

Abundance of acidic compounds in Upper Visean black shales from the Dniepr-Donets Basin (Ukraine): advances in facies and maturity assessment

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Upper Visean Rudov Beds are considered the main source rock for conventional oil deposits in the Ukrainian Dniepr-Donets Basin (DDB) and a prospect for unconventional recently. Understanding maturity and facies variations is key to the economic success of an unconventional target, apart from other commonly accepted quality parameters (e.g. TOC content, thickness and mineralogy). Recent developments of new organic geochemical techniques such as Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with Electrospray Ionisation (ESI) in the negative ion mode (-) helped to refine maturity and facies evaluation, enhancing the predictability of source rock quality.

Maturity- and facies variations are commonly investigated by combining organic petrography and organic geochemical techniques including pyrolysis gas chromatography (Py-GC). However, the analytical window of conventional biomarker analyses and Py-GC are limited to a mass range of m/z 50-300, hence covering mainly low-polarity compounds. ESI(-) FT-ICR MS provides a considerably larger analytical window (up to m/z 2000), allowing detection of high polar compounds (e.g. acidic NSOs). Mahlstedt et al. (2016) and others applied ESI(-) FT-ICR MS to crude oils, bitumen and source rock extracts and obtained valuable insights regarding maturity-related changes in the abundance of acidic compounds and the influence of biodegradation. We use a combination of ESI(-) FT-ICR MS and advanced biomarker analyses to characterize acidic NSO compounds of 10 extracts of Upper Visean shales from the so-called Srebren Bay, located in the NW DDB.

Besides an obvious maturity trend from shallower marginal to deeper basinal positions, marginal samples are predominantly gas-prone, whereas basinal samples hold a potential to yield low-wax P-N-A oils (Misch et al., 2015). Based on these results, a sample set covering different facies zones and a maturity range from 0.6 to 1.2 %Rr was selected for ESI(-) FT-ICR MS measurements and the further characterization of NSOs.

A maturity trend is visible in the methylcarbazole group of NSOs. The benzocarbazole distributions indicate a slight facies influence besides a maturity related overprint. Ny an Ox class compounds analysed with ESI(-) FT-ICR MS dominate over Sz class compounds. A decrease of Ox and an increase of Ny class compounds can be referred to ongoing maturation. Samples from a position outside of the Srebren Bay show slightly increased amounts of Ox class compounds in comparison to samples within the Srebren Bay at comparable maturity. In general, N1O1 compounds decrease with increasing maturity except two samples located outside the Srebren Bay which exhibit low amounts of N1O1, likely due to a facies-related overprint. The applied combination of biomarker analyses and ESI(-) FT-ICR MS helps to verify and refine maturity assessment and to reveal changes in the molecular composition of polar high mass-compounds, either caused by facies changes or other processes (e.g. biodegradation).

References:

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- Misch, D., Sachsenhofer, R.F., Bechtel, A., Gratzner, R., Gross, D., Makogon, V. (2015): Oil/gas-source rock correlations in the Dniepr-Donets Basin (Ukraine): New insights into the petroleum system: *Marine and Petroleum Geology*, 67, p. 720-742.