

PYRIDINIC AND OTHER POLAR “BASIC” COMPOUNDS AS MATURITY MARKERS IN THE EAGLE FORD SHALE, TEXAS.

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Polar NSO (Nitrogen, Sulfur, Oxygen) compounds are ideal molecular marker to describe thermal history and maturation in petroleum systems. Especially nitrogen containing compounds with pyrrolic nitrogen like benzocarbazoles and their higher molecular weight analogs with an extended aromatic system (higher numbers of annelated aromatic rings) have been successfully used for the maturity assessment of source rock bitumen (Poetz et al., 2014) and crude oils (Oldenburg et al., 2014). The increase of aromaticity in a molecule induced by condensation and aromatisation reactions transferring formerly aliphatic carbon from side chains into aromatic carbon embedded in the aromatic ring structure is a major indication for ongoing maturation. In addition, an enrichment of aromatic “core structures” with no or only small number of aliphatic carbon in side chains due to thermal cracking reactions occurs.

Direct infusion ultrahigh resolution mass spectrometry like FT-ICR-MS using Electrospray ionization in negative ion mode was shown to be an ideal tool to detect and describe the compositional changes of acidic and neutral NSO compounds on a molecular level. The Double Bond Equivalent (DBE) distribution of selected compound classes (N_1 , N_1O_1 , N_1S_1) is able to display proceeding aromatisation while the carbon number distribution shows a predominance of aromatic core structures within DBE classes.

Here, we try to establish a complementary maturity assessment for “basic” polar NSO compounds like those containing pyridinic nitrogen or oxygen bound in carbonyl or ester functionalities with carbon or other heteroatoms like sulphur or metals. These compounds can be successfully analysed by FT-ICR-MS with electrospray ionization in positive ion mode ((+)-ESI). We used samples from the Late Cretaceous Eagle Ford formation of southeast Texas deposited across the Cenomanian-Turonian transition which is usually associated with the major Oceanic Anoxic Event 2. It is subdivided into upper and lower stratigraphic layers. A maturity suite comprising source rock bitumen from seven wells with T_{max} values between 431 and 476°C have been analyzed and results were compared with those of our well documented in-house source rock bitumen maturity sample set from the Posidonia Shale, Northwest Germany (T_{max} 419 – 466°C).

The carbonate-marl samples from the Eagle Ford Shale are dominated by S_1O_1 compounds with low DBE which are very likely aliphatic monocyclic (low maturity) and aliphatic polycyclic (high maturity) sulfoxides. Almost no condensation and aromatization reactions of S_1O_1 compounds are observed. In addition, the sample spectra especially of the low maturity samples are dominated by vanadyl porphyrins. The amount as well as the ratio of Etio and DPEP vanadyl porphyrins is well suited for the maturity assessment in the Eagle Ford Shale (see Figure 1). N_1 and N_1O_1 compounds are abundant only in lower amounts contrary to their relative amounts in the Posidonia Shale samples. However, a strong dominance of selected DBE classes representing distinct fully aromatized core molecules is not observed even at high maturities neither for Eagle Ford nor Posidonia samples. This might be related to the

broader range of possible core structures containing pyridinic nitrogen (in comparison to pyrrolic nitrogen). The enrichment of low alkylated compounds due to cracking reactions is found in lesser extent than in carbazole-type compounds.

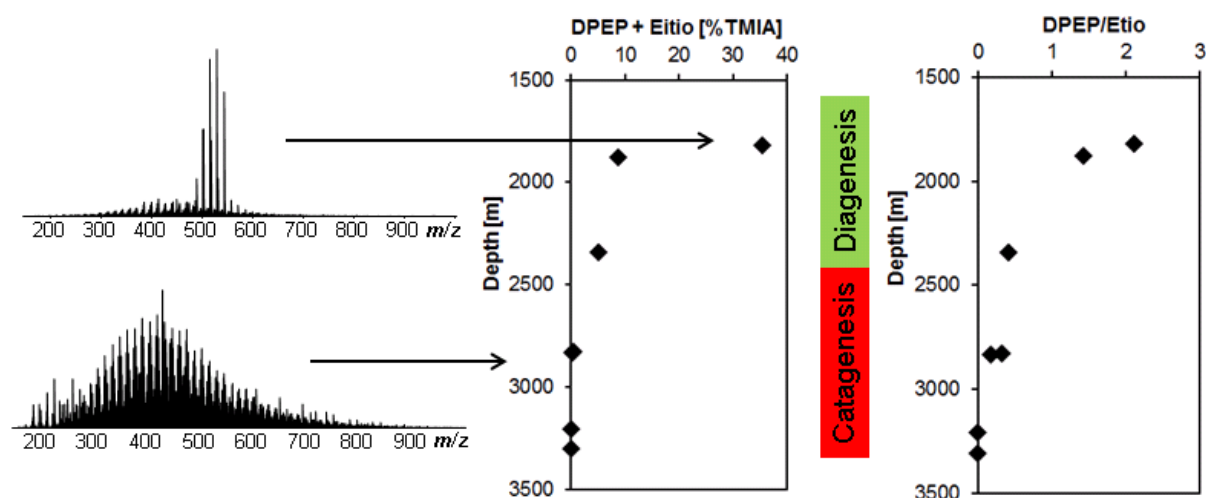


Figure 1 DPEP and Etio vanadyl porphyrins in Eagle Ford source rock bitumen detected by FT-ICR-MS with electrospray ionization in positive ion mode. Left: Spectra of a low maturity sample (top) and a high maturity sample (bottom), middle: Summed relative abundances of vanadyl porphyrins in the spectra, right: Decreasing ratio of DPEP and Etio vanadyl porphyrins with ongoing maturation (depth).

References

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