



## Study of thermochemical sulfate reduction mechanism using compound specific sulfur isotope analysis

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Received 26 November 2015; accepted in revised form 13 May 2016; available online 26 May 2016

### Abstract

The sulfur isotopic fractionation associated with the formation of organic sulfur compounds (OSCs) during thermochemical sulfate reduction (TSR) was studied using gold-tube pyrolysis experiments to simulate TSR. The reactants used included *n*-hexadecane (*n*-C<sub>16</sub>) as a model organic compound with sulfate, sulfite, or elemental sulfur as the sulfur source. At the end of each experiment, the S-isotopic composition and concentration of remaining sulfate, H<sub>2</sub>S, benzothiophene, dibenzothiophene, and 2-phenylthiophene (PT) were measured. The observed S-isotopic fractionations between sulfate and BT, DBT, and H<sub>2</sub>S in experimental simulations of TSR correlate well with a multi-stage model of the overall TSR process. Large kinetic isotope fractionations occur during the first, uncatalyzed stage of TSR, 12.4‰ for H<sub>2</sub>S and as much as 22.2‰ for BT. The fractionations decrease as the H<sub>2</sub>S concentration increases and the reaction enters the second, catalyzed stage. Once all of the oxidizable hydrocarbons have been consumed, sulfate reduction ceases and equilibrium partitioning then dictates the fractionation between H<sub>2</sub>S and sulfate (~17‰).

Experiments involving sparingly soluble CaSO<sub>4</sub> show that during the second catalytic phase of TSR the rate of sulfate reduction exceeds that of sulfate dissolution. In this case, there is no apparent isotopic fractionation between source sulfate and generated H<sub>2</sub>S, as all of the available sulfate is effectively reduced at all reaction times. When CaSO<sub>4</sub> is replaced with fully soluble Na<sub>2</sub>SO<sub>4</sub>, sulfate dissolution is no longer rate limiting and significant S-isotopic fractionation is observed. This supports the notion that CaSO<sub>4</sub> dissolution can lead to the apparent lack of fractionation between H<sub>2</sub>S and sulfate produced by TSR in nature. The S-isotopic composition of individual OSCs record information related to geochemical reactions that cannot be discerned from the δ<sup>34</sup>S values obtained from bulk phases such as H<sub>2</sub>S, oil, and sulfate minerals, and provide important mechanistic details about the overall TSR process.

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**Keywords:** Thermochemical alteration; Organic matter; Sulfur compounds; Sulfate dissolution; Isotopes

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## 1. INTRODUCTION

Thermochemical sulfate reduction (TSR) involves a complex reaction network that ultimately results in oxidation of organic carbon (OC) to CO<sub>2</sub> and reduction of sulfate to H<sub>2</sub>S (Machel et al., 1995; Worden and Smalley, 2001). Experimental and field observations have shown that TSR is a kinetically controlled process with an onset temperature between 100 and 140 °C, and that temperature is the most critical factor controlling the rate and extent of TSR (Machel, 1987, 2001; Heydari and Moore, 1989; Goldstein and Aizenshtat, 1994; Goldhaber and Orr, 1995; Worden et al., 1995 and references therein).

In one of the first laboratory simulations of TSR, Toland (1960) noted that organic compounds were not oxidized when only sulfate was present; however, the presence of even minute amounts of H<sub>2</sub>S (or other reduced sulfur species) were able to initiate sulfate reduction. Subsequent studies supported this view that the presence of reduced sulfur is essential for initiating TSR reactions, and showed that the rate of TSR is directly proportional to the amount of reduced sulfur present in the system (Goldhaber and Orr, 1995; Machel, 2001; Cross et al., 2004; Zhang et al., 2008 and references therein). After temperature, the pH of the aqueous solution is probably the next most important factor controlling TSR reactions (Zhang et al., 2012). The dependence of the extent of TSR on pH conditions has been previously noted, with several laboratory studies of TSR having used highly acidic conditions to promote sulfate reduction (Kiyosu and Krouse, 1990; Goldhaber and Orr, 1995). At low pH conditions aqueous sulfate predominantly occurs as bisulfate (HSO<sub>4</sub><sup>-</sup>), and quantum chemistry molecular modeling calculations have shown that bisulfate ions are much more reactive than stable aqueous sulfate ions (SO<sub>4</sub><sup>2-</sup>) (Ma et al., 2008). The decades-held belief that TSR initiation requires the presence of reduced sulfur was disproven by a series of TSR simulation experiments using aqueous sulfate solutions (CaSO<sub>4</sub>) buffered to pH conditions <4 (Zhang et al., 2012). It was further proposed that in natural environments where pH conditions are likely to be buffered to values >4, TSR reactions predominantly involve [MgSO<sub>4</sub>] contact ion pair (CIP) rather than SO<sub>4</sub><sup>2-</sup> or HSO<sub>4</sub><sup>-</sup> (Ma et al., 2008; Zhang et al., 2012). While reduced sulfur species are not required to initiate the TSR reaction, the presence of H<sub>2</sub>S does enhance the rate of TSR (Zhang et al., 2008). Consequently, a two-stage reaction scheme was proposed to explain this situation. This model postulates that initial sulfate reduction is slow and non-autocatalytic until a threshold concentration of H<sub>2</sub>S is reached, at which point a faster H<sub>2</sub>S-catalyzed sulfate reduction reaction becomes dominant (Zhang et al., 2008, 2012). It was suggested that H<sub>2</sub>S reacts with hydrocarbons to form labile organic sulfur compounds (e.g., thiols, sulfides, polysulfides, etc.) that in turn catalyze TSR (Amrani et al., 2008; Zhang et al., 2008). In addition to the importance of intermediate oxidation-state sulfur species in the catalyzed TSR reaction, Xia et al. (2014) noted the significant role that intermediate oxidized organic compounds (e.g., organic acids, ketones, alcohols, etc.) play at this stage. Further, these authors proposed that once all

of the C<sub>2+</sub> hydrocarbons have been oxidized, the intermediate oxidized organic compounds are no longer available to participate in the catalytic sulfate reduction reaction, and a slow, non-autocatalytic, third stage of TSR commences (Xia et al., 2014). In spite of the substantial progress that has been made in understanding the details of the TSR reaction mechanism, significant knowledge gaps still exist.

Studies of the stable sulfur isotopic systematics of TSR in oil reservoirs have shown that TSR-generated H<sub>2</sub>S typically has δ<sup>34</sup>S values close to those of the source sulfate (gypsum or anhydrite) (Krouse, 1977; Worden and Smalley, 1996; Cai et al., 2003). However, theoretical models predict a substantial kinetic isotope effect associated with initial cleavage of the S–O bond of sulfate (Harrison and Thode, 1957; Goldstein and Aizenshtat, 1994). Laboratory experiments show that the S-isotopic fractionation between SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>S can be greater than 10‰ (Kiyosu, 1980; Kiyosu and Krouse, 1993) and at lower temperatures under open-system conditions can reach ~21‰ (Kiyosu, 1980; Watanabe et al., 2009; Oduro et al., 2011). A possible reason for the apparent contradiction between laboratory and field observations may be that the TSR reaction in oil reservoirs is rate-limited by the dissolution of solid sulfate minerals (Powell and Macqueen, 1984; Machel et al., 1995). In this scenario, aqueous sulfate is reduced faster than it can dissolve and diffuse to the site of reduction, producing <sup>34</sup>S-enriched H<sub>2</sub>S with δ<sup>34</sup>S values close to that of the solid sulfate source (Machel, 2001). Reactions of petroleum with TSR-derived H<sub>2</sub>S have been proposed as a mechanism for producing organic sulfur compounds (OSCs) with <sup>34</sup>S-enriched values, distinct from the original δ<sup>34</sup>S values of sedimentary organic sulfur (Orr, 1974; Powell and Macqueen, 1984; Hanin et al., 2002; Cai et al., 2003, 2009). This makes sulfur isotopes in petroleum potentially useful tracers for the occurrence and extent of TSR (Amrani, 2014).

Analysis of crude oil by gas chromatography (GC) and subsequent <sup>34</sup>S/<sup>32</sup>S ratio measurements by multicollector inductively-coupled plasma mass spectrometry (MC-ICP-MS) enable analysis of individual S compounds (Amrani et al., 2009; Greenwood et al., 2014). Amrani et al. (2012) employed this technique to study a suite of oils from the Gulf of Mexico area (Jurassic Smackover Formation) and observed large variations in δ<sup>34</sup>S (up to ~30‰) between alkylsulfides, alkylbenzothiophenes (BTs), and alkylidibenzothiophenes (DBTs) in a single oil. DBTs were often significantly depleted in <sup>34</sup>S compared with BTs. These δ<sup>34</sup>S variations between DBTs and BTs were interpreted to reflect TSR-affected compounds (BTs) versus the original sedimentary organic sulfur represented by more thermally stable DBTs. More recently, a follow-up study of the Smackover Formation oils showed that thiaadamantanes (TAs), a presumed proxy for TSR (Wei et al., 2007), are also <sup>34</sup>S-enriched relative to DBTs, with δ<sup>34</sup>S values close to those of the solid source sulfate (Gvirtzman et al., 2015). Similar <sup>34</sup>S-enriched values for TAs were also reported in oil samples from the Tarim Basin, China (Cai et al., 2016). Laboratory pyrolysis experiments involving CaSO<sub>4</sub> with distinct δ<sup>34</sup>S values further support this interpretation (Amrani et al., 2012). These experiments also

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