Manuscript Number: JMPG-D-17-00967R3

Title: Geochemical characteristics and significance of heteroatom compounds in lacustrine oils of the Dongpu Depression (Bohai Bay Basin, China) by negative-ion Fourier transform ion cyclotron resonance mass spectrometry

Article Type: Full Length Article

Keywords: Dongpu Depression, saline lacustrine facies, heteroatomic compounds, maturity, ESI FT-ICR MS, GC-ICPMS.

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Abstract: Saline and freshwater lacustrine oils from the Dongpu Depression (Bohai Bay Basin) were characterized by negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). ESI-FT-ICR MS detected a large range of nitrogen and oxygen compounds in the oils, mostly comprising N1, O1, O2 and N1O1 species. The low mature oils are dominated by O1 species with double bond equivalent of 4 (DBE=4; mainly alkylphenols), O2 species with DBE=5-6 (i.e., hopanoid, secohopanoic and steroid acids) and DBE=1 (i.e., fatty acids), indicating a genetic relationship between oxygen compounds and their precursors. The nitrogen and oxygen compounds were significantly influenced by maturity, with the lower maturity oils analysed enriched in O2 species, particularly fatty acids and 4-5 ring naphthenes with biologically sourced hydrocarbon skeletons: ratios of O2/N1 >0.7; C20-30/C15-45-DBE1-O2 >0.4; and DBE5-6/DBE12-22-O2 >3.0 may be useful indicators of low maturity. With increasing maturity, the condensation degree of the compounds increased and the carbon number decreased. The relative abundances of N1 and O1 species with the following specific DBE carbon number ranges were particularly sensitive to maturity: DBE9-12/DBE15-18-N1, C20-28/C29-40-DBE12-N1, C20-30/C31-50-DBE15-N1, DBE9-12/DBE4-20-O1 and C20-30/C31-50-DBE8-O1. In some instances the FT-ICR MS proxies provided a more reliable indication of high maturity levels than traditional sterane based maturity parameters. However, several of these species were also responsive to other influences, namely C20-28/C29-40-DBE12-N1 and C20-30/C31-50-DBE15-N1 ratios reflected an organofacies control and DBE9-12/DBE4-20-O1 and C20-30/C31-50-DBE8-O1 ratios changed with thermochemical sulfate reduction (TSR)- confirmed by $\delta^{34}\text{S}$ variances of OSCs. In light of the multiple controls on the nitrogen and oxygen compounds, DBE9-12/DBE15-18-N1 ratio seems unaffected by organofacies or TSR and was considered the most reliable maturity proxy displaying a similar or better maturity relationship than Ts/(Ts+Tm). Aside from secondary alteration effects, the freshwater samples showed several compositional differences to the

saline samples, albeit from a limited data set, including generally higher O2 and N1 (particularly low MW) product abundances, lower abundances and quite different distribution of O1 products. These distinctions suggest ESI-FT-ICRMS analysis has potential for distinguishing these sample types.

**Geochemical characteristics and significance of heteroatom compounds
in saline lacustrine oils by Negative-ion Fourier Transform Ion
Cyclotron Resonance Mass Spectrometry**

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This is a manuscript about nitrogen- and oxygen compounds in saline lacustrine oils identified by negative-ion ESI FT-ICR MS. Abundant oxygen compounds with biological skeleton are detected in the immature oils investigated suggesting close genetic relationship between heteroatomic compounds and the immature oils. Maturity is suggested to be the most important factors controlling the composition and relative distribution of the NO compounds in the oils, which could be excellent maturity indices for immature to high mature level samples. TSR was suggested to be existed in partial saline lacustrine oils, which seems to have an impact on the NSO compounds. The No compounds in the saline lacustrine oils are essential for unraveling hydrocarbons generation mechanism, and identifying secondary alteration i.e. TSR as well as immature oils, which is profitable for petroleum exploration in the studied area.

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A manuscript prepared for Marine and petroleum geology

June 26, 2018

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Dear Dr. Harry Dembicki, Jr,

We deeply appreciate the reviewers' and your constructive suggestions and many revisions for our manuscript, which have certainly helped improve the quality of the manuscript. We hope the new version of our manuscript is now suitable for *Marine and petroleum geology*.

Thank you once again for your time and help. I look forward to hearing from you.

Sincerely,

Sumei Li

Comments from Reviewer #1

Reviewer #1: The authors improved the manuscript and addressed almost all of my questions and recommendations. I do not want to discuss every single point again, but I will pick out some specific aspects which still raise some concern.

We thank this reviewer for the constructive comments.

1) A main concern was that differences in oil compositions observed using FTICRMS are not discussed specifically in the light of organofacies, biodegradation, TSR, etc (besides maturity) based on results of more conventional analytical methods such as GC-MS. This is improved now but could still be much more to the point in my opinion. For example, one of my personal main questions remains not specifically answered (or is not even specifically addressed and hidden in the reported data): Is the FTICRMS data alone able to tell me whether the oils are of saline or freshwater origin, or can I distinguish between different saline facies? The answer is yes! it is possible but the how has to be stressed a little bit more!

Reply: This manuscript focuses on nitrogen and oxygen compounds (detected by negative ESI FT-ICR MS) in saline lacustrine oils with two fresh-water lacustrine oils included for a simple comparison. More samples of the latter would be necessary to evaluate systematic compositional differences between them. Nevertheless, further observations of the current differences have been added to section 4.3.1 in this revised version to further explain the differences of the oils of saline and freshwater origin, and a brief comment is now included in the abstract to emphasize the potential of these analysis to distinguish these types of lacustrine samples.

Text added to abstract: Aside from secondary alteration effects, the freshwater samples showed several compositional differences to the saline samples, albeit from a limited data set, including generally higher O₂ and N₁ (particularly low MW) product abundances, lower abundances and quite different distribution of O₁ products. These distinctions suggest ESI-FT-ICRMS analysis has potential for distinguishing these sample types.

Added Text:

4.3.1 “A relatively high abundance of O₂ species was observed in freshwater lacustrine oils (16-26%). These were generally more abundant than the saline oils (6-10%), apart from the lowest maturity (i.e., Pu1-120, Ming85 and Wei77-10; 28-35%) and TSR affected (i.e., Phshen18-2, Phshen18 and Hu96-3; 21-49%, discussed in section 4.4.3) saline oils.

4.3.3: “The carbon distribution pattern of the O₁ species with DBE values of 4, 5 and 8 for the

freshwater lacustrine oils (displaying 2~3 main peaks) is also different from that of the saline oils (showing a single main peak) (Fig. 8i, j, k, l)....”

4.3.4: “); the relative abundance of the C₂₂~C₃₄ compounds with DBE=1 of the O₂ species for the freshwater lacustrine oils is much larger than the saline lacustrine oils with similar maturity (Fig. 9j, k, l) , ”

Plus: Observations of N₁ and O₂ differences were previously described in (4.3.1/4.3.2):

4.3.1: “...The oil samples from saline lacustrine facies contain relatively low N₁, but high O₁. For example, the northern oils of well Pu7-18 and Wei42-26 have relative abundance of 48.62%–53.89% (average 51.26%) for N₁ and of 29.8%–34.93% (average 32.37%) for O₁ class species, whereas the freshwater lacustrine oils from Ma24-1 and Ma19-30 in the South Depression have relative abundance of 56.41%–64.55% (average 60.48%) for N₁ and of 13.13%–14.76% (average 13.95%) for O₁ class species (Table 3).”

4.3.2:.....“As mentioned in section 4.3.1, the freshwater lacustrine oils were generally enriched in N₁ class species relative to the saline lacustrine oils (Fig. 5). Compared to the saline oils the N₁ species composition of the freshwater lacustrine oils had a relatively narrow carbon number range (enriched in compounds with relatively low molecular weight; Fig. 6j, k, l), specific DBE values and a greater abundance of high DBEs compounds (Fig. 6b, d, f, h, i, j).”

2) Language: It is polished now, but too much content is still described in past tense. Especially results of your work should be presented in the present tense (also in the abstract)!

Page 13, line 49: ...saline/stratified/reducing depositional conditions... You can't write this like this in a paper, please make a proper sentence out of it! You took this wording directly from my Review-comment that was meant to encourage you a little bit to discuss possible differences in depositional facies a little bit more in detail (and later find those differences in your FTICRMS data)

Reply: The sentence has been revised (The reservoir of the Wei42-26 oil was sealed by salt layers at the top and bottom and is featured by thin bedded alternation of shales (source rock) and sandstones (reservoir rock), which is different from the other oil reservoirs analyzed).

3) Title: ok but even more generic know... I think it should be Bohai Bay (not Baby, right?)

Reply: Yes, sorry! The corrected name is Bohai Bay Basin.

4) Oil Maturity: Page 12 lines 22-33:

Please, do not write immature oils (also according to Peters et al. 2005)!!! Maturity per se is an expression to describe kerogen (not oil), and immature kerogen per definition has not yet generated oil! So "immature oil" is a paradox if you want to describe the thermal stress the source rock has seen to generate the respective oil. In addition, you use "immature oil" in your paper to distinguish it from "oil window mature oil", which sounds very strange. Oils are usually generated in the "oil window", but the oil window is in fact not a fixed thermal stress range for all source rocks. So please replace "immature oils" with "oils generated from low mature source rocks" (you could add a Vitrinite Reflectance value of the source rock, e.g. <0.5% Ro) and replace

"oil window mature oils" with "oils generated from peak oil window mature source rocks (add Ro of the source rock, e.g. ~0.7% Ro). Same for "mature oils"....

Reply: We agree with the definition of the reviewer that "Oils are typically generated in the "oil window", but the oil window itself spans a thermal stress range within which source rocks generate oil". We have changed "immature oil" to "oils generated from low mature source rocks" or "low mature oils". Organic geochemical studies/reports commonly abbreviate this to "low mature oils" "Low/im-/less mature oil and high/over mature oils" are all commonly used literature terms (including in Organic Geochemical "Bible" The Biomarker Guide; Peters et al., 2005).

5) TSR: In my opinion still clearly the weakest topic of the manuscript. I have nothing against discussing possible influences of TSR on some oils, but the topic just takes too much room in an already very long and crowded manuscript where the sample set is not perfectly suited to clearly unravel the effect of TSR (you focused on maturity effects which is perfectly ok). The best indication for that is that in your previous manuscript-version you featured oil Hu96-3 as the end member oil least affected by TSR whereas in the present version oil Hu96-3 is the end member oil most affected by TSR. This just shows that you have still a lot of room for interpretation and that you are missing evidence (from better suited samples) to proof your case. I would suggest you simply indicate in the text for which sample you think TSR played a role (like you already did, stating the literature and some work you did when describing Figure 13), but largely get rid of the extra TSR chapter and Figures 15-17. Perhaps you find a better suite of samples for a next paper with the main topic TSR (similar source and maturity but from different reservoirs with different stages of TSR, like in Walters et al. 2015).

Reply:

1) The CSSIA evidence of TSR confirms the capacity of Positive ESI FT-ICR MS to recognize TSR occurrence. Few OSCs with low thermal stability (DBE=0~9) could be detected from Hu96-3 characterized by relatively high thermal maturity, indicating no TSR or thermal involvement of TSR-related sulfur compounds with low thermal stability into high thermally stability. Our interpretation of Hu96-3 in the primary manuscript is not sufficient. The results about TSR discrimination should be accurate if ESI FT-ICR MS was used and combined with sulfur isotope analysis. As to the TSR degree in the area investigated, further work is necessary next.

2) Our results (compounds distribution and parameters) suggest negative ESI FT-ICR MS data is sensitive to TSR (the occurrence of which confirmed by CSSIA). This is a significant outcome of our study which we believe warrants reporting.

Reviewer #2: This paper applies -ESI-FT-ICR MS in association with conventional biomarker and CSSIA to characterize the heteroatomic species in lacustrine oils from the Dongu Depression and relates the observed differences to source input/environment, thermal maturity, and secondary alteration processes (biodegradation and TSR). This is a well-constructed study with high quality data. I take no issues with the authors' discussion of the result and compounds in scientific conclusions.

I have numerous suggested changes/comments that address minor grammar, syntax and typos. There are only a few places where sentences need to be edited to improve understanding. These changes should be made by the authors so I am suggesting that the manuscript be sent

back for minor revision.

Reply: We would like to thank the reviewer sincerely for his/her support of our work, especially detailed revisions for our manuscript.

General corrections/comments

Reference citations throughout the text should be reordered by date of publication, not alphabetical by author)

Reply: Sorry for the mistakes, we have revised now.

Section 4.2.1: There is a high redundancy as the text frequently describes the values in Table 2. I would advise that this section be edited to just focus on the meaning of the measurements. The reader can see the ranges of values easily enough without these being stated in the text.

Reply: Good idea. A few words have been deleted in this revised version.

Specific corrections/comments

Page 1, Title: "Lacustrine" to "lacustrine"

Abstract: page 2, line 16: "skeleton" to "skeletons"

Abstract: page 2, line 57: "e.g C29" to "e.g., C29"

Introduction, page 3, line 20: "which" to "that"

Section 3.2, page 7, line 32: "<mu>I" to "<mu>L"

Section 3.2, page 7, line 41: "100-<mu>L" to "100 <mu>L"

Section 3.2, page 8, line 19: "200-900." To ""200-900 Da."

Section 3.3, page 9, line 11: "SF6" subscript the 6

Section 4.2.1, page 10, line 32: "botryococcusbrauni" to "Botryococcus brauni"

Section 4.2.1, page 10, line 46: "had relatively low" to "have relatively low"

Section 4.2.1, page 10, line 52: "had higher" to "have higher"

Reply: We are sorry for the mistakes. Many thanks for the revisions. All of the mistakes have been corrected and the suggestions have been adopted.

Section 4.2.1, page 10, line 55: "occurrence f <beta>-carotene" to "occurrence of <beta>-carotane" [I doubt <beta>- carotene is present, rather it is the fully saturated equivalent]

Reply: The mass spectrum of the so-call "β-carotene" in this manuscript is not typical when we compared the "compound" with that of the mass spectrum. The relevant context of β-carotene has been deleted. We are sorry for not checking carefully.

Section 4.2.1, page 11, line 16: "deep oils i.e, Pushen 18-2 (0.72) are relatively low than some immature oils i.e. Wei77-10 (0.77)," to "deep oils, e.g., Pushen 18-2 (0.72), are relatively lower than some immature oils, e.g., Wei77-10 (0.77)."

Section 4.2.1, page 11, line 21: "had significantly" to "have significantly"

Section 4.2.1, page 11, line 30: "Sinninghe" to "Sinninghe Damsté"

Section 4.2.1, page 11, line 52: "or absence" to "or presence"

Section 4.3.2, page 15, line 55: "were dominated" to "are dominated"

Section 4.3.2, page 16, line 10: "There was significant" to "There is significant"

Reply: We are sorry for the mistakes. Many thanks for the revisions.

Section 4.3.2, page 16, line 19: Not sure what is meant by "pre-displacement"??

Reply: We have changed "a pre-displacement" to "a forward movement".

Section 4.3.2, page 16, line 52: "reactions which" to "reactions, which"

Section 4.3.3, page 17, line 27: "with an absolute predominance" to "with a predominance"

Section 4.3.3, page 17, line 30: "(mainly 22-40) (Fig. 8e" to " (mainly 22-40) species (Fig. 8e"

Section 4.3.3, page 17, line 44: "Well Hu96-3 which" to "Well Hu96-3 that"

Section 4.3.5, page 22, line 44: "well Pu7-18 seem to have" to "well Pu7-18 have"

Section 4.1.5, page 23, line 13: "It seems a little complex about the relative abundance of the N1, N1O1, O1~O3 classes with varied maturity, which will be discussed hereafter." This is an awkwardly worded sentence suggest "The relative abundance of the N1, N1O1, O1~O3 classes with varied maturity in a more complex manner"

Section 4.1.5, page 23, line 30: "analysis, is" to "analysis is"

Section 4.1.5, page 23, line 41: had good positive relationships" to "have good positive correlations"

Section 4.1.5, page 23, line 44: "Ts/(Ts+Tm) values. The related coefficient (r) values were in a range" to "Ts/(Ts+Tm) with r values in a range"

Section 4.1.5, page 23, line 46: "also resulted in a good positive relationship with the conventional maturity indicators (r=0.81-0.94, average 0.87)" "also correlate well with the conventional maturity indicators (r=0.81-0.94, average 0.87)"

Section 4.1.5, page 23-24, line 1: "Just as some index could be used to evaluation maturity level for crude oils in the foregoing paragraphs, some of the FT-ICR MS parameters could be utilized to distinguish immature oils from mature ones." to "Other parameters derived from FT-ICR MS can be use to distinguish immature from mature oils."

Section 4.1.5, page 24, line 9: "For example, with the exception of Hu96-3, the ratios of O2/N1 species in immature oils ranged from 0.78 to 0.98 (average 0.87) while the mature oils were in a range of 0.11-0.42 (average 0.3), C20-30/C15-45-DBE1-O2 (mostly fatty acids) of the immature oils ranged from 0.44 to 0.68 (average 0.59) while the ratios for the mature oils were from 0.08 to 0.31 (average 0.17) (Fig. 14a, table 3), and DBE5-6/DBE12-22-O2 of the immature and matured oils were 4.10-13.5 and 0.15-2.68, respectively (Fig. 14b; Table 3)." To

"For example, with the exception of Hu96-3, the ratios of O2/N1, C20-30/C15-45-DBE1-O2 (mostly fatty acids), and DBE5-6/DBE12-22-O2 for the immature and mature oils respectively range from 0.78 to 0.98 (average 0.87) vs. 0.11-0.42 (average 0.3), 0.44 to 0.68 (average 0.59) vs. 0.11-0.42 (average 0.3), and 4.10-13.5 vs. 0.15-2.68 (Fig. 14, Table 3)."

Section 4.1.5, page 24, line 24 "it seems maturity is essential for the crude oils in this study" to "thermal maturity is the main influence on composition for the crude oils in this study"

Section 4.4.2, page 25, line 35 "C35hopanoic" to "C35 hopanoic"

Section 4.4.2, page 25, line 55: "Our recent work showed that the "immature oils" in the Dongpu Depression are actually mixed oils with different maturity with most of them especially the saturated and aromatic fraction were derived from relatively deep source rock with normal maturity (Zhang et al., 2017)." To ""Our recent work showed that the "immature oils" in the Dongpu Depression are actually mixed oils with different maturity with the saturated and aromatic fractions especially influenced by hydrocarbons derived from relatively deep source

rock at higher maturity (Zhang et al., 2017)."

Section 4.4.2, page 26, line 5: "considerable macromolecules like NSO' s compounds in resins and asphaltene were mostly derived from potential source rocks with relatively low maturity." to "a majority of the NSO compounds were derived from source rocks at relatively low maturity."

Section 4.4.3, page 27, line 5: "2015a).The" to ""2015a). The"

Section 4.4.3, page 27, line 8: "We thus suggest" to "We hypothesize" or just "We suggest"

Section 4.4.4, page 30, line 44: "(Fig. 5b) which" to "(Fig. 5b), which"

Section 4.4.4, page 31, line 33: "; Fig.13) which" to "; Fig.13), which"

Section 4.4.4, page 32, line 55: "The present ESI FTICR MS data and more so CSSIA data does reflect a TSR origin, supporting the proposal that these sour gases have migrated from deeper source rocks." "Evidence from ESI FTICR MS and CSSIA analyses indicate TSR alteration, supporting the proposal that these sour gases have migrated from deeper source rocks."

Section 4.4.4, page 33, line 5: "estimated to be ~180°C" should this be "~80°C ?

Section 4.4.4. page 33, line 10 "It appears the TSR evidences concluded from ESI FT-ICR MS are coincided with the geological and geochemical conditions in the Dongpu Depression." {Not exactly sure what is the intended meaning of this sentence. Perhaps change to "ESI FT-ICR MS provides evidence suggesting that TSR alteration has occurred."}]

Reply: Many thanks for the revisions. All of the mistakes have been corrected and the suggestions have been adopted.

Associate editor: The reviewers find the manuscript is still in need of revision prior to publication. After reading the reviewers comments and looking over the manuscript, I agree with the reviewers that additions revisions are needed prior to publication. I urge the authors to carefully consider the suggestions from the reviewers while making revisions. If you do not feel particular suggested revisions are appropriate, please explain your opinion for consideration. Thank you for your continued efforts.

Reply: Many thanks for these constructive suggestions.

Highlights

1. Heteroatom compounds in saline lacustrine oils were detected.
2. Abundant O and N compounds were identified in low mature oils.
3. Parameters of N and O compounds indicating maturity were proposed.
4. NSO compounds in several saline lacustrine oils were probably impacted by TSR.

Geochemical characteristics and significance of heteroatom compounds in lacustrine oils of the Dongpu Depression (Bohai Bay Basin, China) by negative-ion Fourier transform ion cyclotron resonance mass spectrometry

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Abstract: Saline and freshwater lacustrine oils from the Dongpu Depression (Bohai Bay Basin) were characterized by negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). ESI-FT-ICR MS detected a large range of nitrogen and oxygen compounds in the oils, mostly comprising N₁, O₁, O₂ and N₁O₁ species. The low mature oils are dominated by O₁ species with double bond equivalent of 4 (DBE=4; mainly alkylphenols), O₂ species with DBE=5-6 (i.e., hopanoid, secohopanoic and steroid acids) and DBE=1 (i.e., fatty acids), indicating a genetic relationship between oxygen compounds and their precursors. The nitrogen and oxygen compounds were significantly influenced by maturity, with the lower maturity oils analysed enriched in

O₂ species, particularly fatty acids and 4-5 ring naphthenes with biologically sourced hydrocarbon skeletons: ratios of O₂/N₁ >0.7; C₂₀₋₃₀/C₁₅₋₄₅-DBE₁-O₂ >0.4; and DBE₅₋₆/DBE₁₂₋₂₂-O₂ >3.0 may be useful indicators of low maturity. With increasing maturity, the condensation degree of the compounds increased and the carbon number decreased. The relative abundances of N₁ and O₁ species with the following specific DBE carbon number ranges were particularly sensitive to maturity: DBE₉₋₁₂/DBE₁₅₋₁₈-N₁, C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁, C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁, DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁. In some instances the FT-ICR MS proxies provided a more reliable indication of high maturity levels than traditional sterane based maturity parameters. However, several of these species were also responsive to other influences, namely C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁ ratios reflected an organofacies control and DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁ ratios changed with thermochemical sulfate reduction (TSR)—confirmed by δ³⁴S variances of OSCs. In light of the multiple controls on the nitrogen and oxygen compounds, DBE₉₋₁₂/DBE₁₅₋₁₈-N₁ ratio seems unaffected by organofacies or TSR and was considered the most reliable maturity proxy displaying a similar or better maturity relationship than Ts/(Ts+Tm). Aside from secondary alteration effects, the freshwater samples showed several compositional differences to the saline samples, albeit from a limited data set, including generally higher O₂ and N₁ (particularly low MW) product abundances, lower abundances and quite different distribution of O₁ products. These distinctions suggest ESI-FT-ICRMS analysis has potential for distinguishing these sample types.

Key words: Dongpu Depression, saline lacustrine facies, heteroatomic compounds, maturity, ESI FT-ICR MS, GC-ICPMS.

1. Introduction

Although oxygen and nitrogen compounds are minor components of crude oils, they carry important geological and geochemical information that may help unravel hydrocarbon generation and migration mechanisms. Nitrogen or oxygen containing organic products of geological samples have been used to indicate thermal maturity (Li et al., 1995; Clegg et al., 1998; Horsfield et al., 1998; Zhang et al., 2011), origin, paleoenvironment (Clegg et al., 1997) and hydrocarbon migration pathways (Yamamoto, 1992; Li et al., 1995; Larter et al., 1996). However, identification and analysis of polar, high MW heteroatom compounds by traditional geochemical methods has proved challenging. Gas chromatography-mass spectrometry (GC-MS), for example, has generally been limited to the detection of low molecular weight nitrogen compounds such as C₀-C₂ carbazoles, benzocarbazoles and dibenzocarbazoles (Yamamoto et al., 1991; Larter et al., 1996; Bennett et al., 2002). The high resolution and mass accuracy of Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) may support a more comprehensive analysis (Qian et al., 2001; Hughey et al., 2002; Mullins, 2007; Headley et al., 2016). Electrospray ionization (ESI) FT-ICR MS can be used for the molecular characterization of non-basic pyrrolic nitrogen compounds (Qian et al., 2001; Hughey et al., 2004). More sophisticated application of ESI FT-ICR MS has supported detailed characterization of the oxygen and nitrogen product distribution in oil sands, asphalts and heavy crude oils (Roussis et al., 2003; Noah et al., 2015), biodegraded oil (Kim et al., 2005; Liao et al., 2012; Vaz et al., 2013; Pan et al., 2015), mature oil and their polarity based (Cui et al., 2014; Oldenburg et al., 2014; Poetz et al., 2014; Wan et al., 2017), high total acid number (TAN) oils (Barrow et al., 2003; Shi et al., 2010b) and shale oils (Bae et al., 2010;

Chen et al., 2012; Tong et al., 2013; Mahlstedt et al., 2016), as well as tracing oil migration pathways (Liu et al., 2015; Zhang et al., 2016). Early studies recognized the distinctive heteroatom product composition of crude oils from different geological sources or depositional environments, of different maturity level or altered by secondary impacts. For instance, a low maturity, partially biodegraded lacustrine Chinese oil had a higher oxygen (O₂) content than moderately mature marine oils from North America (Hughey et al., 2002); a mature marine-derived oil from the Middle East had a high nitrogen content (Hughey et al., 2002); whilst a North Sea was characterized by a lower relative abundance of O₂ and N₁ (Teräväinen et al., 2007), which were determined by biomass, depositional environment and biodegradation (Hughey et al., 2002).

The freshwater lacustrine-sourced oil from the Nanpu Depression of the Bohai Bay Basin in China was reported recently as having the highest relative abundance of N₁, followed by O₁ and O₂ species (Wan et al., 2017). However, the composition of oxygen and nitrogen compounds in low maturity saline lacustrine oils has not yet been investigated in detail. In this study, negative-ion ESI FT-ICR MS combined with GC-MS was used to investigate the composition and distribution of oxygen and nitrogen compounds in saline/freshwater lacustrine oils of different maturities in the Dongpu Depression of the Bohai Bay Basin. These oils also contained distinctive organic sulfur compounds (OSCs) so compound specific sulfur isotope analysis (CSSIA) was conducted to help assess the potential occurrence and impact of thermochemical sulfate reduction (TSR). The geochemical significance and genetic mechanisms of these compounds are discussed.

2 Geological setting

Saline lacustrine basins of Tertiary age are well developed in China. The NNE-trending Dongpu

Depression in the southeastern part of the Bohai Bay Basin is a typical lacustrine sub-basin containing abundant petroleum (Gao et al., 2015; Wang et al., 2015) (Fig. 1a). The depression covers an area of 5300 km² with narrowing-down topography from northeast to southwest. The Lanliao Fault in the east and the Changyuan Fault in the west exert control on the sedimentation of the depression. In total, four tectonic units of the depression are defined: eastern sub-depression, western sub-depression, central uplift and western slope (Fig. 1a). The Dongpu Depression has undergone two major tectonic cycles (*Es*₄-*Ed* and *Ng*-*Q*), which are subdivided into five evolution stages: initial rifting (depositional episode of the *Es*₄ strata), advanced rifting (*Es*₃), post-rifting (*Es*₂-*Es*₁), rifting termination (*Ed*) and subsidence (*Ng*, *Nm* and *Q*).

The Dongpu Depression developed on Mesozoic and Paleozoic basement, and overlain by Cenozoic sedimentary packages, including the Paleogene Shahejie (*Es*) and Dongying (*Ed*) formations, the Neogene Guantao (*Ng*) and Minghuazhen (*Nm*) formations, and the Quaternary Pingyuan (*Py*) Formation. The *Es* is divided into four members (*Es*₁ to *Es*₄); *Es*₃ and *Es*₄ are further divided into three (*Es*₃¹ to *Es*₃³) and two (*Es*₄¹ and *Es*₄²) sub-members, respectively. The *Es*₄ member and middle-lower *Es*₃ sub-members (*Es*₃²-*Es*₃³) were deposited in a humid climate and consists of extensive and deep lacustrine facies, the *Es*₃¹ sub-member is an arid fluvial facies, and the *Es*₁-*Es*₂ members are shallow lacustrine facies deposited in a humid climate (Liu and Ren, 2007; Zhang et al., 2007; Ji et al., 2015; Li et al., 2015b). The Dongpu Depression contains two apparently different sedimentary facies of Tertiary age: saline lacustrine in the northern sector (hereafter North Depression) and freshwater lacustrine in the southern sector (hereafter South Depression) (Li et al., 2015b; Jiang et al., 2016), which are nearly divided by the Yellow River (Li

et al., 2015b; Jiang et al., 2016) (Fig.1a). The Es contains prominent reservoir-producing layers and two main sets of source rocks, including the Es₁ and Es₃-Es₄ members, among which Es₃ is the most important. Four sets of gypsum salt rocks co-occur with petroleum in the North Depression (Fig. 1b), significantly impacting oil and gas generation and distribution (Gao et al., 2009; Wang et al., 2015). The proven petroleum reservoir is about 5.848×10⁸t with the majority (>90%) distributed in the North Depression where gypsum strata have developed. Low maturity oils (generated from low mature source rocks) were discovered in the Wenmingzhai (WMZ), Pucheng (PC) and Weicheng (WC) oilfields (Gao et al., 2009; Wang et al., 2015) and normal maturity oil, condensate and gas (generated from moderately to highly mature source rocks) can be found in the central Wenliu (WL) Oilfield and the South Depression (Fig.1). We define the oils with C₂₉ sterane $\alpha\alpha\alpha 20S/(S+R)$ and C₂₉ sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta) < 0.4$ as low mature oils (generated from low mature source rocks) (Wang et al., 1995; Peters et al., 2005).

3 Samples and methods

Over 100 crude oils were collected from the Dongpu Depression for detailed geochemical analysis by conventional methods such as GC-MS and carbon isotopic analysis (to be separately reported). Among which, 11 oils were selected for ESI FT-ICR MS analysis. Nine were derived from source rocks deposited in saline lacustrine facies in the North Depression while two were sourced from source rocks formed in freshwater lacustrine facies in the South Depression. The detail of the samples is shown in Fig. 1a and Table 1.

3.1 GC-MS analysis

All oils were separated into saturate, aromatics, resins and asphaltenes fractions (SARA).

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5 Briefly, the oils were deasphalted before fractionation on a neutral alumina chromatographic
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8 column. Saturated hydrocarbons, aromatic hydrocarbons and polar fractions were then obtained by
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10 sequential elution with *n*-hexane, toluene and chloroform. GC-MS analysis of the saturate and
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12 aromatic fractions were separately carried out on an Agilent 6980 gas chromatography coupled with
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14 HP-5MS fused silica columns of 30m×0.25mm×0.25μm and 60m×0.25mm×0.25μm, respectively.
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17 The experimental conditions were the same as those detailed in Li et al. (2010b). Peak
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19 identifications and quantitative methods were reported by Jiang et al. (2001).
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23 24 **3.2 FT-ICR MS analysis**

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27 A total of 10 mg crude oil was dissolved in 1 mL toluene. Twenty micrometer of the solutions
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29 was diluted by 1mL toluene and methanol (1:1, v:v) mixture. A total of 15 μL ammonium
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31 hydroxide solution (28%) was added to facilitate deprotonation of the acids and neutral nitrogen
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33 compounds to yield [M-H]⁻ ions. All solvents were analytical reagent grade, distilled twice and
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35 kept in a glass bottle, which is utilized to solvent handling and transferring except for the steel
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37 pistons of 100μL Hamilton syringes.
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44 The analysis was conducted on a Bruker Apex-Ultra FT-ICR mass spectrometry equipped with
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46 a 9.4-T superconducting magnet. Sample solutions were dissolved by an Apollo II electrospray
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48 source (ESI) at 180 μL/h with a syringe pump. The ESI was operated at negative mode. The spray
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50 shield voltage is 4000V for general operating conditions of negative-ion formation. Capillary
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52 column introduce voltage and end voltage are 4500V and 320V respectively. Ions accumulated for
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54 0.1 s in a hexapole with 2.4 V of direct current (DC) voltage and 400 Vp-p (volts peak to peak) of
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56 radio-frequency (RF) amplitude. The optimized mass for Q1 was m/z 300. An argon-filled
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hexapole collision pool was operated at 5 MHz and 400 Vp-p of RF amplitude, in which ions accumulated for 0.4 s. The extraction period for ions from the hexapole to the ICR cell was 1.2 s. The RF excitation was attenuated at 11.75 dB and used to excite ions over the range of m/z 200–900 Da. Data sets of 4M words were acquired. To enhance signal/noise ratio, 64 scans were co-added. A square sine bell multiplication apodization was carried out, followed by a single zero-fill before fast Fourier transform and magnitude calculation. The threshold for the signal to noise ratio (S/N) used was ≥ 6 , and the calibration error is <1ppm. Data processing was described elsewhere (Shi et al., 2013).

3.3 Compound-specific stable sulfur isotope analyses

Compound specific sulfur isotope analysis (CSSIA) was performed on the aromatic fractions of eight selected Dongpu Depression oils. $\delta^{34}\text{S}$ measurement of OSCs (thioaromatics and thiadamantanes) present in the oils was achieved using an Agilent 6890 GC coupled to a Thermo Neptune Plus multi-collector inductively coupled plasma (ICP) MS (Greenwood *et al.*, 2018). The OSCs were separated on the GC with a DB-5 MS column (30 m $\times$ 0.25 mm i.d. $\times$ 0.1 μm film thickness). The GC oven was heated from 100 $^{\circ}\text{C}$ (held for 0.5 min) to an end temperature of 300 $^{\circ}\text{C}$ (held for 15 min) at a rate of 8 $^{\circ}\text{C}/\text{min}$. The argon gas for the plasma torch was pre-heated and introduced co-axially with the analyses from the GC. The ICPMS-measured $\delta^{34}\text{S}$ values were converted to true $\delta^{34}\text{S}$ - reported as permil (‰) relative to the international sulfur isotope standard Vienna Canyon Diablo Troilite (VCDT) - with a normalisation curve established from the measurement of authentic standards of known $\delta^{34}\text{S}$ values (benzothiophene (BT) = +4.5‰; dibenzothiophene (DBT) = +13.7‰; 1-dodecanthiol (C12SH) = -7.1‰; 1-octadecaenthio (C18SH) = +13.7‰) measured by Elemental Analysis isotope ratio mass

spectrometry calibrated for $\delta^{34}\text{S}$ measurements with international standards provided by IAEA (IAEA-S1, IAEA-S2, IAEA-S3 and NBS127). Two pulses of an SF_6 gas standard were included at both the start and end of all sample analyses to internally calibrate $\delta^{34}\text{S}$ measurements. Where OSC concentrations permitted oils were analyzed twice with the standard variation ($\text{SV}\pm$) between the two duplicates usually better than 1 %.

4 Results and discussion

4.1 Physical properties and group compositions of the crude oils

The physical properties of the crude oils in the North Depression are diverse. Multiple types of oils were discovered, including light, normal and heavy. Most of the heavy oils were situated in a tectonically elevated position in the WMZ and WC oilfields. There is an improvement in the oil quality from the North to the South Depression with a wide range in sulfur content. The density and viscosity of the northern oils in this study ranged from 0.80 to 0.92 g/cm^3 (average 0.87 g/cm^3) and from 4.35 to 748.8 mPa.s (average 96.49 mPa.s), respectively. Most of the oils had relatively high pour points ranging from 6°C to 34°C (26°C on average) and a wide range in wax content (0.16%–13.92%, average 10.32%). The sulfur content of the oils was 0.05%–1.52% (average 0.5%) (Table 1). The crude oils in the South Depression showed relatively homogeneous physical properties, characterized by relatively low density (0.83 g/cm^3), low viscosity (17.36 mPa.s and 5.62 mPa.s), high pour points (30°C–37°C) and a normal to high wax content (6.87%–16.4%) with less than 0.2% sulfur (Table 1). The physical properties of the oils in the South Depression are in accordance with freshwater lacustrine facies, suggesting different origins of the northern and southern oils.

The contents of saturates and aromatics of the crude oils ranged from 31.02% to 91.61% and from

5.11% to 46.06%, respectively. Resins and asphaltene varied from 1.46% to 8.87% and from 0.56% to 34.92%, respectively (Table 1). A generally positive relationship between saturates/aromatics ratios (0.49–17.93) and maturity parameters for the oils analyzed were observed, indicating a distinctive variation in the oil maturity (Table 1).

4.2 Conventional geochemical oil characteristics

4.2.1 Chemistry of the crude oils

Total ion chromatograms (TICs) from the saturate fractions of the oils are shown in Fig. 2. Most of the oils had a bimodal distribution of *n*-alkanes (nC_{11} – nC_{43}), suggesting both microbial and higher plant contributions (Tissot and Welte, 1984; Peters et al., 2005). The long-chain *n*-alkanes likely have a higher plant origin, although they can derive from other sources (e.g., *Botryococcus brauni*, Gelpi et al., 1970). Higher plant input to the Dongpu oils was confirmed by the detection of 1, 2, 5-trimethyl naphthalene and 1, 2, 5, 6-Tetramethyl naphthalene, higher plant diagnostic compounds (Alexande et al., 1988; Strachan et al., 1988). A general decline in the $\delta^{13}C$ value of *n*-alkanes with increasing carbon number was reflective of a larger contribution of relatively ^{13}C depleted plant lipids (Murray et al., 1994). Oils located in the Dongpu Depression have relatively low Pr/Ph values (0.41 to 0.64, Table 2), consistent with deposition in a hypersaline environment (Peters et al., 2005); while more southerly freshwater lacustrine oil have higher Pr/Ph values (1.2) indicating a weakly oxidizing to weakly reducing environment (Connan and Cassou, 1980; Peters et al., 2005). The carbon preference index (CPI) and odd-even predominance (OEP) values are 0.93–1.05 (average 0.96) and 0.92–1.06 (average 0.98), respectively, showing no obvious trends. The ratios of $\sum nC_{21}^- / \sum nC_{22}^+$ and $(nC_{21} + nC_{22}) / (nC_{28} + nC_{29})$ (Table 2) may be influenced by source, thermal maturity or secondary alterations. The

ratios of $\sum nC_{21}^-/\sum nC_{22}^+$ for the deep oils e.g., Pushen 18-2 (0.72), are relatively lower than the low mature oils, e.g., Wei77-10 (0.77) (Table 2), which might be a result of thermal cracking.

The saline lacustrine oils in the North Depression have significantly high amount of gammacerane. The ratios of gammacerane/ C_{30} hopane were 0.56–1.07 (average 0.75) (Table 2). The generally high content of gammacerane in the oils indicates saline conditions and/or a stratified water column during source rock deposition (Sinninghe Damsté et al., 1995; Peters et al., 2005). Another distinguishing characteristic of the northern oils is an obvious predominance of C_{35} and C_{34} hopanes ($C_{35}/C_{34}=0.72$ – 2.31 , average 1.41) (Table 2), which coincides with the features of typical saline lacustrine oils. The ratios of tricyclic/pentacyclic terpene ranged from 0.13 to 2.36; this ratio is affected by thermal maturity (Peters et al., 2005) (Table 2). The southern oils exhibited lower ratios of gammacerane/ C_{30} hopane (0.24–0.34, average 0.29) (Table 2) and C_{35}/C_{34} hopane (0.65–0.79) (Table 2), suggesting that the source rocks were deposited in a freshwater environment. No or little biodegradation of the crude oils were interpreted from the TIC and m/z 177 mass chromatograms of the northern oil saturated fractions because there was no obvious depletion of n -alkanes or presence of C_{25} norhopanes.

The fingerprints of the C_{27} , C_{28} and C_{29} regular steranes in the northern samples showed either an asymmetric (shallow oil samples) or symmetric “V” shape (deep oil samples) due to relatively low C_{28} steranes (Fig. 3). C_{27} steroids are indicative of algal input while C_{29} steroids may come from both algae and higher plants (Moldowan et al., 1983; 1985; Volkman., 1986). A relative predominance of C_{27} $\alpha\alpha\alpha$ (20R) to C_{29} $\alpha\alpha\alpha$ (20R) for the crude oils i.e., Ming85 and Wei77-10 with a relatively low thermal maturity may reflect a higher contribution of algae to the shallow oil precursors (Fig.3). The ratios of C_{29} sterane $\alpha\alpha\alpha$ 20S/(S+R) and C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ of the oils were 0.28–0.57 and

0.28–0.65, respectively (Table 2), demonstrating the oils derived from source rocks with R_c to be 0.67%–1.29% (Table 2): the relatively low values of Ming85, Pu1-120 and Wei 77-10 oils (0.28–0.31; 0.28–0.29) suggests these were all low mature oils (generated from low mature source rocks); higher values of Pu7-18 and Wei42-26 (0.39–0.43; 0.32–0.38) suggested these oils generated from peak oil window mature source rocks; and the higher values of Pushen20, Pushen18-2, Pushen18 and Hu96-3 (0.46–0.57; 0.57–0.65) suggests they were oils generated from high mature source rocks. The C_{29} $\alpha\alpha\alpha 20S/(S+R)$ and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ values of the freshwater oils ranged from 0.36 to 0.40 and from 0.40 to 0.50, respectively, reflecting an oil generation maturity with the R_c of their source rocks around 0.72%~0.75% (Table 2).

These traditional indicators of thermal maturity (i.e., C_{29} sterane isomer ratios; $Ts/(Ts+Tm)$ and others often related to maturity (diasterane/regular sterane and tricyclic terpane/pentacycliterpanes; Table 2) all show the current oil suite spans a broad range of maturities. The vitrinite reflectance equivalent (R_c) converted by the methyl phenanthrene index I (MPI-1) (Radke and Willsch, 1993; Radke et al., 2000) varied between 0.67% to 0.93% (Table 2); however, this might be invalid parameter for the Pusheng 20, Pusheng18 and Pusheng18-2 oils which have all been subject to obvious thermal cracking (see Fig. 3). The R_o of the oil source rocks, based on oil-source rock correlation, was covered the wide range of 0.67%–1.29% (Table 2), consistent with the apparent broad maturity range of the analyzed oils. Conclusively, the maturity level of the crude oils in this study is generally in the order of Pu1-120<Wei77-10<Ming85<Wei42-26<Pu7-18<Chun24-1<Ma19-30<Pushen20<Pushen18<Hu96-3<Pushen18-2 based on maturity parameters of $Ts/(Ts+Tm)$, C_{29} sterane $\alpha\alpha\alpha 20S/(S+R)$ and C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ (Table 2; refer to Fig.13a~c).

4.2.2 Genetic types of crude oil

Two distinct groups of oils were identified based on biomarker parameters and related cross plots (Fig. 4a–d). The northern oils are derived from type II kerogen, while those from the South Depression are mixtures from type II and III kerogens (Fig. 4a, Table 2). The cross plot of pristane/phytane (Pr/Ph) against dibenzothiophene/phenanthrene (DBT/P) (Fig. 4b) is used as paleoenvironment proxy (Hughes et al., 1995). The northern oils aggregated in section C, which represents a saline lacustrine environment whereas the southern oils grouped in section D that indicates other lacustrine environments according to Hughes et al. (1995) (Fig. 4b). The ratios of gammacerane/C₃₀hopane, C₃₅/C₃₄hopane, C_{19–21}/C_{23–24} and C₂₅/C₂₆ tricyclic terpane all divide the oils into the same two families (Fig. 4c, d). Relatively low C_{19–21}/C_{23–24} tricyclic terpane values (<1) and high C₂₅/C₂₆ tricyclic terpane ratios (>1) are usually associated with a highly reducing environment (Sharaf et al., 2007; Peters et al., 2013). A small variation is observed among the north oils. For example, the gammacerane/C₃₀hopane ratios of the Pu7-18 and Wei42-26 oils (0.56) is less than the other saline oils (0.73~0.79) with a relatively low maturity and they also had relatively high Pr/Ph ratios (0.50~0.62; Table.2) which can be ascribed to less saline and/or water stratified as well as reducing depositional conditions of the source rocks. The reservoir of the Wei42-26 oil was sealed by salt layers at the top and bottom and is featured by thin bedded alternation of shales (source rock) and sandstones (reservoir rock), which is different from the other oil reservoirs analyzed.

Two sets of source rocks were assigned for the northern oils from the Dongpu Depression: the mudstone of the Es₁ and Es₃³–Es₄¹ intervals (Zhang, 2011). Fair to good saline lacustrine facies with source rocks were well developed in the Northern Depression, particularly in the WMZ, PC, WC and

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5 HZJ areas, where total organic carbon (TOC) is up to 2.3% (Zhang et al., 2011). The previous oil-source
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8 rock correlation showed that the northern oils mainly derived from the $Es_3^3-Es_4^1$ source rocks from
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10 typical saline lacustrine facies (Chang, 2007; Cheng et al., 2010b; Zhang et al., 2010), while the
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12 southern oils were derived from the $Es_3^M-Es_3^L$ mudstones from typical freshwater lacustrine facies
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15 (Peng et al., 2003). The detailed hydrocarbon generation and accumulation characteristics of the source
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18 rocks in the Dongpu Depression will be described in a subsequent manuscript.
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21 **4.3 Negative-ion ESI FT-ICR MS oil characteristics**

22 **4.3.1 Composition and distribution of nitrogen- and oxygen-containing compounds**

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27 Five neutral acid oxygen and non-basic nitrogen heteroatomic classes, including N_1 (molecules with
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29 one nitrogen atom), N_1O_1 , O_1 , O_2 and O_3 , were detected in the crude oils from the Dongpu Depression
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31 by negative-ion ESI FT-ICR MS (Fig. 5). The N_1 class species are dominant in relative abundance,
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33 ranging from 13.41% to 65.94% (average 48%), followed by O_1 (10.83%–34.93%, average 20.98%)
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35 and O_2 (6.07%–48.8%, average 24.02%) (Table 3). The relative abundance of N_1O_1 and O_3 are lowest
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38 with an average of 3.94% and 3.03%, respectively (Fig. 5, Table 3). The composition and relative
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41 abundance distribution of the N and O class species in the oils are similar to previous studies on the
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44 terrestrial oils from the Nanpu Depression, and an increase in relative abundance of oxygen-containing
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47 compounds was observed with the changes of kerogen from Type I to III for both the source rock
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50 extracts and the relevant oils in the Nanpu Depression (Wan et al., 2017). There are differences in
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53 relative abundance of the N and O compounds found in the saline and freshwater lacustrine oil samples
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56 with similar maturity (Fig. 5). A relatively high abundance of O_2 species was observed in freshwater
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59 lacustrine oils (16-26%). These were generally more abundant than the saline oils (6-10%), apart from
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the lowest maturity (i.e., Pu1-120, Ming85 and Wei77-10; 28-35%) and TSR affected (i.e., Phshen18-2, Phshen18 and Hu96-3; 21-49%, discussed in section 4.4.3) saline oils. The oil samples from saline lacustrine facies contain relatively low N_1 , but high O_1 . For example, the northern oils of well Pu7-18 and Wei42-26 have relative abundance of 48.62%–53.89% (average 51.26%) for N_1 and of 29.8%–34.93% (average 32.37%) for O_1 class species, whereas the freshwater lacustrine oils from Ma24-1 and Ma19-30 in the South Depression have relative abundance of 56.41%–64.55% (average 60.48%) for N_1 and of 13.13%–14.76% (average 13.95%) for O_1 class species (Table 3). Distinctions are also found among the oils with a similar origin. It appears that low mature saline lacustrine oils have a lower relative abundance of N_1 class species but a higher relative abundance of O_2 class species. For instance, the relative abundance of N_1 and O_2 in the low mature oil from well Pu1-120 are 36.29% and 28.3%, respectively; while that from well Pushen20, a relatively high maturity oil, are 65.94% and 10.31%, respectively (Fig. 5; Table 3). This result is also in accordance with the observation of Wan et al. (2017). Samples from well Hu96-3 showed abnormal characteristics in composition, an unusually low relative abundance of N_1 , but exceptionally high O_2 (Fig. 5; Table 3). We assume that thermochemical sulfate reduction (TSR) contributes to the conversions of nitrogen and oxygen and affects their distribution, which will be discussed hereafter.

4.3.2 Composition and distribution of N_1 class species

Pyrrolic nitrogen compounds are widely distributed in source rocks and crude oils of saline lacustrine facies (Bakr and Wilkes, 2002; Ni et al., 2005; Liu and Yang, 2008; Zhang et al., 2008a). There are many studies about the origin and formation mechanisms of nitrogen compounds: from higher plants and blue-green algae (Snyder, 1965; Li et al., 1995, 1999); formation during diagenesis (alkaloid)

(Schimmelmann et al., 1998); or early diagenetic reactions of amino acids (Bennett et al., 2002). The composition of N₁ class species in the crude oils analyzed by negative-ion ESI FT-ICR MS are shown in Fig. 6. The double bond equivalent (DBE) values and carbon numbers of the N₁ class species ranged from 4 to 26 (mainly 9–22) and from 15 to 55 (mainly 18–48), respectively (Fig. 6a–d). The N₁ class species are dominated by compounds with DBE values of 9, 12, and 15 (Fig. 6a–d, e–h), which correspond to carbazoles, benzocarbazoles and dibenzocarbazoles, respectively (Hughey et al., 2002; Shi et al., 2010a, b). Very similar distribution patterns have been observed in terrestrial lacustrine oils from the Nanpu Depression (Wan et al., 2017) and other crude oils (Oldenburg et al., 2014; Poetz et al., 2014; Mahlstedt et al., 2016).

There is significant variation in the N₁ class species of oils with a similar origin. Generally, increasing thermal maturity contributed to an increase in the degree of condensation, also shown by DBE (Fig. 6e–g, a–c) and a decrease in the carbon number range of the N₁ species, as well as a forward movement of the main peak of the N₁ compounds with different DBE values in the northern/saline oils (Fig. 6e–g, i–k). For example, the low mature oil from well Pu1-120 had a predominance of DBE=9 species with the main carbon numbers between C₃₂–C₃₅ (Fig. 6a, e, i), while the relatively high maturity oil from Pushen18-2 well was dominated by DBE=15 species with the main carbon numbers of C₁₅–C₂₃ (Fig. 6c, g, k). A distribution pattern similar to Pu1-120 was previously observed in terrestrial lacustrine oils from the Nanpu Depression (Wan et al., 2017). However, the prevalence of DBE=9 compounds decreased gradually with increasing maturity as species with high DBEs (12 and 15) became dominant (Fig. 6a–c). The relative distribution and thermal evolution trends of the N₁ class species with varied DBEs (Fig. 7a), show the impact of thermal maturity in terms of condensation and aromatization. This

phenomenon has previously been related to thermochemical kinetics (Poetz et al., 2014; Wan et al., 2017). Major mechanistic pathways of thermal cracking include ring opening, side-chain cleavage and heteroatom defunctionalization (which all yield lower MW products) as well as condensation/aromatization reactions, which can involve heteroatoms and leads to an increase in MW (Hughey et al., 2002, 2004; Oldenburg et al., 2014).

As mentioned in section 4.3.1, the freshwater lacustrine oils were generally enriched in N₁ class species relative to the saline lacustrine oils (Fig. 5). Compared to the saline oils the N₁ species composition of the freshwater lacustrine oils had a relatively narrow carbon number range (enriched in compounds with relatively low molecular weight; Fig. 6j, k, l), specific DBE values and a greater abundance of high DBEs compounds (Fig. 6b, d, f, h, i, j). The percentage of DBE=15 in the freshwater lacustrine oils including Chun 24-1 and Ma 19-30 was 9.74~12.6%, which was a little higher than similar maturity saline lacustrine oils i.e. Pu7-18 and Wei42-26 (7.46~8.56%; Fig. 6b, d; Table 3). This is consistent with previous studies (Cui et al., 2014; Wan et al., 2017). Lipids and proteins from reworked lacustrine organisms probably lead to an enhancement in organic nitrogen in the terrestrial lacustrine environment (Cui et al., 2014).

4.3.3 Composition and distribution of O₁ class species

The O₁ class species have DBE values of 0–26 with a predominance of DBE=4 (Fig. 8a–d, e–h) and carbon numbers of 15–55 (mainly 22–40) species (Fig. 8e–h, i–l). The carbon number peaks of the O₁ class species with DBE=4, 5, 8 were around C₂₁, C₂₂, C₂₇ and C₂₈ (Fig. 8i–l). The species with DBE=1 and 4 are likely alcohol and alkylphenols, respectively (Kamga et al., 2014; Shi et al., 2010b), while those with DBE=5 and 6 are likely alkylphenol-bearing indenol rings (Zhang et al., 2011; Liao et

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5 al., 2012) and the species with DBE=8 are probably phenylphenols (Shi et al., 2010b; Kamga et al.,
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8 2014). The alcohols are likely to be intermediate compounds in the conversion of organic matter to
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10 hydrocarbons (Rodrigues et al., 2000). A trace amount of alcohols were detected in the oils analyzed in
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12 this study (Fig. 8a–h). Abundant alkylphenols identified from the aromatic and resin fractions by
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14 GC-MS analysis, and the composition and distribution of these compounds are dependent on the biotic
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16 input and secondary alterations of original organic matter (Taylor et al., 2001; Bastow et al., 2005),
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18 which is significantly influenced by thermal maturity (Taylor et al., 1997; Li et al., 2000). The ESI
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20 FT-ICR MS results indicate that the masses associated with alkylphenols are the most important
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22 component of the O₁ class species in the saline lacustrine oil samples. Generally, two distribution
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24 patterns were found for the northern oils: (1) low mature oils dominated by O₁ class species with
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26 DBE=4 (Fig. 8a, b, e, and f), and (2) medium-high maturity oils containing enhanced compounds with
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28 DBE>4 (Fig. 8c, g). We suggest that the low mature oils of saline lacustrine origin are enriched in
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30 alkylphenols that are assigned to the O₁ DBE=4 species (Shi et al., 2010b; Kamga et al., 2014).
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41 Like N₁ species, the condensation degree of the O₁ class species in the crude oils increases (Fig. 7b;
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43 Fig. 8a–d, e–g) and the carbon number distribution shifts to lower values (Fig. 8e–g, i–k) with the
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45 increasing of thermal maturity. For instance, the oil generated from low mature source rocks from well
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47 Pu1-120 is dominated by species with DBE=4 (Fig. 8a, e) and carbon number of 15–55 with the main
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49 peak of C₂₈ (Fig. 8e, i), while the crude oil generated from high mature source rocks from well
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51 Pushen18-2, has mainly O₁ species with DBE=4–16 with nearly equal relative abundance, and carbon
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53 number ranges of 15–37 (main peak was C₂₀ for the species with DBE=4) (Fig. 8c, g and k). In the
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55 triangular diagram of the relative abundance of DBE=4, 8 and 9 O₁ species (Fig. 7b), it is obvious that
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5 the relatively abundances of the DBE=8 and 9 O₁ species generally increase with the increasing
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7 maturity of the oil samples as the figure 7a displayed, with an exception for the oil from Well Hu96-3
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9 that might have been altered by TSR.
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13 The composition and distribution of the O₁ class species (mainly alkylphenols) are also influenced
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15 by kerogen type (Bennett and Larter, 1997; Lucach et al., 2002; Bastow et al., 2003). The O₁ species
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17 with a lower relative abundance compared with the others, lower DBE values and short alkyl side
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19 chains are observed for the southern oils of freshwater origin. For example, the DBE values (DBE<18)
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21 and carbon number (<45) of well Ma19-30 is significantly lower than well Pu7-18 (DBE<22, carbon
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23 number <55) (Fig. 8f, h, j, l); The carbon distribution pattern of the O₁ species with DBE values of 4, 5
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25 and 8 for the freshwater lacustrine oils (displaying 2~3 main peaks) is also different from that of the
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27 saline oils (showing a single main peak) (Fig. 8i, j, k, l). All of these demonstrate the impact of kerogen
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29 type and/or sedimentary environment on the O₁ species. Alkylphenols are the most abundant
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31 components in the O₁ class species, and the depletion of O₁ class species in the freshwater lacustrine
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33 oils in the South Depression might result from the oxidized paleoenvironment in which these
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35 compounds can be easily be reformed (Bastow et al., 2003). Additionally, TSR is also a crucial factor
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37 controlling the oxygenic species in the crude oil (Walters et al., 2015), which will be discussed later on.
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49 **4.3.4 Composition and distribution of O₂ class species**

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51 The O₂ class species of the crude oils have DBEs of 0–25 (mainly 0–14), dominated by the class
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53 with DBE=1 (Fig. 9a–h), and carbon numbers from 15–51 (mainly 15–40) (Fig. 9a–l). Molecules with
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55 two oxygen atoms are likely carboxylic acids or binary alcohols, of which carboxylic acids are the
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57 primary compounds of O₂ species in crude oils (Shi et al., 2010b; Headley et al., 2016). Many
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5 carboxylic acids, such as phytanic acid, hopanoic acids (C_{28} – C_{32}) and steroidal acids (C_{27} – C_{29}), have
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7 been used as indicators of hydrocarbon origin, migration and biodegradation in petroleum systems
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9 (Jaffé and Gallardo, 1993; Barth et al., 2004; Ding et al., 2004; Wang et al., 2004). The O_2 class species
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11 with one DBE should be aliphatic acids, while those with DBEs of 2–7 correspond to 1–6-ring
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13 naphthenic acids (Barrow et al., 2003; Kim et al., 2005; Shi et al., 2010b). The O_2 class species with
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15 relatively high DBE values (i.e. 2–7) and low carbon numbers are likely multi-ring naphthenic acids,
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17 aromatic acids or phenols with multiple hydroxyl groups (Jones et al., 2001; Barrow et al., 2003; Shi et
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19 al., 2010a, b). The crude oils in the Dongpu Depression are dominated by O_2 species with DBE=1
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21 (mainly fatty acids) (Fig. 9a–h), the C_{16} and C_{18} compounds are relatively abundant with the exception
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23 of a few oils generated from low mature source rocks from wells Ming85, Pu1-120 and Wei77-10 (Fig.
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25 9e–l). The low mature oils are generally dominated by C_{20} compounds of the O_2 class species with
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27 DBE=1 (Fig. 9i). Fatty acids with low molecular weights, such as C_{16} and C_{18} , generally derive from
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29 plankton and bacteria, whereas fatty acids with high molecular weights ($>C_{24}$) originate from higher
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31 land plants (Jaffé and Gallardo, 1993). The C_{16} and C_{18} fatty acids in this study also could be
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33 contaminants introduced during the MS analysis (Teräväinen et al., 2007; Shi et al., 2010a, b;
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35 Oldenburg et al., 2014; Poetz et al., 2014). The distribution pattern of fatty acids with high molecular
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37 weights in crude oils still reflects the input to the source rocks. It should be noted that the C_{16} and C_{18}
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39 compounds with DBE=1 (O_2 class species, mainly unsaturated fatty acids) were not the most abundant
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41 compounds in low mature oils in this study. Instead, C_{20} compounds are abundant in the relatively low
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43 mature oils from wells Pu1-120 and Pu77-10 (Fig. 9e, i), reflecting overall enrichment of considerable
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45 unsaturated acids with various carbon numbers in low mature oils. Biodegradation may also lead to the
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concentration of fatty acids (Kim et al., 2005; Liao et al., 2012; Vaz et al., 2013; Pan et al., 2015). The TIC fingerprints of the saturated hydrocarbons in the Dongpu oils (Fig. 2) show a good preservation of *n*-alkanes; the A/C ratios (acyclic to cyclic naphthenic acids, $\sum O_2 DBE_1 / (\sum O_2 DBE_{(3+4+5)})$) of the Dongpu saline lacustrine oils (1.03~5.46, averaged 3.91; Table 3) is much larger than those of the biodegraded oils (mostly <1) reported by Kim et al (2005), which would decrease with increasing biodegradation. The oils generated from low mature source rocks with a relatively low burial depth in this study have a narrow range of A/C ratios (3.46~5.52) with an exception of the oil from Well Ming85 (1.04) (Table 3). We believe that the O_2 class species with DBE=1 is original components rather than biodegradation products. In general, the degree of condensation of the O_2 class species increase and the carbon number range decrease with increasing maturity (Fig. 9e–g; Fig. 7b), which is similar to the N_1 species.

Four- and five-ring naphthenic acids in crude oils carry special biological skeleton structures, such as steroids and hopanoids, and are commonly used as biomarkers (Cheng et al., 2010a; Shi et al., 2010a, b). The O_2 class species with DBEs of 6 and 5 are likely hopanoic acids and secohopanoic acids/steroidal acids (Shi et al., 2010a, b; Poetz et al., 2014), which are relatively enriched in most of the oil samples generated from low mature source rocks from wells Wei 77-10 and Pu1-120 (Fig. 9a, e and i). These hopanoic acids and secohopanoic acids/steroidal acids with special biological structures are commonly found in modern sediments and other low mature geological samples (Farrimond et al., 2002). They were also detected in the low mature geological samples from the Liaohe Oilfield of the Bohai Bay Basin (Shi et al., 2010b) and Posidonia shale of Germany (Poetz et al., 2014), and were recognized as related immature compounds (Jaffé and Gallardo, 1993; Mpanju and Philp, 1994;

Rodrigues et al., 2000). The southern oils showed some differences to the northern oils in the Dongpu Depression. It appears that the saline lacustrine oils, such as those from well Pu7-18, have more compounds with higher DBE values and a stronger degree of condensation and aromatization than the freshwater lacustrine oils (e.g., well Ma19-30) (Fig. 9b, f, d, h); the relative abundance of the $C_{22}\sim C_{34}$ compounds with DBE=1 of the O_2 species for the freshwater lacustrine oils is much larger than the saline lacustrine oils with similar maturity (Fig. 9j, k, l), suggesting an effect from organic matter input and/or paleoenvironment.

4.3.5 Composition and distribution of N_1O_1 class species

Only a slight variation in the relative abundance of the N_1O_1 species among the crude oils is observed (1.89%–6.88%, Table 3, Fig. 5). The N_1O_1 species in the oils have DBEs of 0–25 (mainly 6–22) (Fig. 10) and the compounds with DBE=2, 15 and 18 relatively are enriched (Fig. 8a–d). N_1O_1 species with DBEs of 10 and 13 correspond to hydroxylatedbenzoquinolines and ketones (benzoquinolinones), and DBEs of 15, 18 and 21 very likely consist of molecules containing a pyrrolic ring or fluorenocarbazoles (Poetz et al., 2014). The carbon numbers of the N_1O_1 species ranged from 15–22, maximizing at DBE=2 with a preference for C_{18} and C_{22} compounds (Fig. 5). Similar to the other nitrogen- and oxygen-containing compounds, the N_1O_1 species are influenced by maturity. The relative abundance of the species showed a slight increasing trend with maturity (Fig. 5). There is apparent increase in condensation for the N_1O_1 species with DBE>2 with increasing maturity (Fig. 10e–g; a–c) as well as an increasing relative abundance of the N_1O_1 species with DBE=2 (Fig. 10e–g; a–c). The kinetic mechanisms of the thermal evolution trends need further investigation. It seems that there are differences between the saline and freshwater lacustrine oils. For example, the saline lacustrine

oil samples from well Pu7-18 have a higher abundance of the species with a relatively higher degree of condensation than oil samples from freshwater lacustrine facies (Fig. 10 b, d, f, and h).

4.4 Geochemical significance of the nitrogen and oxygen compounds

4.4.1 Thermal maturity evaluation

The results discussed above demonstrate that the nitrogen- and oxygen-containing compounds of the N_1 , N_1O_1 , O_1 , O_2 class species are significantly influenced by thermal maturity, particularly the N_1 and O_1 class species. Thus, with increasing maturity we can conclude: (1) the relative abundance of the nitrogen and oxygen compounds changes as the relative abundance of the N_1 and N_1O_1 class species increases while the O_1 and O_2 decreases over the maturity range analyzed in this study (Fig. 5); (2) the condensation degree of the compounds increases (Figs. 6a–h; Fig.7; Figs. 8–9a–h; Fig.10), and (3) small molecules were produced (Figs. 6e–l; Figs.8–9 e–l). The last two points agree with previous reports for the Nanpu Depression (Wan et al., 2017) and Liaohe Oilfield (Li et al., 2010a). Fig. 7 shows a close relationship between thermal maturity and condensation and aromatization. With increasing maturity, macromolecules bound in the kerogen matrix are released and compounds with relatively high DBEs were also formed from those with low DBEs through cyclization of alkyl side chains and aromatization (Poetz et al., 2014). Previous studies showed that hydrocarbon migration also has an impact on the relative abundance of N_1 class (Liu et al., 2015; Zhang et al., 2016; Wan et al., 2017), which may not be essential here because of hydrocarbons trapped in situ with a very short migration distance (Zhang et al., 2011). It seems the relative abundance of the N_1 , N_1O_1 , O_1 ~ O_3 classes with varied maturity in a more complex manner.

Conventional biomarker parameters, such as C_{29} sterane 20S/(20S+20R), C_{29} sterane

$\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ and $Ts/(Ts+Tm)$, are widely used for maturity evaluations. However, the application is invalid with relatively high maturity to overmature material due to the thermal cracking of biomarkers (Peters et al., 2005). It was proposed by Wan et al. (2017) recently that ratios of C_{16-20}/C_{21-50} -DBE₁₂-N₁, DBE₁₂/DBE₉-N₁ and DBE₈₋₉/DBE₄-O₁, from negative-ion ESI FT-ICR MS analysis is, much more effective than the conventional maturity parameters, particularly at a higher maturity stage. Similarly, we found that ratios of the sum of N₁ class species with DBE=9–12 to DBE=15–18 (DBE_{9-12}/DBE_{15-18} -N₁), C₂₀–C₂₈ homologs to C₂₉–C₄₀ homologs with DBE=12 (C_{20-28}/C_{29-40} -DBE₁₂-N₁) and C_{20-30}/C_{31-50} -DBE₁₅-N₁ had good positive correlations with C₂₉ sterane 20S/ (S+R), C₂₉ sterane $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ and $Ts/(Ts+Tm)$ with *r* values in a range of 0.78–0.98 (average 0.89) (Figs. 11–12). Ratios of DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C_{20-30}/C_{31-40} -DBE₈-O₁ also correlate well with the conventional maturity indicators (*r*=0.81–0.94, average 0.87) (Fig. 11–12). We suggest that these ratios can be used as supplementary maturity indices, which are more suitable for geological samples with a relatively wide maturity range from low to moderate mature material relative to those of the biomarkers (Fig. 13a–h).

Other parameters derived from FT-ICR MS could be utilized to distinguish the oils generated from low mature source rocks from the ones from moderately to highly mature source rocks. For example, with the exception of Hu96-3, the ratios of O₂/N₁, C_{20-30}/C_{15-45} -DBE₁-O₂ (mostly fatty acids), and DBE₅₋₆/DBE₁₂₋₂₂-O₂ for the low mature and moderately to highly mature oils, respectively, ranged from 0.78 to 0.98 (average 0.87) vs. 0.11–0.42 (average 0.3), 0.44 to 0.68 (average 0.59) vs. 0.08 to 0.31 (average 0.17), and 4.10–13.5 vs. 0.15–2.68 (Fig. 14, table 3). Although the O₂/N₁ ratio could also be controlled by kerogen type and possibly TSR, thermal maturity is the main influence on composition

for the crude oils in this study. Therefore, abundant O₁ class species) with DBE=4 (mainly alkylphenols), the O₂ class species with DBE=1 with higher carbon numbers (>C₁₈) (mainly fatty acids) and O₂ species with DBE=5 and 6 (mostly hopanoic and secohopanoic acids) could be considered as signatures of low mature oils. In addition, high C₂₀₋₃₀/C₁₅₋₄₅-DBE₁-O₂ (>0.4), DBE₅₋₆/DBE₁₂₋₂₂-O₂ (>3.0) and O₂/N₁ (>0.7) can be used as auxiliary indicators for low mature oils (Fig. 14a–b).

4.4.2 Origin of the lacustrine oils generated at low maturity

Low mature lacustrine oils are widely distributed around the globe including some rift basins in Eastern China, which usually occurs in saline to half-saline tertiary stratum (Pang et al., 2003 and reference therein). Although there are some disputes focusing on quantity and mode of occurrence of such a kind of petroleum reserves (Li et al., 2003), it does exist (Tissot and Welte, 1984). Resins and asphaltenes that contain a large number of NSO heteroatom compounds are important components in the oils generated from low mature source rocks and of significance for unraveling the formation mechanisms of low mature oils (Barakat and Rullkoetter, 1994; Volkman et al., 1980). The low mature oils of the Dongpu Depression were deficient in saturated hydrocarbons (40.63%–57.34%) but abundant in “resins+asphaltenes” (21.77%–42.22%, average 30%). The percentages of “resins+asphaltenes” in the oils shows an obvious declining trend along increasing depth/maturity (Table 1), which provides solid evidence that the crude oils are generally progenetic without secondary alteration, and “resins+asphaltenes” or NSO compounds is intermediate product from kerogen and/or biological macromolecule to hydrocarbons. The negative-ion ESI FT-ICR MS provided important information for the understanding of the low mature oils origin.

Oxygen compounds in crude oils are important constituents and are considered mainly derived

from kerogen and/or lipids, or as products from secondary alteration, such as biodegradation (Hunt, 1979; Barth et al., 2004). Since no obvious signs of biodegradation is found in the Dongpu oils, the oxygen compounds should be considered primary and likely form resins and asphaltenes (Khorasani and Michelsen, 1991; Qin et al., 1997). Research on lower weight oxygen compounds carried out by GC–MS has shown that, the composition and distribution of alkylphenols are significantly affected by parental sources and maturity (Taylor et al., 1997). Fatty acids in resins are meaningful indicators for low mature oil origin (Shi et al., 2001; Zhe et al., 2003; Wang et al., 2004). However which heteroatom compounds are closely related to low mature oils was unclear. In this study, oxygen compounds, such as N_1O_1 , O_1 , O_2 and O_3 class species were affected by maturity to various degrees, while the O_1 and O_2 class species are abundant in low maturity oils (Fig. 5a). The O_1 class species were dominated by compounds with DBE=4 (primarily alkylphenols) in the relatively low mature oils (Fig. 8a–d), and the O_2 class species were the main constituents in the low mature oils, accounting for 28.3%–35.2% in relative abundance with a preference for higher carbon numbers ($>C_{20}$) with DBE=1 (mainly fatty acids) (Fig. 5; Fig. 9i, Table 3). We assume that these higher carbon number molecular compounds contain a large amount of long chain fatty acids with high OEP values (Fig. 9i), which has also been determined for low mature oils from the Lingqing Depression in the Bohai Bay Basin by Zhang and Zhang. (1999). It seems that the OEP of the O_2 class species with DBE=1 (mainly fatty acids) corresponds to the OEP of n -alkanes in the low mature oils, suggesting a close genetic relationship because n -alkanes could be produced from long chain fatty acids by thermal cracking of the carboxyl groups (Clemente and Fedorak, 2005). It has been well recognized that fatty acids of the O_2 class species are the intermediate products during chemical conversion of the organism to hydrocarbons, which generate hydrocarbons

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5 after chemical reaction (Shi et al., 2001). We also observe abundant O₂ species with DBE=5 and 6,
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8 primarily 4- and 5- ring naphthenic acids with special biological structures dominated by C₂₀–C₃₅ (Fig.
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10 9 a, e). These compounds were reported in the low mature oils from the Liaohe Oilfield by Shi et al.
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13 (2010b) and were considered as hopanoic and secohopanoic acids (Jaffé and Gallardo, 1993;
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16 Nascimento et al., 1999). They could be products of microbial degradation from C₃₅ hopanoic polyols,
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19 generally found in low mature oils (Qu et al., 1996). These hopanoic acids were constrained in
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22 macromolecules net by ester bonds or other weak interactions after incorporating into kerogen. Their
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25 occurrence was generally accepted as the marker of low mature oil (Jaffé and Gallardo, 1993;
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28 Nascimento et al., 1999). The content of DBE=5 and 6 compounds in O₂ class species (mostly hopanoic
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31 and secohopanoic acids or steroid acids) has a positive relationship with resins in the crude oils from the
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34 Dongpu Depression (Table 3).

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36 Our recent work showed that the "low mature oils" in the Dongpu Depression are usually mixed
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39 oils with different maturity with the saturated and aromatic fraction especially influenced by
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42 hydrocarbons derived from relatively deep source rock at higher maturity (Zhang et al., 2017). We
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45 presume that a majority of the NSO compounds were derived from low mature source rocks. Obvious
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48 differences were observed among rock extracts and the adjacent oil sands as well as mobile crude oils
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51 suggesting close relationship between them, which will be discussed in another manuscript.

52 **4.4.3 Evidence for thermochemical sulfate reduction**

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55 Thermochemical sulfate reduction (TSR) is a high temperature reaction between sulfate minerals
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58 and petroleum hydrocarbons. It usually occurs in reservoirs containing gypsum salt rocks. H₂S, organic
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61 sulfur compounds (e.g., thiadiamondoids), pyrobitumen, authigenic pyrite and other metal sulfide
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5 compounds are common products of TSR (Ho et al., 1974; Wei et al., 2012). Across the globe TSR has
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8 been detected in many carbonate formations including the Sichuan, Tarim, and Alberta Basins
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10 (Manzano et al., 1997; Zhang et al., 2008b, c; Hao et al., 2008; Cai et al., 2016). TSR was suggested to
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12 have occurred in terrestrial clastic reservoirs, such as North Sea sandstones (Worden et al., 2003) and
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14 the lacustrine sections of Jinxian Sag (Bohai Bay Basin) (Zhang et al., 2005b).
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18 FT-ICR MS has been previously used to successfully identify TSR by the composition and
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20 distribution of sulfur compounds (Li et al., 2011; Walters et al., 2011; Li et al., 2012, 2015a). Oils from
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22 wells Pushen18-2 and Pushen18 wells have undergone extensive TSR based on the large amount of
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24 thermally unstable S₁ class species (DBE<8) detected by positive-ion ESI FT-ICR MS (Fig. 15a–b)
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26 (Chen, 2017), which occurs in oils generated from low mature source rocks. The oils from the
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28 Pushen18-2 and Pushen18 wells have reached a relatively high thermal evolution level with partial
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30 biomarker thermal cracking (Fig. 3), which has a relatively higher concentration of aromatic sulfur
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32 compounds (i.e. dibenzothiophenes, DBTs), up to 10.75% (Pushen18-2) and 8.83% (Pushen18) (Table 2).
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34 High concentrations of DBTs could be a result of TSR (Manzano et al., 1997; Li et al., 2012, 2015a).
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36 The clastic reservoirs of the Pushen18-2 and Pushen18 wells were pinched with gypsum salt rock. We
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38 suggest that the S₁ class species with DBE<8 detected in Pushen18-2 and Pushen18 are products of TSR.
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40 Thick gypsum salt rocks, primarily anhydrite, were well developed in the Dongpu Depression, and part
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42 of the northern oils were deeply buried (3451–4556.1m) with reservoir temperatures reaching
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44 125–150°C, according to the burial history and well testing data, which provides a sound condition for
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46 TSR (Orr, 1974). Free sulfur and authigenic pyrite were commonly observed in drill cores from the
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48 clastic reservoirs, which can be reagents and products of TSR (Orr, 1974; Zhang et al., 2008b).
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Negative-ion ESI FT-ICR MS was recently used to identify TSR. Walters et al. (2015) proposed that nitrogen and oxygen compounds in the Alabama oils underwent varied degrees of TSR, and showed changes with increasing TSR alteration. They also suggested that there is an increasing trend in the relative abundance of the oxygen compounds O₁, O₂ to O₃ with increasing TSR. The O₁ class species, which contain the fewest number of oxygen atoms, were considered to be the one mostly depleted during TSR (Walters et al., 2015; Hosseini et al., 2017) (Fig. 17a). We observed an obvious decrease trend of the relative abundance of the O₁ species whereas an increasing trend of the O₂ and O₃ species for the group-I oils, featured by a relatively low thermal maturity level (Fig.17c) and derived from the Es₃-Es₄ rocks in the Puwei Sag in the order of Pu7-18→Wei42-26→Wei77-10→Ming85 (Fig.17b, c). Although these oils are TSR relevant, they display a decreasing trend of $\delta^{34}\text{S}$ of C₀~C₁-DBTs indicating probably a decreasing trend of TSR in the same order of the oils (Fig.17d), which suggests possibly other action such as maturity also play an important role on the compounds (Fig.17b, c). Therefore, precaution should be taken when the relative abundance of O₁, O₂ and O₃ species were used to identify the extent of TSR, which might be more suitable for the crude oils with relatively high thermal maturity. The group II oils were characterized by a relatively high thermal maturity (Fig.17c), which were sourced from the source rocks with type II kerogen in the Liutun Sag. We observed an in obviously higher $\delta^{34}\text{S}$ value for the oil from Hu96-3 (Fig.16; Fig.17d) and significantly higher abundances of O₂ and O₃ species relative to the oils from Well Pushen 18-2 and Pushen 18 (Fig.17b). Since a lowest $\delta^{34}\text{S}$ value was detected from the oil of Chun24-1 (Fig.16a), a freshwater lacustrine oil generated from source rocks with type II~III kerogen (Fig. 4a, c), it is unlikely that a little more amount of terrestrial organic matter input if possible to the source rocks would caused the abnormal features of the Hu96-3

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5 oils distinguished from the others. TSR might be one of the most important geochemical factors
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7 responsible for the abnormal phenomena. A slight higher $\delta^{34}\text{S}$ values were observed from the oil of
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9 Pushen18 relative to Pushen18-2 (Fig.16b), suggesting a little higher extent of TSR of the later
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11 compared with the former. A decreasing abundance of the O_1 species (Fig.17b) agrees with the
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13 observation of Walters et al. (2015).
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18 A new approach often able to identify oils impacted by TSR is compound specific sulfur isotope
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20 analysis (CSSIA; Amrani et al., 2012; Li et al., 2015a). Different OSCs can have a varied sensitivity to
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22 TSR and a distinction in their $\delta^{34}\text{S}$ values may help identify the early stages of TSR (Amrani et al., 2012;
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24 Gvirtzman et al., 2015). For instance, benzothiophenes (BTs) and dibenzothiophene (DBT) produced by
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26 the reaction of the H_2S from TSR with hydrocarbons will gradually approach a $\delta^{34}\text{S}$ value close to the
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28 sulfate utilized by TSR, but differences in the TSR production rates of BTs and DBTs leads to
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30 differences in $\delta^{34}\text{S}$ values at the early stages of TSR (Amrani et al., 2012). The $\delta^{34}\text{S}$ values of several
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32 alkylated BTs measured for oils from wells Wei77-10 and Min85 in the Wenmingzhai and Weichen
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34 oilfields were distinctly higher than the $\delta^{34}\text{S}$ values of co-occurring DBTs (Fig.16a) which is indicative
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36 of a TSR event. BT concentrations in the other oils analyzed were too low for reliable measurement, but
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38 several alkylated thiadamantanes detected in oil from Well Pu7-18 in the Puchen Oilfield (Fig.16a) were
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40 similarly enriched compared to the DBTs in that oil. Thiadamantane produced by TSR will also be
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42 relatively ^{34}S enriched compared to DBTs which don't fully equilibrate with the isotopically heavier
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44 sulfate source (Gvirtzman et al., 2015; Cai et al., 2016). The compound specific sulfur isotope
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46 differential evident in the OSCs of these oils is consistent with TSR alteration.
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60 **4.4.4 Controls and reliability of the FT-ICR MS indices**

The composition and relative distribution of heteroatomic compounds in crude oils are largely controlled by the secondary processing of kerogen with a potential contribution also from inorganic substances (Li et al., 2010a, 2012; Wan et al., 2017, and references therein). Thermal maturation can have a significant effect on these products. Of the current negative ESI FT-ICR MS data lacustrine oils of the Dongpu Depression, the N_1 and O_1 species showed the strongest relationships with thermal maturity. The freshwater lacustrine oils showed decreasing abundances of N_1 and N_1O_1 species with increasing maturity (Fig. 5b), which was similar to the trend previously reported from analysis of Nanpu Sag oils (Wan et al., 2017). However, saline lacustrine oils in the Dongpu Depression (Fig.5a) showed the opposing trend of increasing abundances of N_1 and N_1O_1 species with increasing maturity. Their abundances (particularly for DBE > 9) increased noticeably at early thermal evolution (matched by a decline in O_2 species, particularly acids with DBE<6) but then did decrease at medium to high thermal maturities (where condensed oxygen compounds increased; Fig.9).

The different effects maturation had on the N_1 and N_1O_1 composition of freshwater and saline lacustrine oils is likely due to the relative thermal stabilities of N and O compounds. Secondary alterations such as TSR, identified to impact several of the saline oils, is known to change the oxygen species composition of oils by decreasing the abundance of O_1 species relative to O_2 and O_3 species (Walters et al., 2015). An organofacies influence cannot be excluded, however, given the heterogeneous nature of organic inputs deposited and preserved under saline conditions.

The effects of thermal maturity were magnified by selectively comparing the relative abundance of N_1 and O_1 species with specific DBE values and carbon number ranges. $DBE_{9-12}/DBE_{15-18}-N_1$, $C_{20-28}/C_{29-40}-DBE_{12}-N_1$, $C_{20-30}/C_{31-50}-DBE_{15}-N_1$, $DBE_{9-12}/DBE_{4-20}-O_1$ and $C_{20-30}/C_{31-50}-DBE_8-O_1$ all

showed clear relationships with thermal maturity, and in some instances seemed more sensitive to the thermal maturity range of the oils than traditional biomarker maturity indicators (e.g., C_{29} sterane $\alpha\alpha\alpha 20S/(S+R)$ and C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$; Fig.13), which can operate over a limited maturity range (Peter et al., 2005). $Ts/(Ts+Tm)$ correlated more closely with $DBE_{9-12}/DBE_{15-18}-N_1$ ($r=0.98$, Fig.11c) than with either C_{29} sterane $\alpha\alpha\alpha 20S/(S+R)$ (0.78, Fig.11a) or C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ (0.93, Fig.11b). $C_{20-28}/C_{29-40}-DBE_{12}-N_1$ showed a similarly strong relationship with $Ts/(Ts+Tm)$ ($r=0.90$, 0.80 and 0.88, respectively; Fig.12a~c; Fig. 13).

Sharp deviations in the values of the N_1 species parameters may reflect controls related to source or other secondary alterations. For example, the relatively low $C_{20-28}/C_{29-40}-DBE_{12}-N_1$ and $C_{20-30}/C_{31-50}-DBE_{15}-N_1$ values of the Chun24-1 and Ma19-30 oils is likely due to different source facies (Figs. 13e and f); and the high $DBE_{9-12}/DBE_{4-20}-O_1$ and $C_{20-30}/C_{31-50}-DBE_8-O_1$ values of the Wei42-26 and Hu96-3 oils are probably a result of TSR (Figs. 13g and h) which can hasten the thermal degradation of petroleum hydrocarbons (Zhang et al., 2005a; 2008a). TSR would likely lead to an enrichment of low DBE and carbon numbers O_1 species. Of the potential thermal maturity indicators based on N_1 -species composition, $DBE_{9-12}/DBE_{15-18}-N_1$ ratio is likely the most effective. It showed the strongest correlation with $Ts/(Ts+Tm)$ (Figs. 13c and d) suggesting minimal distortion by different organofacies or TSR alteration. Of the other N_1 ratios tried, $C_{20-30}/C_{31-50}-DBE_{15}-N_1$ was the next most reliable thermal maturity indicator as it showed a slightly closer correlation to the sterane and terpane parameters than $C_{20-28}/C_{29-40}-DBE_{12}-N_1$ and $C_{20-30}/C_{31-40}-DBE_{12}-O_1$ (Fig. 12).

The DBE and carbon number range of the N_1 and O_1 ratios evaluated here (e.g., $DBE_{9-12}/DBE_{15-18}-N_1$) for their apparent close relationship with the thermal maturity of the Dongpu

Depression oils, were slightly different to those ratios (e.g., $\text{DBE}_{12}/\text{DBE}_9\text{-N}_1$, $\text{C}_{16-20}/\text{C}_{21-25}\text{-DBE}_{12}\text{-N}_1$) evaluated for Nanpu Sag oils by Wan et al (2017). The effectiveness of specific ESI FT-ICR MS measured N_1 and O_1 proxies is likely to vary with heteroatom species composition, whereas molecular based parameters from GC/MS analysis typically measure a relatively fixed relationship between specific biomarkers.

Several saline lacustrine oils from wells in the North Dongpu Depression including from the Wenmingzhai (e.g., Min85) and Weichen (e.g., Wei77-10) oilfields have been reported to contain high H_2S levels (Personal communication with field explorationists). There has been some speculation about the TSR or BSR origin of these sour gases. For instance the former source is favored by a lack of hydrocarbon biodegradation evidence, although low reservoir temperatures (e.g., as low 60~70 °C for Wenmingzhai) are not likely to directly support TSR. Evidence from ESI FTICR MS and CSSIA analyses indicate TSR alteration, supporting the proposal that these sour gases have migrated from deeper source rocks. Source rocks > 3000m ($\text{Es}_3\text{-Es}_4$) are a likely candidate, and their geological temperatures have been estimated to be ~80°C (Zhang et al., 2017). This is also below the temperature range normally expected to initiate TSR, although a 100°C activation temperature has been suggested in certain environments (Walters et al., 2015). We believe the geological and geochemical conditions in the Dongpu Depression are suitable for TSR.

5 Conclusions

Negative-ion ESI FT-ICR MS can provide a detailed characterization of the composition and origins of heteroatom compounds in oils and compliment traditional hydrocarbon biomarker characterizations by GC-MS analysis with additional information about the sources, thermal maturity or

secondary alteration (e.g., TSR) of oils. N_1 (dominant), N_1O_1 , O_1 , O_2 and O_3 class species were detected here in oils from type I–II and II–III kerogens deposited under saline and freshwater lacustrine conditions from the Dongpu Depression (Bohai Bay Basin, China) and spanning a range of maturity levels ($R_c=0.67\%–1.29\%$). Only modest variation was evident in the nitrogen- and oxygen- compound composition of the saline and freshwater lacustrine oils, but much larger differences were detected between low mature oils and moderately to highly mature oils.

Low maturity saline lacustrine oils contained a high relative abundance of O_1 class species with DBE=4 (mainly alkylphenols); O_2 species with DBE=1 (mainly fatty acids); and high MW ($> C_{18}$) O_2 species with DBE=5 and 6 (i.e., terpenoid/steroid acids) or DBE=1 (i.e., fatty acids). These and several other compositional features indicative of the low maturity Donpu oils (e.g., $O_2/N_1 > 0.7$, $C_{20-30}/C_{15-45}\text{-DBE}_1\text{-}O_2 > 0.4$; $DBE_{5-6}/DBE_{12-22}\text{-}O_2 > 4.0$) may serve as useful indicators of low maturity oils. The high maturity oils generally showed a lower and narrower C-number range of products with increased condensation/aromatization, particularly of N_1 , O_1 and O_2 species. Parameters based on the relative abundances of specific species type and range (e.g., $DBE_{9-12}/DBE_{15-18}\text{-}N_1$) may be useful auxiliary maturity indicators which could compliment conventional biomarker based parameters to help resolve maturity progression across the oil window.

Other parameters based on features of the N- and O-composition of the oils showed an organofacies relationship (e.g., $C_{20-28}/C_{29-40}\text{-DBE}_{12}\text{-}N_1$, $C_{20-30}/C_{31-50}\text{-DBE}_{15}\text{-}N_1$) or reflected secondary alterations by TSR ($DBE_{9-12}/DBE_{4-20}\text{-}O_1$, $C_{20-30}/C_{31-50}\text{-DBE}_8\text{-}O_1$) which led to a decreasing percentage of O_1 class species.

Several compositional differences were observed between the freshwater and saline

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5 samples(e.g., relatively high O₂ and N₁ abundances and low O₁ abundances in the two freshwater
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8 samples analyzed) suggest ESI-FT-ICRMS analysis has potential for distinguishing between these
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10 types of lacustrine samples, though more of these samples, particularly from freshwater depositions,
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13 need to be studied to confirm systematic compositional differences.
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18 **ACKNOWLEDGEMENTS**

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21 This study was funded by the Natural Science Funding Council of China (Grant Nos. #41473047
22
23 and #41673055) and the National Science and Technology Major Project (No. 2016ZX05006-004). The
24
25
26 Zhongyuan Oilfield, CNPC, is thanked for providing background geological data and permission to
27
28
29 publish the results. The authors thank Dr. Zulin Chen for excellent experimental assistance. The
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32 reviewers are sincerely acknowledged for helpful comments on an earlier version of this manuscript.
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Caption of figures:

Fig. 1 (a) Regional structural map showing the location of the Dongpu Depression; (b) cross section of the North Depression. See (a) for map location of the cross section.

Fig. 2 Total ion chromatogram (TIC) of the saturates from crude oils.

Fig. 3 Mass chromatograms of m/z 217 and m/z 191 of saturates from the Dongpu Depression crude oils.

Fig. 4 Cross plots of biomarkers showing two oil families for the investigated oils from the Dongpu Depression.

(a) is after Connan and Cassou, 1980; (b) is after Hughes et al., 1995; (c) and (d) is after Peters et al., 2013, Sharaf et al., 2007 respectively).

Fig. 5 Relative intensity/abundance of heteroatom class species in the oils assigned from negative-ion

ESI FT-ICR mass spectra. (a) the saline lacustrine oils in the North Depression; (b) the freshwater lacustrine oils in the South Depression.

Fig. 6 Relative intensity/abundance of the N_1 class species with various DBE values of the crude oils detected by negative-ion ESI FT-ICR MS (left); Plots of DBE versus carbon number of the N_1 class species for the selected oils (middle); Carbon curve of the N_1 class species with DBE = 9, 12 and 15 for the selected oils (right).

Fig. 7 Triangular plots of the relative abundance of the DBE 9, 15 and 18 of N_1 and DBE 4, 8 and 9 of O_1 species showing the condensation and aromatization changes with increasing maturity of the species.

Fig. 8 Relative intensity/abundance of O_1 class species with various DBE values of the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of O_1 class species for the selected oils; Carbon curve of the O_1 class species with DBE = 4, 5 and 9 for the selected oils.

Fig. 9 Relative intensity/abundance of O_2 class species with various DBE values for the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of O_2 class species for the selected oils; Carbon curve of the O_2 class species with DBE=1 for the selected oils.

Fig. 10 Relative intensity of N_1O_1 class species with various DBE values for the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of the N_1O_1 class species for the selected oils.

Fig. 11 Cross plots of negative-ion ESI FT-ICR MS indices on condensation versus GC-MS parameters for the oils.

Fig. 12 Cross plots of negative-ion ESI FT-ICR MS indices on alkyl substitution versus GC-MS

parameters for the oils.

Fig. 13 Plots of negative-ion ESI FT-ICR MS parameters of N₁ and O₁ class species versus GC–MS parameters indicating the maturity difference. A: saline lacustrine oils; B freshwater lacustrine oils.

Fig. 14 Parameters of nitrogen and oxygen compounds from negative-ion ESI FT-ICR MS analysis indicates immature oils of the Dongpu Depression.

Fig. 15 The Composition and distribution of the S₁ class species detected by positive-ion ESI FT-ICR MS (Chen, 2017).

Fig. 16 Compound specific of sulfur isotope for partial oils in the Dongpu Sag.

Note: C3BTi, C3BTii, C3BTiii and C3BTiv represent four isomers of C₃-benzothiophene , and so on for the C4BTi, C4BTii, C4BTiii, C4BTiv, C5BTi and C5BTii; DBT: dibenzothiophene; m: methyl; dm: dimethyl; tm: trimethyl; 1D, 2D and 3D represent 1-cage, 2-cage and 3-cage thiadiamondoids.

Fig. 17 Relationship between relative abundance of O₁ , O₂ and O₃ class species detected by negative-ion ESI FT-ICR MS and TSR. (a) is Alabama oils (Walters et al., 2015); (b) ~ (d) is for the Dongpu oils.

Caption of Tables:

Table 1 Physical properties and group composition for the oils from the Dongpu Depression.

Note: Asph: asphaltenes; Sat: saturates, Aro: aromatics, sat/aro: saturates/aromatics.

Table 2 Basic geochemical parameters of the oil analyzed from the Dongpu Depression.

Note: Pr/Ph: pristane/phytane; Pr/*n*C₁₇: pristane/*n*C₁₇; Ph/*n*C₁₈: phytane/*n*C₁₈; CPI:

$$[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})]/2;$$

OEP: $(C_i + 6C_{i+2} + C_{i+4}) / (4C_{i+1} + 4C_{i+3})$ or $(4C_{i+1} + 4C_{i+3}) / (C_i + 6C_{i+2} + C_{i+4})$, among which $i+2$ is the maximum peak of *n*-alkanes with i corresponding to odd and even member respectively; G/C₃₀H: gammacerane/C₃₀-hopane ratio; C₃₅/C₃₄H: C₃₅/C₃₄ hopane; DBTs (%): Percentage of DBTs among the aromatic recognizable peaks. DBT/P: dibenzothiophene/ phenanthrene; C₂₅TT/C₂₆TT: C₂₅ tricyclic terpane/ C₂₆ tricyclic terpane; C₁₉₋₂₁TT/ C₂₃₋₂₄TT: C₁₉₋₂₁tricyclic terpane/C₂₃₋₂₄tricyclic terpane; 20S/(S+R): ratio of C₂₉ $\alpha\alpha$ steranes; $\alpha\beta\beta / (\alpha\alpha\alpha + \alpha\beta\beta)$: Ratio of C₂₉steranes; Ts/(Ts+Tm): 18 α (H) -/(18 α (H)+17 α (H)) -trisorhopane ratio; Dia/Reg: (C₂₇-C₂₉)-diasterane/(C₂₇-C₂₉)-regular sterane; T/P: tricyclic terpane/ pentacycliterpanes; $R_C = 0.6 \times MPI1 + 0.4$, of which $MPI1 = 1.5 \times (2\text{-methylphenanthrene} + 3\text{-methylphenanthrene}) / (1\text{-methylphenanthrene} + 9\text{-methylphenanthrene} + \text{phenanthrene})$; The R_C of the oils from well Phshen20, Pushen 18-2 and Pushen18 might be invalid because of obvious thermal cracking (see figure 3), and therefore, we list the R_o (in bracket) of the source rocks of the oils based on oil-source rock correlation for reference.

Table 3. Parameters calculated by the results of negative-ion ESI FT-ICR MS for the oils.

Note: A: The ratio of the sum of DBE=9–12 to that of the DBE=15–18 of the N₁ species (DBE₉₋₁₂/DBE₁₅₋₁₈-N₁); B: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₅₀ homologs of the N₁ species with DBE=12 (C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₂-N₁); C: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₅₀ homologs of the N₁ class species with DBE=15 (C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁); D: The ratio of the sum of DBE=9–12 to that of the DBE=4–20 of the O₁ species (DBE₉₋₁₂/DBE₄₋₂₀-O₁); E: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₄₀ homologs of the O₁ species with DBE=8 (C₂₀₋₃₀/C₃₁₋₄₀-DBE₈-O₁); F: The ratio of C₂₀–C₃₀ homologs to C₁₅–C₄₅ homologs of the O₂ species with DBE=1 (C₂₀₋₃₀/C₁₅₋₄₅-DBE₁-O₂); G: The ratio of the sum of

DBE=5–6 to that of the DBE=12–22 of the O₂ species DBE_{5–6}/DBE_{12–22}-O₂; H: The ratio of the O₂ species to the N₁ species (O₂/N₁); I: A/C ratio = ($\sum$ O₂ DBE₁)/($\sum$ O₂ DBE₍₃₊₄₊₅₎)

Geochemical characteristics and significance of heteroatom compounds in ~~Laeustrine-lacustrine~~
oils of the Dongpu Depression (Bohai Bay Basin, China) by negative-ion Fourier transform ion
cyclotron resonance mass spectrometry

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Abstract: ~~Abstract:~~ Saline and freshwater lacustrine oils from the Dongpu Depression (Bohai Bay
Basin, ~~China~~) were ~~molecularly~~ characterized by negative-ion electrospray ionization (ESI) Fourier
transform ion cyclotron resonance mass spectrometry (FT-ICR MS) ~~to further evaluate the source,~~
~~thermal maturity or secondary alterations of these oils.~~ ESI-FT-ICR MS detected a large range of
~~neutral~~ nitrogen and ~~acidic~~ oxygen compounds in the oils, mostly comprising N₁ ~~(molecules with one~~
~~nitrogen atom)~~, O₁, O₂ and N₁O₁ ~~class~~ species. The low mature oils ~~immature saline lacustrine oils were~~
are dominated by O₁ ~~class~~ species with double bond equivalent of 4 (DBE=4; mainly alkylphenols), O₂

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~~class~~ species with DBE=5-6 (i.e., hopanoid, secohopanoic and steroid acids) and DBE=1 (i.e., fatty acids), indicating a genetic relationship between oxygen compounds and their ~~bacterial or algal~~ precursors. The nitrogen and oxygen ~~species composition of the oils compounds~~ ~~were~~ significantly influenced by ~~thermal~~ maturity. ~~Immature, with the lowest~~ ~~with the lower maturity~~ oils ~~analysed were~~ enriched in O₂ species, particularly fatty acids and 4-5 ring naphthenes with biologically sourced hydrocarbon skeletons; ratio ~~values~~ of O₂/N₁ >0.7; C₂₀₋₃₀/C₁₅₋₄₅-DBE₁-O₂ >0.4; and DBE₅₋₆/DBE₀₋₂₆-O₂ >6.0 may be useful indicators of ~~low maturity~~ ~~immaturity~~. With increasing maturity, the condensation degree of the compounds increased and the carbon number decreased. The relative abundances of N₁ and O₁ ~~class~~ species with the following specific DBE carbon number ranges were particularly sensitive to ~~the thermal maturity level of the Dongpu oils~~: DBE₉₋₁₂/DBE₁₅₋₁₈-N₁, C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁, C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁, DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁. In some instances the FT-ICR MS proxies provided a more reliable indication of high maturity levels than traditional sterane based maturity parameters. However, several of these species ~~classes~~ were also responsive to other influences, namely C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁ ratios ~~values~~ reflected an organofacies control and DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁ ratios changed with thermochemical sulfate reduction (TSR). ~~Several oils impacted by TSR~~ confirmed by ~~TSR~~ ~~indicative~~ $\delta^{34}\text{S}$ variances of ~~organic sulfur compounds~~ OSCs ~~measured by complimentary compound-specific isotope analysis (CSSIA)~~ ~~showed a decrease in the abundance of O₄ class species and an increase of O₃ class species.~~ In light of the multiple controls on the nitrogen and oxygen ~~species composition of the oils compounds~~, DBE₉₋₁₂/DBE₁₅₋₁₈-N₁ ratio ~~seemed~~ seems unaffected by organofacies or TSR and was considered the most reliable maturity proxy displaying a similar or better

maturity relationship than ~~the traditional C_{27} -hopane ratio~~ $Ts/(Ts+Tm)$. ~~The FT-ICR MS proxies also provided a more reliable indication of high maturity levels than traditional sterane-based (e.g. C_{29} sterane $\alpha\alpha\alpha 20S/(S+R)$ and C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$) thermal maturity parameters.~~ Aside from secondary alteration effects, the freshwater samples showed several compositional differences to the saline samples, albeit from a limited data set, including generally higher O_2 and N_1 (particularly low MW) product abundances, lower abundances and quite different distribution of O_1 products. These distinctions suggest ESI-FT-ICRMS analysis has potential for distinguishing these sample types.

Key words: Dongpu Depression, saline lacustrine facies, heteroatomic compounds, ~~immature oil~~, maturity, ESI FT-ICR MS, GC-ICPMS.

1. Introduction

Although oxygen and nitrogen compounds are minor components of crude oils, they carry important geological and geochemical information ~~which that~~ may help unravel hydrocarbon generation and migration mechanisms. Nitrogen or oxygen containing organic products of geological samples have been used to indicate thermal maturity (Li et al., 1995; Clegg et al., 1998; Horsfield et al., 1998; ~~Li et al., 1995~~; Zhang et al., 2011), origin, paleoenvironment (Clegg et al., 1997) and hydrocarbon migration pathways (~~Larter et al., 1996~~; Li et al., 1995; Yamamoto, 1992; Li et al., 1995; Larter et al., 1996).

However, identification and analysis of polar, high MW heteroatom compounds by traditional geochemical methods has proved challenging. Gas chromatography-mass spectrometry (GC-MS), for example, has generally been limited to the detection of low molecular weight nitrogen compounds such

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as C₀-C₂ carbazoles, benzocarbazoles and dibenzocarbazoles (~~Bennett et al., 2002; Larter et al., 1996;~~ Yamamoto et al., 1991; Larter et al., 1996; Bennett et al., 2002). The high resolution and mass accuracy of Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) may support a more comprehensive analysis (~~Headley et al., 2016; Hughey et al., 2002; Mullins, 2007;~~ Qian et al., 2001; Hughey et al., 2002; Mullins, 2007; Headley et al., 2016). Electrospray ionization (ESI) FT-ICR MS can be used for the molecular characterization of non-basic pyrrolic nitrogen compounds (Qian et al., 2001; Hughey et al., 2004; ~~Qian et al., 2001~~). More sophisticated application of ESI FT-ICR MS has supported detailed characterization of the oxygen and nitrogen product distribution in oil sands, asphalts and heavy crude oils (Roussis et al., 2003; Noah et al., 2015), biodegraded oil (Kim et al., 2005; Liao et al., 2012; Vaz et al., 2013; Pan et al., 2015; ~~Vaz et al., 2013~~), mature oil and their polarity based (~~Cui et al., 2014; Poetz et al., 2014;~~ Oldenburg et al., 2014; Poetz et al., 2014; Cui et al., 2014; Wan et al., 2017), high total acid number (TAN) oils (Barrow et al., 2003; Shi et al., 2010b) and shale oils (Bae et al., 2010; Chen et al., 2012; Tong et al., 2013; Mahlstedt et al., 2016), as well as tracing oil migration pathways (Liu et al., 2015; Zhang et al., 2016). Early studies recognized the distinctive heteroatom product composition of crude oils from different geological sources or depositional environments, of different maturity level or altered by secondary impacts. For instance, a low maturity, partially biodegraded lacustrine Chinese oil had a higher oxygen (O₂) content than moderately mature marine oils from North America (Hughey et al., 2002); a mature marine-derived oil from the Middle East had a high nitrogen content (Hughey et al., 2002); whilst a North Sea was characterized by a lower relative abundance of O₂ and N₁ (Teräviäinen et al., 2007), which were determined by biomass, depositional environment and biodegradation (Hughey et al., 2002).

The freshwater lacustrine-sourced oil from the Nanpu Depression of the Bohai Bay Basin in China was reported recently as having the highest relative abundance of N₁, followed by O₁ and O₂ species (Wan et al., 2017). However, the composition of oxygen and nitrogen compounds in ~~immature-low~~ maturity saline lacustrine oils has not yet been investigated in detail. In this study, negative-ion ESI FT-ICR MS combined with GC-MS was used to investigate the composition and distribution of oxygen and nitrogen compounds in saline/freshwater lacustrine oils of different maturities in the Dongpu Depression of the Bohai Bay Basin. These oils also contained distinctive organic sulfur compounds (OSCs) so compound specific sulfur isotope analysis (CSSIA) was conducted to help assess the potential occurrence and impact of thermochemical sulfate reduction (TSR). The geochemical significance and genetic mechanisms of these compounds are discussed.

2 Geological setting

Saline lacustrine basins of Tertiary age are well developed in China. The NNE-trending Dongpu Depression in the southeastern part of the Bohai Bay Basin is a typical lacustrine sub-basin containing abundant petroleum (Gao et al., 2015; Wang et al., 2015) (Fig. 1a). The depression covers an area of 5300 km² with narrowing-down topography from northeast to southwest. The Lanliao Fault in the east and the Changyuan Fault in the west exert control on the sedimentation of the depression. In total, four tectonic units of the depression are defined: eastern sub-depression, western sub-depression, central uplift and western slope (Fig. 1a). The Dongpu Depression has undergone two major tectonic cycles (Es₄-Ed and Ng-Q), which are subdivided into five evolution stages: initial rifting (depositional episode of the Es₄ strata), advanced rifting (Es₃), post-rifting (Es₂-Es₁), rifting termination (Ed) and subsidence (Ng, Nm and Q).

The Dongpu Depression developed on Mesozoic and Paleozoic basement, and overlain by Cenozoic sedimentary packages, including the Paleogene Shahejie (*Es*) and Dongying (*Ed*) formations, the Neogene Guantao (*Ng*) and Minghuazhen (*Nm*) formations, and the Quaternary Pingyuan (*Py*) Formation. The *Es* is divided into four members (*Es*₁ to *Es*₄); *Es*₃ and *Es*₄ are further divided into three (*Es*₃¹ to *Es*₃³) and two (*Es*₄¹ and *Es*₄²) sub-members, respectively. The *Es*₄ member and middle-lower *Es*₃ sub-members (*Es*₃²-*Es*₃³) were deposited in a humid climate and consists of extensive and deep lacustrine facies, the *Es*₃¹ sub-member is an arid fluvial facies, and the *Es*₁-*Es*₂ members are shallow lacustrine facies deposited in a humid climate (Liu and Ren, 2007; Zhang et al., 2007; Ji et al., 2015; Li et al., 2015b; Liu and Ren, 2007; Zhang et al., 2007). The Dongpu Depression contains two apparently different sedimentary facies of Tertiary age: saline lacustrine in the northern sector (hereafter North Depression) and freshwater lacustrine in the southern sector (hereafter South Depression) (Jiang et al., 2016; Li et al., 2015b; Jiang et al., 2016), which are nearly divided by the Yellow River (Li et al., 2015b; Jiang et al., 2016; Li et al., 2015b) (Fig. 1a). The *Es* contains prominent reservoir-producing layers and two main sets of source rocks, including the *Es*₁ and *Es*₃-*Es*₄ members, among which *Es*₃ is the most important. Four sets of gypsum salt rocks co-occur with petroleum in the North Depression (Fig. 1b), significantly impacting oil and gas generation and distribution (Gao et al., 2009; Wang et al., 2015). The proven petroleum reservoir is about 5.848×10⁸t with the majority (>90%) distributed in the North Depression where gypsum strata have developed. Immature-Low maturity oils (generated from low mature source rocks) were discovered in the Wenmingzhai (WMZ), Pucheng (PC) and Weicheng (WC) oilfields (Gao et al., 2009; Wang et al., 2015) and normal maturity oil, condensate, mature oil-

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and gas (generated from moderately to highly mature source rocks) can be found in the central

Wenliu (WL) Oilfield and the South Depression (Fig.1). We define the oils with C₂₉ sterane

$\alpha\alpha\alpha 20S/(S+R)$ and C₂₉ sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta) < 0.4$ as ~~immature or less mature~~ low mature oils.

(generated from low mature source rocks) (Wang et al., 1995; Peters et al., 2005).

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3 Samples and methods

Over 100 crude oils were collected from the Dongpu Depression for detailed geochemical analysis by conventional methods such as GC-MS and carbon isotopic analysis (to be separately reported). Among which, 11 oils were selected for ESI FT-ICR MS analysis. Nine were derived from source rocks deposited in saline lacustrine facies in the North Depression while two were sourced from source rocks formed in freshwater lacustrine facies in the South Depression. The detail of the samples is shown in Fig. 1a and Table 1.

3.1 GC-MS analysis

All oils were separated into saturate, aromatic~~s~~, resins and asphaltenes fractions (SARA). Briefly, the oils were deasphalted before fractionation on a neutral alumina chromatographic column. Saturated hydrocarbons, aromatic hydrocarbons and ~~a~~-polar fractions were then obtained by sequential elution with *n*-hexane, toluene and chloroform. GC-MS analysis of the saturate and aromatic fractions were separately carried out on an Agilent 6980 gas chromatography coupled with HP-5MS fused silica columns of 30m×0.25mm×0.25μm and 60m×0.25mm×0.25μm, respectively. The experimental conditions were the same as those detailed in Li et al. (2010b). Peak identifications and quantitative methods were reported by Jiang et al. (2001).

3.2 FT-ICR MS analysis

A total of 10 mg crude oil was dissolved in 1 mL toluene. Twenty ~~microleter~~micrometer of the solutions was diluted by 1mL toluene and methanol (1:1, v:v) mixture. A total of 15 μ ~~L~~L ammonium hydroxide solution (28%) was added to facilitate deprotonation of the acids and neutral nitrogen compounds to yield $[M-H]^-$ ions. All solvents were analytical reagent grade, distilled twice and kept in a glass bottle, which is utilized to solvent handling and transferring except for the steel pistons of 100- μ L Hamilton syringes.

The analysis was conducted on a Bruker Apex-Ultra FT-ICR mass spectrometry equipped with a 9.4-T superconducting magnet. Sample solutions were dissolved by an Apollo II electrospray source (ESI) at 180 μ L/h with a syringe pump. The ESI was operated at negative mode. The spray shield voltage is 4000V for general operating conditions of negative-ion formation. Capillary column introduce voltage and end voltage are 4500V and 320V respectively. Ions accumulated for 0.1 s in a hexapole with 2.4 V of direct current (DC) voltage and 400 Vp-p (volts peak to peak) of radio-frequency (RF) amplitude. The optimized mass for Q1 was m/z 300. An argon-filled hexapole collision pool was operated at 5 MHz and 400 Vp-p of RF amplitude, in which ions accumulated for 0.4 s. The extraction period for ions from the hexapole to the ICR cell was 1.2 s. The RF excitation was attenuated at 11.75 dB and used to excite ions over the range of m/z 200–900 Da. Data sets of 4M words were acquired. To enhance signal/noise ratio, 64 scans were co-added. A square sine bell multiplication apodization was carried out, followed by a single zero-fill before fast Fourier transform and magnitude calculation. The threshold for the signal to noise ratio (S/N) used was ≥ 6 , and the calibration error is <1ppm. Data processing was described elsewhere (Shi et al., 2013).

3.3 Compound-specific stable sulfur isotope analyses

Compound specific sulfur isotope analysis (CSSIA) was performed on the aromatic fractions of eight selected Dongpu Depression oils. $\delta^{34}\text{S}$ measurement of OSCs (thioaromatics and thiadamantanes) present in the oils was achieved using an Agilent 6890 GC coupled to a Thermo Neptune Plus multi-collector inductively coupled plasma (ICP) MS (Greenwood *et al.*, 2018). The OSCs were separated on the GC with a DB-5 MS column (30 m $\times$ 0.25 mm i.d. $\times$ 0.1 μm film thickness). The GC oven was heated from 100 $^{\circ}\text{C}$ (held for 0.5 min) to an end temperature of 300 $^{\circ}\text{C}$ (held for 15 min) at a rate of 8 $^{\circ}\text{C}/\text{min}$. The argon gas for the plasma torch was pre-heated and introduced co-axially with the analyses from the GC. The ICPMS-measured $\delta^{34}\text{S}$ values were converted to true $\delta^{34}\text{S}$ - reported as permil (‰) relative to the international sulfur isotope standard Vienna Canyon Diablo Troilite (VCDT) - with a normalisation curve established from the measurement of authentic standards of known $\delta^{34}\text{S}$ values (benzothiophene (BT) = +4.5‰; dibenzothiophene (DBT) = +13.7‰; 1-dodecanthiol (C12SH) = -7.1‰; 1-octadecanethiol (C18SH) = +13.7‰) measured by Elemental Analysis isotope ratio mass spectrometry calibrated for $\delta^{34}\text{S}$ measurements with international standards provided by IAEA (IAEA-S1, IAEA-S2, IAEA-S3 and NBS127). Two pulses of an SF_6 gas standard were included at both the start and end of all sample analyses to internally calibrate $\delta^{34}\text{S}$ measurements. Where OSC concentrations permitted oils were analyzed twice with the standard variation ($\text{SV}_{\pm}$) between the two duplicates usually better than 1 ‰.

4 Results and discussion

4.1 Physical properties and group compositions of the crude oils

The physical properties of the crude oils in the North Depression are diverse. Multiple types of oils

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10 were discovered, including light, normal and heavy. Most of the heavy oils were situated in a
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12 tectonically elevated position in the WMZ and WC oilfields. There is an improvement in the oil quality
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14 from the North to the South Depression with a wide range in sulfur content. The density and viscosity of
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16 the northern oils in this study ranged from 0.80 to 0.92 g/cm³ (average 0.87 g/cm³) and from 4.35 to
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18 748.8 mPa.s (average 96.49 mPa.s), respectively. Most of the oils had relatively high pour points
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20 ranging from 6°C to 34°C (26°C on average) and a wide range in wax content (0.16%–13.92%, average
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22 10.32%). The sulfur content of the oils was 0.05%–1.52% (average 0.5%) (Table 1). The crude oils in
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24 the South Depression showed relatively homogeneous physical properties, characterized by relatively
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26 low density (0.83 g/cm³), low viscosity (17.36 mPa.s and 5.62 mPa.s), high pour points (30°C–37°C)
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28 and a normal to high wax content (6.87%–16.4%) with less than 0.2% sulfur (Table 1). The physical
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30 properties of the oils in the South Depression are in accordance with freshwater lacustrine facies,
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32 suggesting different origins of the northern and southern oils.
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37 The contents of saturates and aromatics of the crude oils ranged from 31.02% to 91.61% and from
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39 5.11% to 46.06%, respectively. Resins and asphaltene varied from 1.46% to 8.87% and from 0.56% to
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41 34.92%, respectively (Table 1). A generally positive relationship between saturates/aromatics ratios
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43 (0.49–17.93) and maturity parameters for the oils analyzed were observed, indicating a distinctive
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45 variation in the oil maturity (Table 1).
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48 ***4.2 Conventional geochemical oil characteristics***

49 **4.2.1 Chemistry of the crude oils**

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52 Total ion chromatograms (TICs) from the saturate fractions of the oils are shown in Fig. 2. Most of
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54 the oils had a bimodal distribution of *n*-alkanes (*n*C₁₁–*n*C₄₃), suggesting both microbial and higher plant
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contributions (Tissot and Welte, 1984; Peters et al., 2005). The long-chain *n*-alkanes likely have a higher plant origin, although they can derive from other sources (e.g., ~~*botryococcusbrauni*~~*Botryococcus brauni*, Gelpi et al., 1970). Higher plant input to the Dongpu oils was confirmed by the detection of 1, 2, 5-trimethyl naphthalene and 1, 2, 5, 6-Tetramethyl naphthalene, higher plant diagnostic compounds (Alexande et al., 1988; Strachan et al., 1988). A general decline in the $\delta^{13}\text{C}$ value of *n*-alkanes with increasing carbon number was reflective of a larger contribution of relatively ^{13}C depleted plant lipids (Murray et al., 1994). Oils located in the Dongpu Depression ~~had~~have relatively low Pr/Ph values (0.41 to 0.64, Table 2), consistent with deposition in a hypersaline environment (Peters et al., 2005); while more southerly freshwater lacustrine oil ~~had~~have higher Pr/Ph values (1.2) indicating a weakly oxidizing to weakly reducing environment (Connan and Cassou, 1980; Peters et al., 2005).~~The widespread occurrence of β carotene in the northern oils (Fig. 2a) also demonstrates a strongly reducing saline environment for the source rocks in the North Depression (Grba et al., 2014; Koopmans et al., 1997; Philp et al., 1992).~~ The carbon preference index (CPI) and odd-even predominance (OEP) values are 0.93–1.05 (average 0.96) and 0.92–1.06 (average 0.98), respectively, showing no obvious trends. The ratios of $\sum n\text{C}_{21}^-/\sum n\text{C}_{22}^+$ and $(nC_{21}+nC_{22})/(nC_{28}+nC_{29})$ (Table 2) ~~in the northern oils were 0.5–1.11 and 0.86–1.46, respectively (Table 2). The values of these parameters~~ may be influenced by source, thermal maturity or secondary alterations. The ratios of $\sum n\text{C}_{21}^-/\sum n\text{C}_{22}^+$ for the deep oils ~~ie.ge.~~, Pushen 18-2 (0.72), are relatively lower er than ~~some of the immature-low mature oils, ie.ge., Wei77-10 (0.77) (Table 2),~~ which might be a result of thermal cracking.

The saline lacustrine oils in the North Depression ~~had~~have significantly high amount of gammacerane. The ratios of gammacerane/ C_{30} hopane were 0.56–1.07 (average 0.75) (Table 2). The

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generally high content of gammacerane in the oils indicates saline conditions and/or a stratified water column during source rock deposition (Sinninghe Damsté et al., 1995; Peters et al., 2005). Another distinguishing characteristic of the northern oils is an obvious predominance of C₃₅ and C₃₄ hopanes (C₃₅/C₃₄=0.72–2.31, average 1.41) (Table 2), which coincides with the features of typical saline lacustrine oils. The ratios of tricyclic/pentacyclic terpene ranged from 0.13 to 2.36; this ratio is affected by thermal maturity (Peters et al., 2005) (Table 2). The southern oils exhibited lower ratios of gammacerane/C₃₀hopane (0.24–0.34, average 0.29) (Table 2) and C₃₅/C₃₄hopane (0.65–0.79) (Table 2), suggesting that the source rocks were deposited in a freshwater environment. No or little biodegradation of the crude oils were interpreted from the TIC and *m/z* 177 mass chromatograms of the northern oil saturated fractions because there was no obvious depletion of *n*-alkanes or ~~presence~~ absence of C₂₅ norhopanes.

The fingerprints of the C₂₇, C₂₈ and C₂₉ regular steranes in the northern samples showed either an asymmetric (shallow oil samples) or symmetric “V” shape (deep oil samples) due to relatively low C₂₈ steranes (Fig. 3). C₂₇ steroids are indicative of algal input while C₂₉ steroids may come from both algae and higher plants (Moldowan et al., 1983; 1985; Volkman., 1986). A relative predominance of C₂₇ $\alpha\alpha\alpha$ (20R) to C₂₉ $\alpha\alpha\alpha$ (20R) for the crude oils i.e., Ming85 and Wei77-10 with a relatively low thermal maturity may reflect a higher contribution of algae to the shallow oil precursors (Fig.3). The ratios of C₂₉ sterane $\alpha\alpha\alpha$ 20S/(S+R) and C₂₉ sterane $\alpha\beta\beta$ /($\alpha\alpha\alpha$ + $\alpha\beta\beta$) of the oils were 0.28–0.57 and 0.28–0.65, respectively (Table 2), demonstrating the oils derived from source rocks with *R_c* to be 0.67%–1.29% maturity ranged from immature to relatively high maturity (Table 2)(Peters et al., 2005): the relatively low values of Ming85, Pu1-120 and Wei 77-10 oils (0.28–0.31; 0.28–0.29) suggests these

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were all ~~immature~~ low mature oils (generated from low mature source rocks); higher values of Pu7-18 and Wei42-26 (0.39–0.43; 0.32–0.38) suggested these oils generated from an oil peak oil window maturity for these oil source rocks; and the higher values of Pushen20, Pushen18-2, Pushen18 and Hu96-3 (0.46–0.57; 0.57–0.65) suggests they were oils generated from at high mature source rocks maturity. The $C_{29} \alpha\alpha 20S/(S+R)$ and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ values of the freshwater oils ranged from 0.36 to 0.40 and from 0.40 to 0.50, respectively, reflecting an oil generation maturity with the R_c of their source rocks around 0.72%~0.75% (Table 2).

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These traditional indicators of thermal maturity (i.e., C_{29} sterane isomer ratios; $Ts/(Ts+Tm)$ and others often related to maturity (diasterane/regular sterane and tricyclic terpane/pentacycliterpanes; Table 2) all show the current oil suite spans a broad range of maturities. The vitrinite reflectance equivalent (R_c) converted by the methyl phenanthrene index I (MPI-1) (~~Radke et al., 2000~~; Radke and Willsch, 1993; Radke et al., 2000) varied between 0.67% to 0.93% (Table 2); however, this might be invalid parameter for the Pusheng 20, Pusheng18 and Pusheng18-2 oils which have all been subject to obvious thermal cracking (see Fig. 3). The R_o of the oil source rocks, based on oil-source rock correlation, was covered the wide range of 0.67%–1.29% (Table 2), consistent with the apparent broad maturity range of the analyzed oils. Conclusively, the maturity level of the crude oils in this study is generally in the order of

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Pu1-120<Wei77-10<Ming85<Wei42-26<Pu7-18<Chun24-1<Ma19-30<Pushen20<Pushen18<Hu96-3<Pushen18-2 based on maturity parameters of $Ts/(Ts+Tm)$, C_{29} sterane $\alpha\alpha 20S/(S+R)$ and C_{29} sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ (Table 2; refer to Fig.13a~c).

4.2.2 Genetic types of crude oil

Two distinct groups of oils were identified based on biomarker parameters and related cross plots (Fig. 4a–d). The northern oils are derived from type II kerogen, while those from the South Depression are mixtures from type II and III kerogens (Fig. 4a, Table 2). The cross plot of pristane/phytane (Pr/Ph) against dibenzothiophene/phenanthrene (DBT/P) (Fig. 4b) is used as paleoenvironment proxy (Hughes et al., 1995). The northern oils aggregated in section C, which represents a saline lacustrine environment whereas the southern oils grouped in section D that indicates other lacustrine environments according to Hughes et al. (1995) (Fig. 4b). The ratios of gammacerane/C₃₀hopane, C₃₅/C₃₄ hopane, C_{19–21}/C_{23–24} and C₂₅/C₂₆ tricyclic terpane all divide the oils into the same two families (Fig. 4c, d). Relatively low C_{19–21}/C_{23–24} tricyclic terpane values (<1) and high C₂₅/C₂₆ tricyclic terpane ratios (>1) are usually associated with a highly reducing environment (Sharaf et al., 2007; Peters et al., 2013; Sharaf et al., 2007). A small variation is observed among the north oils. For example, the gammacerane/C₃₀hopane ratios of the Pu7-18 and Wei22-Wei42-26 oils (0.56) is less than the other saline oils, immature oils (0.73–0.79), with a relatively low maturity and they also had relatively high Pr/Ph ratios (0.50–0.62; Table.2) which can be ascribed to less saline and/or water stratified as well as reducing depositional conditions of the source rocks. The reservoir of the Wei42-26 oil was sealed by salt layers at the top and bottom and is featured by thin bedded alternation of shales (source rock) and sandstones (reservoir rock), which is different from the other oil reservoirs analyzed.

Two sets of source rocks were assigned for the northern oils from the Dongpu Depression: the mudstone of the Es₁ and Es₃³–Es₄¹ intervals (Zhang, 2011). Fair to good saline lacustrine facies with source rocks were well developed in the Northern Depression, particularly in the WMZ, PC, WC and HZJ areas, where total organic carbon (TOC) is up to 2.3% (Zhang et al., 2011). The previous oil-source

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Phshen18 and Hu96-3; 21-49%, discussed in section 4.4.3) saline oils. The oil samples from saline lacustrine facies contain relatively low N₁, but high O₁. For example, the northern oils of well Pu7-18 and Wei42-26 have relative abundance of 48.62%–53.89% (average 51.26%) for N₁ and of 29.8%–34.93% (average 32.37%) for O₁ class species, whereas the freshwater lacustrine oils from Ma24-1 and Ma19-30 in the South Depression have relative abundance of 56.41%–64.55% (average 60.48%) for N₁ and of 13.13%–14.76% (average 13.95%) for O₁ class species (Table 3). Distinctions are also found among the oils with a similar origin. It appears that ~~immature-low mature~~ saline lacustrine oils ~~generated from low mature source rocks~~ have a lower relative abundance of N₁ class species but a higher relative abundance of O₂ class species. For instance, the relative abundance of N₁ and O₂ in the ~~immature-low mature~~ oil from well Pu1-120 are 36.29% and 28.3%, respectively; while that from well Pushen20, a relatively high maturity oil, are 65.94% and 10.31%, respectively (Fig. 5; Table 3). This result is also in accordance with the observation of Wan et al. (2017). Samples from well Hu96-3 showed abnormal characteristics in composition, an unusually low relative abundance of N₁, but exceptionally high O₂ (Fig. 5; Table 3). We assume that thermochemical sulfate reduction (TSR) contributes to the conversions of nitrogen and oxygen and affects their distribution, which will be discussed hereafter.

4.3.2 Composition and distribution of N₁ class species

Pyrrolic nitrogen compounds are widely distributed in source rocks and crude oils of saline lacustrine facies (Bakr and Wilkes, 2002; ~~Liu and Yang, 2008~~; Ni et al., 2005; Liu and Yang, 2008; Zhang et al., 2008a). There are many studies about the origin and formation mechanisms of nitrogen compounds: from higher plants and blue-green algae (Snyder, 1965; Li et al., 1995, 1999; ~~Snyder,~~

1965); formation during diagenesis (alkaloid) (Schimmelmann et al., 1998); or early diagenetic reactions of amino acids (Bennett et al., 2002). The composition of N₁ class species in the crude oils analyzed by negative-ion ESI FT-ICR MS are shown in Fig. 6. The double bond equivalent (DBE) values and carbon numbers of the N₁ class species ranged from 4 to 26 (mainly 9–22) and from 15 to 55 (mainly 18–48), respectively (Fig. 6a–d). The N₁ class species ~~awere~~ were dominated by compounds with DBE values of 9, 12, and 15 (Fig. 6a–d, e–h), which correspond to carbazoles, benzocarbazoles and dibenzocarbazoles, respectively (Hughey et al., 2002; Shi et al., 2010a, b). Very similar distribution patterns have been observed in terrestrial lacustrine oils from the Nanpu Depression (Wan et al., 2017) and other crude oils (Oldenburg et al., 2014; Poetz et al., 2014; Mahlstedt et al., 2016).

There ~~iwas~~ was significant variation in the N₁ class species of oils with a similar origin. Generally, increasing thermal maturity contributed to an increase in the degree of condensation, also shown by DBE (Fig. 6e–g, a–c) and a decrease in the carbon number range of the N₁ species, as well as a forward movement ~~pre-displacement~~ of the main peak of the N₁ compounds with different DBE values in the northern/saline oils (Fig. 6e–g, i–k). For example, the ~~immature-low mature~~ oil from well Pu1-120 had a predominance of DBE=9 species with the main carbon numbers between C₃₂–C₃₅ (Fig. 6a, e, i), while the relatively high maturity oil from Pushen18-2 well was dominated by DBE=15 species with the main carbon numbers of C₁₅–C₂₃ (Fig. 6c, g, k). A distribution pattern similar to Pu1-120 was previously observed in terrestrial lacustrine oils from the Nanpu Depression (Wan et al., 2017). However, the prevalence of DBE=9 compounds decreased gradually with increasing maturity as species with high DBEs (12 and 15) became dominant (Fig. 6a–c). The relative distribution and thermal evolution trends of the N₁ class species with varied DBEs (Fig. 7a), show the impact of thermal maturity in terms of

condensation and aromatization. This phenomenon has previously been related to thermochemical kinetics ([Poetz et al., 2014](#); Wan et al., 2017; ~~Poetz et al., 2014~~). Major mechanistic pathways of thermal cracking include ring opening, side-chain cleavage and heteroatom defunctionalization (which all yield lower MW products) as well as condensation/aromatization reactions, which can involve heteroatoms and leads to an increase in MW (Hughey et al., 2002, 2004; Oldenburg et al., 2014).

As mentioned in section 4.3.1, the freshwater lacustrine oils were generally enriched in N₁ class species relative to the saline lacustrine oils (Fig. 5). Compared to the saline oils the N₁ species composition of the freshwater lacustrine oils had a relatively narrow carbon number range, enriched in compounds with relatively low molecular weight (Fig. 6j, k, l), specific DBE values and a greater abundance of high DBEs compounds (Fig. 6b, d, f, h, i, j). The percentage of DBE=15 in the freshwater lacustrine oils including Chun 24-1 and Ma 19-30 was 9.74~12.6%, which was a little higher than similar maturity saline lacustrine oils i.e. Pu7-18 and Wei42-26 (7.46~8.56%; Fig. 6b, d; Table 3). This is consistent with previous studies (Cui et al., 2014; Wan et al., 2017). Lipids and proteins from reworked lacustrine organisms probably lead to an enhancement in organic nitrogen in the terrestrial lacustrine environment (Cui et al., 2014).

4.3.3 Composition and distribution of O₁ class species

The O₁ class species have DBE values of 0–26 with an ~~absolute~~ predominance of DBE=4 (Fig. 8a–d, e–h) and carbon numbers of 15–55 (mainly 22–40) species (Fig. 8e–h, i–l). The carbon number peaks of the O₁ class species with DBE=4, 5, 8 were around C₂₁, C₂₂, C₂₇ and C₂₈ (Fig. 8i–l). The species with DBE=1 and 4 are likely alcohol and alkylphenols, respectively (Kamga et al., 2014; Shi et al., 2010b), while those with DBE=5 and 6 are likely alkylphenol-bearing indenol rings ([Zhang et al.,](#)

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2011; Liao et al., 2012; ~~Zhang et al., 2011~~) and the species with DBE=8 are probably phenylphenols (Shi et al., 2010b; Kamga et al., 2014; ~~Shi et al., 2010b~~). The alcohols are likely to be intermediate compounds in the conversion of organic matter to hydrocarbons (Rodrigues et al., 2000). A trace amount of alcohols were detected in the oils analyzed in this study (Fig. 8a–h). Abundant alkylphenols identified from the aromatic and resin fractions by GC-MS analysis, and the composition and distribution of these compounds are dependent on the biotic input and secondary alterations of original organic matter (~~Bastow et al., 2005~~; Taylor et al., 2001; Bastow et al., 2005), which is significantly influenced by thermal maturity (Taylor et al., 1997; Li et al., 2000). The ESI FT-ICR MS results indicate that the masses associated with alkylphenols are the most important component of the O₁ class species in the saline lacustrine oil samples. Generally, two distribution patterns were found for the northern oils: (1) ~~immature~~-low mature oils dominated by O₁ class species with DBE=4 (Fig. 8a, b, e, and f), and (2) medium-high maturity oils containing enhanced compounds with DBE>4 (Fig. 8c, g). We suggest that the ~~immature~~-low mature oils of saline lacustrine origin are enriched in alkylphenols that are assigned to the O₁ DBE=4 species (~~Shi et al., 2010b~~; Kamga et al., 2014; ~~Shi et al., 2010b~~).

Like N₁ species, the condensation degree of the O₁ class species in the crude oils increases (Fig. 7b; Fig. 8a–d, e–g) and the carbon number distribution shifts to lower values (Fig. 8e–g, i–k) with the increasing of thermal maturity. For instance, the ~~immature~~-oil generated from low mature source rocks from well Pu1-120 is dominated by species with DBE=4 (Fig. 8a, e) and carbon number of 15–55 with the main peak of C₂₈ (Fig. 8e, i), while the crude oil generated from high mature source rocks from well Pushen18-2, ~~which has relatively high maturity~~, has mainly O₁ species with DBE=4–16 with nearly equal relative abundance, and carbon number ranges of 15–37 (main peak was C₂₀ for the species with

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DBE=4) (Fig. 8c, g and k). In the triangular diagram of the relative abundance of DBE=4, 8 and 9 O₁ species (Fig. 7b), it is obvious that the relative abundances of the DBE=8 and 9 O₁ species generally increase with the increasing maturity of the oil samples as the figure 7a displayed, with an exception for the oil from Well Hu96-3 ~~which that~~ might have been altered by TSR.

The composition and distribution of the O₁ class species (mainly alkylphenols) are also influenced by kerogen type (~~Bastow et al., 2003~~; Bennett and Larter, 1997; Lucach et al., 2002; Bastow et al., 2003). The O₁ species with a lower relative abundance compared with the others, lower DBE values and short alkyl side chains are observed for the southern oils of freshwater origin. For example, the DBE values (DBE<18) and carbon number (<45) of well Ma19--30 is significantly lower than well Pu7-18 (DBE<22, carbon number <55) (Fig. 8f, h, j, ~~l, -~~); The carbon distribution pattern of the O₁ species with DBE values of 4, 5 and 8 for the freshwater lacustrine oils (displaying 2~3 main peaks) is also different from that of the saline oils (showing a single main peak) (Fig. 8i, j, k, l). All of these ~~which~~ demonstrates the impact of kerogen type and/or sedimentary environment on the O₁ species.

Alkylphenols are the most abundant components in the O₁ class species, and the depletion of O₁ class species in the freshwater lacustrine oils in the South Depression might result from the oxidized paleoenvironment in which these compounds can be easily be reformed (Bastow et al., 2003). Additionally, TSR is also a crucial factor controlling the oxygenic species in the crude oil (Walters et al., 2015), which will be discussed later on.

4.3.4 Composition and distribution of O₂ class species

The O₂ class species of the crude oils have DBEs of 0–25 (mainly 0–14), dominated by the class with DBE=1 (Fig. 9a–h), and carbon numbers from 15–51 (mainly 15–40) (Fig. 9a–l). Molecules with

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two oxygen atoms are likely carboxylic acids or binary alcohols, of which carboxylic acids are the primary compounds of O₂ species in crude oils (Shi et al., 2010b; Headley et al., 2016). Many carboxylic acids, such as phytanic acid, hopanoic acids (C₂₈–C₃₂) and steroidal acids (C₂₇–C₂₉), have been used as indicators of hydrocarbon origin, migration and biodegradation in petroleum systems (Jaffé and Gallardo, 1993; Barth et al., 2004; Ding et al., 2004; Wang et al., 2004). The O₂ class species with one DBE should be aliphatic acids, while those with DBEs of 2–7 correspond to 1–6-ring naphthenic acids (Barrow et al., 2003; Kim et al., 2005; Shi et al., 2010b). The O₂ class species with relatively high DBE values (i.e. 2–7) and low carbon numbers are likely multi-ring naphthenic acids, aromatic acids or phenols with multiple hydroxyl groups (Jones et al., 2001; Barrow et al., 2003; Jones et al., 2001; Shi et al., 2010a, b). The crude oils in the Dongpu Depression are dominated by O₂ species with DBE=1 (mainly fatty acids) (Fig. 9a–h), the C₁₆ and C₁₈ compounds are relatively abundant with the exception of a few ~~immature~~ oils generated from low mature source rocks from wells Ming85, Pu1-120 and Wei77-10 (Fig. 9e–l). The ~~immature-low mature~~ oils are generally dominated by C₂₀ compounds of the O₂ class species with DBE=1 (Fig. 9i). Fatty acids with low molecular weights, such as C₁₆ and C₁₈, generally derive from plankton and bacteria, whereas fatty acids with high molecular weights (>C₂₄) originate from higher land plants (Jaffé and Gallardo, 1993). The C₁₆ and C₁₈ fatty acids in this study also could be contaminants introduced during the MS analysis (Teräsväinen et al., 2007; Shi et al., 2010a, b; Oldenburg et al., 2014; Poetz et al., 2014). The distribution pattern of fatty acids with high molecular weights in crude oils still reflects the input to the source rocks. It should be noted that the C₁₆ and C₁₈ compounds with DBE=1 (O₂ class species, mainly unsaturated fatty acids) were not the most abundant compounds in ~~immature-low mature~~ oils in this study. Instead, C₂₀ compounds are

abundant in the ~~immature~~relatively low mature oils from wells Pu1-120 and Pu77-10 (Fig. 9e, i), reflecting overall enrichment of considerable unsaturated acids with various carbon numbers in ~~immature~~low mature oils. Biodegradation may also lead to the concentration of fatty acids (Kim et al., 2005; Liao et al., 2012; Vaz et al., 2013; Pan et al., 2015; ~~Vaz et al., 2013~~). The TIC fingerprints of the saturated hydrocarbons in the Dongpu oils (Fig. 2) show a good preservation of *n*-alkanes; the A/C ratios (acyclic to cyclic naphthenic acids, $\sum O_2 DBE_1 / (\sum O_2 DBE_{(3+4+5)})$) of the Dongpu saline lacustrine oils (1.03~5.46, averaged 3.91; Table 3) is much larger than those of the biodegraded oils (mostly <1) reported by Kim et al (2005), which would decrease with increasing biodegradation. The ~~immature~~ oils generated from low mature source rocks with a relatively low burial depth in this study have a narrow range of A/C ratios (3.46~5.52) with an exception of the oil from Well Ming85 (1.04) (Table 3). We believe that the O_2 class species with DBE=1 is original components rather than biodegradation products. In general, the degree of condensation of the O_2 class species increase and the carbon number range decrease with increasing maturity (Fig. 9e-g; ~~Fig. 7b~~), which is similar to the N_1 species.

Four- and five-ring naphthenic acids in crude oils carry special biological skeleton structures, such as steroids and hopanoids, and are commonly used as biomarkers (Cheng et al., ~~2010b~~2010a; Shi et al., 2010a, b). The O_2 class species with DBEs of 6 and 5 are likely hopanoic acids and secohopanoic acids/steroidal acids (Shi et al., 2010a, b; Poetz et al., 2014), which are relatively enriched in most of the ~~immature~~ oil samples generated from low mature source rocks from wells Wei 77-10 and Pu1-120 (Fig. 9a, e and i). These hopanoic acids and secohopanoic acids/steroidal acids with special biological structures are commonly found in modern sediments and other ~~immature~~low mature geological samples (Farrimond et al., 2002). They were also detected in the ~~immature~~low mature geological samples from

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the Liaohe Oilfield of the Bohai Bay Basin (Shi et al., 2010b) and Posidonia shale of Germany (Poetz et al., 2014), and were recognized as related immature compounds (Jaffé and Gallardo, 1993; Mpanju and Philp, 1994; Rodrigues et al., 2000). The southern oils showed some differences to the northern oils in the Dongpu Depression. It appears that the saline lacustrine oils, such as those from well Pu7-18, have more compounds with higher DBE values and a stronger degree of condensation and aromatization than the freshwater lacustrine oils (e.g., well Ma19-30) (Fig. 9b, f, d, h); the relative abundance of the C_{22} – C_{34} compounds with DBE=1 of the O_2 species for the freshwater lacustrine oils is much larger than the saline lacustrine oils with similar maturity (Fig. 9j, k, l), suggesting an effect from organic matter input and/or paleoenvironment.

4.3.5 Composition and distribution of N_1O_1 class species

Only a slight variation in the relative abundance of the N_1O_1 species among the crude oils is observed (1.89%–6.88%, Table 3, Fig. 5). The N_1O_1 species in the oils have DBEs of 0–25 (mainly 6–22) (Fig. 10) and the compounds with DBE=2, 15 and 18 relatively are enriched (Fig. 8a–d). N_1O_1 species with DBEs of 10 and 13 correspond to hydroxylatedbenzoquinolines and ketones (benzoquinolinones), and DBEs of 15, 18 and 21 very likely consist of molecules containing a pyrrolic ring or fluorenocarbazoles (Poetz et al., 2014). The carbon numbers of the N_1O_1 species ranged from 15–22, maximizing at DBE=2 with a preference for C_{18} and C_{22} compounds (Fig. 10e–h). Similar to the other nitrogen- and oxygen-containing compounds, the N_1O_1 species are influenced by maturity. The relative abundance of the species showed a slight increasing trend with maturity (Fig. 5). There is apparent increase in condensation for the N_1O_1 species with DBE>2 with increasing maturity (Fig. 10e–g; a–c) as well as an increasing relative abundance of the N_1O_1 species with DBE=2 (Fig. 10e–g;

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a–c). The kinetic mechanisms of the thermal evolution trends need further investigation. It seems that there are differences between the saline and freshwater lacustrine oils. For example, the saline lacustrine oil samples from well Pu7-18 ~~seem to~~ have a higher abundance of the species with a relatively higher degree of condensation than oil samples from freshwater lacustrine facies (Fig. 10 b, d, f, and h).

4.4 Geochemical significance of the nitrogen and oxygen compounds

4.4.1 Thermal maturity evaluation

The results discussed above demonstrate that the nitrogen- and oxygen-containing compounds of the N_1 , N_1O_1 , O_1 , O_2 class species are significantly influenced by thermal maturity, particularly the N_1 and O_1 class species. Thus, with increasing maturity we can conclude: (1) the relative abundance of the nitrogen and oxygen compounds changes as the relative abundance of the N_1 and N_1O_1 class species increases while the O_1 and O_2 decreases over the maturity range analyzed in this study (Fig. 5); (2) the condensation degree of the compounds increases (Figs. 6a–h; Fig.7; Figs. 8–9a–h; Fig.10), and (3) small molecules were produced (Figs. 6e–l; Figs.8–9 e–l). The last two points agree with previous reports for the Nanpu Depression (Wan et al., 2017) and Liaohe Oilfield (Li et al., 2010a). Fig. 7 shows a close relationship between thermal maturity and condensation and aromatization. With increasing maturity, macromolecules bound in the kerogen matrix are released and compounds with relatively high DBEs were also formed from those with low DBEs through cyclization of alkyl side chains and aromatization (Poetz et al., 2014). Previous studies showed that hydrocarbon migration also has an impact on the relative abundance of N_1 class (Liu et al., 2015; [Zhang et al., 2016](#); Wan et al., 2017; [Zhang et al., 2016](#)), which may not be essential here because of hydrocarbons trapped in situ with a very short migration distance (Zhang et al., 2011). It seems the relative abundance of the N_1 , N_1O_1 .

~~O₁~O₃ classes with varied maturity in a more complex manner. It seems a little complex about the relative abundance of the N₁, N₁O₁, O₁~O₃ classes with varied maturity, which will be discussed hereafter.~~

Conventional biomarker parameters, such as C₂₉ sterane 20S/(20S+20R), C₂₉ sterane $\alpha\beta/(\alpha\beta+\alpha\alpha)$ and Ts/(Ts+Tm), are widely used for maturity evaluations. However, the application is invalid with relatively high maturity to overmature material due to the thermal cracking of biomarkers (Peters et al., 2005). It was proposed by Wan et al. (2017) recently that ratios of C₁₆₋₂₀/C₂₁₋₅₀-DBE₁₂-N₁, DBE₁₂/DBE₉-N₁ and DBE₈₋₉/DBE₄-O₁, from negative-ion ESI FT-ICR MS analysis, is much more effective than the conventional maturity parameters, particularly at a higher maturity stage. Similarly, we found that ratios of the sum of N₁ class species with DBE=9–12 to DBE=15–18 (DBE₉₋₁₂/DBE₁₅₋₁₈-N₁), C₂₀–C₂₈ homologs to C₂₉–C₄₀ homologs with DBE=12 (C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁) and C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁ had good positive relationships correlations with C₂₉ sterane 20S/ (S+R), C₂₉ sterane $\alpha\beta/(\alpha\beta+\alpha\alpha)$ and Ts/(Ts+Tm) with *r* values. The related coefficient (*r*) values were in a range of 0.78–0.98 (average 0.89) (Figs. 11–12). Ratios of DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₄₀-DBE₈-O₁ also resulted in a good positive relationship correlate well with the conventional maturity indicators (*r*=0.81–0.94, average 0.87) (Fig. 11–12). We suggest that these ratios can be used as supplementary maturity indices, which are more suitable for geological samples with a relatively wide maturity range immature from low to moderate mature material relative to those of the biomarkers (Fig. 13a–h).

~~Just as some index could be used to evaluation maturity level for crude oils in the foregoing paragraphs, some of the~~ Other parameters derived from FT-ICR MS parameters could be utilized to

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distinguish ~~immature-the~~ oils generated from low mature source rocks from ~~mature-the~~ ones from moderately to highly mature source rocks. For example, with the exception of Hu96-3, the ratios of O_2/N_1 , C_{20-30}/C_{15-45} -DBE₁-O₂ (mostly fatty acids), and DBE₅₋₆/DBE₀₋₂₆-O₂ for the low mature and moderately to highly mature oils, ~~species in immature oils~~ respectively, ranged from 0.78 to 0.98 (average 0.87) ~~vs. while the mature oils were in a range of~~ 0.11–0.42 (average 0.3),- C_{20-30}/C_{15-45} -DBE₁-O₂ (mostly fatty acids) of the immature oils ranged from 0.44 to 0.68 (average 0.59) while the ratios for the mature oils were from ~~vs.~~ 0.08 to 0.31 (average 0.17), ~~and -7.56–22.9 vs.~~ 1.33–4.63 (Fig. 14a, table 3), ~~and DBE₅₋₆/DBE₀₋₂₆-O₂ of the immature and matured oils were 4.10–13.5 and 0.15–2.68, respectively (Fig. 14b; Table 3).~~ Although the O_2/N_1 ratio could also be controlled by kerogen type and possibly TSR, thermal maturity is the main influence on composition for the crude oils ~~it seems maturity is essential for the crude oils~~ in this study. Therefore, abundant O₁ class species) with DBE=4 (mainly alkylphenols), the O₂ class species with DBE=1 with higher carbon numbers (>C₁₈) (mainly fatty acids) and O₂ species with DBE=5 and 6 (mostly hopanoic and secohopanoic acids) could be considered as signatures of ~~immature-low mature~~ oils. In addition, high C_{20-30}/C_{15-45} -DBE₁-O₂ (>0.4), DBE₅₋₆/DBE₀₋₂₆-O₂ (>6.0) and O_2/N_1 (>0.7) can be used as auxiliary indicators for ~~immature-low mature~~ oils (Fig. 14a–b).

4.4.2 Origin of the lacustrine oils generated at low maturity~~immature oils~~

~~Immature~~Low mature lacustrine oils ~~are widely distributed around the globe~~ ~~ss mature oil was reported world widely~~ including some rift basins in Eastern China, which usually occurs in saline to half-saline tertiary stratum (Pang et al., 2003 and reference therein). Although there are some disputes focusing on quantity and mode of occurrence of such a kind of petroleum reserves (Li et al., 2003), it

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does exist (Tissot and Welte, 1984). Resins and asphaltenes that contain a large number of NSO heteroatom compounds are important components in ~~immature-the~~ oils generated from low mature source rocks and of significance for unraveling the formation mechanisms of ~~immature-low mature~~ oils (Barakat and Rullkoetter, 1994; Volkman et al., 1980). The ~~immature-low mature~~ oils of the Dongpu Depression were deficient in saturated hydrocarbons (40.63%–57.34%) but abundant in “resins+asphaltenes” (21.77%–42.22%, average 30%). The percentages of “resins+asphaltenes” in the oils shows an obvious declining trend along increasing depth/maturity (Table 1), which provides solid evidence that the crude oils are generally progenetic without secondary alteration, and “resins+asphaltenes” or NSO compounds is intermediate product from kerogen and/or biological macromolecule to hydrocarbons. The negative-ion ESI FT-ICR MS provided important information for the understanding of the ~~immature-low mature~~ oils origin.

Oxygen compounds in crude oils are important constituents and are considered mainly derived from kerogen and/or lipids, or as products from secondary alteration, such as biodegradation (Hunt, 1979; Barth et al., 2004). Since no obvious signs of biodegradation is found in the Dongpu oils, the oxygen compounds should be considered primary and likely form resins and asphaltenes (Khorasani and Michelsen, 1991; Qin et al., 1997). Research on lower weight oxygen compounds carried out by GC–MS ~~have-has~~ shown that, the composition and distribution of alkylphenols are significantly affected by parental sources and maturity (Taylor et al., 1997). Fatty acids in resins are meaningful indicators for ~~immature-low mature~~ oil origin (Shi et al., 2001; Zhe et al., 2003; Wang et al., 2004). However which heteroatom compounds are closely related to ~~immature-low mature~~ oils was unclear. In this study, oxygen compounds, such as N₁O₁, O₁, O₂ and O₃ class species were affected by maturity to various

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degrees, while the O₁ and O₂ class species are abundant in ~~immature~~low maturity oils (Fig. 5a). The O₁ class species were dominated by compounds with DBE=4 (primarily alkylphenols) in the ~~immature~~relatively low mature oils (Fig. 7a8a-d), and the O₂ class species were the main constituents in the ~~immature~~low mature oils, accounting for 28.3%–35.2% in relative abundance with a preference for higher carbon numbers (>C₂₀) with DBE=1 (mainly fatty acids) (Fig. 5; Fig. 9i, Table 3). We assume that these higher carbon number molecular compounds contain a large amount of long chain fatty acids with high OEP values (Fig. 9i), which has also been determined for ~~immature~~low mature oils from the Lingqing Depression in the Bohai Bay Basin by Zhang and Zhang (1999). It seems that the OEP of the O₂ class species with DBE=1 (mainly fatty acids) corresponds to the OEP of *n*-alkanes in the low ~~mature~~immature oils, suggesting a close genetic relationship because *n*-alkanes could be produced from long chain fatty acids by thermal cracking of the carboxyl groups (Clemente and Fedorak, 2005). It has been well recognized that fatty acids of the O₂ class species are the intermediate products during chemical conversion of the organism to hydrocarbons, which generate hydrocarbons after chemical reaction (Shi et al., 2001). We also observe abundant O₂ species with DBE=5 and 6, primarily 4- and 5-ring naphthenic acids with special biological structures dominated by C₂₀–C₃₅ (Fig. 9 a, e). These compounds were reported in the ~~immature~~low mature oils from the Liaohe Oilfield by Shi et al. (2010b) and were considered as hopanoic and secohopanoic acids (Jaffé and Gallardo, 1993; Nascimento et al., 1999). They could be products of microbial degradation from C₃₅ hopanoic polyols, generally found in ~~immature~~low mature oils (Qu et al., 1996). These hopanoic acids were constrained in macromolecules net by ester bonds or other weak interactions after incorporating into kerogen. Their occurrence was generally accepted as the marker of ~~immature~~low mature oil (Jaffé and Gallardo, 1993; Nascimento et

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al., 1999). The content of DBE=5 and 6 compounds in O₂ class species (mostly hopanoic and sec-hopanoic acids or steroid acids) has a positive relationship with resins in the crude oils from the Dongpu Depression (Table 3).

Our recent work showed that the "~~low mature~~~~immature~~ oils" in the Dongpu Depression are ~~actually-usually~~ mixed oils with different maturity with ~~most of them especially~~ the saturated and aromatic fraction ~~especially influenced by~~ ~~were hydrocarbons~~ derived from relatively deep source rock ~~with normal~~ at higher maturity (Zhang et al., 2017). We presume that a majority of the NSO compounds were derived from low mature source rocks. ~~considerable macromolecules like NSO's compounds in resins and asphaltene were mostly derived from potential source rocks with relatively low maturity.~~

Obvious differences were observed among rock extracts and the adjacent oil sands as well as mobile crude oils suggesting close relationship between them, which will be discussed in another manuscript.

4.4.3 Evidence for thermochemical sulfate reduction

Thermochemical sulfate reduction (TSR) is a high temperature reaction between sulfate minerals and petroleum hydrocarbons. It usually occurs in reservoirs containing gypsum salt rocks. H₂S, organic sulfur compounds (e.g., thiadiazonoids), pyrobitumen, authigenic pyrite and other metal sulfide compounds are common products of TSR (Ho et al., 1974; Wei et al., 2012). Across the globe TSR has been detected in many carbonate formations including the Sichuan, Tarim, and Alberta Basins (~~Cai et al., 2016; Hao et al., 2008;~~Manzano et al., 1997; Zhang et al., 2008b, c; Hao et al., 2008; Cai et al., 2016).

TSR was suggested to have occurred in terrestrial clastic reservoirs, such as North Sea sandstones (Worden et al., 2003) and the lacustrine sections of Jinxian Sag (Bohai Bay Basin) (Zhang et al., 2005b).

FT-ICR MS has been previously used to successfully identify TSR by the composition and distribution of sulfur compounds ([Li et al., 2011](#); [Walters et al., 2011](#); Li et al., 2012, 2015a; ~~Li et al., 2011; Walters et al., 2011~~). Oils from wells Pushen18-2 and Pushen18 wells have undergone extensive TSR based on the large amount of thermally unstable S₁ class species (DBE<8) detected by positive-ion ESI FT-ICR MS (Fig. 15a–b) (Chen, 2017), which occurs in ~~less mature~~ oils generated from low mature source rocks. The oils from the Pushen18-2 and Pushen18 wells have reached a relatively high thermal evolution level with partial biomarker thermal cracking (Fig. 3), which has a relatively higher concentration of aromatic sulfur compounds (i.e. dibenzothiophenes, DBTs), up to 10.75% (Pushen18-2) and 8.83% (Pushen18) (Table 2). High concentrations of DBTs could be a result of TSR (Manzano et al., 1997; Li et al., 2012, 2015a). The clastic reservoirs of the Pushen18-2 and Pushen18 wells were pinched with gypsum salt rock. We ~~thus~~ suggest that the S₁ class species with DBE<8 detected in Pushen18-2 and Pushen18 are products of TSR. Thick gypsum salt rocks, primarily anhydrite, were well developed in the Dongpu Depression, and part of the northern oils were deeply buried (3451–4556.1m) with reservoir temperatures reaching 125–150°C, according to the burial history and well testing data, which provides a sound condition for TSR (Orr, 1974). Free sulfur and authigenic pyrite were commonly observed in drill cores from the clastic reservoirs, which can be reagents and products of TSR (Orr, 1974; Zhang et al., 2008b).

Negative-ion ESI FT-ICR MS was recently used to identify TSR. Walters et al. (2015) proposed that nitrogen and oxygen compounds in the Alabama oils underwent varied degrees of TSR, and showed changes with increasing TSR alteration. They also suggested that there is an increasing trend in the relative abundance of the oxygen compounds O₁, O₂ to O₃ with increasing TSR. The O₁ class species,

which contain the fewest number of oxygen atoms, were considered to be the one mostly depleted during TSR ([Walters et al., 2015](#); Hosseini et al., 2017; ~~Walters et al., 2015~~) (Fig. 17a). We observed an obvious decrease trend of the relative abundance of the O₁ species whereas an increasing trend of the O₂ and O₃ species for the group-I oils, featured by a relatively low thermal maturity level (Fig.17c) and derived from the Es₃-Es₄ rocks in the Puwei Sag in the order of Pu7-18→Wei42-26→Wei77-10→Ming85 (Fig.17b, c). Although these oils are TSR relevant, they display a decreasing trend of $\delta^{34}\text{S}$ of C₀~C₁-DBTs indicating probably a decreasing trend of TSR in the same order of the oils (Fig.17d), which suggests possibly other action such as maturity also play an important role on the compounds (Fig.17b, c). Therefore, precaution should be taken when the relative abundance of O₁, O₂ and O₃ species were used to identify the extent of TSR, which might be more suitable for the crude oils with relatively high thermal maturity. The group II oils were characterized by a relatively high thermal maturity (Fig.17c), which were sourced from the source rocks with type II kerogen in the Liutun Sag. We observed an ~~in~~ obviously higher $\delta^{34}\text{S}$ value for the oil from Hu96-3 (Fig.16; Fig.17d) and ~~a~~ significantly higher abundances of O₂ and O₃ species relative to the oils from Well Pushen 18-2 and Pushen 18 (Fig.17b). Since a lowest $\delta^{34}\text{S}$ value was detected from the oil of Chun24-1 (Fig.16a), a freshwater lacustrine oil generated from source rocks with type II~III kerogen (Fig. 4a, c), it is unlikely that a little more amount of terrestrial organic matter input if possible to the source rocks would caused the abnormal features of the Hu96-3 oils distinguished from the others. TSR might be one of the most important geochemical factors responsible for the abnormal phenomena. A slight higher $\delta^{34}\text{S}$ values were observed from the oil of Pushen18 relative to Pushen18-2 (Fig.16b), suggesting a little higher extent of TSR of the later compared with the former. A decreasing abundance of the O₁ species (Fig.17b)

agrees with the observation of Walters et al. (2015).

A new approach often able to identify oils impacted by TSR is compound specific sulfur isotope analysis (CSSIA; Amrani et al., 2012; Li et al., 2015a). Different OSCs can have a varied sensitivity to TSR and a distinction in their $\delta^{34}\text{S}$ values may help identify the early stages of TSR (Amrani et al., 2012; Gvirtzman et al., 2015). For instance, benzothiophenes (BTs) and dibenzothiophene (DBT) produced by the reaction of the H_2S from TSR with hydrocarbons will gradually approach a $\delta^{34}\text{S}$ value close to the sulfate utilized by TSR, but differences in the TSR production rates of BTs and DBTs leads to differences in $\delta^{34}\text{S}$ values at the early stages of TSR (Amrani et al., 2012). The $\delta^{34}\text{S}$ values of several alkylated BTs measured for oils from wells Wei77-10 and Min85 in the Wenmingzhai and Weichen oilfields were distinctly higher than the $\delta^{34}\text{S}$ values of co-occurring DBTs (Fig.16a) which is indicative of a TSR event. BT concentrations in the other oils analyzed were too low for reliable measurement, but several alkylated thiadamantanes detected in oil from Well Pu7-18 in the Puchen Oilfield (Fig.16a) were similarly enriched compared to the DBTs in that oil. Thiadamantane produced by TSR will also be relatively ^{34}S enriched compared to DBTs which don't fully equilibrate with the isotopically heavier sulfate source (Gvirtzman et al., 2015; Cai et al., 2016). The compound specific sulfur isotope differential evident in the OSCs of these oils is consistent with TSR alteration.

4.4.4 Controls and reliability of the FT-ICR MS indices

The composition and relative distribution of heteroatomic compounds in crude oils are largely controlled by the secondary processing of kerogen with a potential contribution also from inorganic substances (Li et al., 2010a, 2012; Wan et al., 2017, and references therein). Thermal maturation can have a significant effect on these products. Of the current negative ESI FT-ICR MS data lacustrine oils

of the Dongpu Depression, the N₁ and O₁ species showed the strongest relationships with thermal maturity. The freshwater lacustrine oils showed decreasing abundances of N₁ and N₁O₁ species with increasing maturity (Fig. 5b), which was similar to the trend previously reported from analysis of Nanpu Sag oils (Wan et al., 2017). However, saline lacustrine oils in the Dongpu Depression (Fig. 5a) showed the opposing trend of increasing abundances of N₁ and N₁O₁ species with increasing maturity. Their abundances (particularly for DBE > 9) increased noticeably at early thermal evolution (matched by a decline in O₂ species, particularly acids with DBE < 6) but then did decrease at medium to high thermal maturities (where condensed oxygen compounds increased; Fig. 9).

The different effects maturation had on the N₁ and N₁O₁ composition of freshwater and saline lacustrine oils is likely due to the relative thermal stabilities of N and O compounds. Secondary alterations such as TSR, identified to impact several of the saline oils, is known to change the oxygen species composition of oils by decreasing the abundance of O₁ species relative to O₂ and O₃ species (Walters et al., 2015). An organofacies influence cannot be excluded, however, given the heterogeneous nature of organic inputs deposited and preserved under saline conditions.

The effects of thermal maturity were magnified by selectively comparing the relative abundance of N₁ and O₁ species with specific DBE values and carbon number ranges. DBE₉₋₁₂/DBE₁₅₋₁₈-N₁, C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁, C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁, DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁ all showed clear relationships with thermal maturity, and in some instances seemed more sensitive to the thermal maturity range of the oils than traditional biomarker maturity indicators (e.g., C₂₉ sterane $\alpha\alpha\alpha 20S/(S+R)$ and C₂₉ sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$; Fig. 13), which can operate over a limited maturity range (Peter et al., 2005). Ts/(Ts+Tm) correlated more closely with DBE₉₋₁₂/DBE₁₅₋₁₈-N₁ ($r=0.98$,

Fig.11c) than with either C₂₉ sterane $\alpha\alpha\alpha 20S/(S+R)$ (0.78, Fig.11a) or C₂₉ sterane $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ (0.93, Fig.11b). C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁ showed a similarly strong relationship with Ts/(Ts+Tm) ($r=0.90$, 0.80 and 0.88, respectively; Fig.12a~c; Fig. 13).

Sharp deviations in the values of the N₁ species parameters may reflect controls related to source or other secondary alterations. For example, the relatively low C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁ values of the Chun24-1 and Ma19-30 oils is likely due to different source facies (Figs. 13e and f); and the high DBE₉₋₁₂/DBE₄₋₂₀-O₁ and C₂₀₋₃₀/C₃₁₋₅₀-DBE₈-O₁ values of the Wei42-26 and Hu96-3 oils are probably a result of TSR (Figs. 13g and h) which can hasten the thermal degradation of petroleum hydrocarbons (Zhang et al., 2005a; 2008a). TSR would likely lead to an enrichment of low DBE and carbon numbers O₁ species. Of the potential thermal maturity indicators based on N₁-species composition, DBE₉₋₁₂/DBE₁₅₋₁₈-N₁ ratio is likely the most effective. It showed the strongest correlation with Ts/(Ts+Tm) (Figs. 13c and d) suggesting minimal distortion by different organofacies or TSR alteration. Of the other N₁ ratios tried, C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁ was the next most reliable thermal maturity indicator as it showed a slightly closer correlation to the sterane and terpane parameters than C₂₀₋₂₈/C₂₉₋₄₀-DBE₁₂-N₁ and C₂₀₋₃₀/C₃₁₋₄₀-DBE₁₂-O₁ (Fig. 12).

The DBE and carbon number range of the N₁ and O₁ ratios evaluated here (e.g., DBE₉₋₁₂/DBE₁₅₋₁₈-N₁) for their apparent close relationship with the thermal maturity of the Dongpu Depression oils, were slightly different to those ratios (e.g., DBE₁₂/DBE₉-N₁, C₁₆₋₂₀/C₂₁₋₂₅-DBE₁₂-N₁,) evaluated for Nanpu Sag oils by Wan et al (2017). The effectiveness of specific ESI FT-ICR MS measured N₁ and O₁ proxies is likely to vary with heteroatom species composition, whereas molecular based parameters from GC/MS analysis typically measure a relatively fixed relationship between

specific biomarkers.

Several saline lacustrine oils from wells in the North Dongpu Depression including from the Wenmingzhai (e.g., Min85) and Weichen (e.g., Wei77-10) oilfields have been reported to contain high H₂S levels (Personal communication with field explorationists). There has been some speculation about the TSR or BSR origin of these sour gases. For instance the former source is favored by a lack of hydrocarbon biodegradation evidence, although low reservoir temperatures (e.g., as low 60~70 °C for Wenmingzhai) are not likely to directly support TSR. ~~The present Evidence from ESI FTICR MS data~~ and ~~more so~~ CSSIA ~~analyses indicate data does reflect a~~ TSR ~~origin alteration~~, supporting the proposal that these sour gases have migrated from deeper source rocks. Source rocks > 3000m (Es₃-Es₄) are a likely candidate, and their geological temperatures have been estimated to be ~480°C (Zhang et al., 2017). This is also below the temperature range normally expected to initiate TSR, although a 100°C activation temperature has been suggested in certain environments (Walters et al., 2015). ~~It appears the TSR evidences concluded from ESI FT ICR MS are coincided with~~ ~~We believe~~ the geological and geochemical conditions in the Dongpu Depression ~~are suitable for TSR.~~

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5 Conclusions

Negative-ion ESI FT-ICR MS can provide a detailed characterization of the composition and origins of heteroatom compounds in oils and compliment traditional hydrocarbon biomarker characterizations by GC-MS analysis with additional information about the sources, thermal maturity or secondary alteration (e.g., TSR) of oils. N₁ (dominant), N₁O₁, O₁, O₂ and O₃ class species were detected here in oils from type I–II and II–III kerogens deposited under saline and freshwater lacustrine conditions from the Dongpu Depression (Bohai Bay Basin, China) and spanning a range of maturity

levels ($R_c=0.67\%–1.29\%$). Only modest variation was evident in the nitrogen- and oxygen- compound composition of the saline and freshwater lacustrine oils, but much larger differences were detected between ~~immature~~low mature oils and moderately to highly mature oils and mature oils.

Low maturity saline lacustrine oils contained a high relative abundance of O_1 class species with DBE=4 (mainly alkylphenols); O_2 species with DBE=1 (mainly fatty acids); and high MW ($> C_{18}$) O_2 species with DBE=5 and 6 (i.e., terpenoid/steroid acids) or DBE=1 (i.e., fatty acids). These and several other compositional features indicative of the low maturity Donpu oils (e.g., $O_2/N_1 > 0.7$, $C_{20-30}/C_{15-45}-DBE_1-O_2 > 0.4$; $DBE_{5-6}/DBE_{0-26}-O_2 > 6.0$) may serve as useful indicators of ~~immature~~low maturity oils. The high maturity oils generally showed a lower and narrower C-number range of products with increased condensation/aromatization, particularly of N_1 , O_1 and O_2 species. Parameters based on the relative abundances of specific species type and range (e.g., $DBE_{9-12}/DBE_{15-18}-N_1$) may be useful auxiliary maturity indicators which could compliment conventional biomarker based parameters to help resolve maturity progression across the oil window.

Other parameters based on features of the N- and O-composition of the oils showed an organofacies relationship (e.g., $C_{20-28}/C_{29-40}-DBE_{12}-N_1$, $C_{20-30}/C_{31-50}-DBE_{15}-N_1$) or reflected secondary alterations by TSR ($DBE_{9-12}/DBE_{4-20}-O_1$, $C_{20-30}/C_{31-50}-DBE_8-O_1$) which led to a decreasing percentage of O_1 class species.

Several compositional differences were observed between the freshwater and saline samples(e.g., relatively high O_2 and N_1 abundances and low O_1 abundances in the two freshwater samples analyzed) suggest ESI-FT-ICRMS analysis has potential for distinguishing between these types of lacustrine samples, though more of these samples, particularly from freshwater depositions.

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need to be studied to confirm systematic compositional differences.

ACKNOWLEDGEMENTS

This study was funded by the Natural Science Funding Council of China (Grant Nos. #41473047 and #41673055) and the National Science and Technology Major Project (No. 2016ZX05006-004). The Zhongyuan Oilfield, CNPC, is thanked for providing background geological data and permission to publish the results. The authors thank Dr. Zulin Chen for excellent experimental assistance. The reviewers are sincerely acknowledged for helpful comments on an earlier version of this manuscript.

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Caption of figures:

Fig. 1 (a) Regional structural map showing the location of the Dongpu Depression; (b) cross section of the North Depression. See (a) for map location of the cross section.

Fig. 2 Total ion chromatogram (TIC) of the saturates from crude oils.

Fig. 3 Mass chromatograms of m/z 217 and m/z 191 of saturates from the Dongpu Depression crude oils.

Fig. 4 Cross plots of biomarkers showing two oil families for the investigated oils from the Dongpu Depression.

(a) is after Connan and Cassou, 1980; (b) is after Hughes et al., 1995; (c) and (d) is after Peters et al., 2013, Sharaf et al., 2007 respectively).

Fig. 5 Relative intensity/abundance of heteroatom class species in the oils assigned from negative-ion ESI FT-ICR mass spectra. (a) the saline lacustrine oils in the North Depression; (b) the freshwater lacustrine oils in the South Depression.

Fig. 6 Relative intensity/abundance of the N_1 class species with various DBE values of the crude oils detected by negative-ion ESI FT-ICR MS (left); Plots of DBE versus carbon number of the N_1 class

species for the selected oils (middle); Carbon curve of the N_1 class species with DBE = 9, 12 and 15 for the selected oils (right).

Fig. 7 Triangular plots of the relative abundance of the DBE 9, 15 and 18 of N_1 and DBE 4, 8 and 9 of O_1 species showing the condensation and aromatization changes with increasing maturity of the species.

Fig. 8 Relative intensity/abundance of O_1 class species with various DBE values of the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of O_1 class species for the selected oils; Carbon curve of the O_1 class species with DBE = 4, 5 and 9 for the selected oils.

Fig. 9 Relative intensity/abundance of O_2 class species with various DBE values for the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of O_2 class species for the selected oils; Carbon curve of the O_2 class species with DBE=1 for the selected oils.

Fig. 10 Relative intensity of N_1O_1 class species with various DBE values for the crude oils detected by negative-ion ESI FT-ICR MS; Plots of DBE versus carbon number of the N_1O_1 class species for the selected oils.

Fig. 11 Cross plots of negative-ion ESI FT-ICR MS indices on condensation versus GC-MS parameters for the oils.

Fig. 12 Cross plots of negative-ion ESI FT-ICR MS indices on alkyl substitution versus GC-MS parameters for the oils.

Fig. 13 Plots of negative-ion ESI FT-ICR MS parameters of N_1 and O_1 class species versus GC-MS parameters indicating the maturity difference. A: saline lacustrine oils; B freshwater lacustrine oils.

Fig. 14 Parameters of nitrogen and oxygen compounds from negative-ion ESI FT-ICR MS analysis

indicates immature oils of the Dongpu Depression.

Fig. 15 The Composition and distribution of the S₁ class species detected by positive-ion ESI FT-ICR MS (Chen, 2017).

Fig. 16 Compound specific of sulfur isotope for partial oils in the Dongpu Sag.

Note: C3BTi, C3BTii, C3BTiii and C3BTiv represent four isomers of C₃-benzothiophene, and so on for the C4BTi, C4BTii, C4BTiii, C4BTiv, C5BTi and C5BTii; DBT: dibenzothiophene; m: methyl; dm: dimethyl; tm: trimethyl; 1D, 2D and 3D represent 1-cage, 2-cage and 3-cage thiadiamondoids.

Fig. 17 Relationship between relative abundance of O₁, O₂ and O₃ class species detected by negative-ion ESI FT-ICR MS and TSR. (a) is Alabama oils (Walters et al., 2015); (b) ~ (d) is for the Dongpu oils.

Caption of Tables:

Table 1 Physical properties and group composition for the oils from the Dongpu Depression.

Note: Asph: asphaltenes; Sat: saturates, Aro: aromatics, sat/aro: saturates/aromatics.

Table 2 Basic geochemical parameters of the oil analyzed from the Dongpu Depression.

Note: Pr/Ph: pristane/phytane; Pr/*n*C₁₇: pristane/*n*C₁₇; Ph/*n*C₁₈: phytane/*n*C₁₈; CPI:

$$[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})]/2;$$

OEP: $(C_i+6C_{i+2}+C_{i+4})/(4C_{i+1}+4C_{i+3})$ or $(4C_{i+1}+4C_{i+3})/(C_i+6C_{i+2}+C_{i+4})$, among which *i*+2 is the maximum peak of *n*-alkanes with *i* corresponding to odd and even member respectively; G/C₃₀H:

gammacerane/C₃₀-hopane ratio; C₃₅/C₃₄H: C₃₅/C₃₄ hopane; DBTs (%): Percentage of DBTs among the

aromatic recognizable peaks. DBT/P: dibenzothiophene/phenanthrene; C₂₅TT/C₂₆TT: C₂₅ tricyclic

terpane/ C₂₆ tricyclic terpane; C₁₉₋₂₁TT/ C₂₃₋₂₄TT: C₁₉₋₂₁tricyclic terpane/C₂₃₋₂₄tricyclic terpane;
 20S/(S+R): ratio of C₂₉ $\alpha\alpha$ steranes; $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$: Ratio of C₂₉steranes; Ts/(Ts+Tm): 18 α (H)
 -/(18 α (H)+17 α (H)) -trisanthracene ratio; Dia/Reg: (C₂₇-C₂₉)-diasterane/(C₂₇-C₂₉)-regular sterane; T/P:
 tricyclic terpane/ pentacycliterpanes; R_C=0.6×MPI1+0.4, of which
 MPI1=1.5×(2-methylphenanthrene+3-methylphenanthrene)/
 (1-methylphenanthrene+9-methylphenanthrene+phenanthrene); The R_C of the oils from well Phshen20,
 Pushen 18-2 and Pushen18 might be invalid because of obvious thermal cracking (see figure 3), and
 therefore, we list the R_o (in bracket) of the source rocks of the oils based on oil-source rock correlation
 for reference.

Table 3. Parameters calculated by the results of negative-ion ESI FT-ICR MS for the oils.

Note: A: The ratio of the sum of DBE=9–12 to that of the DBE=15–18 of the N₁ species
 (DBE₉₋₁₂/DBE₁₅₋₁₈-N₁); B: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₅₀ homologs of the N₁ species with
 DBE=12 (C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₂-N₁); C: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₅₀ homologs of the N₁
 class species with DBE=15 (C₂₀₋₃₀/C₃₁₋₅₀-DBE₁₅-N₁); D: The ratio of the sum of DBE=9–12 to that of
 the DBE=4–20 of the O₁ species (DBE₉₋₁₂/DBE₄₋₂₀-O₁); E: The ratio of C₂₀–C₃₀ homologs to C₃₁–C₄₀
 homologs of the O₁ species with DBE=8 (C₂₀₋₃₀/C₃₁₋₄₀-DBE₈-O₁); F: The ratio of C₂₀–C₃₀ homologs to
 C₁₅–C₄₅ homologs of the O₂ species with DBE=1 (C₂₀₋₃₀/C₁₅₋₄₅-DBE₁-O₂); G: The ratio of the sum of
 DBE=5–6 to that of the DBE=0–26 of the O₂ species DBE₅₋₆/DBE₀₋₂₆-O₂; H: The ratio of the O₂ species
 to the N₁ species (O₂/N₁); I: A/C ratio = ($\sum$ O₂ DBE₁)/($\sum$ O₂ DBE₍₃₊₄₊₅₎)

(10)

Figure 2

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Figure 3
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Figure 5
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Figure 6
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A: saline lacustrine oil

B: fresh water lacustrine oil

Figure 7
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Figure 8
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A: saline lacustrine oil

B: fresh water lacustrine oil

Figure 9
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Figure 10

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Table 1

Table 1											
Well	Saline lacustrine oil									Freshwater lacustrine oil	
	Pu1-120	Wei77-10	Ming85	Wei42-26	Pu7-18	Pushen20	Pushen18	Hu96-3	Pushen18-2	Chun24-1	Ma19-30
Burial depth (m)	2421.4-2408.4	2734-2799	1612.2-1630	3451-3466.6	3233.5-3517	4329.5-4556.1	3886.4-4237.1	4039.3-4105.5	4167-4207.3	2714.8-2727.9	2848.4-2900.6
Strata	Es ₁	Es ₄ ^U	Es ₂ ^U	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M
Density (g/cm ³)	0.94	0.87	0.92	0.90	0.91	0.82	0.83	0.84	0.80	0.83	0.83
Viscosity(mPa.s)	748.80	9.25	36.21	28.47	21.57	4.58	5.35	9.8	4.35	17.36	5.62
Pour point (°C)	/	21.00	33.00	22.00	34.00	29.00	23.00	32	16.00	30.00	37.00
Sulfur (%)	0.87	1.46	1.52	0.05	0.32	0.12	0.06	0.04	0.05	0.11	0.05
Wax (%)	9.00	12.42	12.73	11.25	11.83	13.92	/	0.16	11.25	16.40	6.87
Sat (%)	57.34	40.63	51.72	56.39	45.36	79.51	31.02	91.61	90.68	81.59	84.26
Aro (%)	20.89	17.14	24.14	21.80	46.06	14.48	63.19	5.11	6.50	11.72	12.77
Resin (%)	8.44	7.30	8.87	2.26	3.78	2.73	4.53	1.46	2.26	5.02	2.13
Asp (%)	13.33	34.92	15.27	19.55	4.81	3.28	1.25	1.82	0.56	1.67	0.85
Sat/Aro	2.75	2.37	2.14	2.59	0.98	5.49	0.49	17.93	13.96	6.96	6.60

Table 2

Table 2

Well	Saline lacustrine oil								Freshwater lacustrine oil		
	Pu1-120	Wei77-10	Ming85	Wei42-26	Pu7-18	Pushen20	Pushen18	Hu96-3	Pushen18-2	Chun24-1	Ma19-30
Depth (m)	2421.4-	2734-	1612.2-	3451-	3233.5-	4329.5-	3886.4-	4039.3-	4167-	2714.8-	2848.4-
	2408.4	2799	1630	3466.6	3517	4556.1	4237.1	4105.5	4207.3	2727.9	2900.6
Strata	Es ₁	Es ₄ ^U	Es ₂ ^U	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M	Es ₃ ^M
Pr/Ph	0.41	0.43	0.41	0.62	0.50	0.64	0.51	0.51	0.54	1.20	1.20
Pr/ <i>n</i> C ₁₇	0.93	0.65	0.94	0.58	0.69	0.53	0.52	0.52	0.44	0.33	0.30
Ph/ <i>n</i> C ₁₈	2.59	1.56	1.99	1.03	1.49	0.90	1.11	1.11	0.88	0.31	0.28
CPI	0.97	0.93	0.97	1.05	0.99	1.02	0.95	0.94	1.02	0.97	0.97
OEP	0.95	0.92	0.94	0.97	0.97	1.02	0.97	1.06	1.02	0.97	0.96
$\sum nC_{21}^{-}/\sum nC_{22}^{+}$	0.75	0.77	0.90	0.50	0.80	0.79	0.96	1.11	0.72	0.98	1.24
$(nC_{21}+nC_{22})/(nC_{28}+nC_{29})$	0.86	0.96	1.43	0.92	1.05	0.98	1.40	1.46	0.98	1.15	1.43
G/C ₃₀ H	0.74	0.73	0.75	0.56	0.56	0.79	0.77	1.07	0.74	0.34	0.23
C ₃₅ /C ₃₄ H	1.32	1.58	1.62	0.72	1.13	1.29	1.44	1.29	2.31	0.65	0.79
DBTs (%)	4.43	5.72	8.53	4.68	4.67	3.67	8.83	4.63	10.75	4.32	5.14
DBT/P	0.21	0.27	0.24	0.32	0.28	0.35	0.11	0.05	0.35	0.43	0.43
C ₂₅ TT/C ₂₆ TT	1.40	1.43	1.46	1.45	1.36	1.10	1.30	1.19	1.18	0.81	0.69
C ₁₉₋₂₁ TT/ C ₂₃₋₂₄ TT	0.68	0.71	0.67	0.65	0.74	0.76	0.74	0.75	0.79	1.06	1.02
20S/(20S+20R)	0.28	0.31	0.32	0.39	0.43	0.48	0.57	0.49	0.46	0.36	0.40
$\alpha\beta\beta/(aaa+\alpha\beta\beta)$	0.29	0.29	0.28	0.32	0.38	0.63	0.57	0.64	0.65	0.40	0.50
Ts/(Ts+Tm)	0.26	0.21	0.23	0.24	0.27	0.50	0.66	0.68	0.87	0.39	0.43
Dia/Reg	0.14	0.16	0.15	0.18	0.19	0.35	0.52	0.80	0.91	0.27	0.39
T/P	0.13	0.17	0.13	0.21	0.19	0.51	2.32	1.68	1.34	0.34	0.57
Rc (%)	0.78	0.67	0.67	0.67	0.67	0.74(1.29)	0.78 (1.24)	0.87(1.27)	0.93 (1.28)	0.72	0.75

Table 3

Table 3

Well	Strata	(%)					A	B	C	D	E	F	G	H	I	N ₁ (%)				O ₁ (%)			O ₂ (%)	
		N ₁	N ₁ O ₁	O ₁	O ₂	O ₃										DBE ₉	DBE ₁₂	DBE ₁₅	DBE ₁₈	DBE ₄	DBE ₅	DBE ₈	DBE ₁	
Pu1-120	Es ₁	36.29	3.67	25.38	28.3	6.35	0.33	0.57	0.45	0.11	0.95	0.66	22.99	0.78	3.46	34.13	15.86	4.31	1.16	42.42	19.4	6.16	52.81	
Wei77-10	Es ₄ ^U	36.06	2.9	23.57	35.19	2.28	0.38	0.88	0.79	0.14	1.04	0.68	12.78	0.98	5.32	32.95	18.16	5.47	1.5	44.07	16.3	7.23	71.27	
Ming85	Es ₃ ^M	38.52	2.57	23.46	33.16	2.28	0.47	1.27	1.23	0.16	1.23	0.44	7.56	0.86	1.04	25.44	19.43	6.65	1.59	35.78	19.9	6.88	34.35	
Wei42-26	Es ₃ ^M	48.62	5.08	29.8	15.88	0.61	0.49	1.3	1.56	0.19	1.76	0.2	2.98	0.33	3.64	25.63	20.17	8.56	2.24	32.67	17.1	7.23	49.18	
Pu7-18	Es ₃ ^M	53.89	2.92	34.93	6.07	2.19	0.57	1.32	1.53	0.18	1.34	0.31	4.63	0.11	4.89	23.18	19.15	7.46	2.22	33.94	16.6	7.51	43.12	
Pushen20	Es ₃ ^M	65.94	4.95	18.31	10.31	0.49	1.07	1.97	3.33	0.3	1.85	0.14	1.82	0.16	2.17	12.17	17.55	14.2	4.05	12.81	8.61	11.51	55.95	
Pushen18	Es ₃ ^M	59.7	6.88	10.83	21.21	1.39	1.2	1.99	3.68	0.34	1.92	0.13	1.4	0.36	3.67	9.2	16.55	16.3	4.91	5.4	3.69	9.19	62.16	
Hu96-3	Es ₃ ^M	13.41	1.89	20.41	48.84	15.44	1.25	1.88	4.18	0.40	3.19	0.22	1.39	3.64	2.08	8.96	17.08	17.48	5.25	2.33	5.48	6.70	33.29	
Pushen18-2	Es ₃ ^M	55.02	4.06	16.19	23.35	1.37	1.76	2.71	4.01	0.33	2.19	0.08	1.33	0.42	4.57	4.1	14.42	18	6.04	3.85	4.45	11.29	63.66	
Chun24-1	Es ₃ ^M	64.55	4.31	14.76	16.1	0.27	0.63	1.12	1.18	0.24	1.56	0.4	3.99	0.25	5.46	22.03	19.25	9.74	2.83	23.68	12.8	10.16	53.37	
Ma19-30	Es ₃ ^M	56.41	4.06	13.13	25.77	0.64	0.82	1.52	1.78	0.26	1.82	0.38	2.76	0.46	4.69	17.64	18.8	12.6	3.62	21.06	10.6	11.16	67.85	