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Composition and distribution of NSO compounds in two different shales at the early maturity stage characterized by negative ion electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry

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Abstract

Gas chromatography/mass spectrometry (GC/MS) can only analyze volatile molecular compounds, and it has limitations when applied to determine the complex components of crude oils and hydrocarbon source rocks. Based on Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and GC/MS analyses, the molecular compositions of NSO compounds in extracts from the Permian Dalong Formation, Sichuan Basin and the Permian Lucaogou Formation, Junggar Basin in China were compared. Analyses of types of heteroatoms present (S_1, S_2, S_3, OS, OS_2, O_2S, NS, and NOS compounds) suggest that marine shales from the Dalong Formation are mainly composed of carboxylic acids (O_2 compounds) with a high abundance of fatty acids, indicating a marine phytoplankton organic source. However, lacustrine shales from the Lucaogou Formation are dominated by pyrrolic compounds (N_1 compounds) with abundant dibenzocarbazole. It suggests that the organic source materials may be derived from lower aquatic organisms and lacustrine algae. Overall, FT-ICR-MS has potential for applications in analyses and determination of depositional environments and organic sources in petroleum geology.

Keywords Fourier transform ion cyclotron resonance mass spectrometry · Dalong Formation · Lucaogou Formation · NSO compounds · Sedimentary environment

1 Introduction

Crude oils are composed of complex hydrocarbons and nonhydrocarbons. Traditionally, column chromatography is used to separate the aliphatic hydrocarbons, aromatics, resins, and asphaltenes. Aliphatic and aromatic hydrocarbons are then analyzed by gas chromatography (GC), GC–MS, and GC along with coupled tandem mass spectrometry. However, for nonhydrocarbons and bitumen with strong polarity and high molecular weights, it is difficult to analyze them systematically and comprehensively using these traditional methods. Although nitrogen, sulfur and oxygen (NSO) compounds are not predominant in crude oils, their distribution and composition greatly affect the characteristic of crude oils. For example, the amount of sulfur directly determines the quality of crude oils. Considering that the distribution and characteristics of NSO compounds are related to the source material, depositional environment and other factors thus the analysis of NSO

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compounds can help determine the formation, generation and evolution of petroleum (Wang 2002; Wang et al. 2004; Li et al. 2001).

Currently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is widely used to determine the differences of polar compounds in crude oils from different districts with various maturity and biodegradation degrees (Qian et al. 2001; Hughey et al. 2004, 2007). But the geological background of the source rock and biomarkers were not taken into consideration in many studies. Certain standards and indexes have not been proposed yet (Kim et al. 2005; Stanford et al. 2007). In addition, limited research concerning the differences among the NSO compounds from lacustrine shales and marine shales has been reported. This research is to investigate the NSO compounds of shale extracts from the Dalong Formation in the Sichuan Basin (Fu et al. 2010; Liang et al. 2009; Xia et al. 2010) and the Lucaogou Formation in the Junggar Basin, China (Zhao et al. 1994; Peng et al. 2011) using negative ion electrospray ionization (ESI) coupled with FT-ICR-MS, and compare their differences and similarities from analyses of the composition of the acidic and neutral nitrogen heteroatom compounds.

2 Samples and experimental methods

2.1 Samples

Marine shale from the Dalong Formation (Kushan Liang Section) in the Sichuan Basin is characterized by relatively high total organic carbon (TOC = 10.60%), type II_1 organic matter, and low maturity (R_o = 0.74%). However, the total organic carbon of lacustrine shale from the Dalong Formation (Dalongkou Section) in the southern part of the Junggar Basin is relatively lower than that of marine shale with a value of 7.82%. Lacustrine shale is in an early thermal stage (R_o = 0.78%) with type I organic matter (Table 1).

2.2 The method of GC–MS

Using the mass spectrometer (6890 N GC/5975 MSD developed by the company of Agilent), the chloroform bitumen "A" was analyzed by gas chromatography mass

spectrometry after Soxhlet extraction and rotational evaporation. The chromatographic conditions are 30 m × 0.25 mm × 0.25 μm, with conventional chromatographic column type of HP-5MS. The operating temperature for the pulse-splitless inlet was 300 °C using constant current mode, in which the flow rate was 1.0 mL/min, the temperature program was at 50, 20 °C/min to 100 °C, 3 °C/min to 310 °C and the constant temperature should be held for 21 min. MS conditions: using electron impact (EI) ionization mode, with an ionization energy of 70 eV, a filament current of 34.6 mA scan mode full scan (50–550 Da) ion scanning, the temperature of ions is 230 °C and the temperature of the four stage pole is 150 °C.

2.3 The experiments and analysis for ESI FT-ICR-MS

Bitumen "A" was extracted by Soxhlet extraction and rotary evaporation. Then, we dissolved 10 mg bitumen "A" in 1 mL of toluene, diluted with toluene/methanol (1:3) to give a final content of 0.2 mg/mL, and added 1 μL of ammonia (Lu et al. 2013; Shi et al. 2010). Finally, the solution was shaken gently to stimulate the acidic compounds and neutral nitrogen to generate the ion $[M - H]^-$.

The samples were analyzed using a Bruker Apex-ultra FT-ICR-MS equipped with a Bruker 9.4 T actively shielded superconducting magnet. The sample solution was infused via an Apollo IV electrospray source at 180 μL/h using a syringe pump. The operating conditions for negative ion formation were − 3.5 kV emitter voltage, − 4.0 kV capillary column front end voltage, and − 4.0 kV capillary column end voltage. Ions were accumulated for 0.01 s in a hexapole. The quadrupole (Q1) was optimized to obtain a broad range for ion transfers. An argon-filled hexapole collision cell was operated at 5 MHz and 400 Vp-p RF amplitude, in which ions accumulated for 0.02 s. The extraction period for ions from the hexapole to the ICR cell was set to 1.2 ms. The excitation was attenuated at 12 dB and was used to excite ions over the range of 110–800 Da. 128 scans were used to enhance the signal-to-noise ratio and the dynamic range.

We used software from the China University of Petroleum (Beijing) to calculate the combination of various molecular compounds C, H, O, N and S atoms, and the

Table 1 Basic geochemical data for TOC, vitrinite reflectance, and Rock–Eval results of the Dalong and Lucaogou Formations

Sample	Formation	Bitumen "A", %	TOC, %	S1 + S2, mg/g	HI, %	T_{max}, °C	R_o, %	Pr/Ph	Type
1	Dalong	0.51	10.6	29.91	305	442	0.74	0.89	II_1
2	Lucaogou	0.41	7.82	41.18	502	448	0.78	1.13	I

molecular mass peak corresponding to the type (the subscript of $C_cH_hO_oN_nS_s$ represented the number of different atoms). All types of molecular compounds in the sample would be given with DBE (Double Band Equivalence) which is equal to the number of molecular structure of naphthenic rings added with the number of double bands. The formula for calculating DBE is $DBE = c - h/2 + n/2 + 1$ (Kendrick 1963; Liu et al. 2010; Shi et al. 2013).

3 Results and discussion

3.1 The results of GC–MS

The Dalong Formation shale has a large content of n-alkanes with the highest content of nC_{15}. The pristine/phytane ratio is 0.89, while the abundance of gammacerane is relatively low (Fig. 1) with a ratio of 0.06 for the index of gammacerane (gammaceranes/C_{30-}αβhopanes), indicating a reducing environment. Ts and C_{29}Ts are also in low abundance, but the concentrations of Tm and C_{29} hopanes are fairly high. The Ts/(Ts + Tm) and C_{29}Ts/C_{29} hopanes ratios are 0.17 and 0.09, respectively. In addition, as the number of carbon atoms increases, the abundance of C_{31}^+ hopanes increase, too. The abundances of pregnanes and homopregnanes are relative high, while the (pregnanes + homopregnanes)/total regular steranes ratio is 0.18. The relative abundances of the C_{28} and C_{29} steranes are higher than the C_{27} steranes (the relative abundances of C_{28} steranes are 17.1%, C_{27} steranes are 33.1%, and C_{29} steranes are 49.9%), so the compositional fingerprint of C_{27}-C_{28}-C_{29} steranes is V-shaped (Fig. 1). The index of maturity 20S/(C_{29}20S + C_{29}20R) of C_{29} steranes is 0.53 with the index of C_{29}ββ/(C_{29-}ββ + C_{29}αα) is 0.45. And C_{31} sublimation hopanes 22S/(22S + 22R) is 0.60. These values indicate the shales from the Dalong Formation are mature (Luo et al., 2016).

The shale extracts from the Permian Lucaogou Formation have a severe loss of n-alkanes, while the abundances of pristine and phytane are higher than the C_{17} and C_{18} alkanes. This indicates the Lucaogou Formation suffered slight biodegradation in the early history of deposition or in the diagenesis stage (Bao 1996). The total ion chromatogram (TIC) shows that a relatively higher abundance of pentacyclic triterpenoids, while the main peak is C_{30} hopanes. As the number of carbon atoms increases, the abundance of C_{31}^+ hopanes decline. The pristine/phytane ratio is 1.02, and the abundance of β-carotanes is high too. But the gammaceranes have a moderate abundance (Fig. 1) with a ratio of 0.14, indicating a reducing depositional environment. The abundances of Ts and C_{29}Ts are relative low, but Tm and C_{29} hopanes are higher, which is similar to the Dalong Formation. The ratio of Ts/(Ts + Tm) is 0.12, while the C_{29}Ts/C_{29} hopanes is 0.08. The abundance of pregnanes and homopregnanes is also high, with the (pregnanes + homopregnanes)/total regular steranes ratio is 0.19. The relative abundances of C_{27} steranes are lower than the amount of C_{28} and C_{29} steranes (the relative abundance of C_{27} sterane are 17.0%, the C_{28} sterane are 36.1%, and the C_{29} steranes are 46.9%), so the compositional fingerprint of C_{27}–C_{28}–C_{29} steranes is line-shaped (Fig. 1). The index of maturity 20S/(C_{29}20S + C_{29}20R) of C_{29} steranes is 0.48, and C_{29}ββ/(C_{29}ββ + C_{29}αα) is 0.52. And C_{31} homopregnanes 22S/(22S + 22R) ratio is 0.48,
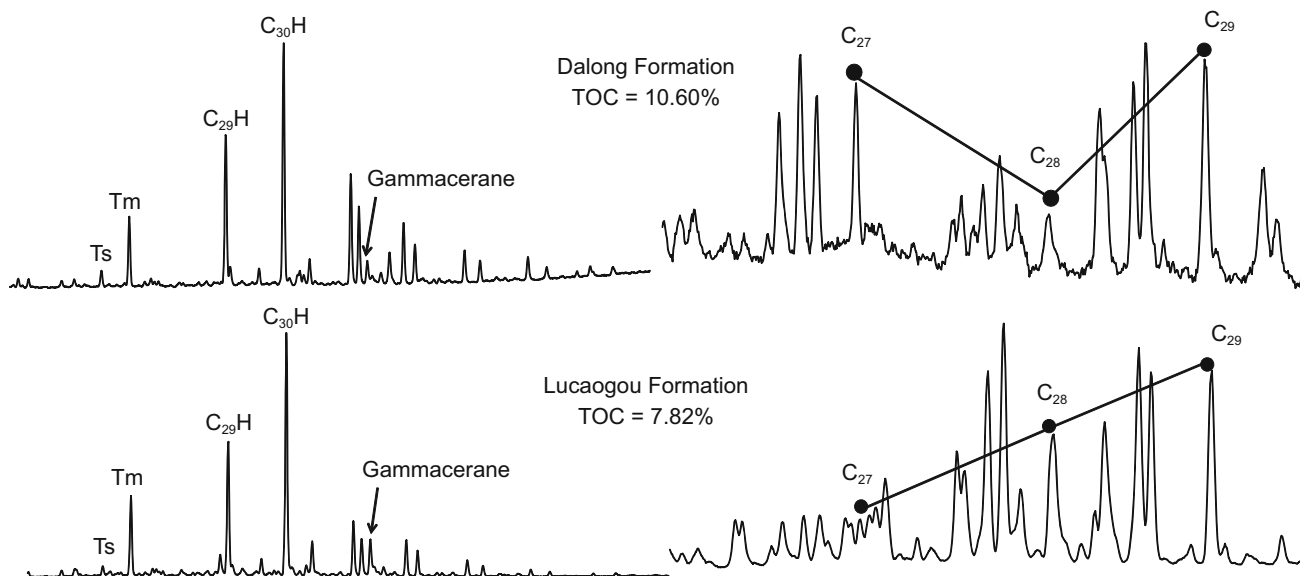

Fig. 1 Mass chromatogram segments (m/z = 191 and m/z = 217) for the pentacyclic triterpenoids (left) and steranes (right) of the Dalong Formation and the Lucaogou Formation

indicates the Lucaogou Formation is also mature (Luo et al. 2016, 2017).

The above analyses show that the abundance of organic material is high both in the Dalong and Lucaogou Formations. The types of organic material are II_1 and I, and both of them are at the early stage of maturity, indicating the two formations are very good source rocks. However, as for the biomarkers, there are several differences: the Dalong Formation has low abundances of gammacerane, pristine/phytane ratio, C_{28} steranes, and absent of β-carotane; while the Lucaogou Formation has higher abundances of these four biomarkers.

3.2 Distribution of heteroatoms in the extraction of two different source rocks

The broadband negative ion ESI FT-ICR mass spectrograms show the distributions of different molecular types from the Dalong and Lucaogou Formations. Figure 2 shows that the abscissa is m/z with continuous mass spectra peaks It also shows the CG (center of mass) is around $m/z = 400$. The abscissa also represents the distribution of the acidic compounds because the negative ion ESI only ionizes the $[M - H]^-$. Figure 2 indicates that the characteristics of the two mass spectrograms are different. The mass

spectrogram of the extraction from the Dalong Formation is ordinary, and there are a series of mass spectra peaks with adjacent mass number of 14 that distribute continuously to an odd predominance. The mass spectrogram of the Lucaogou Formations is more complex.

Taking the $m/z = 382.10–382.40$ fragment of the spectrogram shown in Fig. 3 as an example, 7–8 mass spectrum peaks at the $\Delta(m/z) = 0.3$ can be detected. The NSO compounds of the two samples have significant differences, while the molecular composition of these NSO compounds can be confirmed through their accurate molecular weights (Table 2). There is little deviation from the theoretical molecular weight because of the high resolution. The measured molecular weights and the NSO compounds also have obvious differences between the extracts from marine shale and lacustrine shale. Characterizing the acidic compounds and neutral nitrogen compounds by negative ESI FT-ICR MS works well, it indicates that their diversity can be analyzed.

Figure 4 shows the distributions of different compounds classes for the two shales, which includes the types and the quantities of the NSO compounds. The marine shale of the Dalong Formation has many types of NSO compounds, such as N_1, N_1O_1, N_1O_2, N_1O_3, N_1O_4, $N_1O_1S_1$, O_1, O_2, and O_3. The O_2 compounds have the highest abundance, while
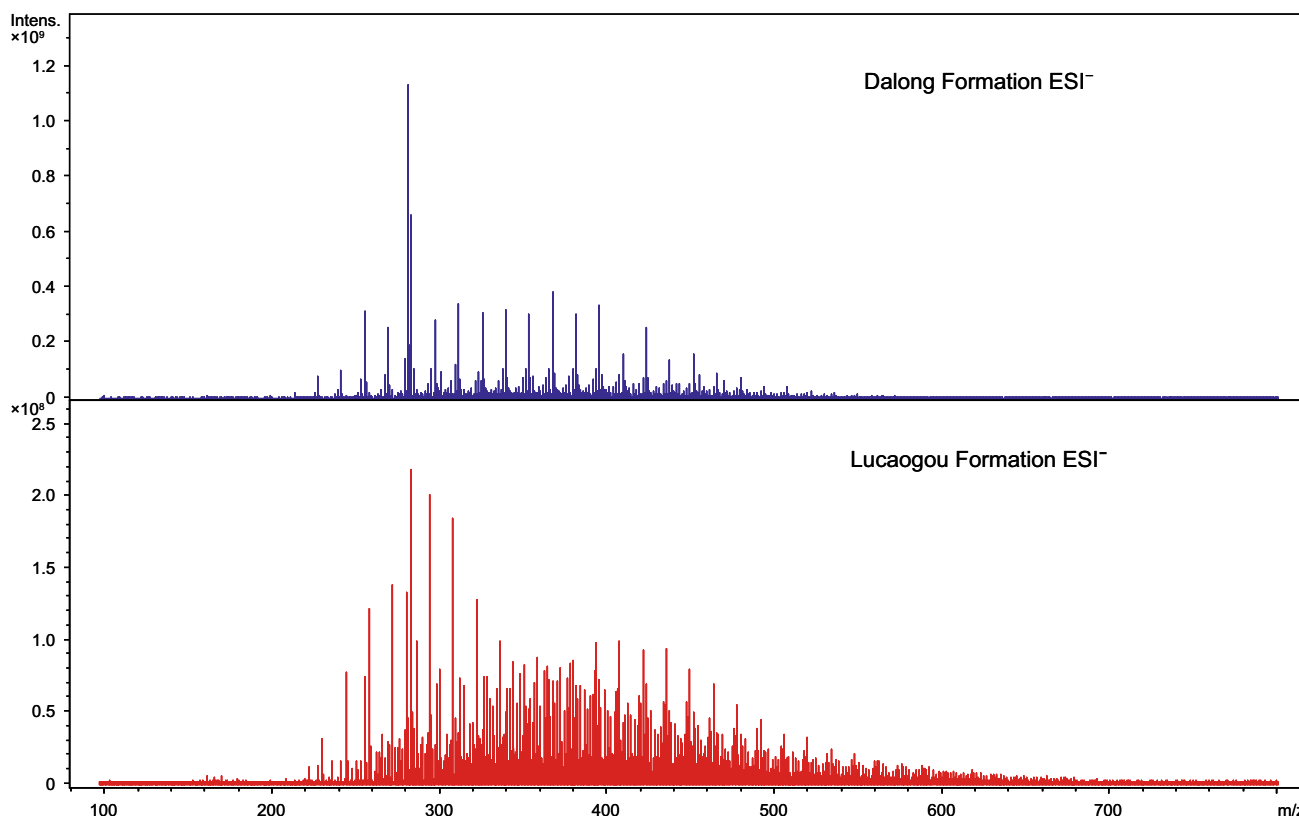

Fig. 2 Broadband negative ion ESI FT-ICR mass spectra of the two asphalts from different sources
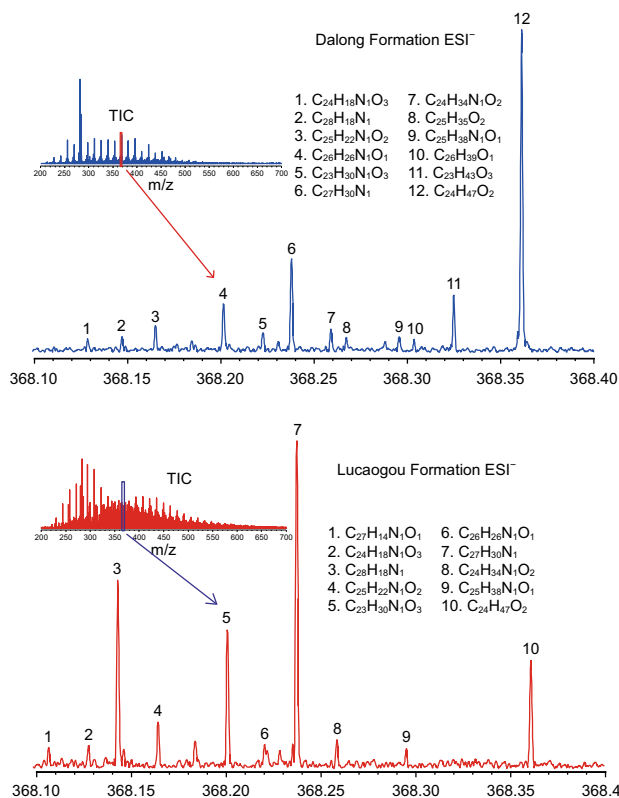
Fig. 3 Expanded negative ion ESI FT-ICR mass spectra of the two asphalts from different sources
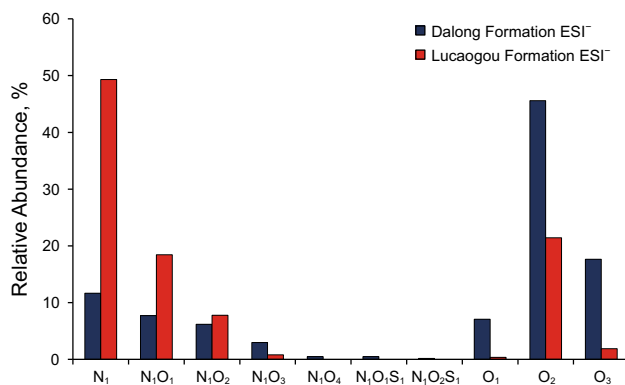

Fig. 4 Relative abundance of heteroatom classes assigned from the negative ion ESI FT-ICR mass spectra of the two asphalts

with the Lucaogou Formation, it also has many types of molecules such as N_1, N_1O_1, N_1O_2, N_1O_3, O_1, O_2, and O_3. The N_1 compounds have the most abundance, while the contents of N_1O_1 compounds and O_2 compounds are lower than N_1 compounds. The N_1O_3 compounds, O_1 compounds, and O_3 compounds have the lowest proportions. The shale of the Lucaogou Formation is lacking of N_1O_4 compounds and $N_1O_1S_1$ compounds.

3.3 Comparison of the shales

The analysis of the negative ion ESI FT-ICR MS demonstrates the marine and lacustrine source rocks have the same elemental compositions. The NSO compounds of the marine shale in Sichuan Basin and the lacustrine shale in Junggar Basin have obvious differences. For example, the

the contents of O_3 compounds and N_1 compounds are lower than O_2 compounds, with the lowest proportions of the N_1O_4 compounds and $N_1O_1S_1$ compounds. Compared

Table 2 Data for the broadband negative ion ESI FT-ICR mass spectra between m/z = 382.10–382.40 of the two asphalts from different sources

Formation	Serial number	Molecular formula	Theoretical value	Measured value	Abundance	ppm
Dalong Formation	1	$C_{25}H_{20}NO_3$	382.14	382.15	5,159,845	0.40
	2	$C_{26}H_{24}NO_2$	382.18	382.18	10,906,558	0.44
	3	$C_{23}H_{28}NO_2S_1$	382.18	382.18	2,651,072	0.12
	4	$C_{27}H_{28}NO$	382.22	382.22	16,096,214	0.43
	5	$C_{24}H_{32}NO_3$	382.24	382.24	3,854,309	0.24
	6	$C_{28}H_{20}N$	382.25	382.25	31,706,095	0.39
	7	$C_{25}H_{36}NO_2$	382.28	382.28	6,255,613	0.15
	8	$C_{26}H_{40}NO$	382.31	382.31	3,687,445	0.53
Lucaogou Formation	1	$C_{28}H_{16}NO$	382.12	382.12	11,853,644	0.30
	2	$C_{25}H_{20}NO_3$	382.14	382.14	2,628,444	0.07
	3	$C_{29}H_{20}N$	382.16	382.16	38,897,511	0.23
	4	$C_{26}H_{24}NO_2$	382.18	382.18	9,322,359	0.36
	5	$C_{27}H_{28}NO$	382.22	382.22	21,886,866	0.32
	6	$C_{28}H_{32}N$	382.25	382.25	59,336,621	0.31
	7	$C_{25}H_{36}NO_2$	382.28	382.28	5,318,589	0.23
	8	$C_{26}H_{40}NO$	382.31	382.31	4,040,664	0.66

Dalong Formation has the highest abundance of O_2 compounds with the detected $N_1O_1S_1$ compounds which contain sulfur. The Lucaogou Formation has the highest abundance of N_1 compounds without S compounds, which indicates the marine shale has sulfur. Barrow et al. (2003), Stanford et al. (2007), Bae et al. (2010), and Li et al. (2013) studied oils and shale oils from different geological sources, and found that the composition and distribution of the NSO compounds varies from different source rocks and source oils. The following discussion is mainly based on two compound types (O_2 compounds and N_1 compounds), because the samples are rich in O_2 compounds or N_1 compounds (Fig. 4).

In negative-ion ESI, the neutral nitrogen compounds and the acids are ionized selectively, so the N_1 compounds and O_2 compounds are neutral nitrogen compounds and acidic compounds. The N_1 compounds contain pyrrole rings (Liu et al. 2014). The Dalong Formation has 11.7% of N_1 compounds and 45.6% of O_2 compounds; while the Lucaogou Formation has 49.3% of N_1 compounds and 21.4% of O_2 compounds. The geological nitrogen compounds are composed of amino acids, which originate from the sedimentary organic material reformed by diagenesis (Baxby et al. 1994). The main compositions of plankton and bacteria in the organic matter are protein (over 50%), while higher plants mainly contain lignin and cellulose with a content of protein of only 3%–10% (Zhu et al. 1997). Previous studies hold the view that the sedimentary environment has a predominant effect on the content of pyrroles, especially the neutral nitrogen compounds. They concluded that there are more pyrroles (nitrogen compounds) in salt lake and marine facies than in fresh water lacustrine environments (Zhu et al. 1997; Li et al. 1999). However, the results of this study differ from previous research. The source of organic material has an influence on the content of N_1 compounds. The sedimentary environment of the Dalong Formation is a platform environment, which contained silicon and phosphorus. There are many benthic macroalgae, nematothallus, and acritarchs (Liang et al. 2009) in this environment. The type of organic material in the Dalong Formation is II_1, which contains less protein. The sedimentary environment of the Lucaogou Formation is a deep or semi-deep lacustrine reducing environment, which cause that the type of organic material is I. Thus, the source material of the Lucaogou formation is lower aquatic organisms and phytoplankton, which contain lots of protein in the lacustrine reducing environment (Shen et al. 2015). Other studies concluded that the metabolisms of the micro-organisms need a lot of nitrogen compounds and that they can utilize inorganic nitrogen (Xiao et al. 2005). So the Lucaogou Formation is rich in pyrrolic nitrogen compounds, while the Dalong Formation is lacking them.

3.4 The causes of the differences

O_2 compounds with DBE = 1 are fatty acids, while O_2 compounds with DBE = 2–4 are naphthenic acids to tricyclic naphthenic acids. The main O_2 compounds of the Dalong Formation are fatty acids (DBE = 1) with an even number carbon preference, however, the naphthenic acids (DBE = 2, 3, 4) have lower contents. As for the Lucaogou Formation, the main O_2 compounds are naphthenic acids (DBE = 2), which also have an even number carbon preference; the fatty acids (DBE = 1) and bicyclic naphthenic acids (DBE = 3) have slightly lower contents than the naphthenic acids (Fig. 5). The fatty acids are one of the most abundant lipid markers, which are widely generated from marine phytoplankton (marine microalgae and macrophytes), zooplankton, terrestrial higher plants, and bacteria. However, the main source of fatty acids is marine microalgae. This is the reason that fatty acids in the Dalong Formation have the highest content of the O_2 compounds and the lowest content of naphthenic acids. The higher
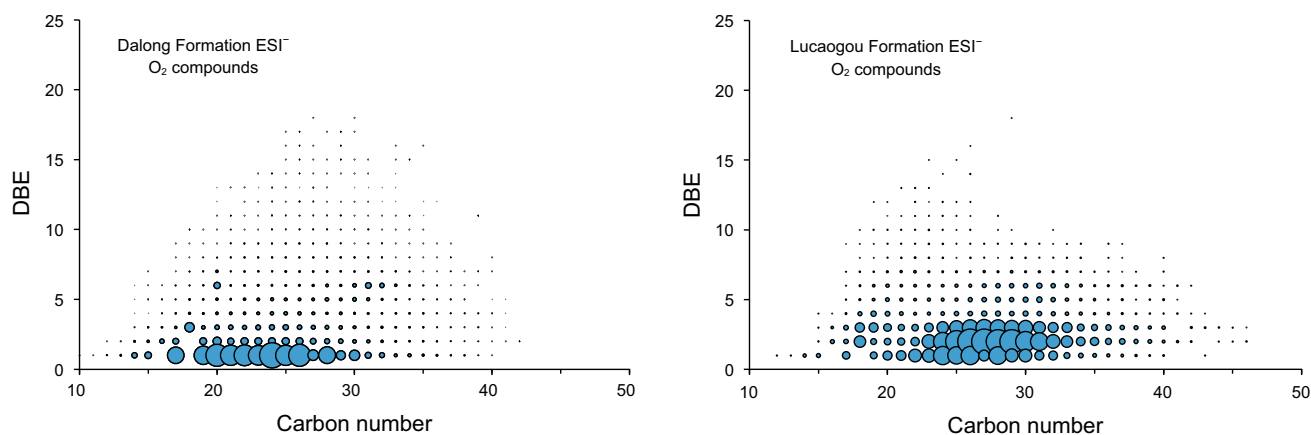

Fig. 5 Distribution of O_2 compounds in DBE and carbon number of the two asphalts from different sources
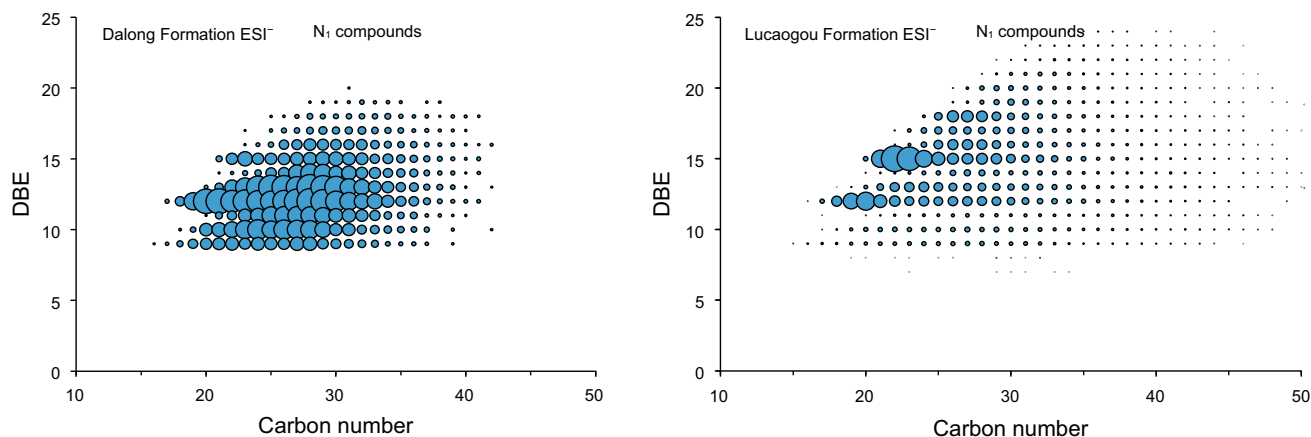
Fig. 6 Distribution of N_1 compounds in DBE and carbon number of the two asphalts from different sources

content of naphthenic acids in the Lucaogou Formation is caused by slight biodegradation (Dou et al. 2007; Jing et al. 2014).

N_1 compounds with DBE = 9 are carbazole compounds, while N_1 compounds with DBE = 12 are benzocarbazole compounds. As for, N_1 compounds with DBE = 15 are dibenzocarbazole compounds, N_1 compounds with the DBE = 10 and 13 are the benzocarbazole compounds and dibenzocarbazole compounds which have a naphthenic ring. The N_1 compounds in the Dalong Formation are rich in benzocarbazole compounds (DBE = 12), with naphthenic carbazole (DBE = 13). The carbazole (DBE = 9), alkylcarbazole (DBE = 10), and dibenzocarbazole (DBE = 15) compounds have similar contents. The Lucaogou Formation has the highest contents of benzocarbazole and dibenzocarbazole, while other N_1 compounds have lower contents (Fig. 6). Sumei Li holds the view that there may be few carbazole compounds in the marine sedimentary environment that cause the different distribution of DBE in the Dalong Formation and the Lucaogou Formation.

4 Conclusions

1. Based on the negative ESI FT-ICR MS technology, this research analyzed the distribution of the NSO compounds in two different sedimentary environments, and found that the asphalts from the Dalong Formation are composed mostly of carboxylic acids (O_2 compounds), especially fatty acids. The Lucaogou Formation asphalt is composed mostly of pyrrolic compounds, especially carbazole compounds (N_1 compounds).

2. The sedimentary environment of the Dalong Formation is a platform environment, which contains silicon and phosphorus. The main source material may be benthic macroalgae, nematothallus, and acritarchs, which contain less protein. The sedimentary environment of the Lucaogou Formation is a deep or semi-deep lacustrine reducing environment, in which the salinity of the water is quite high. The source material may be lower aquatic organisms and phytoplankton which contain abundant protein.

3. The technology of Fourier transform ion cyclotron resonance mass spectrometry works well for analyzing information about the sedimentary environment and the source material. In addition, this technology cannot only be used for the analysis of oils and oil fractions, but also for the analysis of source rocks and the extracts of source rocks.

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