

## The Effect of Organic Matter Maturation and Porosity Evolution on Methane Storage Potential in Shale-Gas Reservoirs

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**Abstract :** Formation of organic matter (OM)-hosted nanopores upon thermal maturation are one of the key factor controlling methane storage potential in unconventional shale-gas reservoirs. In this study, the subcritical CO<sub>2</sub> and N<sub>2</sub> gas adsorption measurements combined with scanning electron microscopy and supercritical methane adsorption have been used to characterize pore system and methane storage potential in black shales from the Baltic Basin (Poland). The samples were collected from a virtually equivalent Llandovery strata across the basin and represent a complete diagenetic sequence, from thermally immature to overmature. The results demonstrate that the thermal maturation is a dominant mechanism controlling the formation of OM micro- and mesopores in the Baltic Basin shales. The formation of micro- and mesopores occurs in the oil window (vitrinite reflectance; leavedVR; ~0.5-0.9%) as a result of oil expulsion from kerogenleft OM highly porous. The generated hydrocarbons then turn into solid bitumen causing pore blocking and substantial decrease in micro- and mesopore volume in late-mature shales (VR ~0.9-1.2%). Both micro- and mesopores are regenerated in a middle of the catagenesis range (VR 1.4-1.9%) due to secondary cracking of OM and gas formation. The micropore volume in investigated shales is almost exclusively controlled by the OM content. The contribution of clay minerals to micropore volume is insignificant and masked by a strong contribution from OM. Methane adsorption capacity in the Baltic Basin shales is predominantly controlled by microporous OM with pores < 1.5 nm. The mesopore volume (2-50 nm) and mesopore surface area have no effect on methane sorption behavior. The adsorbed methane density equivalent, calculated as absolute methane adsorption divided by micropore volume, revealed a decrease of the methane loading potential in micropores with increasing maturity. The highest methane loading potential in micropores is observed for OM before metagenesis (VR < 2%), where the adsorbed methane density equivalent is greater than the density of liquid methane. This implies that, in addition to physical adsorption, absorption of methane in OM may occur before metagenesis. After OM content reduction using NaOCl solution methane adoption capacity substantially decreases, suggesting significantly greater adsorption potential for OM microstructure than for the clay minerals matrix.

**Keywords :** maturation, methane sorption, organic matter, porosity, shales

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