



Research paper

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 analyzed enriched in O₂ species, particularly fatty acids and 4–5 ring naphthenes with biologically sourced hydrocarbon skeletons: ratios of O₂/N₁ > 0.7; C_{20–30}/C_{15–45}-DBE₁-O₂ > 0.4; and DBE_{5–6}/DBE_{12–22}-O₂ > 6.0 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: DBE_{9–12}/DBE_{15–18}-N₁, C_{20–28}/C_{29–40}-DBE₁₂-N₁, C_{20–30}/C_{31–50}-DBE₁₅-N₁, DBE_{9–12}/DBE_{4–20}-O₁ and C_{20–30}/C_{31–50}-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 C_{20–28}/C_{29–40}-DBE₁₂-N₁ and C_{20–30}/C_{31–50}-DBE₁₅-N₁ ratios reflected an organofacies control and DBE_{9–12}/DBE_{4–20}-O₁ and C_{20–30}/C_{31–50}-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, DBE_{9–12}/DBE_{15–18}-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-ICR MS analysis has potential for distinguishing these sample types.

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).

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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 oils (Kim et al., 2005; Liao et al., 2012; Vaz et al., 2013; Pan et al., 2015), mature oils 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 oil 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 (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 (Es₁ to Es₄); Es₃ and Es₄ are further divided into three (Es₃¹ to Es₃³) and two (Es₄¹ and Es₄²) sub-members, respectively. The Es₄ member and middle-lower Es₃ sub-members (Es₃²-Es₃³) were deposited in a humid climate and consists of extensive and deep lacustrine facies, the Es₃¹ sub-member is an arid fluvial facies, and the Es₁-Es₂ 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 ααα20S/(S + R) and C₂₉ sterane αββ/(ααα + αββ) < 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 saturates, aromatics, resins and asphaltenes (SARA). Briefly, the oils were deasphalted before fractionation on a neutral alumina chromatographic column. Saturated hydrocarbons, aromatic hydrocarbons and 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 30 m × 0.25 mm × 0.25 μm and 60 m × 0.25 mm × 0.25 μm, 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 micrometer of the solutions was diluted by 1 mL toluene and methanol (1:1, v:v) mixture. A total of 15 μL 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 μL Hamilton syringes.

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