Thermal evolution of porosity in organic- rich shales: The influence of Soxhlet- extractable bitumen/oil

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Bitumen and oil generated in maturing shale can fill pore space, block pore connectivity, and reduce porosity. Lowpressure N2 and CO2 adsorption techniques were used to quantify mesoporosity (pore size 2-50 nm) and microporosity (pore size <2 nm) in four New Albany Shale samples of Devonian age from Indiana and Illinois ranging from marginally mature (vitrinite reflectance R_o=0.55%) to postmature ($R_0 = 1.41\%$). The same shale samples were subsequently Soxhlet solvent-extracted in refluxing dichloromethane and their meso and microporosities remeasured. Finally, the same samples were extracted in refluxing toluene and again characterized porosimetrically.

The maturation sequence of original, non-extracted shales expressed an initial increase in mesoporosity that was followed along increasing maturity by an intermittent decrease, and a subsequent increase in mesoporosity. The intermittent decrease in mesoporosity is consistent with partial filling of pore space with bitumen/oil until secondary cracking reclaims some of the lost open pore space from liquid hydrocarbon phases. Organic matter transformation is thus a pivotal cause for the observed evolution of mesoporosity in these original, non-extracted shales.

Solvent extraction of soluble bitumen and oil from the four shales generally opens additional pore space for N_2 and CO_2 adsorption, although the specific effects on mesoporosity and microporosity depend on maturity, total organic carbon (TOC) content, type of solvent, and grain size of the Soxhlet-extracted shales. The mesopore volume increases more in extracted samples with higher maturity, whereas the strongest gain in micropore volume occurs at elevated TOC content and highest maturity. Comparative porosities of original and Soxhlet-extracted shale samples constrain the evolution of porosity along maturation and the effect of partial oil/bitumen filling of pores.