

CHARACTERIZATION AND CHEMICAL STRUCTURE MODELING OF SOLID BITUMENS ASSOCIATED WITH THERMAL CHEMICAL ALTERATION AND THERMOCHEMICAL SULFATE REDUCTION

Simon R. KELEMEN¹, Clifford C. WALTERS¹, Peter. J. KWIATEK¹, Mobae AFEWORKI¹, Michael SANSONE¹, Howard FREUND¹, Robert J. POTTORF², Hans MACHEL³, Tongwei ZHANG⁴, Geoffrey ELLIS⁴, Yongchun TANG⁴ and Kenneth E. PETERS⁵

¹ ExxonMobil Research and Engineering Co. 1545 Route 22 East, Annandale NJ, 08801

² ExxonMobil Upstream Research Company, PO Box 2189, Houston, TX 77252

³ University of Alberta, Edmonton, AB, T6G 2E3

⁴ Power, Environmental, and Energy Research Center, California Institute of Technology, Covina, CA 91722

⁵ U.S. Geological Survey, 345 Middefield Road, Menlo Park, CA, 94025

Solid bitumens can arise from a variety of reservoir processes. These highly aromatic insoluble residues can form by oxidative processes associated with thermochemical sulfate reduction (TSR), as well as by thermal chemical alteration (TCA) of petroleum. TCA may be preceded by several low temperature processes: 1) severe biodegradation can alter oil to form viscous tars that may not flow under reservoir conditions; and 2) asphaltenes may precipitate by the addition of light hydrocarbons (gas deasphalting), or by 3) depressurization. It is difficult to distinguish solid bitumens formed by TCA of petroleum from those formed by TSR because both processes occur under relatively high temperatures of >100 °C.

The focus of the present work is on the characterization of solid bitumen samples formed by TSR or TCA using a combination of solid-state ¹³C NMR, X-ray Photoelectron Spectroscopy (XPS), and Sulfur X-ray Absorption Near Edge Structure Spectroscopy (S-XANES). Naturally occurring solid bitumens from three locations were investigated, i.e., from the Nisku Fm., Brazeau River area (TSR-related); LaBarge Field, Madison Fm, (TSR-related); and Alaska North Slope (TCA-related). These samples are compared to organic solids generated during laboratory simulations of TSR and TCA. The solid-state characterization data enable the creation of average chemical structure models of solid bitumens, and they offer the prospect of distinguishing the alteration processes that gave rise to their origin.

Figure 1 shows the amounts of organic nitrogen and organic sulfur plotted versus the percent aromatic carbon for natural solid bitumens. TCA-associated samples from the Alaskan North Slope are less aromatic and contain much more organic nitrogen than those associated with TSR. Organic sulfur in the TCA samples is present in non-aromatic as well as aromatic forms. In contrast, the TSR-associated samples are highly aromatic, contain little or no nitrogen and the organic sulfur is almost exclusively aromatic. Extremely high levels of

organic sulfur appear in both the LaBarge and Nisku solid bitumens. On average the LaBarge samples contain one sulfur for every two aromatic rings, corresponding to a sulfur level found in benzothiophene. Despite these chemical differences, the average number of aromatic carbons per cluster for all solid bitumen samples were comparable corresponding between 4 to 6 ring polynuclear aromatic units.

Laboratory simulation of the TCA process by staged pyrolysis (up to an equivalent $R_o=2.0$) of a diverse selection of petroleum vacuum residua asphaltenes produced solid bitumens with nitrogen, organic sulfur, and aromatic carbon levels comparable to the North Slope samples. Laboratory simulation of the TSR process by reacting *n*-alkanes with $MgSO_4$ and H_2O in sealed gold tubes ($20^\circ C/hour$ to maximum temperatures of 275 to $550^\circ C$) produced organic residues rich in aromatic carbon and sulfur. The organic compositions of residues from the high temperature experiments ($T \geq 375^\circ C$) were comparable to the Nisku and LaBarge samples.

The composition and structure of nitrogen and sulfur in TCA and TSR solid bitumens can be understood in terms of 1) hydrocarbon precursor molecules, 2) the mode of sulfur incorporation, and 3) alteration of their concentration during thermal stress. Sulfur-rich and nitrogen-poor solids associated with TSR are likely related to the low levels of nitrogen in the hydrocarbon precursors and the incorporate copious amounts of sulfur in aromatic carbon via back-reactions H_2S (3-12 S per 100 C). The nitrogen-rich solids associated with TCA are due to relatively high levels of nitrogen in the polar precursors that further concentrate in the solid during thermal maturation. Moderate levels of organic sulfur (<3 per 100 C) in TCA-related solids are likely due to precursor concentrations and a combination of preservation and elimination reactions.

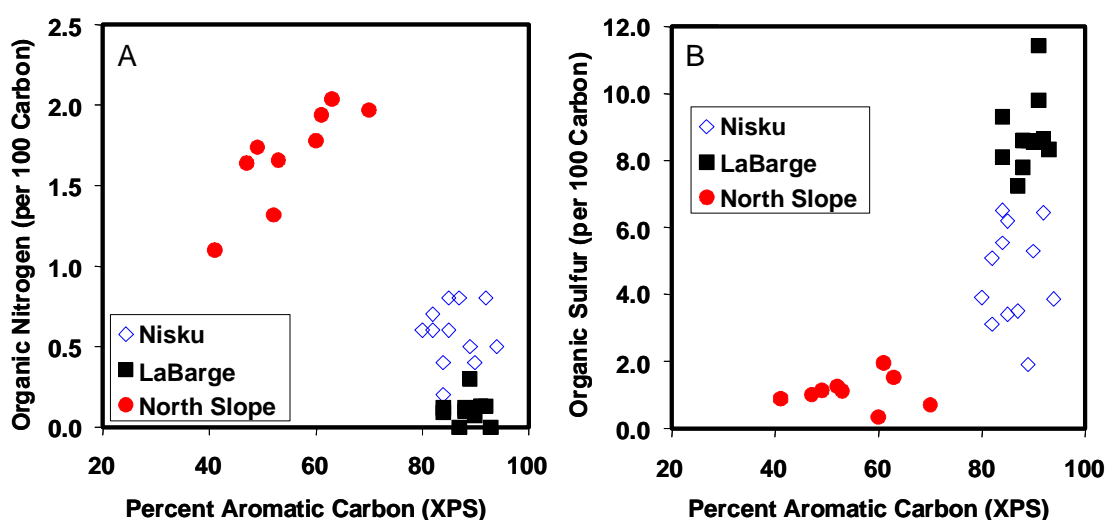


Figure 1. A) Organic nitrogen and B) organic sulfur vs. aromatic carbon for solid bitumens.

SULFUR ISOTOPES AS MARKERS OF OIL-SOURCE CORRELATION AND THERMOCHEMICAL SULPHATE REDUCTION IN CENTRAL TARIM

Chunfang CAI¹, Hongtao LI¹, Guanhui WU², Kaikai LI¹, Mei LI² and Lixin CHEN²

1. Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029 P R China

2. Tarim Oilfield Company, PetroChina, Kuerle, Xinjiang 841000 P R China

Oils and natural gas have been found from the Carboniferous, Silurian and Ordovician in Central Tarim. However, there still exists debate on the source of the petroleum since the potential source rocks (Cambrian and Lower Ordovician and/or the Middle-Upper Ordovician) show high maturity and similar biomarker and carbon isotopic composition. Thus, we report an attempt to apply $\delta^{34}\text{S}$ values to oil-source rock correlation here.

Two potential source rock samples were analyzed for $\delta^{34}\text{S}$ values. One is marlstone taken from the Upper Ordovician from Well TZ12 with TOC of 0.8% and vitrinite reflectance value (R_o) of 0.8%. The other is mudstone from Well TD2 with TOC of 1.8% and R_o of 1.7%. Kerogen separated from the Middle-Upper Ordovician marlstone has $\delta^{34}\text{S}$ value of 0.86‰. The value is much lower than that of kerogen from the Cambrian mudstone (22.5‰).

Whole oils from the Ordovician are relatively sulphur-poor, and have $\delta^{34}\text{S}$ values from 13.6 to 19.9‰ (n=6) and $\delta^{13}\text{C}$ values from -31.3 to -32.7‰ (n=4). Carboniferous and Silurian oils are relatively rich in sulphur, and have $\delta^{34}\text{S}$ values from 20.0 to 25.8‰ and $\delta^{13}\text{C}$ values from -30.3 to -32.6‰ (n=5). The oils show similarly low $\delta^{13}\text{C}$ value, but significantly higher $\delta^{34}\text{S}$ values than the Upper Ordovician kerogen. If an oil is directly decomposed from kerogen, ^{32}S -rich components are expected to be preferentially cracked down, producing an oil with relatively low $\delta^{34}\text{S}$ value and residual kerogen with high $\delta^{34}\text{S}$ value. Thus, based on the $\delta^{34}\text{S}$ values, it can be concluded that the oils in the Central Tarim are unlikely to have been derived from the Middle-Upper Ordovician kerogen, but most likely from the Cambrian and Lower Ordovician. The proposal is supported by the fact that most of the oils have $\delta^{34}\text{S}$ values lower than the Cambrian kerogen. However, one oil sample from the Silurian has $\delta^{34}\text{S}$ value of 25.8‰, being significantly higher than the Cambrian kerogen. Additionally, positive correlative relationship occurs between sulphur content and $\delta^{34}\text{S}$ value. The features can not be explained by kerogen decomposition, but have been concluded to be a result of incorporation of TSR-derived ^{34}S -rich H_2S into biodegraded oils. TSR in Central Tarim is further supported by new data in this study, as explored in the following.

In the Ordovician, 0.1% to 2% H_2S by volume were detected in gas cap associated with oil pools or in separated gas pools. H_2S may be up to 3.75% after acidification and

abundant pyrite were found in the reservoirs such as in wells TZ83 and TZ12 in Central Tarim. H₂S and pyrite have $\delta^{34}\text{S}$ from 15 to 29.7‰. In the Silurian and Carboniferous, up to 3% cubic pyrite was found in sandstone reservoirs but no sulphate minerals occur. The $\delta^{34}\text{S}$ values of pyrite have a wide range from 9.5 to 34‰ (Cai et al., 2001). Abundant sulphides (H₂S and pyrite) and variable $\delta^{34}\text{S}$ values have been concluded to have a complex origin, i.e., from both TSR in the Cambro-Ordovician and epigenic BSR (Cai et al., 2001).

Anhydrite and barite veins in Ordovician limestone show $\delta^{34}\text{S}$ values from 24.5 to 45.9‰ (n=3), and from 45.3 to 46.6‰ (n=2), respectively. Most of the values are significantly higher than that of unaltered anhydrite in the Ordovician and Cambrian with $\delta^{34}\text{S}$ of 26‰ and 34‰, respectively. Replacement of barite by calcite and high homogenization temperatures of barite and calcite (90 to 140°C) indicate that abnormally ³⁴S-rich sulphates may be a residue of TSR (Alonso-Azcarate et al., 2001) but not of BSR since the temperatures are generally thought to be too high for bacteria to grow. Given TSR occurs in the veins, H₂S and pyrite with low $\delta^{34}\text{S}$ values are expected to generate due to sulphur isotope fractionation, thus sulphides with $\delta^{34}\text{S}$ values from 9.5 to 20‰ may have resulted from TSR in Upper Ordovician vein, organic and/or epigenic BSR origin. In contrast, H₂S with high $\delta^{34}\text{S}$ values may have been derived from TSR in the Cambrian and Lower Ordovician (Cai et al., 2001), resulting in cubic pyrite in the Ordovician and Silurian reservoirs with $\delta^{34}\text{S}$ values higher than 25‰.

In summary, TSR may have occurred in Cambro-Ordovician, resulting in ³⁴S-rich residual sulphates. Oils from the Palaeozoic reservoirs were unlikely derived from Upper Ordovician kerogen but most likely from the Cambrian based on $\delta^{34}\text{S}$ values. Subsequently, TSR-derived ³⁴S-rich sulphides may have been incorporated into the oils, resulting in part of the oils have $\delta^{34}\text{S}$ values higher than the potential source rock and positive relationship between $\delta^{34}\text{S}$ value and sulphur content.

ACKNOWLEDGEMENTS

The research was financially supported by National Natural Sciences Foundation of China (40573034) and China National Major Basic Development Program “973” (2006CB202304), and FANEDD.

REFERENCES

- Alonso-Azcarate J., Bottrell, S. H. and Tritlla, J. (2001) Sulfur redox reactions and formation of native sulfur veins during low grade metamorphism of gypsum evaporites, Cameros Basin (NE Spain). *Chemical Geology*, **174**, 389–402.
- Cai C. F., Hu, W. S. and Worden R. H. (2001) Thermochemical sulphate reduction in Cambro-Ordovician carbonates in Central Tarim. *Marine and Petroleum Geology*, **18**, 729-741.

KINETICS AND MECHANISMS OF HYDROCARBON OXIDATION BY THERMOCHEMICAL SULFATE REDUCTION

Geoffrey S. ELLIS^{1,2}, Tongwei ZHANG¹, Qisheng MA¹ and Yongchun TANG¹

¹*Power, Environmental, and Energy Research Center
California Institute of Technology, Pasadena, California, USA*
²*Present address: U. S. Geological Survey, Box 25046, MS 939
Denver, CO 80225-0046 USA*

Although the process of thermochemical sulfate reduction (TSR) has been recognized by geochemists for nearly fifty years, it has proven extremely difficult to simulate in the laboratory under conditions close to those encountered in geologic settings. Published estimates of the kinetic parameters that describe the rate of the TSR reaction vary widely and are often inconsistent with geologic observations. Consequently, the prediction of the hydrogen sulfide generation potential of a reservoir prior to drilling remains a major challenge for the oil industry.

New experimental and theoretical evidence suggests that magnesium plays a significant role in controlling the rate of TSR in petroleum reservoirs. A novel reaction mechanism for TSR is proposed that involves the formation of contact ion-pairs between Mg and SO₄. The formation of [MgSO₄] contact ion pairs changes the symmetry of the sulfate ion [SO₄²⁻] from T_d to C_{2v} and consequently increases the S-O bond length making sulfate easier to be reduced. *Ab initio* quantum chemical calculations have been applied to this model in order to locate a potential transition state and determine the activation energy for this reaction pathway (56 kcal/mol). Detailed experimental work confirms previous reports that the presence of H₂S is capable of catalyzing sulfate reduction and significantly increases the rate of reaction (Machel, 2001). These results suggest that TSR may proceed as a two-stage reaction initially involving the slow reduction of MgSO₄ to H₂S followed by a more rapid sulfate reduction reaction catalyzed by H₂S (Figure 1). The recognition that the overall TSR process may be the result of two different reaction mechanisms with very distinct kinetics may help to explain why previous estimates of TSR activation energies were so divergent.

While the details of the mechanisms of the H₂S catalyzed reaction are still under investigation, preliminary experimental evidence suggests that this reaction involves the formation of sulfur radicals during the thermal decomposition of labile organic sulfur compounds (e.g., thiols and sulfides), which in turn enhance the formation of unsaturated hydrocarbons (C=C) that are more easily oxidized. A new conceptual model for understanding the process of TSR in geologic environments has been developed that does not

require the initial presence of reduced sulfur (e.g., H_2S or S°) but rather invokes an H_2S threshold concentration in order to sustain rapid sulfate reduction rates. While this approach appears to be more consistent with field observations than previous mechanisms, further validation of this model will require detailed integration with other geologic data in basin models. These findings may explain the common association of H_2S -rich hydrocarbon deposits with dolomitic rocks (CaMgCO_3), and have important implications for the maximum possible depth of oil occurrence within a sedimentary basin and estimates of global fossil fuel reserves.

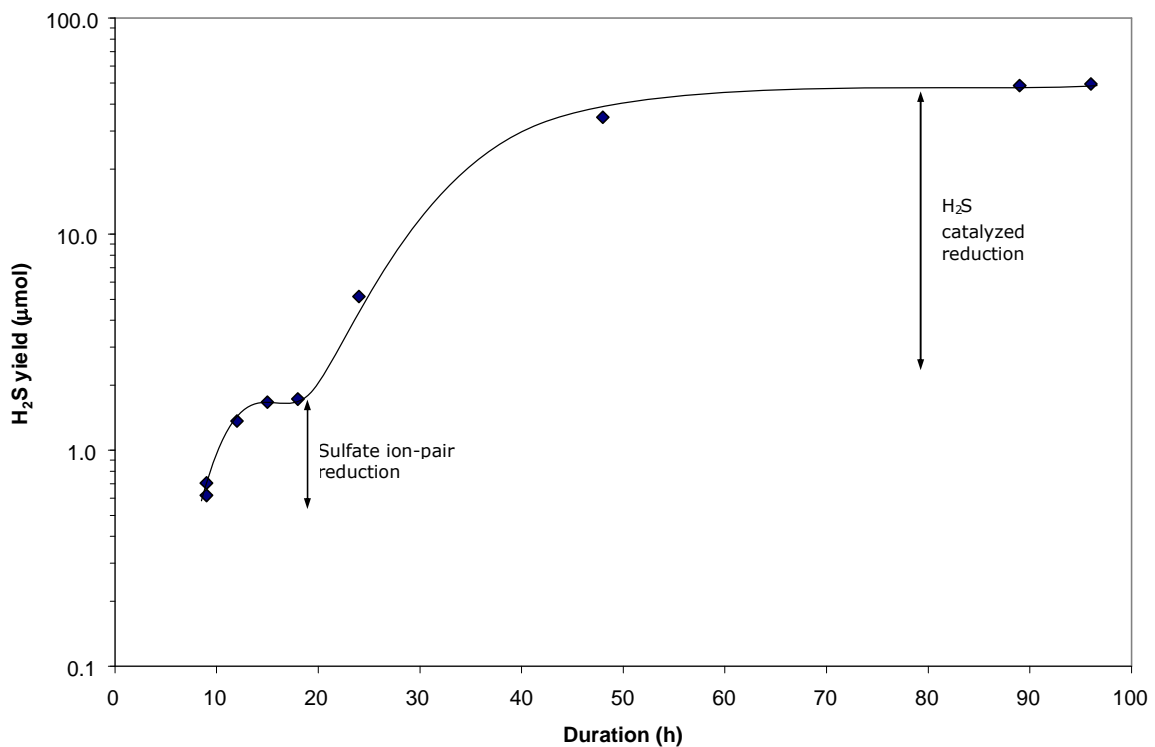


Figure 1. Hydrogen sulfide generation from TSR simulation experiments conducted in sealed gold-tubes containing a pure paraffin mixture + MgCl_2 + CaSO_4 + H_2O heated isothermally at 360°C with the *in situ* pH buffered to 3.0 using talc and silica. These results show an initial slower sulphate reduction reaction followed by the rapid H_2S catalyzed reaction.

REFERENCES

Machel, H. G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights. *Sedimentary Geology* **140**, 143-175.