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Research paper

Identification of polycyclic sulfides hexahydrodibenzothiophenes and their implications for heavy oil accumulation in ultra-deep strata in Tarim Basin

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ABSTRACT

Heavy oil accumulation in deep Ordovician carbonate stratum was discovered at present burial depths greater than 6600 m in the northern Tarim Basin, NW China. Density of the unusual ultra-deep heavy oils is greater than 0.92 g/cm^3 at 20 °C. Crude oil produced from 6598 to 6710 m interval of the Ha9 well was selected for the thiophenic and sulfidic compounds characterization in order to understand the mechanism of heavy oil accumulation in the ultra-deep strata. In addition to the common thiophenic compounds, four homologues of novel polycyclic sulfides named as 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9*b*-hexahydrodibenzothiophenes (H_6DBTs, 9-alkyl = H, methyl, ethyl, and propyl, respectively) were identified in Ha9 well crude oil, and it is the first time these biomarkers were detected in natural occurrence. H_6DBTs were generated from isoprenoid-related precursors reacted with reduced-state sulfur in early diagenesis stage by bacterial sulfate reduction. The occurrence of H_6DBTs further indicated biodegradation of the reservoir oil at a relatively mild temperature (60–65 °C), a favorable condition for microorganism survival. According to the history of reservoir forming, oil and gas accumulation occurred in reservoirs during the Late Permian period and then being uplifted, suffering biodegradation. Oil quality was significantly altered as a result of strong biodegradation since the Triassic. Heavy oil reservoir was buried deeper around. 5 Ma, leading to a rapid increase in reservoir temperature up to 150 °C at a burial depth of 6600 m. The quick burial and elevated temperature of the reservoir were favorable to the preservation of H_6DBTs.

1. Introduction

Heavy oils are important resources that are widely distributed in sedimentary basins around the world (Demaison, 1977; Hunt, 1979; Head et al., 2003). Heavy oils, composed of a low abundance of saturated hydrocarbons, are also characterized by high density, viscosity, acidity, sulfur and asphaltene contents. Most scientists believe that biodegradation of crude oil is an anaerobic biological process (Rueter et al., 1994; Zengler et al., 1999; Van Aarssen et al., 1999; Anderson and Lovely, 2000; Kniemeyer et al., 2007; Jones et al., 2008) that would cease at temperatures above 75–80 °C (Bernard et al., 1992; Peters and Moldowan, 1993; Larter et al., 2003). Therefore, heavy oils around the world are mainly distributed in shallow strata (Zhu et al., 2012).

A variety of hopanes and steranes have been widely used as geochemical proxies for the formation of heavy oils in shallow strata and outcrops (Bennett et al., 2006, 2009; Eiserbeck et al., 2012; Oliveira et al., 2012; Tian et al., 2012). In addition, some new sulfur-containing biomarkers were also identified in heavy oils, which provides further understanding of burial history and formation mechanisms of shallow heavy oils (Lu et al., 2013a, 2013b; Schaeffer et al., 2006). Nevertheless, biomarkers with geochemical significance have been rarely studies in heavy crude oils in deep reservoirs. Recently, a series of polycyclic sulfides were reported in catalytic hydrodesulfurization diesels from refinery units, which were identified as hexahydrodibenzothiophenes (H_6DBTs) (Charrié-Duhaut et al., 2003; Japes et al., 2009). H_6DBTs were speculated to be derived from certain carotenoid biological precursors, and the formation of H6DBTs was closed to microbial actions such as bacterial sulfate reduction and biodegradation and

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(Charrié-Duhaut et al., 2003). Nevertheless, the above speculation has not been firmly evidenced, since H6DBTs were only determined in artificial processed diesels.

In present study, hexahydrodibenzothiophenes were elaborately separated from a heavy crude oil in northern Tabei of Tarim Basin, providing a solid evidence for the natural occurrence of these sulfur compounds. In recent years, a huge of heavy oil resources with a reserve greater than 3 billion tons have been discovered in deep Ordovician carbonate reservoirs (at depths of 6000–7500 m and reservoir temperatures of 140–160 °C) in the northern Tarim Basin (Tabei area) in China. Such heavy oil has a density of 0.90–1.05 g/cm^3 (20 °C), viscosities of 20–9142 mPa s, and freezing points of -16–30 °C. The original gas-to-oil ratio (GOR) is 50 m^3/m^3 on average.

In this work, the thiophenic and sulfidic compounds were selectively separated from the crude oil of Ha9 well. Detailed characterization of sulfur compounds facilitates a deeper understanding of the geological and geochemical history of this ultra-deep paleo-oil reservoir.

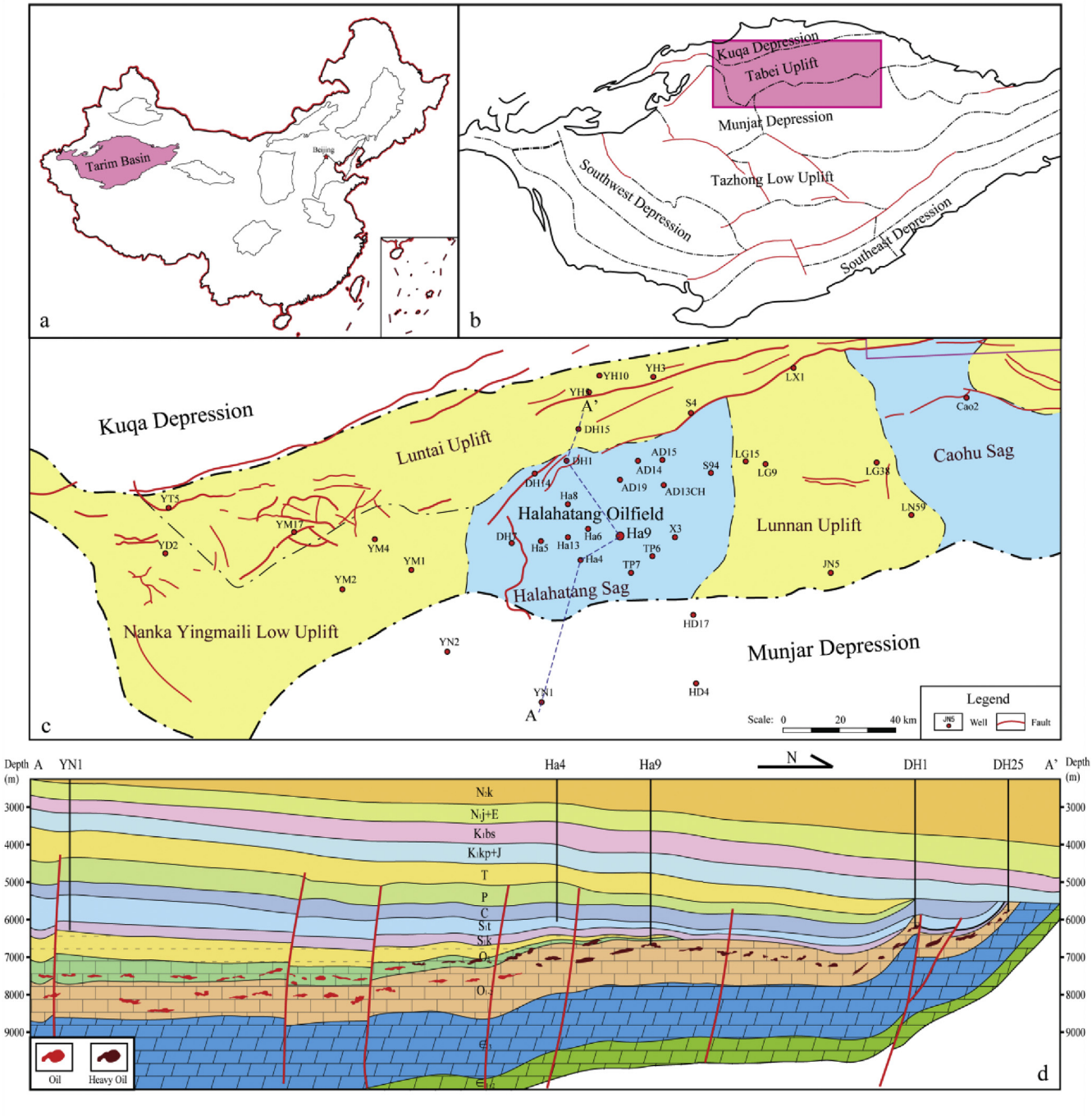

Fig. 1. Tectonic settings and oil/gas distribution in Ordovician reservoir in Tabei Uplift. (a) Location of Tarim Basin; (b) structural unit division of Tarim Basin; (c) structural unit division and main wells in Tabei area; (d) E–W cross section of reservoir in Tabei area. Well names along top of graph. Red lines are faults; red blobs are oil reservoirs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)