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Geochemistry of alkylbenzenes in the Paleozoic oils from the Tarim Basin, NW China

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ABSTRACT

Monoaromatic hydrocarbons (alkylbenzenes) in Paleozoic oils/condensates from the Tarim Basin were quantitatively analyzed using gas chromatography–mass spectrometry. Their relative abundances and distributions show large variation, which are most likely controlled by the temperature and duration of the catagenesis stage of petroleum maturation. Relatively high abundance of long chain linear substituted alkylbenzenes and alkyltoluenes in the studied samples implies that source rocks of these oils/condensates contain high contents of algal material. The dominance of dodecylbenzene in these n-alkylbenzenes suggests the formation of alkylbenzenes from fatty acids via lactone formation (dehydration). The 1,2,3,4-tetramethylbenzene (TeMB), 1-methyl-3-phytanylbenzene (1-M-3-PyB) and aryl isoprenoids are mainly derived from carotenoids produced by Chlorobiaceae and their occurrence may indicate a highly reducing depositional environment. However, the concentration of these compounds diminishes significantly at high maturity. With increasing thermal maturity, the prominent trend of demethylation of alkylbenzenes is accompanied by shortening of alkyl side chains. Large variation in the C_4-alkylbenzene isomer distribution is also controlled by thermal maturity. The 1,2,3,5-TeMB and 1,2,4,5-TeMB isomers are more stable than other TeMB isomers and the overall thermodynamic stability of TeMBs is lower than that of dimethylethylbenzenes. Therefore, several maturity parameters can be derived based on alkylbenzene stability. Absolute concentrations of alkylbenzenes generally increase with increasing thermal maturity, but concentrations of 1-M-3-PyB and aryl isoprenoids decrease significantly at high maturity. Maturity parameters obtained from alkylbenzenes are especially useful for highly mature oils and condensates when most biomarkers are depleted. Caution is advised when interpreting the paleoenvironment and thermal maturity of an oil from the alkylbenzene signatures because they are affected by various other processes such as evaporative fractionation, thermal cracking and biodegradation as well.

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1. Introduction

Monoaromatic hydrocarbons are very important components in crude oils and source rock extracts. This compound class consists predominantly of alkylbenzene isomers ranging to > 40 carbon atoms. They are not synthesized directly by living organisms, but are formed from organic substances present in them by thermochemical transformations via dehydration, cyclization and aromatization reactions (Ostroukhov et al., 1983; Koopmans et al., 1997; Kissin, 1998). The C–C bond cleavage of the side chain by which the aromatic moiety is linked to the macromolecular structure fosters the production of alkylbenzenes. The most probable sequence of events leading to aromatization includes cracking of saturated hydrocarbon chains to olefins, cracking of olefins to dienes, cyclization of dienes to cyclodienes and aromatization of cyclodienes (Kissin, 1998). The composition and concentration of alkylbenzenes in crude oils are controlled by source input, depositional environments, thermal evolution and secondary alteration processes (Sinninghe Damsté et al., 1991, 1993; Hartgers et al., 1994; Pedentchouk et al., 2004) resulting in distributions that are quite diverse.

Some alkylbenzenes preserve information about their biological precursors and are, therefore, important from a paleoenvironmental perspective. The n-alkylbenzenes and n-alkyltoluenes may be formed from linear precursor carbon skeletons such as fatty acids

(Sinninghe Damsté et al., 1991; Ellis et al., 1999; Gorchs et al., 2003; Ivanova et al., 2007). The 1,2,4-trimethylbenzene (TMB) is possibly sourced from plastoquinones (Hartgers et al., 1994). The 1,2,3,4-tetramethylbenzene (TeMB) and a series of aryl isoprenoids are often regarded as the diagenetic products of di-aromatic carotenoids (e.g., isorenieratene) from anaerobic photosynthetic green sulfur bacteria (Chlorobiaceae) (Summons and Powell, 1987; Sinninghe Damsté et al., 1988; Requejo et al., 1992; Sinninghe Damsté et al., 1993; Hartgers et al., 1994; Koopmans et al., 1996).

When two substituents are present on a benzene ring, there is a large predominance of the 2-methyl isomer (*ortho-*) over the others (i.e., *meta-* and *para-*alkyltoluenes). Isomerization reactions of initially formed *o*-alkyltoluenes may lead to the formation of thermodynamically more stable isomers at higher thermal maturity (Albaiges et al., 1986; Sinninghe Damsté et al., 1991; Lis et al., 2008). Hill et al. (2004) noticed that the relative abundances of C_4-alkylbenzene isomers show systematic changes during pyrolysis and that their isomer ratios could be used as thermal maturity indicators.

Alkylbenzenes are one of the most abundant aromatic compound classes in the Tarim oils. Like many other well known biomarkers, the occurrence of isotopically ^{13}C enriched 1,2,3,4-TeMB and aryl isoprenoids has been used for source rock depositional environment identification and oil-source correlation in previous studies (Sun et al., 2003; Jia et al., 2007). However, the geochemistry of alkylbenzenes has not been thoroughly investigated. Their formation mechanisms and reasons for the difference in their occurrences and distributions in oils remain poorly understood. This study examines the geochemistry of alkylbenzenes in selected oils/condensates from the cratonic region of the Tarim Basin. Our data suggest that thermal evolution exerts a substantial impact on the abundances and distributions of alkylbenzenes in oils, which is important for deciphering and interpreting source inputs and depositional conditions of source rocks.

2. Geological background

The Tarim Basin, with an area of 560,000 km², is a superimposed basin with a Paleozoic craton and a Mesozoic–Cenozoic foreland depression (Fig. 1). Its geological characteristics have been summarized by numerous investigations (Li et al., 1996; Jia and Wei, 2002; Zhang and Huang, 2005; Zhang et al., 2005, 2011, 2014). The cratonic region mainly consists of the Manjiaer Depression and the adjacent Tabei and Tazhong uplifts. The Paleozoic strata were deposited almost entirely in marine settings. The Cambrian–Lower Ordovician strata comprise mainly shallow marine to lagoonal carbonates, whereas the Middle–Upper Ordovician was deposited during a marine transgression event. The Silurian and Devonian are composed largely of fine-grained red beds and tidal sandstones, while the Carboniferous is mainly marine and continental transitional sediments. Oil and gas accumulations occur in the Cambrian–Ordovician carbonates and in the overlying sandstones. Multiple charges and various secondary alterations including biodegradation, evaporative fractionation, thermal cracking and thermochemical sulfate reduction may have altered these accumulations (Xiao et al., 2000; Zhang et al., 2000, 2005, 2011, 2014; Li et al., 2010; Zhu et al., 2012; Pang et al., 2013).

Marine oils in the cratonic region of the Tarim Basin are thought to be derived from two main source rock systems in the Cambrian–Lower Ordovician and the Middle–Upper Ordovician. The former is currently over mature and the latter is mature. It is generally assumed that the Lower–Middle Cambrian was deposited under an oxygen deficit sedimentary environment with more phosphorite and black shale, while the Middle–Upper Ordovician was deposited in an under filled marginal basin and slope environments with more planktonic algal organic facies (Zhang et al., 2000; Sun et al., 2003;

Jia et al., 2007; Yu et al., 2011; Li et al., 2012). However, the main contributor to the accumulated oil remains a controversial issue due to the relatively high thermal maturity of the oils, complicated charge history, mixing and secondary alterations and the scarcity of deep wells that have penetrated likely source rock intervals. There are a few oil samples which are widely accepted as end member based on biomarkers, specific isotopic compositions and geological conditions (Zhang and Huang, 2005; Li et al., 2010).

3. Methods

Thirty-eight (38) oil/condensate samples were collected at well head separators from the cratonic region of the Tarim Basin. The crude oil/condensate samples were spiked with a suite of internal standards and then separated into fractions using a small scale column (pipette) liquid chromatography method (Bastow et al., 2007). The sample was applied to the top of a mini column of activated silica gel. The saturated hydrocarbon fraction was eluted with *n*-pentane (2 ml) and the aromatic hydrocarbon fraction with dichloromethane (2 ml). The saturated and aromatic hydrocarbon fractions were analyzed without any solvent evaporation by gas chromatography–mass spectrometry (GC–MS).

The GC–MS analyses of the hydrocarbon fractions were performed using an Agilent 5975C MSD system interfaced to an Agilent 7890A gas chromatograph. A DB-1MS fused silica capillary column (60 m × 0.32 mm i.d. × 0.25 µm film thickness) and a HP-5MS column (60 m × 0.32 m × 0.25 µm) were used for saturated and aromatic hydrocarbon fractions, respectively. The oven temperature was initially set at 40 °C for 5 min, programmed to reach 325 °C at 3 °C/min and held for 20 min. Helium was used as the carrier gas with constant flow rate of 1 ml/min. Both interface temperature and injector temperature were 300 °C. The transfer line temperature was 250 °C, and the ion source temperature was 230 °C. The ion source was operated in the electron ionization (EI) mode at 70 eV and selected ion monitoring (SIM) was performed.

Quantification of individual compounds was achieved by extracted ion chromatograms and peak area integration, using $m/z = 92$ (*n*-alkylbenzenes), $m/z = 106$ (*n*-alkyltoluenes), $m/z = 120$ (C_3-alkylbenzenes), and $m/z = 134$ (C_4-alkylbenzenes and aryl isoprenoids). The compounds were identified based on relative retention times and comparisons with published data (Summons and Powell, 1987; Sinninghe Damsté et al., 1988, 1991; Hartgers et al., 1992, 1994; Hill et al., 2004). D8-naphthalene was used as an internal standard for calculation of absolute concentrations and no response factor calibration was applied.

4. Results

4.1. Physical properties and bulk compositions

The studied samples are characterized by a broad range of physicochemical properties ranging from colorless condensates and light oil to dark, viscous heavy oils (Table 1). The wide variation is characterized by an API gravity range of 22.5–54.6° at 20 °C, viscosity of 0.8–381 cP at 50 °C, sulfur content of 0.02–1.69% and wax content of 2.2–37.8%, which spans most of the maturity window for oil generation from marine source rocks. The bulk compositional fractions of the oils/condensates display a wide range of saturated hydrocarbon, aromatic hydrocarbon, resins and asphaltenes (SARA) concentrations in the range 17.0–84.2%, 5.5–48.1%, 0.9–29.1% and 0.3–33.4%, respectively (Table 1).

4.2. Distribution patterns of alkylbenzenes

The alkylbenzene distributions varies significantly among the studied oils/condensates as indicated by the summed mass