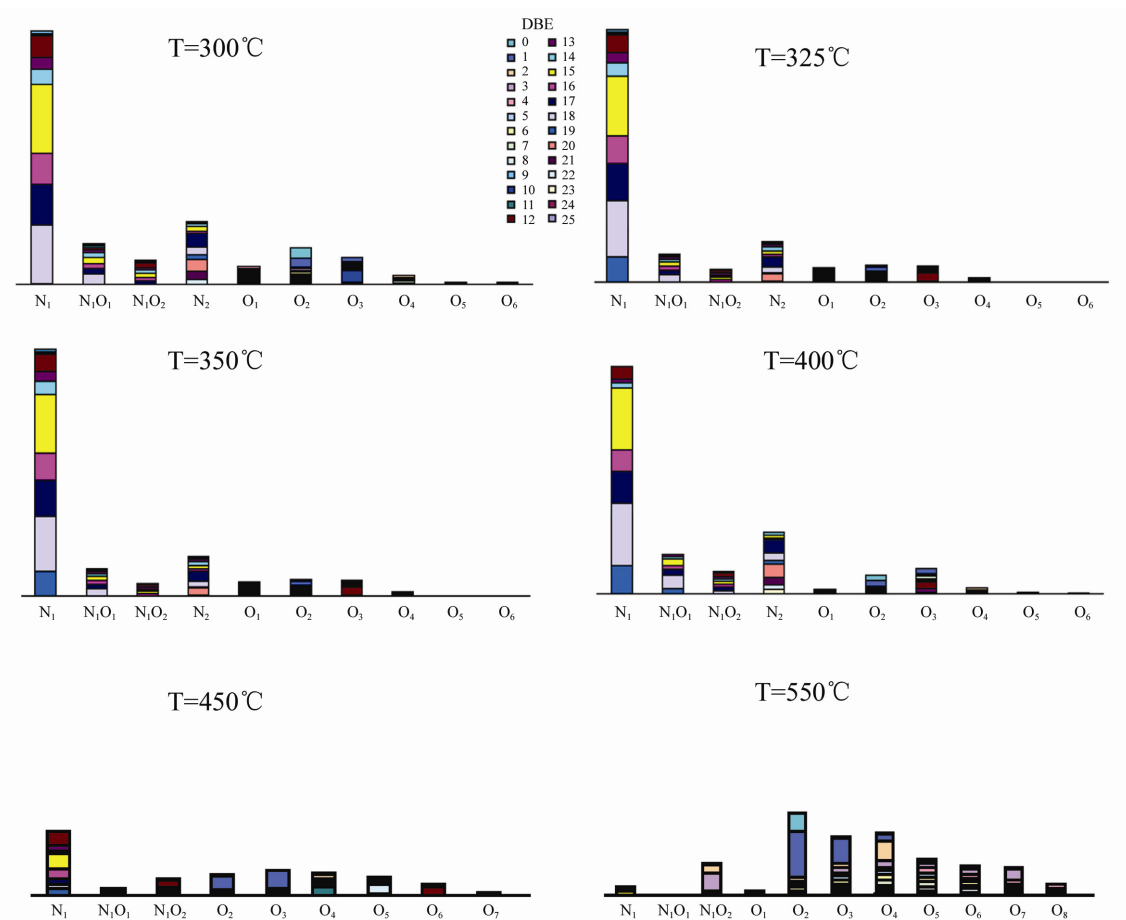


Fig. 7. Comparison of the classes of polarized macromolecular compounds in shale oils of various temperatures with samples taken from the Ordos Basin.

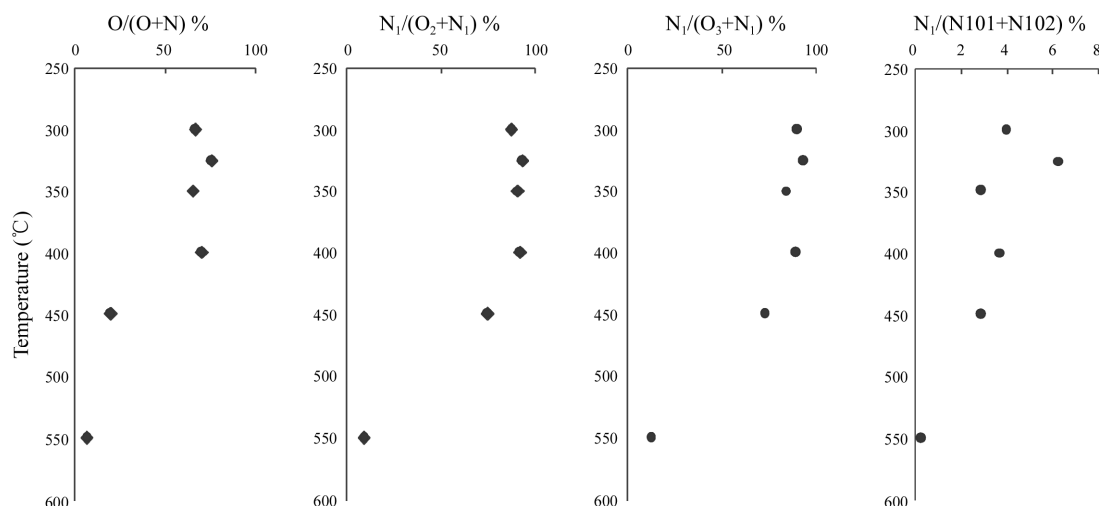


Fig. 8. Proportional profile of the polarized macromolecular compounds and temperatures for low mature shales (for diagenesis physical simulation) in the Ordos Basin.

4 Conclusions

The main peaks of the compounds of classes N₁ and O₂ are important parameters for identifying the lacustrine oil and marine oil, respectively. Proportional figures between N₁- and O₂-class compounds are indicative of the mixed sources of oil in Well Qu1. Concurring with the regular biomarkers shows the accuracy and applicability of the indicators. The diagenesis physical simulation experiments showed that shale oils generated from the Ordos shales under various temperature and pressure conditions, showing that nitrogen compounds/(nitrogen compounds and oxygen compounds), e.g. N₁/(O₂+N₁), N₁/(O₃+N₁), N₁/(N₁O₁+N₁O₂) are proposed as the maturity indicators. This study on the polar macromolecular compounds is of significance for further shale oil accumulation mechanism study.

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