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Molecular composition assessment of biodegradation influence at extreme levels – A case study from oilsand bitumen in the Junggar Basin, NW China

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ABSTRACT

In order to understand the effects of extreme biodegradation on petroleum molecular compositions, a series of shallow buried oilsands from the northwestern margin of the Junggar Basin, NW China has been investigated using geochemical methods. Most samples have experienced at least level 8 biodegradation on the scale of Peters and Moldowan, but their molecular compositions still show dramatic variations. The bi- and tricyclic aromatic compounds are almost completely removed with aromatic steroid hydrocarbons being the only visible molecules in the aromatic hydrocarbon fraction. However, aromatic steroids are not sensitive to the assessment of biodegradation extent possibly due to mixed effects with water washing. At an extreme level of biodegradation after diasteranes were attacked, pregnanes, tri- and tetracyclic terpanes, non-hopane pentacyclic terpanes such as 18 α -30-norneohopane, C₃₀ diahopane and gammacerane remain prominent. The post extreme level of biodegradation can be further differentiated on the basis of the presence and absence of these 'refractory' components together with 25-norhopanes (NHs), 17-nortricyclic terpanes (NTTs) and C₂₃ demethylated tetracyclic terpane (C₂₃NTeT). These NHs, NTTs and C₂₃NTeT are produced from corresponding hopanes, tri- and tetracyclic terpanes during biodegradation but they are biodegradable as well. Extreme plus 1 level of biodegradation is characterized by the attack of pregnanes and tricyclic terpanes. Extreme plus 2 level of biodegradation is characterized by the attack of tetracyclic terpanes and non-hopane pentacyclic terpanes. When biodegradation level reaches to extreme plus 3, NHs and NTTs are largely depleted. At extreme plus 4 level, the only traceable components are C₂₃NTeT and C₂₉NH. While different basins or reservoirs may have their unique features of the biodegradation process, relative rates of biodegradation of the different hydrocarbon classes that occur in the Junggar Basin may provide a protocol for intensity assessment after the extreme level of biodegradation is reached.

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1. Introduction

The effect of biodegradation on the molecular composition of oil has been comprehensively studied for the hydrocarbon fraction. Progressive biodegradation of crude oil tends to remove saturated hydrocarbons first, concentrating heavy polar and asphaltene components in the residual oil (Connan, 1984; Peters and Moldowan, 1993; Wenger et al., 2002; Head et al., 2003; Huang et al., 2004a; Larter et al., 2006). One feature is the increasing magnitude of the unresolved complex mixture (UCM) in gas chromatograms of

both the saturated and aromatic hydrocarbon fractions with increasing extent of biodegradation (Volkman et al., 1983). The sequential removal of certain compound classes of the oil during biodegradation forms the basis of biodegradation scales. These scales are essentially based on the presence or absence of key compound classes (Connan, 1984). Volkman et al. (1983) presented a nine point scale which ranked oils according to the extent to which the distribution of saturated hydrocarbons had been altered by biodegradation. Later, they expanded this scale to include aromatic hydrocarbons (Volkman et al., 1984). Another more widely used ten point scale was proposed by Peters and Moldowan (1993) (PM scale) with PM1 (least altered) to PM10 (most altered). The normal removal sequence appears to start with *n*-alkanes followed by acyclic isoprenoids and then more resistant compounds such as

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cyclic alkanes. However, the PM scale did not include aromatic hydrocarbons except aromatic steroids. Recently, Larter et al. (2012) developed Manco (Modular Analysis and Numerical Classification of Oils) scale, based on integrating the extent of biodegradation of various aromatic compounds and steranes. The authors noted wide variation of alkyl aromatic compounds (e.g., alkyltoluenes, alkyl-naphthalenes, alkylphenanthrenes and alkyl-dibenzothio-phenes) in samples degraded to uniform levels on standard PM scales, which may show variation in local degradation systematics related to biodegradation mechanisms and extent of oil mixing. However, the Manco scale was only applicable to oils biodegraded in the range of PM levels 4–8.

In severely biodegraded oils, no simple alkyl-naphthalenes or alkylphenanthrenes are present but monoaromatic steroids are unaffected (level 8). Alteration of diasteranes and aromatic steroid hydrocarbons suggests an extreme level of biodegradation (level 9 of Volkman et al., 1983, 1984; and PM 9–10 of Peters and Moldovan, 1993). Existing scales widely used to describe the extent of biodegradation of petroleum have insufficient resolution at extreme biodegradation levels (level 8+) as the behavior of some biodegradation resistant compounds such as pregnanes, tri- and tetracyclic terpanes and non-hopane pentacyclic terpanes has not been included. The biodegradation influence and the susceptibility among them may not have been fully understood simply due to the lack of cases which systematically record such extreme biodegradation. Some studies indicated that tricyclic terpanes (TTs) can be biodegraded as biodegradation proceeds (Peters, 2000; Alberdi et al., 2001), and even 25-norhopanes (NHs) are not sustainable in aerobic settings under laboratory conditions (Bost et al., 2001) and natural biodegraded reservoirs (Li et al., 2015). In the present study the behavior of 'refractory' components during biodegradation has been investigated in a series of oilsands from the northwestern margin of the Junggar Basin, NW China. Residual oils (bitumens) in shallow reservoirs experienced extreme levels of biodegradation, which offers one of the best natural examples of molecular changes to an oil at this level of biodegradation.

2. Geological background and methods

2.1. Geological background

The Junggar Basin, with an area of 1.3×10^5 km², is located in the northern part of Xinjiang Uygur Autonomous Region, NW China. It is bounded by the Kelameili Mountains to the east, the Tianshan Mountains to the south, and the Zhayier Mountains to the northwest. The basic characteristics of petroleum geology and geochemistry in this area have been investigated in numerous studies (Chen and Zhang, 1993; Clayton et al., 1997; Wang and Kang, 1999; Huang, 2000; Chen et al., 2003; Wang and Chen, 2004). The basin is developed on the Junggar terrane, consisting of the Precambrian crystallized basement, formed before 800 Ma, and slightly metamorphic Palaeozoic basement. It has undergone several evolution stages from rift basin, collision foreland basin, intraplate depression basin to rejuvenated foreland basin since the Carboniferous (Wang and Chen, 2004; Cao et al., 2005). The main source rocks for this region are the Permian lacustrine sediments including the Jiamuhe, Fengcheng and Wuerhe formations, which form the base of the giant Permian petroleum system along the northwestern margin of the Junggar Basin. All source rocks were matured enough to generate oil before the Late Jurassic uplift event (Carroll, 1998; Chen et al., 2003; Cao et al., 2005). Alluvial conglomerates and sandstones of the Permian, Triassic, Jurassic and Cretaceous strata serve as reservoir rocks. Conventional oils and heavy oils are mainly produced from the Middle Triassic

Karamay Formation, while oilsands are in shallow reservoirs in the Lower Cretaceous Tugulu Group.

The study area is situated on northwestern margin of the basin, where more than 10 oil and gas fields have been discovered and oil seeps are widely distributed (Fig. 1). The oils in the Chepaizi area were mostly derived from Permian Wuerhe Formation (Chen et al., 2016). Petroleum exploration revealed that a large-scale thrust fault system in this region controls oil and gas distribution patterns (Chen and Zhang, 1993; Wang and Chen, 2004; Cao et al., 2005, 2010; Xiang et al., 2015; Lu et al., 2016). Crude oils in shallow reservoirs in western part of the basin were severely biodegraded (Zhang et al., 1988; Jiang et al., 1990). In order to investigate oilsand potential at the basin margins, a large number of shallow wells were drilled recently. Samples in the present study are from these shallow boreholes within the mineable depth (Fig. 1).

2.2. Experimental methods

Fifty-six samples for the present study were collected from 9 wells on the upper block of Hong-Che fault zone (Table 1). Commercial oil fields such as Hongshanzui and Chepaizi are located on its lower block (Fig. 1).

Core samples were extracted with a mixture of dichloro-methane:methanol (93:7) via Soxhlet extraction for 24 h. The extracts (ca. 50 mg) were de-asphalted to obtain a hexane soluble fraction that was readily amenable to the following solid phase extraction (SPE) procedure (Bennett and Larter, 2000). An aliquot of the de-asphalted extract was loaded onto a C18 non-end capped (NEC) SPE cartridge and allowed to absorb. The hydrocarbon-containing fraction was collected with *n*-hexane. Squalane and 1,1-binaphthyl were added to the maltene fraction as internal standards prior to further separation into aliphatic and aromatic hydrocarbon fractions using a silver nitrate-silica gel SPE column, eluting with hexane and dichloromethane, respectively.

Detailed analysis of the aliphatic and aromatic hydrocarbon fractions was performed on an HP 5890 gas chromatograph fitted with a DB-5 fused silica capillary column (30 m × 0.32 mm i. d. × 0.25 μm film thickness; J&W Scientific) and coupled to an HP 5970B quadrupole mass selective detector. Samples were analyzed in selected ion monitoring (SIM) mode with an electron ionization energy of 70 eV, filament current of 220 μA, source temperature of 250 °C and multiplier voltage of 2000 V. The oven temperature program was 40 °C (initial time, 2 min) to 175 °C at 10 °C/min to 225 °C at 6 °C/min to 300 °C at 4 °C/min and held at 300 °C for 20 min. The mass spectrometer was operated in selected ion monitoring (SIM) mode for both fractions. Monitoring ion mass-to-charge ratios (*m/z*) include 85, 123, 177, 191, 205, 217, 218, and 259 (saturated fraction) and *m/z* 91, 105, 128, 142, 156, 166, 168, 170, 178, 184, 192, 202, 206, 220, 228, 231, and 253 (aromatic fraction). Peak area was used for concentration and molecular parameter calculations. No response factor calibration was applied for analyses of either fraction.

3. Results

The bitumen contents vary from 0.5–8.9 wt% with an average value of 2.7% in the studied samples and show no clear correlation with burial depth. The bulk composition analysis indicates that the core extracts have enriched resin plus asphaltene contents (41.9–96.6%) whereas the saturated hydrocarbons ranged between 2.6% and 43.1% and the aromatic hydrocarbon fraction ranged from 0.8–19.5% (Fig. 2).

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