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Project Title: Evolution of Nanopore Networks in Unconventional Chalk-Rich Reservoirs: Integrating the Effects of Catagenesis with Mineral Diagenesis

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Understanding heterogeneity in the pore networks of unconventional hydrocarbon reservoirs is critical to a successful production strategy. One poorly understood source of heterogeneity is the spatial distribution of hydrocarbons in the voids, and the continued catagenesis of those hydrocarbons. Organic compounds can segregate, with large polar components becoming immobile and blocking pores while others remain mobile. Continued catagenesis can also produce pores within the organic matter. A major obstacle to fully understanding both of these critical processes has been the inability to obtain *in situ* data on the types and distribution of organic matter at the nano- to micro-scale of individual pores. Standard extractive techniques spatially average the consortium of hydrocarbons, and traditional spectroscopic techniques have too coarse a resolution.

This study is evaluating infrared scattering-scanning near-field optical microscopy (IR *s*-SNOM¹⁻²) as a tool to overcome the above obstacles. The tool can image, map, and identify organic and inorganic components in fields of view up to 100 microns on a side with a spatial resolution of 10 nm. Variation of IR *s*-SNOM across geologic materials have recently been used to characterize individual organic maceral in source rocks³⁻⁴. The current study, however, is the first to use IR *s*-SNOM to characterize the effect of reservoir bitumen (i.e., migrated hydrocarbons) on porosity in a fabric-selective context. The test case is the unconventional chalk-marl reservoirs of the Niobrara Formation in Wattenberg Field, Colorado. Samples were chosen from the main reservoir zone across a thermal gradient ranging from R_o values of 0.72 to 1.40 (i.e., onset of oil generation to dry gas window). The project represents a completely new research direction for the PI, forms the basis for ~ 1/3rd of a Geology PhD student's research, and introduces a chemical physics PhD student to new problems in the field of organic geochemistry.

The main accomplishments in year one of the study were three-fold. First, total lipid extractions were performed on a suite of Niobrara rocks in order to characterize the bulk organic composition and identify vibrational modes to pursue with IR *s*-SNOM. The extractions produced an admixture of aliphatic, non-volatile aromatic, and resinous/asphaltic hydrocarbons. Asphaltene and maltene extracts were analyzed as thin films using attenuated total reflectance FTIR spectroscopy. These full-range mid-IR far-field spectra identified between 2 and 6 resonances within both families that contrast sharply to the surrounding mineral matrix, and between 4 and 8 resonances in the asphaltene family that could be used to assess intra- and inter-pore heterogeneity. Column chromatography was also used to separate the maltene family into three polar fractions, and the least polar fraction was analyzed via gas chromatography mass spectrometry. These data provide qualitative estimates of degradation, asphaltene/maltene weight ratios, and other metrics that allow for the prioritization of particular rock samples.

With ideal vibrational resonances identified, a suite of aggregate-intensity near-field IR images and spatio-spectral near-field IR arrays were collected in collaboration with Dr. Markus Raschke's (CU-Boulder Physics) Center for Ultrafast Nano-Optics. This initial data set included samples from all but the most thermally mature material, which the total lipid analysis showed to be extremely lipid-lean. A qualitative estimate of heterogeneity was done via aggregate intensity imaging and a quantitative metric for heterogeneity was pursued via spatio-spectral analysis. A significant portion of time was spent modifying well-established methods for IR *s*-SNOM of monolayers, synthetic metal carbonyls, and other materials exhibiting interesting physical chemistry behaviors. Such modifications were necessary to maximize near-field intensity given the non-reflective, non-conductive, and chemically complex nature of the Niobrara rocks. These challenges forced a disappointing ratio of "good" fields of view to low-intensity fields of view. In particular, vibrational modes with smaller transition dipole moments and those near the edge of the laser's tunable frequency range (roughly 1100 to 2200 wavenumbers) suffered from low intensity and low signal-to-noise ratios. A small pilot of nano-mechanical imaging⁵ was also tested in an effort to bolster near-field IR results. These analyses capitalize on the properties of the tapping probe to capture data such as the reduced Young's modulus, the adhesion, and the deformation of the sample material at each pixel. Because these data require no chemical specificity, they are easier to collect in a robust fashion; however, they cannot be correlated to a bulk metric the way near-field IR can, so their utility is dependent on corroborating IR evidence.

Overall, the best IR *s*-SNOM data collected to date suggest that there is statistically significant pore-scale heterogeneity in the spectral character of the reservoir bitumen (Fig. 1). However, there is little spectroscopic or nano-mechanical evidence that any particular phase of hydrocarbon associates closely with mineral surfaces or pore throats,

as previously suggested by reservoir geoscientists⁶⁻⁷. It is possible that such pore-rimming behavior exists, and remains below the resolution of the tapping probe (~10-30nm). However, it is also possible that asphaltic hydrocarbons travel in suspension, either as dissolved species or colloids, as suggested by *ex-situ* hydrocarbon analyses/models⁸⁻⁹.

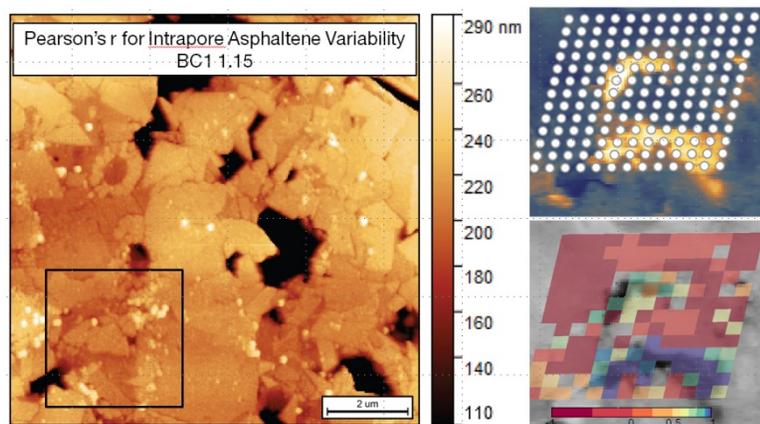


Figure 1: Pairwise statistical correlation metrics for each point of a spatio-spectral array, relative to point 128 (an arbitrarily defined local reference within the array). Images are AFM topography (left) and broadband nearfield second harmonic (right, false color with array location and grayscale with point-by-point Pearson's R overlain). Cool colors (lower right) show close replication of the reference spectrum; warm colors suggest a poor replication. Heterogeneity in colors thus indicates heterogeneity within the hydrocarbon consortia within the pore. Center frequency = 1600 cm^{-1} .

Plans for year two include efforts to test the additional utility of narrowband near-field IR imaging. Because of the difficulties described above that are inherent to collecting spatially referenced IR spectra on natural samples, it would be advantageous to find a method that approximates spatio-spectral arrays but which can be executed and interpreted over a shorter time frame (ideally, in real time). Due to the relative broadness of spectral features in extracted hydrocarbons (often >30 wavenumbers at the full-width-half-max), we anticipate that aggregate intensity imaging with a narrowband light source may produce near-field IR images that approximate the information contained in a spatially reference spectrum collected within the broadband window (150+ wavenumbers wide). That is, the narrowband light source may stimulate IR intensity from only one IR feature, making the narrowband aggregate intensity image a potentially useful approximation of a “peak” within the greater IR spectrum for one sample location. This stands in contrast to the collection of features that are typically stimulated by a broadband light source and which contribute to the aggregate intensity image; these features require robust spectral data to deconvolute across the full spectral window, which is data that has thus far been time consuming and difficult to routinely collect.

References Cited

1. Muller, E. A.; Pollard, B.; Raschke, M. B., Infrared chemical nano-imaging: Accessing structure, coupling and dynamics on molecular length scales. *The Journal of Physical Chemistry Letters* **2015**, *6*, 1275-1284.
2. Huth, F.; Govyadinov, A.; Amarie, S.; Nuansing, W.; Keilmann, F.; Hillenbrand, R., Nano-FTIR absorption spectroscopy of molecular fingerprints at 20 nm spatial resolution. *Nano Letters* **2012**, *12*, 3973-3978.
3. Yang, J.; Hatcherian, J.; Hackley, P. C.; Pomerantz, A. E., Nanoscale geochemical and geomechanical characterization of organic matter in shale. *Nature Communications* **2017**, *8* (2179), 9.
4. Hao, Z.; Bechtel, H. A.; Kneafsey, T.; Gilbert, B.; Nico, P. S., Cross-scale molecular analysis of chemical heterogeneity in shale rocks. *Nature Scientific Reports* **2018**, *8* (2552), 9.
5. Pollard, B.; Raschke, M. B., Correlative infrared nanospectroscopic and nanomechanical imaging of block copolymer domains. *Beilstein Journal of Nanotechnology* **2016**, *7*, 605-612.
6. Zhang, S.; Canter, L.; Sonnenfeld, M., Capillary fluid dynamics within unconventional rocks investigated by scanning electron microscopy. *AAPG Bulletin* **2017**, *101* (11), 1759-1765.
7. Pernyeszi, T.; Patzko, A.; Berkesi, O.; Dekany, I., Asphaltene adsorption on clays and crude oil reservoirs. *Colloids and Surfaces A* **1998**, *137*, 373-384.
8. Liu, J.; Zhang, L.; Xu, Z.; Masliyah, J., Colloidal interactions between asphaltene surfaces in aqueous solutions. *Langmuir* **2006**, *22* (4), 1485-14925.
9. Khoshandam, A.; Alamdari, A., Kinetics of asphaltene precipitation in a heptane-toluene mixture. *Energy & Fuels* **2010**, *24*, 1917-1924.