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Research paper

# Recognition of a novel Precambrian petroleum system based on isotopic and biomarker evidence in Yangtze platform, South China

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ABSTRACT

The Precambrian Doushantuo Formation is regarded as a possible petroleum source rock horizon with TOC values of 0.85–1.85% and type I kerogen in northwestern Sichuan Basin, Yangtze platform, South China, while showing high-to post-mature thermal maturity. A set of outcropping bitumen and oil sands from various reservoirs display overall depleted values of $\delta^{13}C$ from −36 to −32‰ (average −35‰), typical of a Precambrian source. In addition, the sterane distributions in these bitumens and oils are unusual compared to marine Phanerozoic oils with a predominance of $C_{29}$ members, as well as their triaromatic counterparts. High amounts of 20-*n*-alkylpregnane with very low diasteranes indicate restricted, sulfur-rich conditions, typical of an anoxic carbonate source rock. This interpretation is supported by some other specific biomarkers such as abundant 30-norhopane and $C_{24}$-tetracyclicterpane, and elevated $C_{35}$ hopane. Furthermore, the presence of gammacerane indicates a saline, stratified water column. Hydrocarbons extracted from the solid bitumen and oil sands have many compositional characteristics in common with other oils derived from Precambrian carbonate source rocks from elsewhere. This implies the existence of a Precambrian marine petroleum system in the Yangtze platform, with the Doushantuo carbonate as the likely source. It is supposed that the reduction of temperature and pressure following basin uplift resulted in petroleum fractionation (deasphalting) in Lower Paleozoic reservoirs with the fractionated oils having migrated along the faults becoming trapped in stratigraphically younger reservoirs, where the petroleum underwent heavy biodegradation.



## 1. Introduction

While it is not common that petroleum systems derived from Precambrian source rocks have been preserved, there are a number of significant Precambrian petroleum systems known (Grantham, 1986; Fowler and Douglas, 1987; Peters et al., 1995; Grosjean et al., 2009; Everett, 2012; Dutta et al., 2013). In particular, the composition and distribution of their biomarkers, or molecular fossils, which were derived from once living organisms on the earth, are unusual when compared to Phanerozoic sediments (Peters et al., 2005). This suggests that Precambrian microbial ecosystems were different in composition than those of younger sedimentary environments (Summons and Walter, 1990). Algae, cyano- and other bacteria increased in abundance through the middle Proterozoic until the latest Proterozoic when metazoa first appeared (e.g. Knoll, 1983; Zhu and Chen, 1995; Love et al., 2009).

Field investigations and geochemical analysis reveal that widely occurring solid bitumen in veins and oil in seeps in northwestern Sichuan, could be derived from the Doushantuo Formation (Wang et al., 2005; Huang and Wang, 2008), although some workers argue that the oil seeps in the Jurassic succession are related to Lower Cambrian source rocks (Dai et al., 2007; Liu et al., 2010). A detailed oil-source rock correlation could not be conducted as both the two stratigraphic units, i.e. the Doushantuo Formation and Lower Cambrian, are over mature or suffered slight metamorphism. In this work, biomarker and isotopic compositions of a suite of outcropping bitumen and oil sands were investigated, in order to define their source and age. This work will provide further evidence

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for the existence of a novel marine petroleum system in the Yangtze platform, South China.

The late Neoproterozoic Doushantuo Formation was widely deposited across the Yangtze platform, South China. It preserves an exceptional record of multicellular life forms just before the Ediacaran radiation of macroscopic animals (Li et al., 1998; Xiao et al., 1998; Yin et al., 2007). Along northwest to southeast of the Yangtze and Cathaysia blocks, a generalized paleogeographic reconstruction during the Doushantuo deposition is characterized by inner shelf (peritidal dominated carbonate facies), intrashelf basin/shelf lagoon (subtidal shale-carbonate facies), shelf margin (carbonate shoal complex), and slope/basin (shale dominated) (Jiang et al., 2011). However, the formation around the studied area was deposited on a carbonate shelf; the rim of which enclosed a lagoon between tidal flats onshore and the deeper ocean. This lagoon was periodically anoxic or euxinic (containing hydrogen sulfide), which might contribute to excellent fossil preservation (Jiang et al., 2011). Organic-rich shales and carbonates were generally inclusive in the Doushantuo Formation.

## 2. Samples and methods

### 2.1. Samples and geological settings

For this study, four solid bitumen samples and two oil sand samples, each one ca. 500g, from different sites and from strata of different ages were collected from open or abandoned mines in the northwestern Sichuan Basin (Fig. 1, Table 1). These samples include: two black bitumen specimens obtained by hand from the Lower Cambrian of Tianba, one black bitumen obtained at the mine from the Silurian of Macun, and one bitumen obtained by hand from the interface of the Triassic/Permian fault of Changjianggou. The two oil sands samples came from the Lower Devonian of Tianjingshan and the Middle Jurassic of Houba, obtained at a mine and by hand, respectively. Additionally, four possible source rocks were sampled from outcrops of the Doushantuo Formation and the Lower Cambrian. All the samples were acquired as massive except for B3 that was in powder form.

Stratigraphy of the Doushantuo Formation (ca. 635–551 Ma) was established based on the Yangtze Gorges area, and generally consists of four members. At the base of Doushantuo Formation, member 1 comprises a 5-m-thick carbonate cap, whereas member 2 includes alternating organic-rich shales, clastics and carbonates. Member 3 is predominantly carbonates, while member 4 refers to the 10-m-thick black, organic-rich shales at the top of the Doushantuo Formation (Jiang et al., 2011). In the studied areas, the Doushantuo Formation comprises a 130–250-m thick succession of clastics, gray carbonates and black shales that lie disconformably above the glaciogenic rocks of the Nantuo Tillite and conformably beneath the carbonates of the Dengying Formation (Fig. 2). The Lower Cambrian, i.e. Guojiaba Formation here, is composed of marine regressive deposits, ranging from 600 to 2000m in thickness. It is dominated by black siliceous shales with thin phosphorus beds.

### 2.2. Methods

Source rock samples were powdered to less than 120 mesh for total organic carbon (TOC) analysis and Rock–Eval pyrolysis. Solid bitumens were powdered to less than 80 mesh and the oil sands were broken into pieces for TOC determination, with a small number of treated samples being subject to Soxhlet extraction with $CH_2Cl_2$ for 24 h. The extracts were deasphaltened and then fractionated using column chromatography (silica gel/alumina, 3:1) into saturate, aromatic and polar fractions. The sequential elution solvents were *n*-hexane, $CH_2Cl_2$ with *n*-hexane (7:3), and $CHCl_3$ with $CH_3OH$ (1:1).

Bulk carbon isotopic ratios were measured for the whole extract and each fraction using an elemental analyzer coupled to a Finnigan Delta Plus XP according to standard sealed tube combustion techniques (Sofer, 1980). Results ($\delta^{13}C$ values) are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard. Organic carbon was converted to $CO_2$ at 980 °C in the FLASH 2000 EA reactor filled with Cu and chromium (III) oxide, and then the $CO_2$ was transferred into a MAT 253 mass spectrometer to determine isotopic composition, with an ionization energy of 70 eV.

The saturated and aromatic hydrocarbons were analyzed by gas chromatography-mass spectrometry (GC–MS). GC–MS was carried out with an Agilent 6890 gas chromatograph coupled to an Agilent 5975i mass spectrometer, using a HP-5MS capillary GC column (60 m × 0.25 mm × 0.25 μm film thickness). For saturate analysis, the oven temperature was programmed from 50 °C (1 min) to 120 °C at 20 °C/min, then to 310 °C (hold 25 min) at 3 °C/min, whereas for aromatics analysis, the oven temperature was programmed from 80 °C (1 min) to 310 °C (hold 16 min) at 3 °C/min. The carrier gas in all cases was He at a constant flow rate (1 ml/min). The temperatures set for the injector and transfer line were 300 °C and 280 °C, respectively. The mass spectrometer was operated in the full scan mode or in the selected ion monitoring (SIM) mode with an ionization energy of 70 eV.

For saturate fraction GC-MS-MS analysis, an Agilent 6890 gas chromatograph interfaced to a Quatro II mass spectrometer was used. A DB-5 column (60 m × 0.25 mm × 0.25 lm film thickness) was used with split injection (20:1); the temperature was programmed from 100 °C (1 min) to 320 °C at 4 °C/min; isothermal at 320 °C for 20 min. The carrier gas was He at constant flow (1 ml/min). The mass spectrometer was run in the parent-daughter mode for the following transitions: (1) $m/z$ 260 + 14$n$ ($n$ = 0 to 11) → 217 for 20-*n*-alkylpregnanes and $C_{27}$ to $C_{30}$ steranes; (2) $m/z$ 372 + 14$n$ ($n$ = 0 to 3) → 217 for regular and rearranged steranes; (3) $m/z$ 370 + 14$n$ ($n$ = 0 to 3) → 191 for hopanes; and (4) $m/z$ 356 + 14$n$ ($n$ = 0 to 3) → 177 for 25-norhopanes. The dwell time was 100 ms for each transition, with a 20 ms interchannel delay. The ionization energy was 70 eV, and Ar was used as collision gas at $2 \times 10^{-4}$ mbar, with a collision energy of 20 eV.

## 3. Results and discussion

### 3.1. Distribution of the bitumen veins and oil seeps

Solid bitumen veins are widely observed at Tianba, Kuangshanliang, and Tianjingshan anticlines in the northwestern Sichuan Basin (Figs. 1 and 3a). The veins mainly occur as fill in faults, fractures, and interlaminations of Lower Cambrian to Middle Silurian marine deposits, accounting for as much as 54%, 31% and 16% of the total veins, respectively. The size of the veins varies significantly from a couple of centimeters to a few meters (Fig. 3a, b and c), including some veins over 8 m in width, which local residents have mined as fossil fuels in past decades. In addition to the outcropping solid bitumen veins, oil sands occur in Middle Jurassic fluvial reservoirs, stretching about 25 km along the length of Houba (Fig. 1).

### 3.2. Petroleum alteration and formation of the bitumen

The bitumen and oil sand samples were collected from Paleozoic to Mesozoic marine carbonate and nonmarine sandstone reservoirs. Compared with commercial crude oils (Tissot and Welte, 1984), saturate fraction percentages of the samples are low in a range from 1% (sample B2) to 24% (sample B3; Table 1). Furthermore, the saturate/aromatics ratios are generally less than 1.1,