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

Simon R. KELEMEN[1], Clifford C. WALTERS[1], Peter. J. KWIATEK[1], Mobae AFEWORKI[1], Michael SANSONE[1], Howard FREUND[1], Robert J. POTTORF[2], Hans MACHEL[3], Tongwei ZHANG[4], Geoffrey ELLIS[4], Yongchun TANG[4] and Kenneth E. PETERS[5]

[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 ^{13}C 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°C/hour to maximum temperatures of 275 to 550°C) produced organic residues rich in aromatic carbon and sulfur. The organic compositions of residues from the high temperature experiments (T≥375 °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.

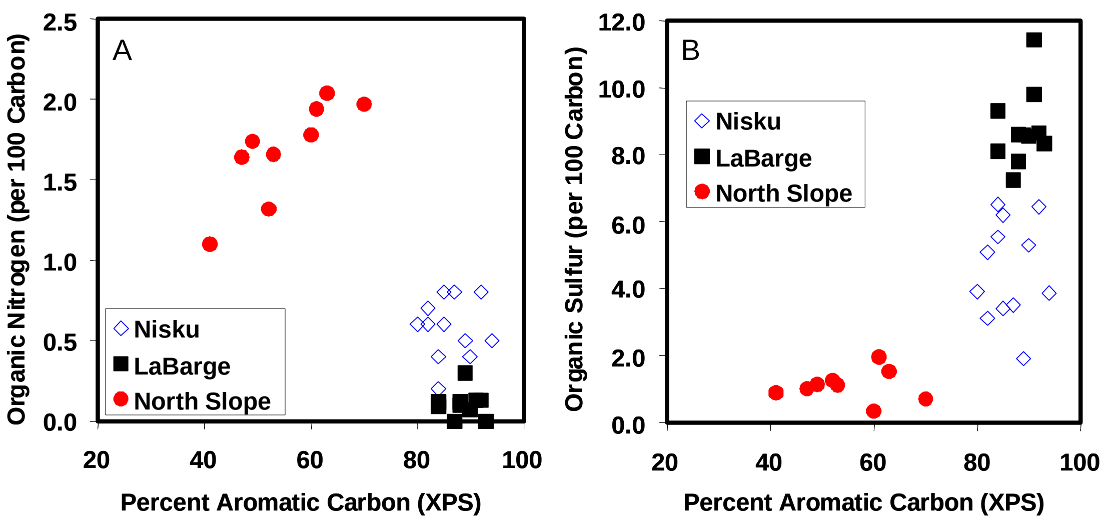

Figure 1. A) Organic nitrogen and B) organic sulfur vs. aromatic carbon for solid bitumens.