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Application of Raman Spectroscopy as Thermal Maturity Probe in Shale Petroleum Systems: Insights from Natural and Artificial Maturation Series

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Amorphous organic matter (AOM) is virtually ubiquitous in fine grained, marine hemi-pelagic to pelagic sediments while the amount of terrestrial organic matter is significantly reduced. Therefore, solid bitumen, which generally derives from AOM, dominates the composition of organic matter if such sediments become subject to diagenesis. Consequently, solid bitumen and AOM represent ideal material to assess thermal maturity in shale rich sequences by means of optical microscopy or, more recently, Raman spectroscopy.
The latter was studied as a thermal maturity probe in a series of Upper Devonian Ohio Shale samples from the Appalachian Basin spanning from immature to dry gas conditions. Raman spectroscopy also was applied to samples spanning a similar thermal range created from 72-h hydrous pyrolysis (HP) experiments of the Ohio Shale at temperatures from 300 to 360 °C and isothermal HP experiments lasting up to 100 days of similar Devonian−Mississippian New Albany Shale.
Raman spectra were treated by automated evaluation software based on iterative and simultaneous modeling of signal and baseline functions to decrease subjectivity. Spectra show robust correlation to measured solid bitumen reflectance (BRo) values and were therefore used to construct logarithmic regression relationships for calculation of BRo equivalent values. Raman spectra show considerable differences between natural samples and HP residues with similar measured BRo values, indicating as-yet undetermined differences in carbon chemistry. We speculate this result may be due to differences in the sampling interactions of Raman vs reflectance measurements, and the incomplete nature of maturation reactions in the time-limited hydrous pyrolysis residues.
Samples used in this study are similar in organic assemblage (dominantly solid bitumen) to other commonly exploited North American shale petroleum systems, which implies that the presented results may be broadly applicable to other shale plays. However, caution is suggested and Raman spectroscopy as a thermal probe may need individual calibration in each shale play due to differences in solid bitumen carbon chemistry.