

Geochemical Explication of Sulfur Organics Characterized by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry on Sulfur-Rich Heavy Oils in Jinxian Sag, Bohai Bay Basin, Northern China

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ABSTRACT: For the sulfur-rich heavy oils in Jinxian Sag, Bohai Bay Basin, northern China, high abundances of organic sulfur compounds (OSCs), including benzothiophenes and dibenzothiophenes, were detected in aromatic hydrocarbon fractions. Short-chain (such as 20-thienylpregnanes and thienylandrostanes) and regular carbon-numbered S-containing steroids are also present in the saturate hydrocarbon fractions. In addition, a series of short-chain steranes (C_{21-26}), unusual short-chain lanostanes (C_{24-25}), 4-methyl steranes (C_{22-23}), 4,4-dimethyl steranes (C_{22-24}), and androstanes (C_{19-20}) were found, accompanied with high-molecular-weight analogues, C_{27-30} regular steranes, C_{27-30} 4-methyl steranes, and C_{28-30} 4,4-dimethyl steranes. The distinctive distribution characteristics and dominance of the short-chain steroids in these oils are believed to be derived from the cleavage of the weak C–S bond at C-17 and C-20 positions of extensively sulfurized steroids with subsequent microbial attack or bacterial reworking. To overcome the limitations of routine gas chromatography mass spectrometric analysis, which are only suitable for analyzing volatile and nonpolar saturate and aromatic hydrocarbon fractions, and to obtain more information and overall cognition on macromolecular OSCs in highly complicated petroleum substrates, such as polar NSO and asphaltene fractions, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry was employed for the analysis of Jinxian heavy oils after methylation pretreatment. The results revealed that very complicated sulfur (S_1 , S_2 , and S_3) and oxidized sulfur (OS and OS_2) compounds were present in the Jinxian heavy oils, with the absence of nitrogen-containing compounds. In addition, the distribution of the most abundant S_1 -type OSCs was featured by a series of compounds with a wide range of double bond equivalent (DBE) values of 1–14 and carbon numbers of 10–44. On the basis of the reported carbon number distributions of steroid biomarkers in these oils, the most abundant OSCs in Jinxian oils with DBE = 5–7 in the vicinity of C_{19-22} and C_{28-30} might come from the short-chain and regular S-containing steroids. The occurrence of abundant S-containing steroids was the results of extensive sulfurization during early diagenetic stages because much more double bonds, hydroxyl groups, and carbonyl groups exist in sterols and sterenes, which are prone to attack by inorganic sulfur.

1. INTRODUCTION

Atypical distributions of biomarkers occurred in the oilsand and oil samples in Jinxian Sag, Bohai Bay Basin, northern China.^{1–7} Very high abundances of short-chain steranes (C_{21-22} pregnanes and homopregnanes) present in concentrations higher than regular steroids.^{2–7} A series of unusually short-chain lanostanes (C_{24-25}), 4-methyl steranes (C_{22-23}), 4,4-dimethyl steranes (C_{22-24}), short-chain steranes (C_{23-26}), and androstanes (C_{19-20}) together with S-containing steroids (20-thienylpregnanes and thienylandrostanes) were also detected and identified in these oils, accompanied by their high-molecular-weight analogues, such as regular steranes (C_{27-30}), 4-methyl steranes (C_{27-30}), and 4,4-dimethyl steranes (C_{28-30}).^{2–7} The distinctive distribution of short-chain steroids that dominated in these oils was believed to be derived from the cleavage of the weak C–S bonds at C-17 and C-20 positions during extensive sulfurization of steroids and subsequent microbial attack or bacterial reworking.⁷

The crude oils in Jinxian Sag have a high density of 1.0830 kg/m³, high viscosity of 1879 mPa s at 50 °C, high sulfur content of 14.69%, and high percentage of asphaltene and polar

fractions (34.55%), typical for sulfur-rich heavy oils. A high concentration of H₂S imparts a strong odor. All of these characteristics are consistent with the explanation of the origin of short-chain steroids through cleavage of C–S bonds.⁷ To further understand this process, studies were shifted and focused on the S-containing steroids and other organic sulfur compounds (OSCs). The OSCs detected in the aromatic hydrocarbon fractions are composed mainly of a benzothiophene series (base peak at m/z of 147, 161, and 175 in their electron-impact ionization mass spectra) and a dibenzothiophene series (base peak at m/z 184, 198, 212, 226, 240, 254, 268, 282, and 296).^{6–8} A high abundance of S-containing steroids structurally connected to the D ring of the steroid nucleus, such as thiophenic ring linked to C-17 of the sterane skeleton and in the side chain at C-20, was identified in saturate hydrocarbon fractions of these oils.⁹ In addition, the S-containing

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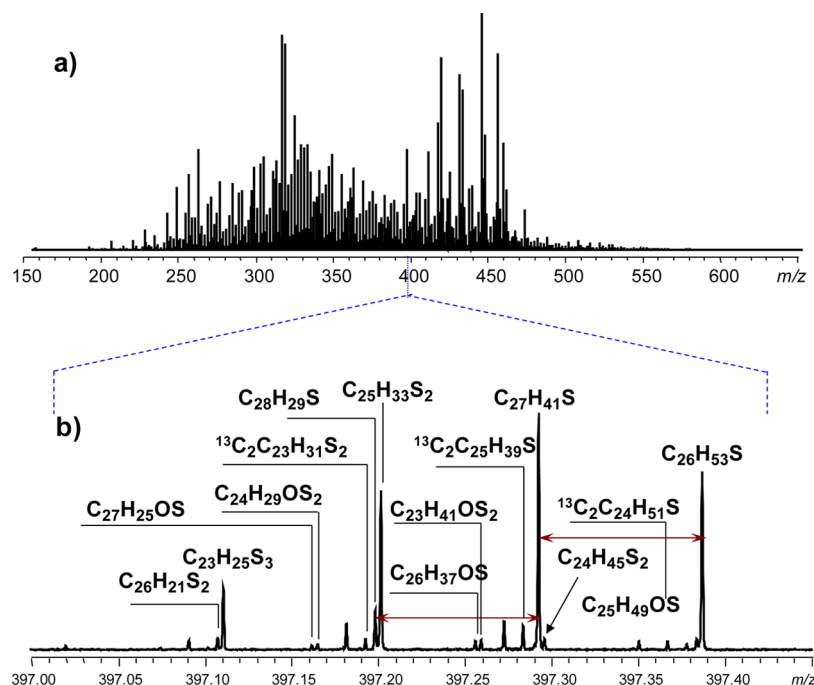


Figure 1. FT-ICR MS of (a) methylsulfonium salt and (b) enlarged spectrum in the m/z range of 397.0–397.5 of Jinxian sulfur-rich heavy oil Zhao-7.

steroids eluted in the saturate hydrocarbon fractions consisting of a saturated thiophanic ring condensed at C-16 and C-17 of the D ring of the sterane nucleus.⁹ As a result, sulfur was regarded as a very important factor influencing the diagenetic pathway of organic matter^{10,11} in the Jinxian Sag sediment, and we proposed that successful hydrogenation/sulfurization leads to the formation of the side-chain S-containing steroids, whereas unsuccessful cyclization and/or sulfurization result in the generation of short-chain steranes.⁹

In the process of studying S-containing steroids and OSCs, we strongly felt the limitation of conventional gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) techniques for the characterization of OSCs, because of its suitability for analyzing only volatilized low-molecular-weight hydrocarbon compounds in the saturate and aromatic fractions. More information is needed for overall cognition and knowledge on macromolecular OSCs in more complicated petroleum substrates, such as polar NSO and asphaltene fractions, which frequently contain heteroatomic compounds with much higher molecular weights beyond the mass range of conventional GC/MS analysis.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) provides ultrahigh resolution and measurement accuracy to obtain unambiguous accurate mass with complete separation of components of different elemental compositions in a mass range of 200–1000 Da, allowing for the more complete molecular-level characterization of petroleum.^{12,13} Previous studies have shown that, through methylation, thioethers and thiophenic OSCs in crude oils can be ionized in electrospray ionization (ESI) and analyzed by FT-ICR MS for their distributions.^{14–21} In this study, an ESI source and the method of iodomethane methylation with conversion of OSCs into methylsulfonium salts were used for FT-ICR MS analysis of the Jinxian heavy oils^{14,15} and we intend to probe into possible geochemical significance based on the molecular compositions and distribution characteristics of the OSCs.

2. SAMPLES AND ANALYSIS

2.1. Samples. The crude oil samples in the Jinxian Sag were collected from Zhao-7 (2280 m, Es₄-Ek₁) and Zhao-9 (2360.6–2390.0 m, Es₄-Ek₁) wells, which have been reported previously for their distinct biomarker distributions.^{2–7} The oil in the Zhao-7 well has a high density of 1.0830 kg/m³, high viscosity of 1879 mPa s at 50 °C, high sulfur content of 14.69%, and high percentage of asphaltene and polar fractions (34.55%), typical for sulfur-rich heavy oils. A strong odor indicative of a high concentration of dissolved H₂S is present.

2.2. Methylation and Pretreatment. The methylation procedure has been described elsewhere.^{18,20,21} Generally, the oil sample was split into three portions with approximately 100 mg each to be weighted and methylated. A total of 2 mL of dichloroethane was used to dilute the oil sample, and then 50 μ L of iodomethane and 2 mL of silver boric tetrafluoride dissolved in dichloromethane (0.5 mol/L) were added to the solution. After ultrasonication for homogeneity, the solution was kept under room temperature for 24 h with no exposure to light. The process was repeated 3 times to obtain high methylation conversion. Silver iodide was precipitated and removed from the solution by centrifugation. The methyl thiophenium salts and the unreacted oil were obtained by evaporating CH₂Cl₂ from the centrifuged solution. The methyl thiophenium salts were deposited as solid material that cannot be dissolved into hexane. Hence, the unreacted oil was washed off by 5 mL of hexane. Thiophenium salts (about 10 mg) were diluted with 1 mL of CH₂Cl₂. A total of 5 μ L of a thiophenium salt solution was diluted with 1 mL of a toluene/methanol/CH₂Cl₂ (3:3:4) solution for positive-ion ESI FT-ICR MS analysis.

2.3. Mass Spectral Analysis and Data Processing. A Bruker Apex-Ultra 9.4T Fourier-transform ion cyclotron resonance mass spectrometer was used for analysis under the positive-ion ESI mode. The samples were injected with a syringe pump at 180 μ L/h under the –2.5 kV nozzle voltage. The electronic voltages for the capillary inlet and exit were –3.0 kV and 320 V, respectively. The ion-transfer parameters for quadrupole Q1 were optimized at m/z 150. The radio frequency for the ion store pool was 5 MHz under 400 V_{pp}. The impact pool was set with a rate of argon flow at 0.3 L/h under the energy of –1.5 eV and with 1 s collection time. The ions were led into an analytic pool within 1.1 ms. The masses were in the range of 150–700 Da with a 4 M sampling. A group of 128 time domain spectra were summed for signal-to-noise enhancement.

The mass calibration was performed through the response of an alkyl dibenzothiophene series in a standard sample before and after the signal collection. All of the mass spectral peaks with a signal-to-noise ratio greater than 6 were entered into the Excel data sheet. The accurate masses and molecular compositions for the target compounds were calculated by data-processing software with the method described in the literature.²²

3. RESULTS AND DISCUSSION

3.1. Chemical Compositions and Distributions of the OSCs. The wide-band ESI FT-ICR mass spectrum of the methylsulfonium salt of the Zhao-7 Jinxian heavy oil in the range of m/z 200–550 is shown in Figure 1a. It can be seen that a bimodal distribution is present in the methylated Jinxian oils, which is similar to the total ion chromatograms (TICs) of saturate hydrocarbon fractions obtained in the GC/MS analysis.^{4–7} The *n*-alkane series are absent because much more abundant iso-alkanes, cyclic hydrocarbons, aromatic hydrocarbons, and even heteroatomic compounds (e.g., OSCs) are present in the methylsulfonium salt extract prepared for FT-ICR MS analysis.

To clearly display the distribution of OSCs, Figure 1a is expanded for a range of m/z 397.0–397.5 as shown in Figure 1b. It can be seen that almost 20 peaks appeared in this narrow mass range of no more than 0.3 Da and all are identified as OSCs. Because the compounds detected in the mass spectrum correspond to the ions of the methylsulfonium salt, the most abundant peak labeled as $C_{27}H_{41}S$ should be originated from a compound with a molecular formula of $C_{26}H_{38}S$ [double bond equivalent (DBE) = 8]. If we use S_1 to represent the heteroatomic compounds with only one sulfur atom in their molecules, the S_1 class compounds identified at m/z 397 also include $C_{27}H_{26}S$ as $C_{28}H_{29}S^+$ (DBE = 15) and $C_{25}H_{50}S$ as $C_{26}H_{53}S^+$ (DBE = 1). These S_1 class compounds have different hydrogen deficiencies.²³ Compounds with two (S_2) or three (S_3) sulfur atoms in molecules were also present in Jinxian oils in high abundances. Oxygen-bearing OSCs, such as OS_2 ($C_{23}H_{26}OS_2$ and $C_{22}H_{38}OS_2$) and OS ($C_{26}H_{22}OS$ and $C_{25}H_{34}OS$), were also found in Jinxian oils. Furthermore, the number of heavy ^{13}C isotopes in a molecule can be calculated from the accurate mass measurement, as shown in Figure 1b for $^{13}C_{22}C_{22}H_{28}S_2$, $^{13}C_{24}C_{24}H_{36}S$, and $^{13}C_{23}C_{23}H_{48}S$ as $^{13}C_{23}C_{23}H_{31}S_2^+$, $^{13}C_{25}H_{39}S^+$, and $^{13}C_{24}H_{51}S^+$, respectively. Only those peaks with sufficient abundances can be detected and calculated for ^{13}C contributions because the natural abundance of ^{13}C is only 1.1% relative to the corresponding ^{12}C species and limited dynamic range of approximately 10^3 offered by the FT-ICR mass spectrometer.

More than 10 000 ionic species are included in the FT-ICR mass spectrum, shown in Figure 1a; thus, only those with accurate masses processed by software within a finite window of the theoretical values of corresponding molecular formulas were identified and listed,²² which account for over 95% of the ionic species detected. Generally, the heteroatomic compounds are grouped into several compound types, including S_3 , S_2 , S_1 , OS_2 , OS , O_2S_2 , O_2S , NS , and NOS . In addition, various degrees of hydrogen deficiency (or molecular condensation) exist in the same compound type, expressed as DBE values to show the number of rings and double bonds in the molecule. The distribution of OSCs with different compound types in the oil samples can be expressed by the NOS heteroatomic group types and DBE values within each type, as shown in Figure 2. The DBE values versus carbon number can be used for more

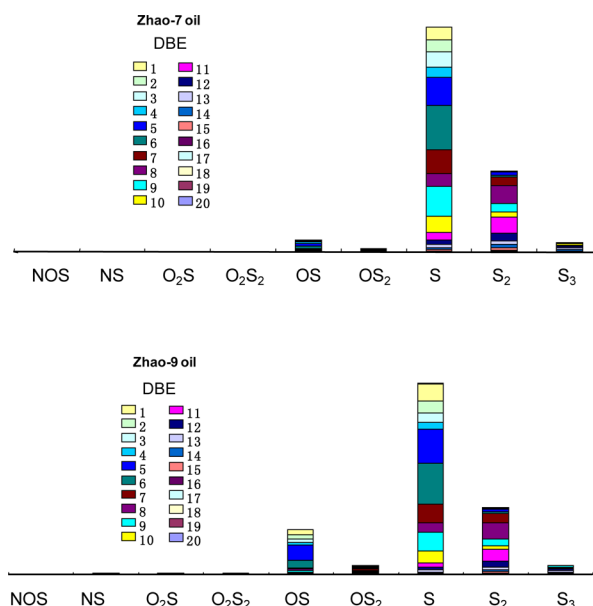


Figure 2. Distribution of OSC types in the Jinxian heavy oils based on the NOS heteroatomic assembly and DBE values.

detailed compound distributions, shown in Figure 3 for the most abundant S_1 type. The size or diameter of the circle dots corresponds to the relative abundance of compounds.

In the Jinxian oils, S_1 compounds are most abundant and dominated by species with DBE values in the range of 5–10 (Figure 2) and with carbon numbers in ranges of C_{19} – C_{22} and C_{27} – C_{30} . The S_2 compounds are the second most abundant and mainly composed of those with DBE values in the range of 7–12 (Figure 2). Surprisingly, almost no NOS , NS , O_2S , and O_2S_2 compounds were detected in the Jinxian oils. The carbon numbers of the OSCs are in the range of C_{10} – C_{44} and mainly in the range of C_{14} – C_{35} (Figure 3), and the DBE values are in the range of 1–14, dominated by 2–11 (Figure 3).

Generally, the high-resolution mass spectral results alone cannot be used directly for elucidating the specific structures; however, the structural type for most of the compounds can be rationalized on the basis of the DBE value and carbon number distributions, as shown in Figure 3 for S_1 . For example, the DBE = 0 OSCs correspond to cateniform thioether series. For DBE = 1 and 2, the OSCs are likely cyclic thioethers with one and two rings. For DBE = 3, the identified OSCs might be cyclic thioethers with three saturated rings or in the thiophene series. Higher DBE values for identified OSCs imply even more possible structures. Figure 3 shows relatively low concentrations of cateniform thioethers being present in the Zhao-9 well. Cyclic thioethers with 1 and 2 saturated rings are present in relatively higher concentrations in the Jinxian oils.

There are several reaction pathways possible for inorganic sulfur entering into organic/biological molecules with the generation of some possible/specific structures:^{24,25} (1) incorporating into the cateniform compounds in the form of H_2S , leading to the generation of thiols; (2) adding onto double bonds, such as isoprenoids, by elemental sulfur, H_2S , HS^- , etc., resulting in the generation of S_1 -type compounds, such as thiols, that can cyclize to form thioethers and be further dehydrogenated to form thiophenic compounds; (3) reacting between complex polysulfides and organic matter; hereinto, the former was formed by the reaction between sulfides and elemental sulfur or as the intermediate products of H_2S oxidation,

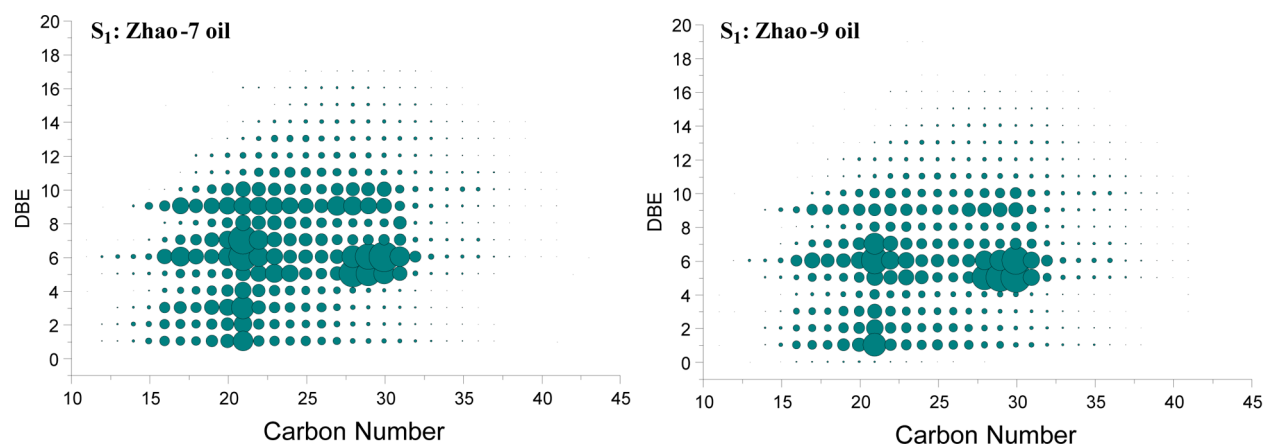


Figure 3. Distribution of DBE versus carbon number of the most abundant S_1 -type, OSC-type methylated ions in typical sulfur-rich heavy oils in Jinxian Sag (note that the results are methylated ions and the corresponding neutral molecules are one carbon less than the numbers shown).

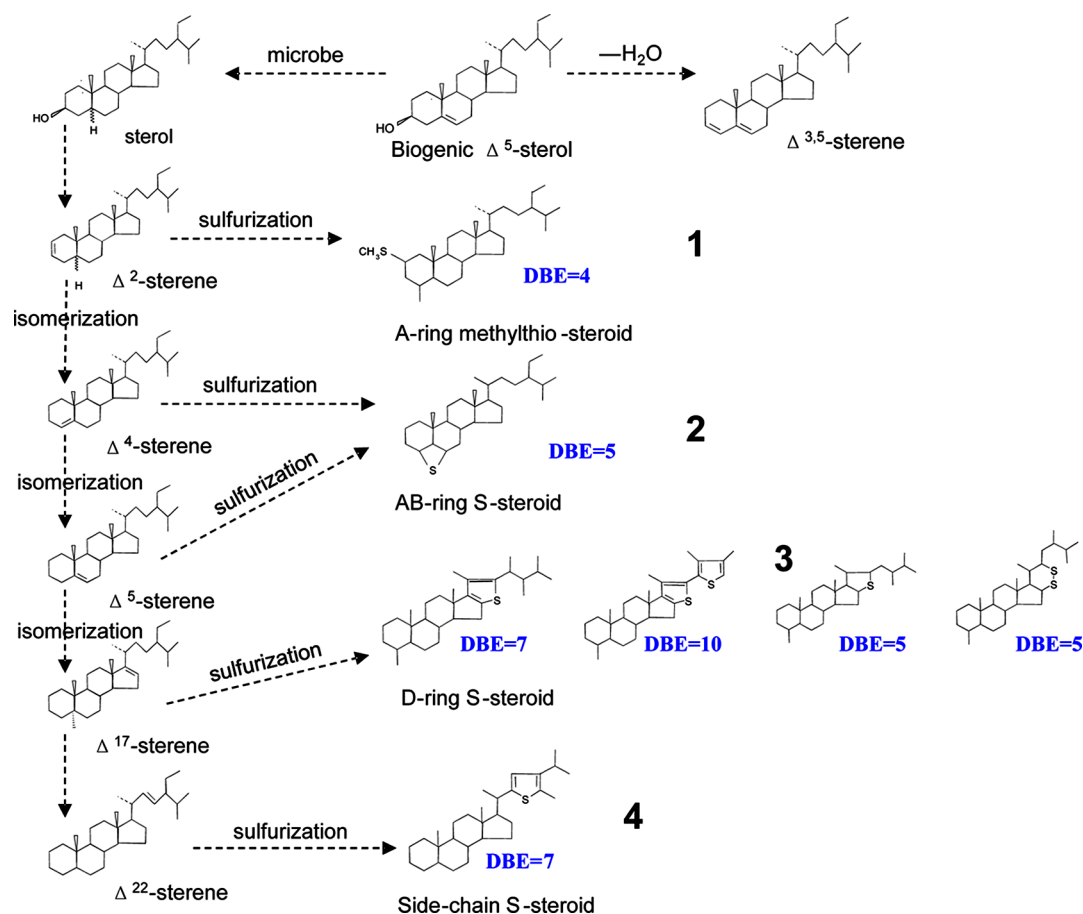
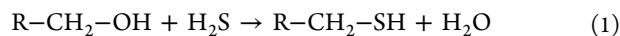


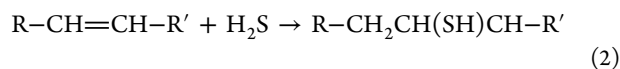
Figure 4. Proposed reaction pathway of the S-containing steroids.

leading to the formation of S_2 - and S_3 -type compounds; and (4) entering into the structure of organic compounds through sulfate assimilation, in which OS- and OS_2 -type compounds can also be formed as redox products with sulfate.

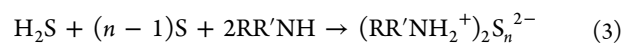
substitution reactions



addition reactions



complex sulfide reactions²⁶



sulfate assimilation



The most abundant S_1 - and S_2 -type and less abundant S_3 -type compounds can come from the reactions 1–3 through the formation of sulfide (HS^-) and polysulfides (HS_n^-) ions.

The occurrence of OS- and OS₂-type compounds should be the result of sulfate assimilation. With regard to no occurrence of NS- and NOS-type compounds that are more possibly from nitrate assimilation, the high abundance of H₂S and high sulfur content from bacteria sulfate reduction (BSR)²⁷ in the reservoir indicate strong sulfate assimilation occurring in the gypsum sediments, prohibiting nitrate assimilation as a result of suppression between denitrifying bacteria and sulfate-reducing bacteria.^{28–30}

Larger OSCs, such as cyclic thioethers of DBE = 1–3, benzothiophenes, dibenzothiophenes, and S-containing steranes, are present in the Jinxian Sag oils. They could be derived from the reactions of 1–4, followed by additional molecular transformation, such as isomerization, decomposition, and disproportionation, to form more complex sulfides and thiophenes.

3.2. Explanation for the Wide Carbon Number Distribution of OSCs. The most distinguished characteristics in the Jinxian heavy oils are featured by their higher DBE values and wide carbon number distributions, with two high abundance areas as shown in Figure 3 for S₁.

The reported S-containing steroids can be classified into four groups with DBE values consisting of the numbers of rings as in the steroid nucleus plus a thiophene ring and possible double bond, as shown in Figure 4. (1) A-ring methylthio-steroids (DBE = 4): the double bond in Δ^2 -sterenes of the dehydroxyl product of sterols was attacked and produced the S-containing steroids with a methylthio group at C-2 or C-3 in the A ring.^{31–33} (2) AB-ring intramolecular S-containing steroids (DBE = 5): the double bond in Δ^5 -sterenes was attacked to introduce sulfur atom into the $\Delta^{5,7}$ -sterol molecule, forming the AB-ring intramolecular S-containing steroids.³⁴ (3) D-ring S-containing steroids (DBE = 5, 7, and 10): when the double bond was attacked, cyclization easily occurred because of the existence of angular carbon in rearranged $\Delta^{16,17}$ -sterene or $\Delta^{17,20}$ -sterene, which had been previously reported in the Jinxian oilsand sample.^{5,6} Thus, S-containing steroids were produced with the thiophene ring merged at the D ring. (4) Side-chain S-containing steroids (DBE = 5 and 7): the double bond in the side chain of Δ^{22} -sterenes cyclized and/or directly linked with the thiophene ring when attacked, resulting in the formation of S-containing steroids with a side-chain thiophene ring.⁹

The carbon numbers of the most abundant OSCs in Jinxian oils are predominantly in the vicinity of C₂₀ and the range of C₂₇–C₃₀. The former (\sim C₂₀) was very similar to that of phytol and phytane, which was consistent with the occurrence of a high abundance of phytane in this region.^{4–7} Of course, C₂₀ may come from the contribution of short-chain S-containing steroids (C₂₀-thienylpregnanes and thienylandrostanes).^{7,9} Similarly, the carbon numbers of the second most abundant S₁-type OSCs in the Jinxian oils were in the range of C₂₇–C₃₀, similar to the carbon number range of regular steroids commonly reported as typical biomarkers.^{1–7} Furthermore, some OSCs are present in the range of C₂₃–C₂₇, which agrees with the previously reported carbon numbers of C₂₃–C₂₆ short-chain steranes and sterenes in Jinxian oils.^{2–7} Therefore, sulfur atoms in OSCs in Jinxian heavy oils should be closely related to those steroids with continuous carbon number distribution. As a result, abundant OSCs occurred with a wide carbon number range. As a matter of fact, a wide range of sulfurization occurred with many sedimentary steroid biomarker precursors because only sterols have much more double bonds, hydroxyl groups, and carbonyl groups, which are prone to attack by inorganic sulfur, leading to natural sulfurization.^{35–37}

4. CONCLUSION

The ultrahigh mass resolving power and high mass accuracy of FT-ICR MS allow us with the assignment of an unique elemental composition (C, H, O, N, and S) to each peak in the mass spectrum, which can be used to determine chemical composition of various complicated compounds in a complex petroleum mixture at the molecular level. To effectively avoid the limitation of routine GC/MS analysis that can only be suitable for analyzing more volatile saturate and aromatic hydrocarbon fractions and to provide more information and overall cognition on macromolecular OSCs in highly complicated petroleum substrates, such as polar NSO and asphaltene fractions, FT-ICR MS was used for the characterization of sulfur-rich heavy oils in Jinxian Sag, Bohai Bay Basin, northern China, after methylation pretreatment of sulfur species for ESI.

ESI FT-ICR MS analysis revealed that very complicated sulfur (S₁, S₂, and S₃) and oxidized sulfur (OS and OS₂) compounds were present in the Jinxian heavy oils with no presence of nitrogen-containing compounds. The distribution of the most abundant S₁-type OSCs were featured by a series of compounds with a wide range of DBE values of 1–14 and carbon numbers of 10–44. According to the reported carbon number distributions of steroid biomarkers in these oil samples, the most abundant OSCs in Jinxian oils with DBE = 5–7 in the vicinity of C_{19–22} and C_{28–30} might come from the short-chain and regular S-containing steroids. A high abundance of S-containing steroids was the result of extensive sulfurization during early stages of diagenesis because much more double bonds, hydroxyl groups, and carbonyl groups exist in sterols and sterenes, which are prone to attack by inorganic sulfur.

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Notes

The authors declare no competing financial interest.

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