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High abundance of alkylated diamondoids, thiadiamondoids and thioaromatics in recently discovered sulfur-rich LS2 condensate in the Tarim Basin

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ABSTRACT

Molecular and stable sulfur isotopic ($\delta^{34}S$) analysis of petroleum recently discovered in the Bachu uplift of the Tarim Basin (China) was conducted to characterize the oil and assist future regional petroleum correlation studies. Sulfur-rich condensate from the Lower Ordovician – Upper Cambrian reservoir rock in the LS2 well showed abundant aromatic hydrocarbons and organic sulfur compounds. Extensive distributions of alkylated caged hydrocarbons (i.e., diamondoids) and caged sulfur compounds (thiadiamondoids), including many additional isomers not previously detected in petroleum, were resolved by GC × GC–MS analysis. The thiadiamondoid products and thioaromatics (i.e., benzothiophenes, dibenzothiophenes), also detected in LS2, products were attributed to a major thermochemical sulfate reduction (TSR) event, which resulted in elevated H_2S (3.66%) and dry gas in the condensate. TSR might also have contributed to the generally heavier $\delta^{34}S$ values of the benzothiophenes (+26 to +28‰) compared to dibenzothiophenes (+20 to +27‰). The LS2 reservoir has no sulfate evaporites and the temperature (144 °C) is relatively low for TSR, implying that it is a secondary reservoir for migrated TSR-derived gas, possibly derived from deeper and hotter (>200 °C) Cambrian strata.

1. Introduction

The Tarim Basin is the largest oil- and gas-bearing basin in China and continues to afford tremendous exploration opportunities. A new and potentially lucrative petroleum play was confirmed in the LS2 well drilled a few years ago in the Bachu uplift of the Tarim Basin (Fig. 1). The Lower Ordovician - Upper Cambrian dolomite reservoir at a depth of 5741–5830 m is now producing commercially viable condensate. This resource, like most petroleum recovered from deep Tarim Basin strata, is condensate-rich and has high H_2S content (3.66%). H_2S concentrations >3% are typically attributed to thermochemical sulfate reduction (TSR), a high temperature redox reaction between hydrocarbons and inorganic sulfate (Orr, 1974; Krouse et al., 1988; Claypool and Mancini, 1989; Heydari and Moore, 1989; Machel et al., 1995; Machel, 1998; Worden et al., 1995, 2000; Carrigan et al., 1998; Hao et al., 2008; Zhang et al., 2008a).

To further evaluate the sources and TSR impacts on the LS2 petroleum, as well as provide useful organic geochemical data for regional petroleum correlation studies, we conducted detailed molecular and stable sulfur isotopic analysis on the LS2 condensate with particular focus on characterisation of abundant caged and organic sulfur compounds (OSCs) in the LS2 condensate. Several distinctive organic sulfur products (e.g., thiols, isoprenoid thiophenes, thioaromatics, thiadiamondoids) can be diagnostic of TSR (Cai et al., 2005, 2016; Zhang et al., 2005; Worden and Cai, 2006), although some of these products can also originate by diagenetic sulfurization (Sinninghé Damste and de Leeuw, 1990). These products can show varied sensitivity to TSR and the $\delta^{34}S$ values of thioaromatic products may help identify the early stages of TSR (Amrani et al., 2012). The organic geochemical information acquired was integrated with the lithology and mineral composition of the LS2 reservoir.

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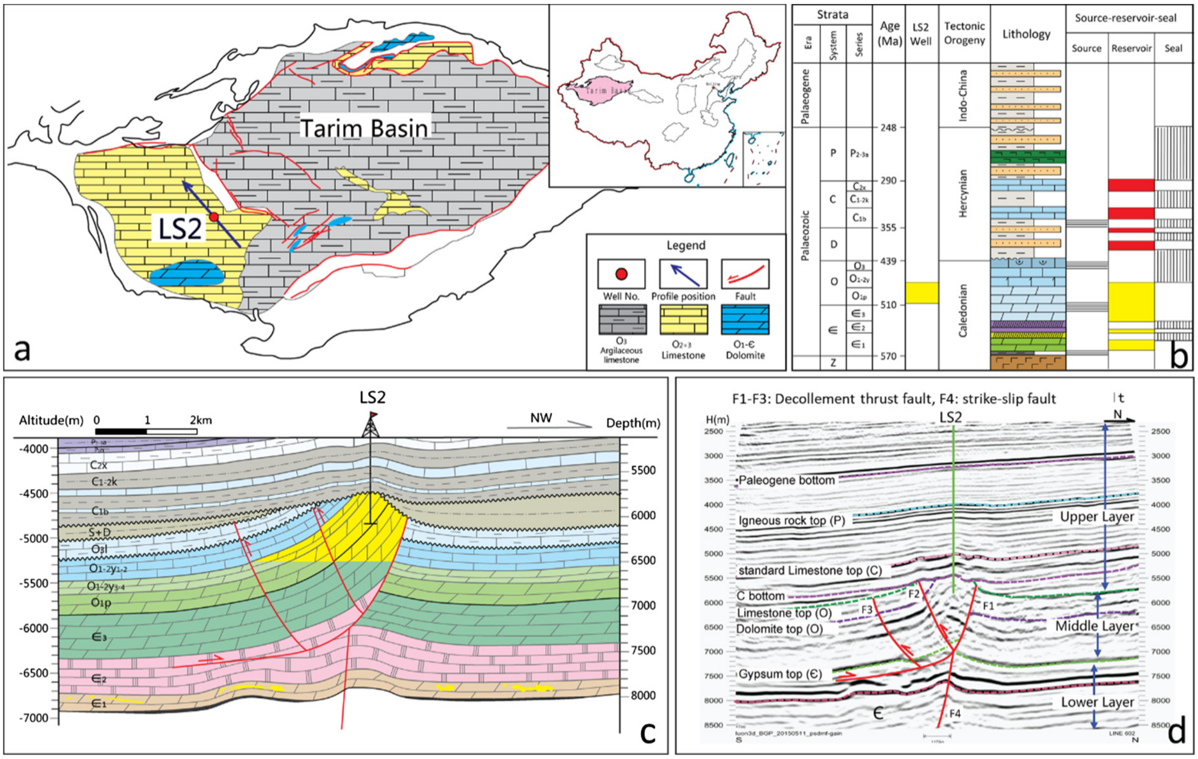

Fig. 1. Geological information for the LS2 well and gas reservoir in Bachu uplift of Tarim Basin, China. (a) Paleogeologic map of Tarim Basin showing LS2 location; (b) Stratigraphic column of Maigaiti slope in Bachu uplift; (c) Structural profile of LS2; (d) Seismic profile and structural model of LS2.

2. Materials and methods

2.1. Well location and physical properties of condensate samples

The LS2 petroleum reservoir is located in the LS2 structure of the Luonan structural belt on the Maigaiti slope in the southwest depression of the Tarim Basin (Fig. 1a). It was drilled in 2016 to a depth of 6080 m and produced light crude oil with low density, viscosity, wax and sulfur content. Daily gas and oil production rates are ~215,000 m^3 and 3 m^3, respectively. For the present study, condensate samples were taken from the Ordovician Penglaiba (O_{1p}) Formation at 5741–5830 m in the well (Fig. 1b–d). The physical and bulk geochemical character of four separately analysed petroleum samples were relatively stable with an average oil density of 0.826 g/cm^3; viscosity between 1.084 MPa and 1.131 MPa; freezing point <−30 °C; wax content 1.2–1.4%; sulfur content 2.1–3.2%; high H_2S content (3.27–4.05%); colloid content 0.13–0.84% and asphaltene content 0.23–0.79%.

Mesozoic formations were missing from the entire Bachu uplift (Fig. 1b), while Devonian and Silurian sections were also absent from the LS2 well (Fig. 1c). The Ordovician LS2 strata were deposited as marine sediments and mainly consist of the Lower Ordovician Penglaiba Formation (O1p), which unconformably overlies Carboniferous strata. The Penglaiba Formation mainly comprised thick-bedded grey dolomitic limestone, and some light grey limestone with thin beds of grey dolomitic conglomerates also occur in the middle and lower sections. The Carboniferous and Permian strata are typical marine-terrigenous units (e.g., thick bed marlstones, calcareous mudstones and mudstones). Paleogene to Quaternary sedimentation was dominated by continental sandstone and mudstone.

The thermal gradient through the formation varied from highs of 28–34 °C/km in Cambrian/Ordovician strata (moderated in Cambrian to lower end of this range by 600–1000 m gypsum and salt layers having relatively high thermal conductivity) to ~25 °C/km in the Mesozoic and Cenozoic due to the development of post-Paleozoic intracratonic and subsequent foreland phases in the basin (Qiu et al., 2012).

2.2. GC × GC-TOFMS analysis

Whole oil samples were analysed on a Leco Corporation GC × GC-TOFMS instrument equipped with two Agilent GCs interfaced to a Pegasus 4D TOF mass spectrometer. A 50 m × 0.2 mm × 0.5 µm J&W DB-petro capillary column and a 3 m × 0.1 mm × 0.1 µm DB-17ht capillary column were used for the first and second dimension GC, respectively. The concentrations of diamondoids, thiadiamondoids and other products were quantified on the basis of peak areas relative to an internal standard (D_{16}-adamantane). Further details of the sample pretreatment procedures and operating conditions for the GC × GC-TOFMS analysis of gas condensate can be found elsewhere (Zhu et al., 2013b).

2.3. Carbon isotopes of gaseous hydrocarbons

Carbon isotope analysis of the hydrocarbon constituents of the natural gas samples, collected in steel bottles at the production well site, were measured using a GC interfaced to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer. All $\delta^{13}C$ values are given in per mil (‰, VPDB) according to delta notation with standard deviation of ±0.10‰.

2.4. $\delta^{34}S$ measurement of OSCs

Compound-specific sulfur isotope analysis (CSSIA) of the aromatic fraction (isolated by liquid chromatography) of the LS2 oils was conducted using an Agilent 6890 GC coupled to a Thermo Neptune Plus multi-collector inductively coupled plasma mass