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A case study of crude oil alteration in a clastic reservoir by waterflooding

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ABSTRACT

The objective of this research was to evaluate the effect of waterflooding on the chemical properties of crude oils. Geochemical characteristics were investigated using GC, GC–MS and stable carbon isotope in 36 oils from three recovery stages spanning an 8-month interval for 12 productive wells in the Qudi oilfield. Waterflooded oils exhibit decreases in aromatics and increases in saturates contents, with an initial increase in NSO content and subsequent decrease; a decrease of $\sum n\text{-}C_{21}^{-}/\sum n\text{-}C_{22}^{+}$ ratio; a slight more positive stable carbon isotope ratios for the NSO fractions; an increase of 4-MDBT/DBT ratio $C_{15}8\beta$(H)-drimane/$C_{16}8\beta$(H)-homodrimane ratio values, which are consistent with the effect of water washing. However, the irregular variation of Pr/n-C_{17} and pH/n-C_{18} ratios and the a random change of naphthalene related parameters values imply a complex fluid flow behavior influenced by the strata chromatography adsorption and the change of aqueous solubility for certain compound during the waterflooding development, except the predominant water washing. The source- and maturity-related and unchanged diterpane, triterpane, sterane, phenanthrene, dibenzothiophene, and TAS biomarker parameters are minimally affected or unchanged by waterflooding and, therefore, can be reliably used for its geochemical interpretation.

1. Introduction

The initial composition of a crude oil is controlled by the organic matter type, maturity of the source rock, hydrocarbon migration, and post-generative alteration (Lafargue and Barker, 1988; Kuo, 1994). Waterflooding is one of the most commonly used methods for enhancing oil recovery, and in-situ and injected water may selectively remove some soluble components from oil (Chang et al., 2010). For the waterflooded oil, water washing is probably the dominant process affecting oil composition in the subsurface where bacterial degradation and thermal maturation is precluded. Over long timescales, the oil composition may be significantly modified, though oil components have a low solubility in water (de Hemptinne et al., 2001).

The simulation experiments and case studies of waterflooding suggest that oil components with high API and low viscosity are firstly expelled (Li et al., 2000), and compounds with low molecular weight and high solubility are preferentially removed (Bailey et al., 1973; Guo et al., 2007), resulting in the rise of mean molecular weight, decrease of aromatics, and increase of NOS fraction abundances for recovered oils (Kuo, 1994; Buckley et al., 1996; Li et al., 2000; Chang et al., 2009). Water washed oils feature: (1) lower API gravities, higher viscosity, and higher freezing point (Kuo, 1994; Liu et al., 2000; Xu et al., 2000; Chen et al., 2000; Chang et al., 2009), lower abundances of low carbon number fractions and oil saturations (Zhu et al., 2007), higher abundances of polycyclic aromatic hydrocarbons (PAH) (Zhu et al., 2003); (2) decrease of $\sum n\text{-}C_{21}^{-}/\sum n\text{-}C_{22}^{+}$ and Pr/pH ratios (Liu et al., 2000; Chen et al., 2000; Zhu et al., 2003; Chang et al., 2009), increase of Pr/n-C_{17} and pH/n-C_{18} ratios (Kuo, 1994; Chang et al., 2009); (3) complete depletion of drimane series compounds, decrease of tricyclic diterpanes, pentacyclic triterpanes, pregnane, homopregnane, diasteranes (Zhang and Zhang, 2000) and 18α (H) trinorhopane (Palmer et al., 1984), enhancement of gammacerane (Zhang and Zhang, 2000) and 17α (H) norhopane (Palmer et al., 1984); (4) slight decrease of bicyclic and tricyclic aromatic hydrocarbons, marked increase of tetracyclic and pentacyclic aromatic hydrocarbons (Zhang and Zhang, 2000), selective loss of dibenzothiophenes followed by loss of aromatic hydrocarbons (Palmer et al., 1984) or even complete depletion (Lafargue and Le, 1996), distinct increase of methylphenanthrene index (MPI), slight

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increase of triaromatic steroid maturity indicators, and systematic decrease of DBT/MDBT and phenanthrene/methylphenanthrene ratios (Kuo, 1994); (5) stable carbon isotopes that are slightly more negative in the saturate fraction, unchanged in the aromatic fraction, and significantly more negative in the NSO fraction (Palmer, 1984; Kuo, 1994).

However, different discoveries were also reported: (1) Lafargue and Le (1996) demonstrated in laboratory experiments that no loss of pristane, phytane, steranes, or terpanes occurred in the C_{15}^{+} fraction influenced by water washing. Kuo (1994) asserted that water washing had negligible effect on diterpane, triterpane, and sterane biomarkers. The ratios of *n*-hexane to benzene, *n*-hexane to cyclohexane and *n*-heptane to methylcyclohexane remained almost constant under water washing conditions (de Hemptinne et al., 2001). (2) Guo et al. (2007) showed that naphthalene abundances in aromatics were nearly unaltered in a correlation of six oil samples with the waterflooding development interval of about 20 years from three wells. Based on a field case in Sha-33 oil reservoir from the Nanpu sag, Xu et al. (2012) proposed that the Pr/pH, pH/n-C_{18}, Pr/n-C_{17}, benzocarbazole [a]/([a]+[c]), C_{31} hopane 22S/(22S+22R), C_{29}20S/(20S+20R) and $C_{29}\beta\beta/(\alpha\alpha+\beta\beta)$ sterane ratios, Ts/(Ts+Tm), MPI_1 and MPI_2 were slightly changed with the waterflooding while 4-/1-MDBT and tricyclic terpane/(tricyclic terpane+C_{30} hopanoid) varied markedly even over a short time.

In this study, we investigate the modification of oil compositions during the process of waterflooding. We present results of biomarker and stable carbon isotope analyses, and attempt to infer their availability and validation in petroleum geology and geochemistry research.

2. Geological setting

The Qudi oilfield covers an area of about 200 km^2 and is located in the Qudi nose structure of Huimin Sag, Jiyang Basin of Eastern China, which is bounded by the Xiakou fault to the north, the Qudi fault to the south, the Baiqiao fault to the east and the Xianan

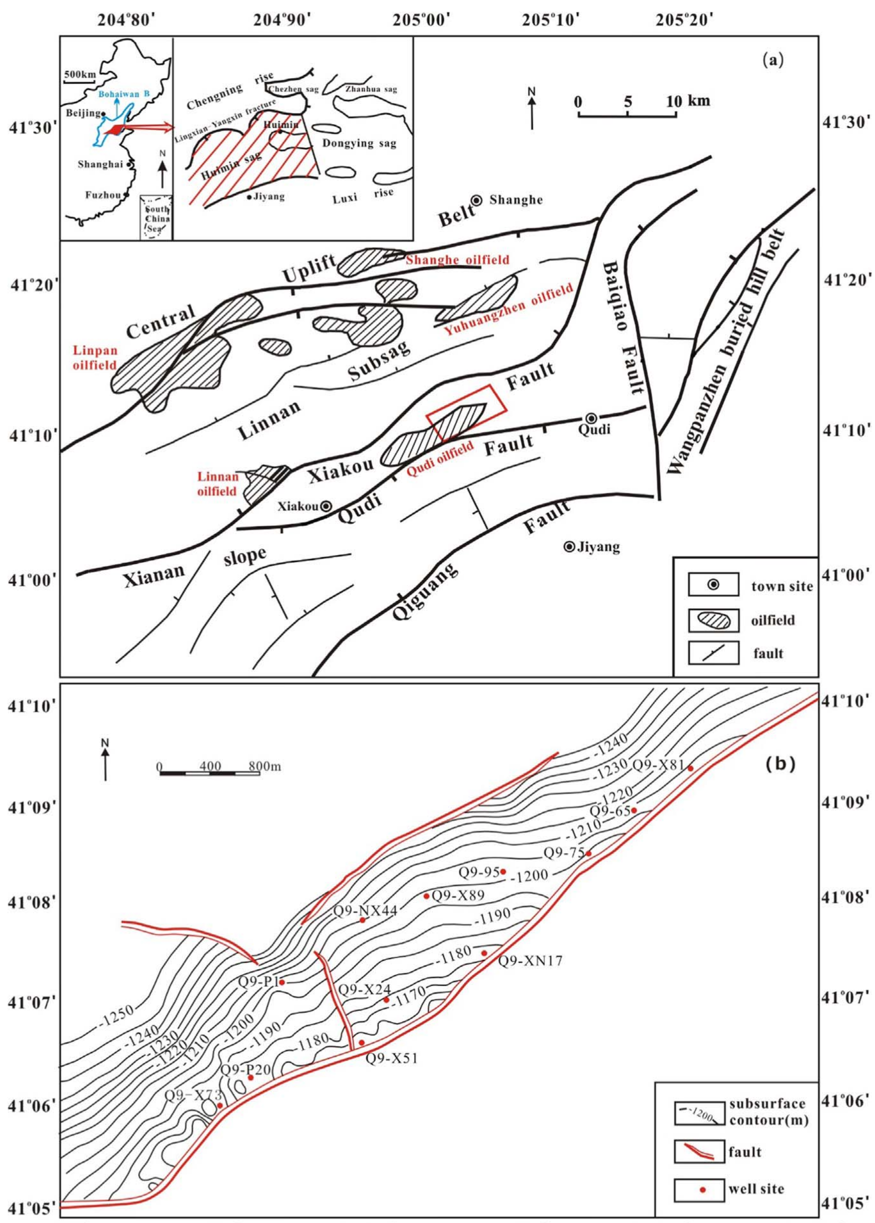

Fig. 1. Map showing the locality of the study area with sample locations identified. Huimin Sag of Jiyang Basin, Q9 reservoir are shown in (a) and (b), respectively.