

## Molecular characterization of sulfur compounds in some special sulfur-rich Chinese crude oils by FT-ICR MS

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Routine GC/MS analysis may apply to the volatilized Low-Molecular-Weight compounds in saturate and aromatic hydrocarbon fractions; thus, relative studies using this technique inevitably bring about some limitations on distribution of miscellaneous sulfur atom. In this article, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) with high resolution is employed to investigate the distribution of organic sulfur compounds (OSCs) in the crude oil typically derived from the Eocene carbonate-evaporite sediments with further chemical compositional characterization in molecular level by miscellaneous atomic type, carbon number, and double bond equivalent (DBE). A variety of miscellaneous atomic types with S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, OS, OS<sub>2</sub>, O<sub>2</sub>S, O<sub>2</sub>S<sub>2</sub>, NS, and NOS etc. (S<sub>1</sub> means those OSCs with one sulfur atom in a molecule) were identified in OSCs in these oil samples. High levels of alkyl thioether series compounds with one ring structure were presented mainly in the crude oil in the Jiangnan Basin whereas high amounts of benzothiophene, dibenzothiophene etc. compounds with higher values in DBE and carbon number range occurred in the sulfur-rich heavy oil in the Jinxian Sag. Although carbonate-evaporite sediments deposited in the saline lacustrine facies in the Eocene basin both occurred in the Jinxian Sag and Jiangnan Basin, obviously, they possess different chemical diagenetic pathway of sulfur under various microbial reactions, leading to diverse distributional characteristics on biomarkers, OSCs, and even different hydrocarbon generation mechanism of immature crude oil.

**ESI, FT-ICR MS, organic sulfur compounds, sulfur-rich oil, Jiangnan Basin, Jinxian Sag**

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Chemical compositional analysis of organic sulfur compounds (OSCs) as an important orientation in organic geochemistry has been developed in the past thirty years (Sinninghe Damsté et al., 1990). Hundreds of OSCs had been identified in crude oil and source rocks by GC and GC/MS techniques (Wang, 1993; Shen et al., 1998). Hereinto, some OSCs have typical biomarker characteristics (Song et al.,

2007; Lu et al., 2013) whilst dibenzothiophenes were used to study the maturity and migration of crude oil in subsurface (Shen et al., 1998; Li et al., 2005; Wang et al., 2005). Although many progresses have been made on the petroleum sulfur-containing compounds, which contain the majority of miscellaneous atomic compounds, overall cognition and knowledge, especially in the compositional information of macromolecular OSCs, were lacking due mainly to the following: the chemical compositions of OSCs in the crude oil were very complicated for the frequent occurrence of some

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other hetero-atoms in which molecular weight is much larger than the distribution ranges and structural types beyond conventional GC/MS analysis. GC/MS that is conventionally catered for analysis of hydrocarbons in saturate and aromatic fractions is hard to distinguish macromolecular OSCs, especially in more complicated petroleum substrate (e.g., polar NSO and asphaltene fractions). GC analysis is only appropriate for some volatilized low-molecular-weight compounds usually in saturate and aromatic hydrocarbon fractions.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) provides a novel technique with extra-high resolution and mass precision, which can achieve a complete separation of compounds with different elemental constituents within petroleum mass range (200–1000 Da) and further get an accurate calculation of the elemental (C, H, O, N, S) constituents, thus it realizes studying petroleum chemical compositions at molecular level (Shi et al., 2010a, 2010b; Liu et al., 2010a, 2010b). Recently, a new concept and research method of Petroleomics had been formed in the field of petroleum chemistry, which mainly studies the relationship between the molecular constituents and their physical, chemical properties, process performance etc. (Marshall et al., 2004; Rodgers et al., 2005), based on the elaborate characterization of the petroleum molecules at molecular level. Previous studies showed that through chemical methylation treatment, thioether, and thiophenic etc. OSCs in crude oil can be ionized for selective oxidation in the Electrospray Ionization (ESI) mode (Müller et al., 2005; Shi et al., 2010a, 2010b; Pan et al., 2010; Liu et al., 2010a, 2010b, 2011), or in the Atmospheric Pressure Photo-Ionization (APPI) mode (Purcell et al., 2007; Liu et al., 2010a, 2010b) in order to conduct FT-ICR MS analysis to characterize their distributions.

Methylated FT-ICR MS analysis on OSCs in oil was first conducted by Jan Andersson groups at University of Munich (Müller et al., 2005). Purcell et al. (2007) further compared the results in the APPI and ESI mode (Purcell et al., 2007) and showed that methylation pretreatment performed a relatively stronger selectivity on those OSCs with low DBE values and proved incapable on those OSCs with high DBE values. In fact, different ionization method on OSCs analysis cannot have the same results (Panda et al., 2009). Using model compounds, Shi et al. (2010a) evaluated the reaction selectivity and conversion rate of methylation method, and found that at least most OSCs in the middle distillate of crude oil can get high efficient conversion (Pan et al., 2010), which proved its rationality on OSCs analysis in heavy oil (Shi et al., 2010a).

The Eocene carbonate-evaporite sediments with typical gypsum facies occurred in the hypersaline lacustrine environment in the Jiangnan Basin and Jinxian Sag. For the abundant production of sulfur-rich heavy crude oil, many characteristic biomarkers in saturate hydrocarbon fractions and OSCs were identified and reported (Yang et al., 1983;

Sheng et al., 1986, 1988; Jiang, 1988; Zeng et al., 1989; Peng et al., 1989; Wang et al., 1989; Pan et al., 1988, 1991; Chen et al., 1991; Fu et al., 1991, 1992; Lin et al., 1993; Zhang et al., 2000; Bao et al., 2006, 2009; Liu et al., 2008; Wang et al., 2009; Chen et al., 2009; Lu et al., 2009), which revealed great disparity presented in the geochemical distributions (Bao et al., 2006) in the same geologic conditions. However, no further explanation has been done of these geochemical distributional differences. Regionally, sulfur was regarded as a very important factor influencing the diagenetic pathway of organic matter (Bao et al., 2006; Lu et al., 2011). Thus, in this study, the method of iodomethane methylation was applied to converting the OSCs into methylsulfonium salts by reacting with them in the presence of tetrafluoride boric silver, which can be under performed by ESI FT-ICR MS in order to analyze their molecular compositions and distributional characteristics and probe into their geochemical significance.

## 1 Samples and analysis

### 1.1 Samples

The crude oil samples in the Jinxian Sag were collected from wells of Zhao 7 (2280 m, Es<sub>4</sub>–Ek<sub>1</sub>) and Zhao 9 (2360.6–2390.0 m, Es<sub>4</sub>–Ek<sub>1</sub>). The oil in well Zhao 7 presented with a high density of 1.0830 kg/m<sup>3</sup>, high viscosity of 1879 mPa·S under 50°C, high sulfur content of 14.69%, and high percentage of asphaltene plus polar fractions (34.55%), which typically belong to sulfur-rich heavy oil. Thick stink in the oil indicated a high concentration of H<sub>2</sub>S gas. The crude oil in the Jiangnan Basin was sampled from various oilfields, including Wangchang (Wang 12-3, Wang 3 and Wang 21 wells), Zhongshi (Zhong 71 well), and Yajiao (Ya 10 well) oilfields, which occurred mainly in the 1st and 2nd members of Qianjiang Formation. The geological distribution information is listed in Table 1.

### 1.2 Methylation and pretreatment

All the analytical reagents include 1,2-dichloroethane, dichloromethane (DCM), iodomethane, tetrafluoride boric silver, *n*-hexane, toluene and methanol.

Three portions of oil samples with approximately 100 mg were weighed and methylated for three times. Each time for methylation, 2 mL dichloroethane was used to dilute the oil samples, then 50 μL iodomethane and 2 mL tetrafluoride boric silver dissolved in dichloromethane (0.5 mol/L) were added into for ultrasonic vibration until evenly, and after that it was held from light for 24 h under room temperature.

The silver iodide precipitates were eliminated from the centrifuged solution, then *n*-hexane was used for extraction, and solid methylsulfonium salts came out, which were dissolved with the oil samples in DCM. Then it was diluted by toluene-methanol (1:1, v/v) into 0.02 and 0.5 g/L, and after

**Table 1** Distribution information for the sulfur-rich heavy oil in the Jinxian Sag and Jiangnan Basin in China

Sample No.	type	Region	Well name	Depth (m)	Formation
1#	oil	Jinxian Sag	Zhao 7	2280.0	Es <sub>4</sub> -Ek <sub>1</sub>
2#	oil	Jinxian Sag	Zhao 9	2360.6–2390.0	Es <sub>4</sub> -Ek <sub>1</sub>
3#	oil	Jiangnan Basin	Wang 12-3	1165.0–1177.4	Eq <sub>2</sub>
4#	oil	Jiangnan Basin	Wang 3	761.1–784.3	Eq <sub>1</sub>
5#	oil	Jiangnan Basin	Zhong 71	1248.4–1258.4	Eq <sub>2</sub>
6#	oil	Jiangnan Basin	Wang 21	1371.0	Eq <sub>2</sub>
7#	oil	Jiangnan Basin	Y10	901.0–1082.6	Eq <sub>2</sub>

that gently shaken for uniformity and prepared for the ESI FT-ICR MS analysis.

### 1.3 Mass spectral analysis and data processing

The Apex-Ultra 9.4T type instrument (American Bruker Company) was used for FT-ICR MS analysis under the positive ion mode with ESI ionization source. The samples were injected with a velocity of 180  $\mu\text{L}/\text{h}$  under the  $-2.5$  kV nozzle voltage. The electronic voltages for the capillary inlet and export were  $-3.0$  kV and 320 V, respectively. The transfer parameters for quadrupole Q1 were optimized at  $m/z$  150. The radio frequency for the ion store pool was 5 MHz under 400 Vpp. The impact pool was set with a rate of argon flow of 0.3 L/h under the energy of  $-1.5$  eV and with 1 s of collect time. The ions were led into analytic pool within 1.1 ms. The mass range should be in range of 150–700 Da with a 4 M sampling numbers. The chromatogram was folded for 128 times in order to enhance the signal-to-noise performance.

The mass calibration for the instrument was performed through the response of alkyl dibenzothiophene series compounds in real samples before and after the signal collection. All the mass spectral peaks with a signal-to-noise ratio larger than 6 were gathered into the Excel data sheet. The corresponded molecular compositions for the target compounds were calculated by the data processing software whose calculation method was described in detail in the references (Shi et al., 2008, 2010b, 2013).

## 2 Results and discussion

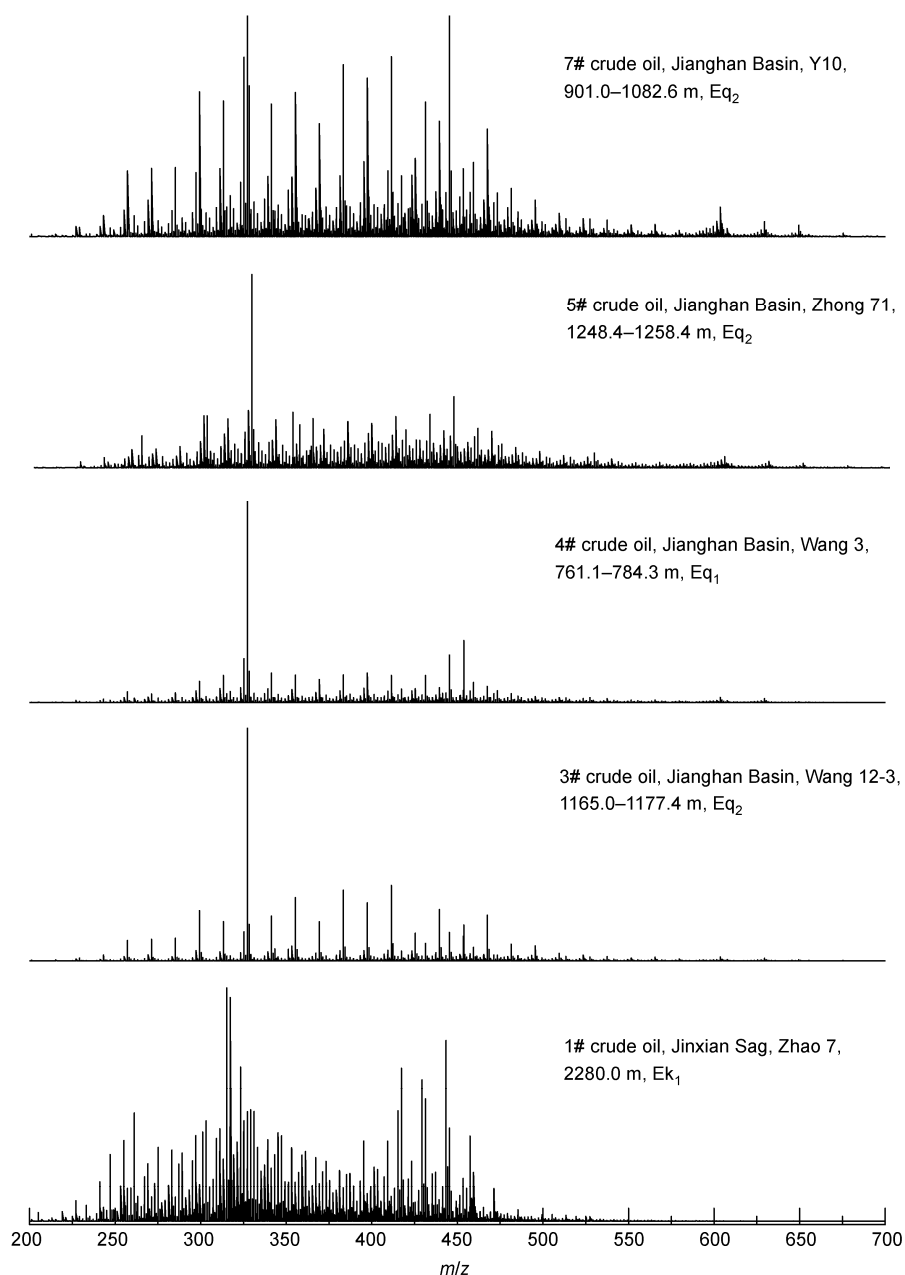
### 2.1 Chemical compositions and distributions for the OSCs

Chromatograms of the methylsulfonium salts by the ESI-FT ICRMS analysis for the sulfur-rich heavy oil were shown in Figure 1, in which the mass was in the range of  $m/z$  200–550. It is obvious that they are remarkably different for oil in these two regions. Very complicated chromatograms with bimodal distribution presented in oil of Zhao 7 well in the Jinxian Sag whereas relatively simple chromatograms with

a continuous series of peaks within 14 discrepancy between adjacent mass numbers occurred in the oil in the Jiangnan Basin, especially with certain odd-even predominance.

Very high resolution ratio in FT-ICR MS analysis can be illustrated by the factor that its width can achieve more than 200 m if the chromatogram expanded to an extent of recognizing every mass spectral peak by human eyes. In Figure 2, chromatograms for positive-ion ESI FT-ICR mass spectra for the methylsulfonium salts of crude oil are partially enlarged in a narrow range of  $m/z$  397.1–397.5. Again, very complicated chromatogram showed in oil from Zhao 7 well in the Jinxian Sag. Almost 20 peaks presented in the narrow range of mass number no more than 0.3 Da and they are all identified as OSCs. For example, because the compound detected in the mass spectrum corresponded to the ion after protonation of methylsulfonium salts, thus, the climax peak labeled as  $\text{C}_{27}\text{H}_{41}\text{S}$  should be originally with a molecular formula of  $\text{C}_{26}\text{H}_{38}\text{S}$ . If we use  $\text{S}_1$  to indicate those hetero-atom compounds with one sulfur in its molecule, the  $\text{S}_1$  class compounds identified at  $m/z$  397 also include  $\text{C}_{28}\text{H}_{29}\text{S}$  and  $\text{C}_{26}\text{H}_{53}\text{S}$ . These  $\text{S}_1$  class compounds have an identical integer molecular mass with expression of accurate discrepancy between neighboring peaks that equals  $\text{CH}_2$  (14). Similarly, those compounds with two ( $\text{S}_2$ ) or three ( $\text{S}_3$ ) sulfur atoms in one molecule occurred with relative abundance in all oil samples. Meanwhile, oxygen-bearing OSCs with  $\text{OS}_2$  ( $\text{C}_{24}\text{H}_{29}\text{OS}_2$ ,  $\text{C}_{23}\text{H}_{41}\text{OS}_2$ ) and  $\text{OS}$  ( $\text{C}_{27}\text{H}_{25}\text{OS}$ ,  $\text{C}_{26}\text{H}_{37}\text{OS}$ ) group can be identified in all oil samples. According to the accurate mass values, how many numbers of  $^{13}\text{C}$  in a molecule can even be calculated. Of course, the occurrence of these stable isotopes will seriously impact the identification of compounds if resolution ratio of mass spectrum is not high enough in the distinction of heavy carbon isotopes.

Relatively high abundance of  $\text{C}_{26}\text{H}_{53}\text{S}$  presented in the oil in the Jiangnan Basin. Theoretically, those occurrences of peak compounds with very high concentrations will restrain the response of other compounds and lead to a less detection of those peaks with a low abundance, since a dynamic range of approximately  $10^3$  existed in the mass spectra instrument. Slightly complicated chromatograms showed in the oil in Zhong 71 well, which only illustrated the relative abundance rather than the absolute concentrations of OSCs.



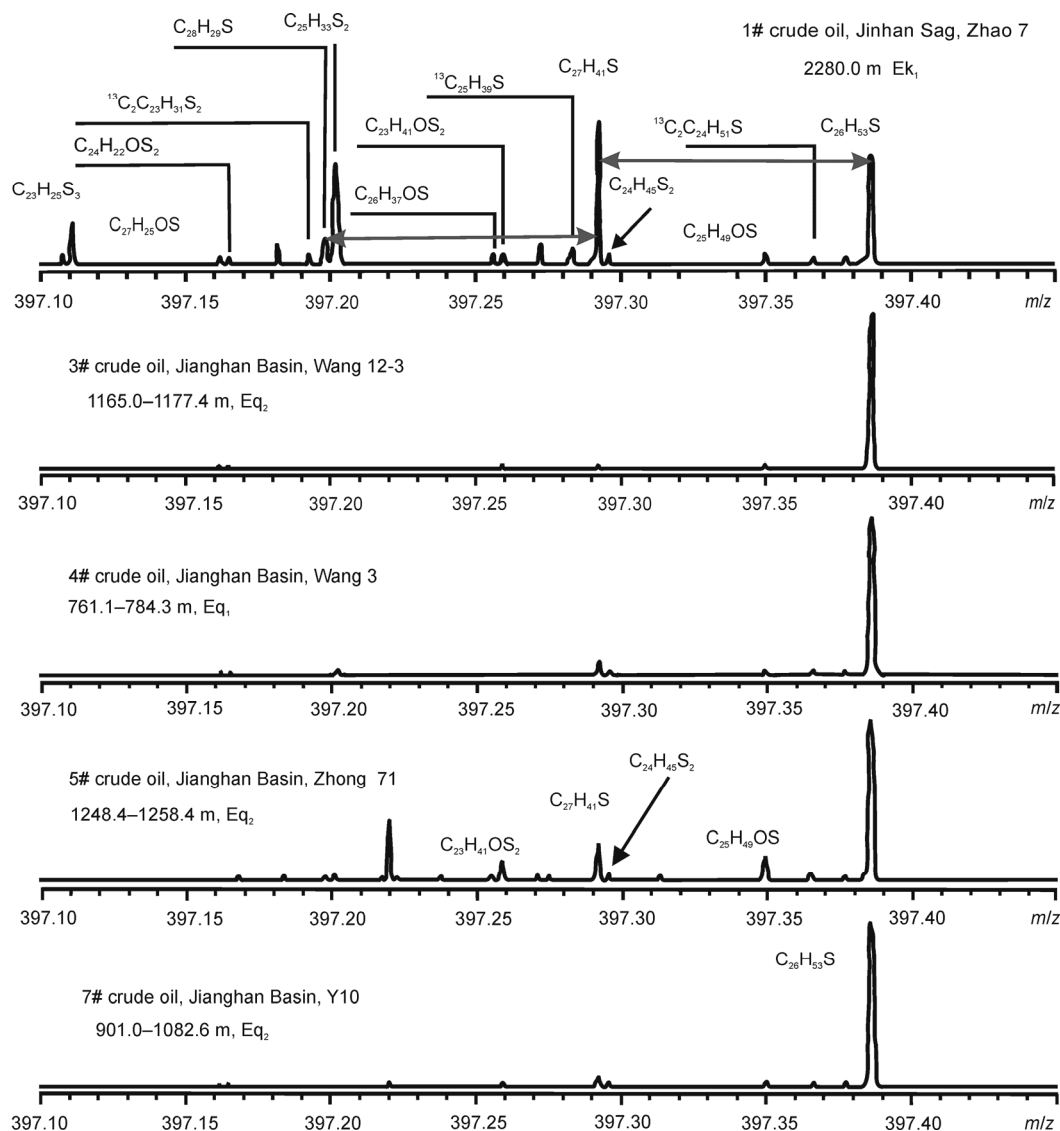
**Figure 1** Chromatograms of the methylsulfonium salts by the ESI FT-ICR MS analysis for the sulfur-rich heavy crude oil.

More than ten thousands of mass spectral peaks can be included in a mass chromatogram, and thus only those corresponded molecular formulas with accurate mass larger than 95% processed by software will be identified and listed. The identified compound types include  $S_3$ ,  $S_2$ ,  $S_1$ ,  $OS_2$ ,  $OS$ ,  $O_2S_2$ ,  $O_2S$ ,  $NS$ , and  $NOS$ . In addition, various molecular condensation degrees existed even in the same type compounds, which usually use the DBE values (Double Bond Equivalent) to show the number of rings and double bonds in one molecule. Every DBE value should be corresponded to a series of compounds with various carbon atomic numbers. As a result, the “class” distribution of OSCs compounds in oil samples can be expressed by the NOS het-

ero-atomic group vs. DBE values as shown in Figure 3. Meanwhile, the DBE values vs. carbon number ranges as shown in Figure 4 was further used to show the distribution of the type  $S_1$  OSCs, in which the size of diameter of circle dot was applied to showing the relative abundance of compounds.

In all analyzed oil samples, type  $S_1$  compounds showed the highest abundance and type  $S_2$  and  $SO$  compounds showed in the second place. On the whole, the carbon number in molecules of OSCs occurred in the range of  $C_{10}$ – $C_{60}$  (mainly in  $C_{15}$ – $C_{35}$ ) and the DBE values were in the range of 0–20.

Generally, the analysis results from the high resolution

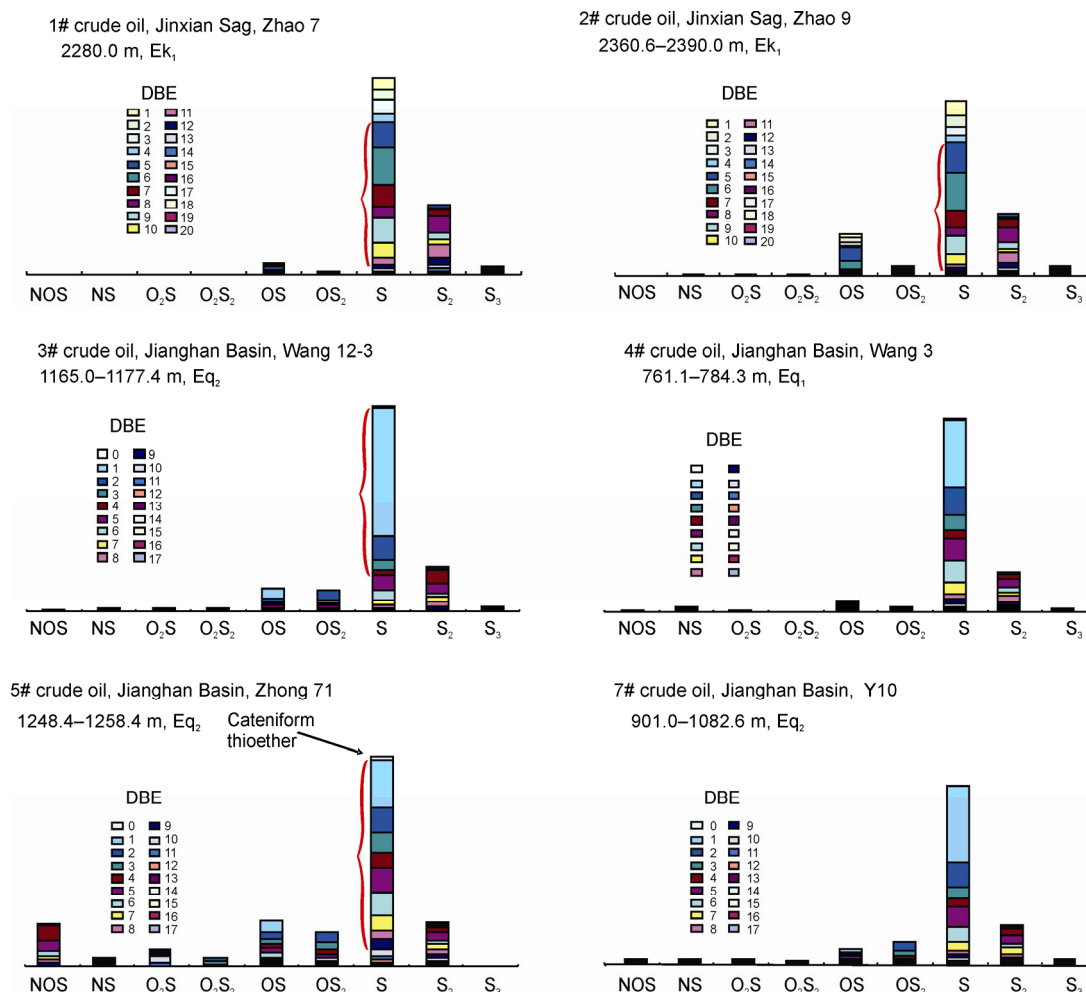


**Figure 2** Chromatograms for positive-ion ESI FT-ICR mass spectra for the methylsulfonium salts of crude oil in enlarged chromatogram at  $m/z$  397.1–397.5.

mass spectra cannot directly illustrate the specific structural information, but the structural type for the most compounds can be speculated based on the DBE values and carbon numbers (Figure 4). For example, if the DBE=0, the identified OSCs should be corresponded to cateniform thioether series compounds; if DBE=1 or 2, the corresponded OSCs might be the cyclic thioethers with one or two rings. If DBE=3, the identified OSCs might be the cyclic thioethers with three rings or thiophene series. Higher DBE values for identified OSCs implied even more possible structures. As shown in Figure 4, relatively low concentration of cateniform thioethers presented in oil, which can explain the devoid detection of these compounds in all analyzed oil samples.

Recently, great progresses have been made through studies on the OSCs based on the FT-ICR MS analysis, including crude oil (Panda et al., 2007; Liu et al., 2010a, 2010b), heavy distillate oils (Liu et al., 2011), residual oil (Liu et al.,

2010a), oilsand asphaltenes (Shi et al., 2010a), petroleum asphaltenes (Walters et al., 2011) and separated fractions from various samples (Liu et al., 2010b). These studies demonstrated that most OSCs were dominant by thiophene type compounds with low concentration of thiophenes and predominant of benzothiophenes and dibenzothiophenes (Li et al., 2012). Compared to those above results, a distinguished characteristic lies in that high concentration of thioether compounds presented in oil in this study. Cyclic thioethers with 1–2 rings occurred with relatively higher concentration in the oil in two regions and the OSCs in the Jiangnan Basin were constituted mostly by one ring cyclic thioethers. Remarkable distributional difference showed by DBE values vs. carbon numbers existed in the type  $S_1$  OSCs in the oil in two regions. Obviously, much more OSCs with higher DBE values presented in the Jinxian oil, which might be polycyclic thioethers and/or thiophene compounds. High



**Figure 3** The “class” distribution of OSCs compounds in crude oil samples based on the NOS hetero-atomic group and DBE values.

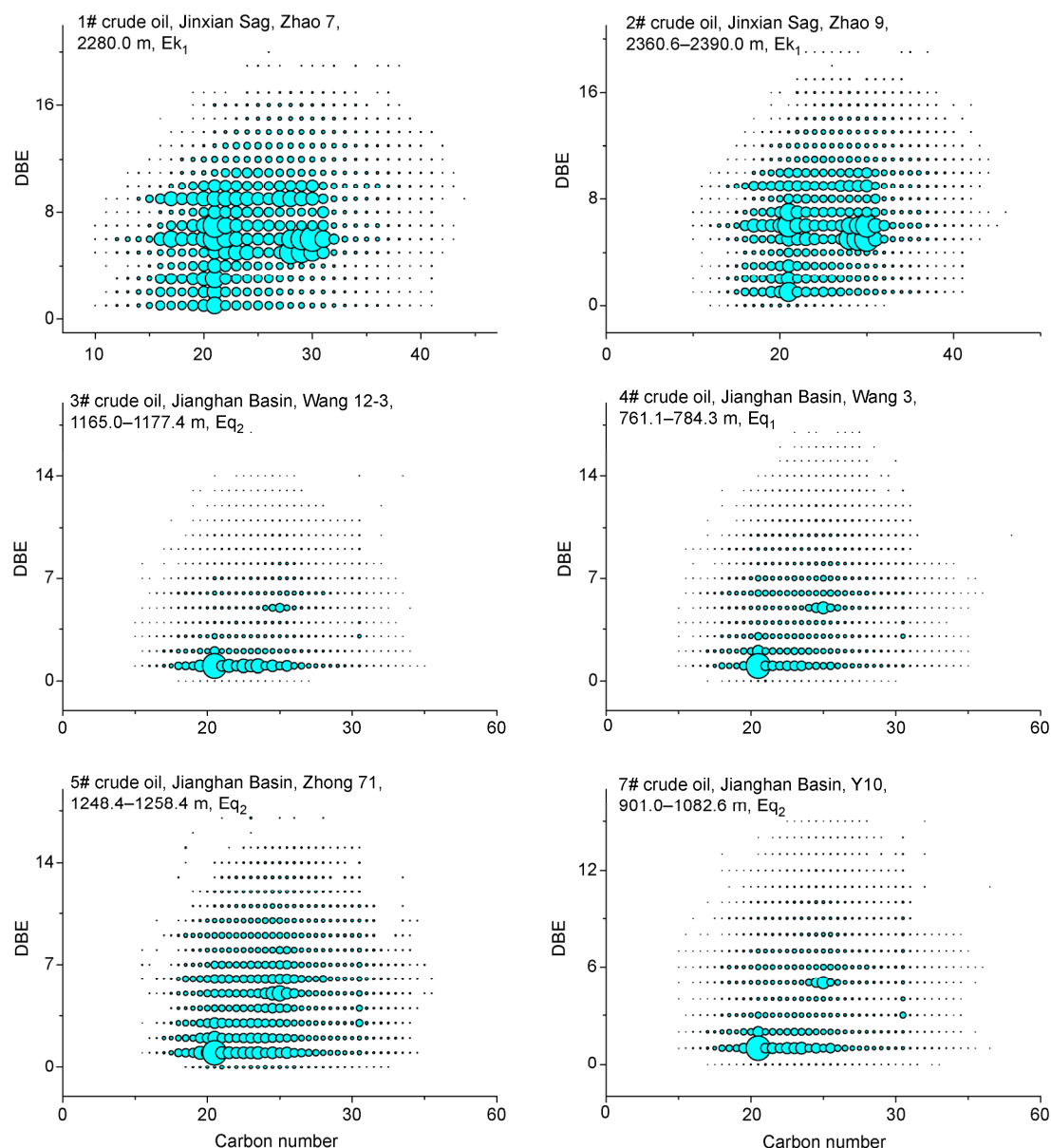
abundance of OSCs with DBE=5 or 6 in the vicinity of  $C_{27-30}$  (Figure 4), generally absent in routine crude oil, might come from the S-containing steranes that have been identified and detected in the saturate hydrocarbon fraction in the same oil in the Jinxian Sag (Lu et al., 2013).

## 2.2 Explanation for the different distribution of OSCs

First, let us see the carbon number distribution of OSCs. The carbon numbers of high abundant OSCs in Jiangnan oil were predominantly in the range of  $C_{20}$  and  $C_{21}$ , very similar to that of phytol and phytane, which was consistent with the occurrence of high abundant phytane in this region (Peng et al., 1989; Fu et al., 1991, 1992). Contrarily, the carbon numbers of high abundant OSCs in Jinxian oil were in the ranges of  $C_{19}-C_{22}$  and  $C_{26}-C_{30}$ , exactly identical to that of reported short-chain steranes and regular steroids (Sheng et al., 1988; Zhang et al., 2000; Wang et al., 2009; Chen et al., 2009; Pan et al., 1991; Zeng et al., 1989). Furthermore, some OSCs presented in the range of  $C_{23}-C_{26}$ , which agreed with the carbon numbers of those detected  $C_{23}-C_{26}$  short-chain steranes and short-chain sterenes (Zhang et al., 2000;

Chen et al., 2009; Pan et al., 1991; Lu et al., 2009, 2011) in the oil of the Jinxian Sag (Table 2). Therefore, sulfur atoms in OSCs in Jinxian oil should be closely combined with those steroids with a continuous carbon number distribution; as a result, it explained the occurrence of high abundant OSCs with wide carbon number ranges. In factor, it is absolutely realistic and true for the wide sulfurization of steroids in many compounds in sediments because only sterols have much more double bond, hydroxyl group, and carbonyl group, which are prone to combine with inorganic sulfur leading to natural sulfurization (Schouten et al., 1993; Schaeffer et al., 1995; Hartgers et al., 1997).

Secondly, according to the diagenetic pathway sketches (Sinninghe Damsté et al., 1990) of OSCs, it can be seen that the cateniform olefins, alkyl thiophene series compounds were first formed through the addition of inorganic sulfur, then turned into alkyl tetrahydrothiophene (thiolanes), and finally evolved into benzothiophenes and dibenzothiophenes through the merge of benzene ring. This means that, following the going deep into sulfurization, the merge of benzene ring itself naturally increased the DBE values. Therefore, it is clear that the detected alkyl thiophenes and



**Figure 4** The distribution of DBE values and carbon number ranges of the OSCs compounds in typical sulfur-rich heavy oil in the Jinxian Sag and Jiangnan Basin.

tetrathiophenes (thiolanes) (Peng et al., 1989; Pan et al., 1988) in Jiangnan oil should be the product of light sulfurization on the phytanic acids and phytols, whereas the benzothiophenes, dibenzothiophenes, and benzonaphthiophenes (Pan et al., 1988; Lu et al., 2009; Bao et al., 2006), especially those high abundant S-containing steranes detected in the Jinxian oil, are the results of deep sulfurization on the sterols and sterenes.

Finally, we need to consider the existence form of inorganic sulfur and their pathway entering into the structures of organic matter. In the hypersaline lakebed sediments that were solidified in the early stages, sulfur atoms existed in the following forms: (1) gaseous or dissolved  $H_2S$ , which can be utilized as energy and food by green sulfur bacteria

(*chlorobiaceae*) with reverse carboxylic acid metabolism occurred in the Jiangnan Basin. (2) Sulfate ions ( $SO_4^{2-}$ ) and sulfur cyanide ions ( $HS^-$ ) in aqueous solution. (3) Sulfate and pyrite in the solid medium. (4) Thioester in the biomacromolecules.

According to Wikipedia, thioester can be formed in the following two pathways. Firstly, one sulfur atom is combined with a molecular acyl group (alkane connected with a carbon-oxygen molecule with double bond which can be regarded as dehydroxylation results of organic acid) as a form of covalent bond, its general formula expressed as  $R-S-CO-R''$ . Another way is that the oxygen atom in the acyl group of a lipid bond was substituted by sulfur atom, generally shown as  $R-O-CS-R'$ . Or more simply understood

as that, thioester can be formed by a hydrosulphonyl group (R-SH) combined with a carboxyl group (R'-COOH) if releasing a molecular H<sub>2</sub>O, then the product was R-S-CO-R'. Therefore, the geochemical significance of thioester lies in the process of entering into organic matter through the sulfate assimilation under the microbial reaction, and then it can further access into the sediments in the form of organic compounds with primary production of organism sterols. In the Swiss Sesson Lake, organic sulfur occurred predominantly in the form of thioester and amino acid with sulfur atom bonding to carbon, which sufficiently account for this point (Loshner et al., 1993). In the sediments and planktonic organic matter in the Swiss Lake, almost all the sulfur atom was bonded in the form of organic thioester, which occupy 30–40 percentage of the total sedimentary sulfur. Thioester was the biggest storing monomer and the only S-containing compound with significance on bonding carbon (Loshner et al., 1993). Thus, this illustrated the significance of thioester on the level of total quantity and the possible existence of bio-residual hydrocarbons (Wang et al., 1994; Qin et al., 1997; Liang et al., 2001). For example, stratified water body often presented in hypersaline lakes, and in the upper surface layer, ample oxygen and salty minerals generally provide a good condition favorable for the growth of planktonic aquatic organisms instead of external terrestrial plants. In the bottom of water body, the strong reductive environment with a high concentration of H<sub>2</sub>S will help abundant anaerobes utilizing the descending, dead body of planktonic organisms (primary production), resulting in the combination of sulfur and sterols; after further diagenetic evolution, finally sulfur and sterols were preserved in the form of bio-residual hydrocarbons, and thus this explained the carbon number distribution of OSCs in this study.

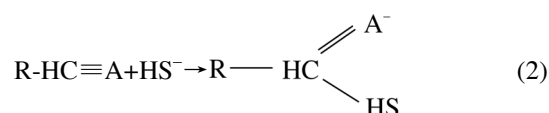
There are several possible chemical mechanisms for the inorganic sulfur entering into the structure of organic matter

(Loshner et al., 1993; Francois, 1987). (1) Access into the cateniform compounds in the form of H<sub>2</sub>S, leading to the generation of thioethers. (2) Entering by the form of sulfur-cyanide ions (HS<sup>-</sup>). (3) Generated by reaction between complex sulfides and organic matter. Hereinto, the former was formed by the reaction between sulfides and elemental sulfur or as the intermediate products of H<sub>2</sub>S oxidation. (4) Entering into the structure of organic compounds through sulfate assimilation.

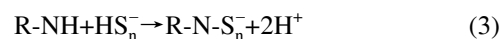
Substitution reactions:



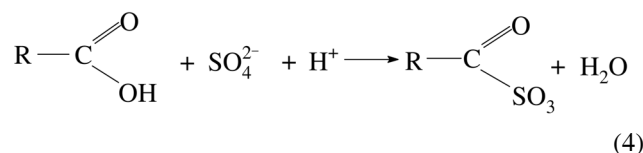
Addition reactions:



Complex sulfide reactions:



Sulfate assimilation:



According to these theories, and based on the structures and distribution of OSCs, the most abundant cyclic thioethers with one ring presented in the Jiangnan Basin should come from the reaction formula (1) plus (2), whereas more complicated OSCs occurred in the Jinxian Sag, such as thioethers with DBE=1–3, benzothiophenes, dibenzothiophenes, benzonaphthiphenes, and abundant S-containing steranes with higher DBE values, should be derived from the reactions (1) and (2) together with reactions (3) and (4), which are formed by more complicated complex sulfides and thioesters.

**Table 2** Identified and reported characteristic biomarkers and OSCs in the Jinxian Sag and Jiangnan Basin

Nos	Classes	Jiangnan Basin	References	Jinxian Sag	References
1		N-alkanes with even carbon number predominance	Jiang, 1988; Peng et al., 1989	C <sub>20</sub> –C <sub>26</sub> short-chain steranes	Pan et al., 1991
2		phytane	Jiang, 1988; Peng et al., 1989	C <sub>19</sub> –C <sub>26</sub> short-chain steranes	Chen et al., 2009; Lu et al., 2009
3	Biomarkers	alkyl benzenes	Peng et al., 1989	Short-chain lanostanes	Lu et al., 2011
4		C <sub>31</sub> –C <sub>35</sub> homo hopanes	Fu et al., 1989	Diginanes	Wang et al., 2009
5		gammaceranes	Fu et al., 1990, 1991; Peng et al., 1989	High abundant steranes	Sheng et al., 1987
6		porphyrins	Peng et al., 2000; Lin et al., 1993	C <sub>24</sub> –C <sub>30</sub> tetracyclic terpanes	Chen et al., 2009; Lu et al., 2009
7		long-chain alkyl thiophenes	Sheng et al., 1986; Sheng et al., 1987; Liu et al., 2008	Long-chain alkyl thiophenes	Pan et al., 1988
8		Long-chain alkyl thiolanes	Sheng et al., 1986, 1987	Long-chain alkyl thiolanes	Pan et al., 1988
9	OSCs	bithiophenes		dibenzothiophenes	Pan et al., 1988
10		trithiophenes		Alkyl benzothiophenes	Lu et al., 2009
11		Sulfur-cyclohexane			
12		S-containing steroids		S-containing steroids	Lu et al., 2013



### 3 Conclusions

The ultra high mass resolving power and high mass accuracy of FT-ICR MS allows the assignment of a unique elemental composition (C, H, O, N, S) to each peak in the mass spectrum. Thus, it has made a significant breakthrough in "petroleomics" research, which can characterize the chemical composition on a level of molecular elemental constituents for those various complicated compounds. Through methylation pretreatment and using electrospray ionization (ESI) source, FT-ICR MS was successfully conducted to realize the analysis of all OSCs in crude oil and provide a general view for the whole distribution of sulfur atoms (hetero-atom pairs, carbon number and DBE etc.), which effectively avoided the limitation of routine GC/MS analysis that can be only used for saturate and aromatic hydrocarbon fractions.

ESI FT-ICR MS analysis on the OSCs of methylated crude oil revealed that the chemical composition and distribution of sulfur in the Jinxian Sag were obviously different from those in the Jiangnan Basin. In the Jiangnan Basin, high abundant OSCs were composed dominantly of those DBE=1 series, corresponded to cyclic thioethers with one ring and little cateniform thioether, in which the carbon in rings was substituted by sulfur. The highest peak of OSCs was  $C_{21}H_{43}S_1$ , which shares the same carbon number ( $C_{21}$ ) with phytanic acid, phytol and reported high abundant phytane in this region. The occurrence of OSCs with cyclic thioethers, alkyl thiophenes, and alkyl thiolanes was possibly the results of light sulfurization, in which they entered into carboxylic acid, fatty acid, and fatty alcohol etc. in the forms of  $H_2S$  and  $HS^-$ .

In the sulfur-rich heavy oil in the Jinxian Sag, high abundant OSCs were dominated mainly by benzothiophenes, dibenzothiophenes, and S-containing steranes, illustrating that most of them were formed by combining benzene ring and thiophene ring into various compounds with different carbon numbers, leading to wide DBE values, as high as above 20 ( $1-20^+$ ). The DBE values for those high abundant OSCs are in the range of 1–10. However, some special OSCs whose DBE values ranged in 20–31 were identical to the carbon number distribution of reported steranes and steranes in this region. The complex distribution for the OSCs and the coincidence for carbon number distribution on biomarkers illustrate that inorganic sulfur can enter into the structure of sterols and sterenes etc. organic matter by simple forms of  $H_2S$  and  $HS^-$ , together with some more complicated forms of complex sulfides and thioesters.

Therefore, to sum up, different diagenetic pathways were shown in the sulfur evolution in the Jinxian Sag and Jiangnan Basin, although they both belong to the hypersaline lacustrine Eocene basin and share the same carbonate-evaporite sediments. In the Jiangnan Basin,  $H_2S$  and  $HS^-$ , after utilized by green sulfur bacteria and purple sulfur bacteria, entered into carboxylic acid, fatty acid, and fatty alcohol

resulting in the formation of cyclic thioethers. In the Jinxian Sag, plentiful sulfate reduction bacteria presented in the water body and bottom sediments, thus complex sulfides and thioesters etc., through the sulfate assimilation under microbial reactions, can access into the sediments and sterols, sterenes etc. organic compounds directly by the form of primary production (e.g., sterols). Thus, the formation and occurrence of biomacromolecules such as thioesters made it possible that the immature crude oil in the Jinxian Sag was generated by the form of bio-residual hydrocarbons proposed previously. At last, remarkably different distribution of biomarkers, OSCs and even the hydrocarbon generation mechanism occurred in the two regions were ascribed to the different diagenetic pathways of sulfur under various microbial reactions.

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