

VARIATIONS OF POLAR NSO COMPOUNDS IN FREE AND BOUND BITUMENS FROM A THERMAL MATURATION SHALE SEQUENCE BY ESI FT-ICR MS

Yinhua Pan^{1,2,3}, Maowen Li², Yongge. Sun³, Zhiming Li², Peng Liu², Yuhong Liao¹

¹ Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China

² Wuxi Institute of Petroleum Geology, Sinopec Petroleum Exploration & Production Research Institute, China

³ Zhejiang University, China

To evaluate petroleum generation and expulsion processes, pyrolysis experiments that simulate increased overburden pressures were conducted on an immature organic-rich shale with type-II kerogen from the Eocene Qianjiang Formation of the Jiangnan Basin. Expelled oils and residual rocks with different maturities covering the oil window were recovered from the experiments. The residual rocks were subjected to stepwise extraction in conjunction with stepwise dissolution of the carbonate and silicate minerals to obtain free and bound bitumen fractions (Spiro, 1984). The compositions of polar NSO compounds in the expelled oils, free and bound bitumens, were investigated by negative-ion electrospray (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The objective of this study is to characterize the nature of polar components in the soluble organic matter that was free or in association with minerals and kerogen during shale oil generation, expulsion and retention.

The ESI FT-ICR MS results showed that the molecular weight distribution of polar components in bitumen tends to be closer to that in expelled oil during maturation of kerogen, indicating the decomposition of bitumen to oil. The polar NSO compounds found in the expelled oils contain the most heteroatom classes, which are dominated by O₂ class, followed by a series of multiple oxygen classes (O₃–O₆), nitrogen-containing classes (N₁, and N₁O₁–N₁O₅) and sulfur-containing classes (O₂S₁–O₅S₁) (Fig. 1a). The free bitumen fraction (bitumen 1) that was extracted from the heated shale powder contain almost as many heteroatom classes as the expelled oil (Fig. 1b), different from the bound bitumens (Fig. 1c and d). The bitumen 2 and bitumen 3 are soluble organic fractions in the bound phase that were associated with mineral matrix and kerogen and only released after demineralization of carbonates and silicates, respectively. O₂–O₅ classes, which are tentatively proposed to be acidic compounds containing carboxylic functional group(s), are prevalent in the polar compounds of bound bitumen. These bitumen acids can act as a coupling material between the mineral surface and bitumen–kerogen matrix, to a large extent, via the formation of ester-linked complexes or salts (Vandegrif et al., 1980). Neutral nitrogen compounds (N₁ and N₁S₁ classes) are only present in the expelled oil and free bitumen. Nevertheless, a series of oxygenated (acidic) nitrogen compounds (N₁O₁–N₁O₅ classes) were also found in the bound bitumen. The oxygen atoms in these oxygenated nitrogen compounds are presumably in the form of phenolic hydroxyl and/or carboxyl at adjacent ring carbon atoms of pyrrolic core. It is similar for O₂S₁–O₅S₁ classes in such a scenario. Therefore, it seems that oxygenated nitrogen/sulfur compounds are associated with mineral matrix and kerogen through chemical bonding (e.g., ionic bonds and ester bonds) and comparatively stronger hydrogen bonding, as in the case with the multiple oxygen compounds.

Semiquantitative results of the acidic compounds reveal that the distributions of acidic compounds in both free and bound bitumens vary throughout the oil window stage. With ongoing maturation, the acidic compounds in free bitumen generally show a slight decrease

in the relative concentration. While the relative concentrations of acidic compounds in the bound bitumen, especially of O₂ and O₄ classes (corresponding to carboxylic acids), decrease progressively in the Easy%*R*_o range of 0.50–0.92. It may indicate that decarboxylation of the acidic compounds occurs progressively during maturation. However, these acidic compounds increase rapidly at advanced maturation stage (Easy%*R*_o = 0.92 to 1.37) where an intense oil expulsion occurred. It is plausible that acidic compounds were redistributed among expelled oil, free and bound bitumens during hydrocarbon expulsion from shale.

In general, the present study exhibits significant differences in the distributions of polar components between free and bound bitumens during maturation of kerogen. These results enhance the understanding of shale oil generation, expulsion and retention processes, and may provide some new insight into the enrichment of soluble organic matter in shale during maturation.

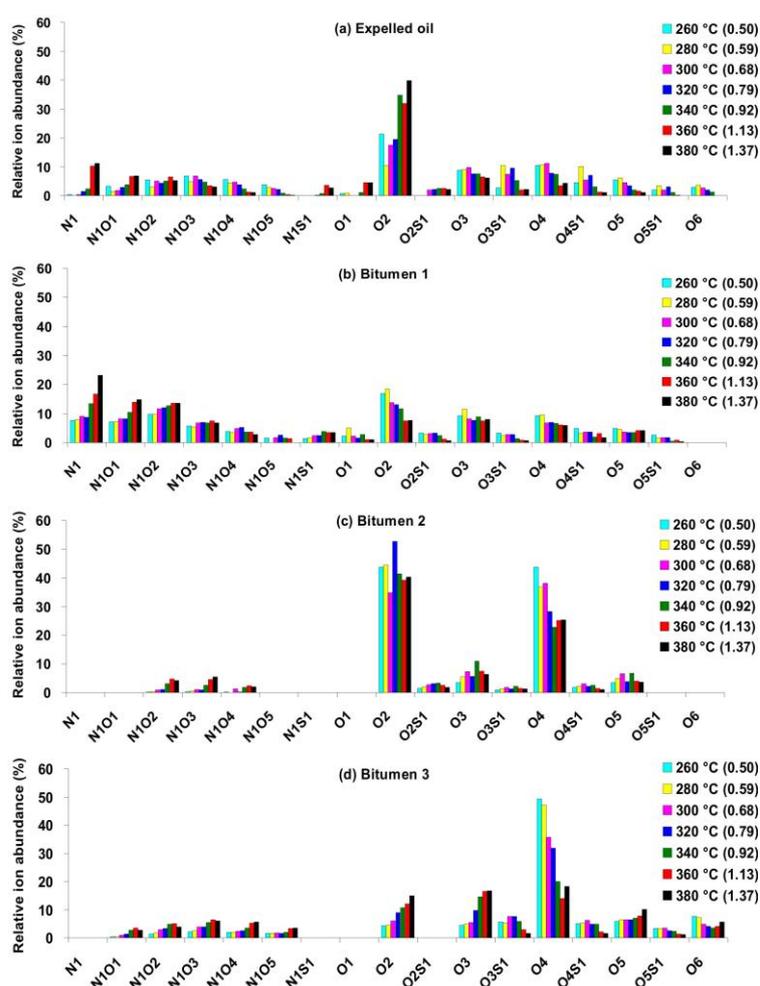


Figure 1 Relative ion abundances of heteroatom classes assigned from negative-ion ESI FT-ICR mass spectra: (a) expelled oil; (b) bitumen 1; (c) bitumen 2; (d) bitumen 3. The values given in the brackets are corresponding Easy%*R*_o values for pyrolysis temperatures.

References

- Spiro, B., 1984. Effects of mineral matrix on the distribution of geochemical markers in thermally affected sedimentary sequences. *Organic Geochemistry* 6, 543–559.
- Vandegrift, G.F., Winans, R.E., Scott, R.G., Horwitz, E.P., 1980. Quantitative study of the carboxylic acids in Green River oil shale bitumen. *Fuel* 59(9), 627–633.