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Micron-scale compositional variation of solid bitumen as a function of mineral association in hydrous pyrolysis residues

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This study presents Raman spectroscopic data paired with scanning electron microscopy (SEM) and optical images to assess solid bitumen composition and porosity development as a function of texture and association with minerals in a set of artificially matured New Albany Shale samples. A series of isothermal hydrous pyrolysis (HP) experiments (1-103 days, 300-370°C) were performed using a low maturity (0.25% solid bitumen reflectance), high total organic carbon (14.0 wt. %) New Albany Shale sample as the starting material. Pyrolysis residues were designed to evaluate reactions associated with evolving solid bitumen aromaticity and organic porosity development at increments of increasing temperature and experimental duration. Solid bitumen was analyzed by Raman spectroscopy using a 532 nm laser wherein point data was collected from accumulations that ranged in size, pore density, and degree of association with the mineral matrix. The results show that with increasing temperature and duration of HP experiments, solid bitumen aromaticity increases and compositional variability decreases. Coarse-grained solid bitumen (analysis spot >1.3 µm from nearest mineral grain) tends to have fewer pores and consistently higher, but less variable aromaticity than fine-grained solid bitumen, which is more closely associated with the mineral matrix (analysis spot <1.3 µm from nearest mineral grain). The Raman data and correlated SEM images indicate that solid bitumen porosity and degree of aromaticity are inversely related, and these parameters are correlated to the textural relationships of the organic matter within the rock. The controlling processes leading to these results were not explicitly addressed in this study; however, we hypothesize that compositional variability may be due to chromatographic and/or size fractionation during local migration, and that pore development is in part a function of differences in mechanical stiffness between the fine- (less aromatic) and coarse-grained (more aromatic) solid bitumen. These results further underscore the complicated nature of rock fabric and mineralogy on the processes of artificial and natural maturation and hydrocarbon production. As hydrocarbons from unconventional reservoirs become increasingly difficult to find and extract, a more complete understanding of how specific rock attributes influence maturation and petroleum generation will aid in recoverability estimates in unconventional resources.