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Sulfur and carbon isotopic compositions of the Permian to Triassic TSR and non-TSR altered solid bitumen and its parent source rock in NE Sichuan Basin

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ABSTRACT

Reservoir solid bitumens from the Permian to Triassic and potential source rocks in the northeastern Sichuan Basin were measured for elemental and stable carbon ($\delta^{13}C$) and sulfur ($\delta^{34}S$) isotopic compositions to determine the chemical and isotopic composition of non-TSR and TSR-altered solid bitumen and to develop proxies to reflect the extent of bitumen alteration by TSR. Non-TSR altered reservoir bitumen samples showed S/C atomic ratios $\leqslant 0.03$ and had $\delta^{13}C$ values closer to Longtan Formation (P_3l) kerogen than to the Lower Silurian and Cambrian kerogens, and $\delta^{34}S$ values slightly more enriched than P_3l kerogens. The TSR-altered solid bitumens have incorporated significant amounts of TSR-derived H_2S resulting in S/C atomic ratios (0.047–0.074) and $\delta^{34}S$ values (13.4–24.0‰) being significantly higher than those of the solid bitumen not altered by TSR (S/C: 0.013–0.030; $\delta^{34}S$: 5.8–9.6‰) and the potential source rock kerogen. The incorporation has produced a decrease in N/C ratio and negative shift of −2.7‰ in $\delta^{13}C$ values that resulted from increasing TSR-H_2S back reactions with ^{12}C-rich *n*-alkanes from the gas phase, soluble solid bitumen or paleo-oil to generate organic sulfur compounds such as ethanethiol that were incorporated into the solid bitumens, which is followed by further aromatization and polymerization. The solid bitumens show positive relationships of S/C ratios and $\delta^{34}S$ values to the associated gas $H_2S/(H_2S + \Sigma C_{1-6})$ or TSR extents, and thus the S/C ratios and $\delta^{34}S$ values can be used as proxies to reflect TSR extents.

1. Introduction

Solid bitumen is precipitated in pores and fractures of sandstone and carbonate rock reservoirs from migrating or trapped hydrocarbons that are altered by various processes (Powell and Macqueen, 1984; Curiale, 1986; George et al., 1994; Stasiuk, 1997; Cai et al., 2001, 2010). Highly aromatic, insoluble solid bitumens may develop in reservoir rock either by thermal chemical alteration (TCA) or thermochemical sulfate reduction (TSR; Machel et al., 1995; Kelemen et al., 2008). TSR is a redox reaction between dissolved sulfate and petroleum at temperatures higher than about 130 °C to generate calcite, CO_2, H_2S, and organic sulfur compounds including thiols, thiolanes, benzothiophene, dibenzothiophenes and thiadiamondoids (Orr, 1977; Hanin et al., 2002; Cai et al., 2003, 2009b, 2015a, 2016a; Wei et al., 2007, 2012; Amrani, 2014; Walters et al., 2015) and likely diamondoids (Cai et al., 2016b). These organic sulfur compounds, especially thiols, can be readily oxidized by the HSO_4^- or $MgSO_4$ contact ion pair to produce intermediate valance sulfur species which, in turn, react with hydrocarbons to form more H_2S and organic sulfur compounds and thus will further sustain the auto-catalyzed reaction (Zhang et al., 2008).

Abundant solid bitumen is associated with commercial natural gases in the Carboniferous to the Upper Triassic reservoirs in the northeastern Sichuan Basin. Natural gases from the Upper Permian

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Changxing (P_3ch) to Lower Triassic Feixianguan (T_1f) formations from northwestern and northeastern parts of the Sichuan Basin contain H_2S ranging from nil to 20%, and show alteration in chemical and isotopic composition by TSR to different degrees (Cai et al., 2004, 2013; Hao et al., 2008; Hu et al., 2013). Both sweet and sour gases are associated with abundant solid bitumen, and are considered to have been derived from oil cracking in the reservoirs (Cai et al., 2004, 2013, 2014; Li et al., 2005; Ma et al., 2007, 2008; Hao et al., 2008; Wang et al., 2008). Significant differences in chemical composition and $\delta^{13}C$ values exist between eastern gas fields (e.g., MB, PG, LJ and Po) and western gas fields (e.g., HB, YB and LG), and thus are proposed, although not proven, to have been derived from different source rocks (Cai et al., 2011, 2013; Hu et al., 2013).

The potential source rocks of paleo-oils for the gases and the associated solid bitumen include Lower Cambrian, Lower Silurian and Upper Permian Longtan formations' mudstone, shale and marlstone and Upper Permian Dalong Formation shale and mudstone (Li et al., 2005; Liang et al., 2008). Organic matter in these source rocks was derived from marine aquatic organisms dominated by algae and thus is primarily a sapropelic and humic-sapropelic type kerogen, and exhibits similar biological precursor-related parameters, but different maturity-related parameters such as C_{21}/C_{23} tricyclic terpane ratios and $\delta^{13}C$ values (Li et al., 2005; Zhu et al., 2012; Jin et al., 2014).

Since no residual oils have been found in the study area (Cai et al., 2004, 2013, 2014), the sources for the gases have been determined based on correlation of biomarkers and $\delta^{13}C$ values of the source rocks and solid bitumen (pyrobitumen) in reservoirs (Li et al., 2005; Zhu et al., 2012; Jin et al., 2014). This is based on the assumption that biomarkers and $\delta^{13}C$ values reflect primary information. However, most of the solid bitumen is associated with high H_2S gas in this area and thus was formed by TSR (Cai et al., 2010), and may have $\delta^{13}C$ values altered based on a case study from the Jurassic Smackover Formation where solid bitumen formed during TSR has been proposed to deplete $\delta^{13}C$ values by $-5‰$ to $-7‰$ compared to solid bitumen formed by thermal cracking (Sassen, 1988). The depletion in $\delta^{13}C$ values has been considered to result from the incorporation of isotopically light alkanes or saturates via polymerization (Machel et al., 1995).

Thermogenic solid bitumen may have $\delta^{34}S$ values slightly depleted or identical to its parent crude oil depending on the resin and asphaltene content (Machel et al., 1995). Solid bitumen formed by TSR via sulfurization of crude oil or solid bitumen is considerably enriched in sulfur, shows much higher S/C and lower N/C atomic ratios than that by TCA, and has $\delta^{34}S$ values close to the parent sulfate. Thus, S/C and N/C ratios and $\delta^{34}S$ values of solid bitumens can be used to distinguish those formed by TSR from TCA (Powell and Macqueen, 1984; Cai et al., 2001, 2010; Kelemen et al., 2008, 2010; King et al., 2014). These properties are expected to be better proxies for the extent of TSR than the present H_2S concentration or $H_2S/(H_2S + \Sigma C_{1-6})$ because H_2S may be lost due to precipitation as pyrite or increase due to ex-solution from formation water during production (Cai et al., 2010, 2013, 2015b). However, it should be noted that nitrogen-poor, sulfur-rich solid bitumens are not necessarily derived from TSR of crude oils, as proposed by Hao et al. (2015). They may be formed via TSR of solid bitumen as documented by Powell and Macqueen (1984). It is hard to distinguish the two processes by means of elemental composition.

TCA or non-TSR altered solid bitumens are expected to have S/C and N/C ratios, and $\delta^{13}C$ and $\delta^{34}S$ values closer to the parent oil and kerogen assuming that the cracking of kerogen to oil and oil to solid bitumen occurs in a closed system. It is possible to correlate non-TSR altered solid bitumen with its parent kerogen using these parameters. For correlation of TSR-solid bitumen to its source, the effects imposed by TSR on elemental composition, carbon and sulfur isotopes need to be determined and then corrected to a pre-TSR state.

In this study, solid bitumens from the Upper Permian and Lower Triassic, and source rocks from the Lower Cambrian, Lower Silurian and Upper Permian were analyzed for biomarkers, elemental composition, $\delta^{13}C$ and $\delta^{34}S$ values. The specific objectives of this study were to determine: (1) chemical and C and S isotopic alteration of solid bitumens with increasing back reactions with TSR-H_2S; and (2) proxies that can be used to indicate TSR extents in addition to H_2S concentration.

2. Geological setting

2.1. Stratigraphy and structure

The Sichuan Basin in southwest China (Fig. 1) is one of China's largest natural gas provinces with gas found in Jurassic, Triassic, Permian, Carboniferous and Upper Ediacaran (Sinian) strata. It is a late Mesozoic-Cenozoic foreland basin overlying an Ediacaran (or Sinian) Middle Mesozoic passive margin. The Upper Ediacaran to the Middle Triassic sedimentation is dominated by shallow marine carbonates and black shale with thickness from 6000 to 7000 m (Cai et al., 2003). As a result of the Yinzi Orogeny between the Middle and Upper Triassic, the Sichuan Basin was uplifted and exposed. Upper Triassic to Cretaceous strata are composed of freshwater lacustrine-alluvial clastics with local coal beds with thicknesses of 2000–5000 m (Fig. 2).

2.2. Source rocks

Potential source rocks in the basin include: the Lower Cambrian black shale (Cam_1), Lower Silurian Longmaxi Formation (S_1l) mudstone and shale, Upper Permian Longtan Formation (P_3l) or isochronous Wujiaping Formation (P_3w) and Upper Permian Dalong Formation (P_3d) or isochronous Changxing Formation (P_3ch). The Upper Permian Longtan Formation source rocks have been proposed, but not proven, as the major source for the gases in the NE Sichuan Basin (Li et al., 2005; Ma et al., 2007, 2008; Liang et al., 2008; Borjigin et al., 2014; Jin et al., 2014).

Upper Permian Longtan (P_3l) Formation source rocks include gas-prone and oil-prone kerogen. The gas-prone source rock was deposited in a marine–terrigenous transitional environment with the deposition of marine black shale and terrigenous mudstone and laminar coal seams in the middle and southern part of NE Sichuan Basin (Ma et al., 2007, 2008; Cai et al., 2010; Zhu et al., 2012). Oil-prone or sapropelic-dominated source rocks were deposited in the Bazhong-Dazhou depression in the northern Sichuan basin in a quiet and restricted deep water shelf as evident in wells HB1, MB3 and PG5 (Zhu et al., 2012; Borjigin et al., 2014). TOC for the samples from these wells range from 0.64% to 10.8% with an average of 2.06% ($n = 53$) (Qin et al., 2008). The thickness for the source rocks in the Bazhong-Dazhou area ranges from 40 m to 140 m with the maximum of 160 m in MB, PG and DU gas fields. The accumulative thickness is about 110 m in wells MB3 and PG5 and relatively thin in well HB1 toward the north (Zhu et al., 2012).

2.3. Burial and thermal history and petroleum generation from the potential source rocks

Burial and geothermal histories of wells PG2, PG5 and YB2 in the Bazhong-Dazhou area (Fig. 3A–C; Hao et al., 2008; Ma et al., 2008; Cai et al., 2014) indicate that rapid sedimentation and burial took place during the Late Permian to the Middle Cretaceous. The