Nanoscale Organic Matter Expulsion and Molecular Fractionation within Unconventional Petroleum Source Beds

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Fractionation of petroleum during migration through sedimentary rock matrices has been observed across length scales of meters to kilometers. Selective adsorption of specific chemical moieties at mineral surfaces and/or the phase behavior of petroleum during pressure changes are typically invoked to explain this behavior. Given current emphasis on unconventional (continuous) shale resources, there is a need to understand petroleum fractionation occurring during expulsion and migration at the nanometer to micron scale, due to the fine-grained nature of petroliferous mudrocks and the observation that fractionation processes are occurring in both source and reservoir rocks.

Here we will discuss results showing organic matter compositional differences observed across nanometers to microns within kukersite petroleum source beds (containing acritarch *Gloeocapsomorpha prisca*) from the Ordovician Stonewall Formation in North Dakota using a combined infrared spectroscopy-atomic force microscopy (nanoIR) approach. The nanoIR technique is capable of providing spatial resolutions approaching 100 nm allowing for clear assessment of kukersite molecular fingerprint across well-defined transition zones from organic-rich ‘source’ layers into micron(s)-distant carbonate ‘reservoir’ layers. Our results indicate that the molecular composition of kukersite organic matter is altered immediately following expulsion from source layers, with loss of C=O moieties and a concomitant increase in the CH_3/CH_2 ratio, a proxy for alkyl chain length reduction, as migration distance increases. These chemical transitions are correlated with a fluorescence decrease and reflectance increase in the organic matter. These findings will be discussed in the context of evaluating the role that nano- and micro-scale molecular fractionation processes may play for petroleum composition from continuous reservoirs following expulsion.