3D imaging and Spectroscopy of Organic Matter Diagenesis in Mudrocks with Linear and Nonlinear Laser Scanning Confocal Microscopy (LSCM)

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ABSTRACT

We are using several 3D laser scanning confocal microscopy (LSCM) techniques to characterize organic matter (OM) in situ within organic-rich mudrocks. Our goal is to chemically differentiate the types of organic matter at the grain scale and identify 3D networks that may impact petroleum generation and expulsion processes. Although optical techniques cannot achieve the spatial resolution possible with SEM methods, the focused laser beam in LSCM can achieve the diffraction limit of high numerical aperture objectives. For example, raster scanning a visible light wavelength laser beam in an objective with numerical aperture (NA) = 1.4 can achieve a lateral resolution at the 80% Rayleigh criterion of -160 nm, although axial resolution is poorer, - 1.1 0 m. In addition, image contrast can be recorded spectroscopically, providing chemical information from electronic (fluorescence) or vibrational (Raman scattering) transitions within the molecular structure of OM. Furthermore, with digital focus control, images can be recorded at a series of focal planes (Z-stacks) to create 3D image volumes that can be manipulated and displayed with standard visualization software. Well-focused Z-stacks are-15 O m with linear LSCM and >30 O m in total thickness with nonlinear optical methods. Separation of individual focal planes is typically- 250 nm. We believe that the spatial and spectroscopic resolution of LSCM can provide new insights to the diagenetic alteration of sedimentary OM to kerogen, bitumen, oil, and gas as the 3D framework of minerals, OM, and porosity evolves during burial diagenesis.

At thermal maturities within the early stages of the oil window (R, < 0.8%), Iiptinitic organic matter is brightly fluorescent, providing high contrast images and spectra with good signal to noise (SIN) ratio. The Leica* SP5 LSCM equipped with a tunable "white-light" laser can record images with emission and excitation spectra from 470 nm to 750 nm in each pixel. Observations on a maturation sequence from 0.4% to 0.8% R, show progressive red-shift of both excitation and emission with decreasing emission intensity. However, the intensity ofthe fluorescence completely overwhelms conventional Raman scattering, thereby precluding observation of vibrational spectra that could chemically differentiate kerogen from neo-formed bitumen.

We are exploring application of multiphoton, nonlinear optical (NLO) imaging and spectroscopy to distinguish types of organic matter within the oil window using methods originally were developed for biomedical research on cellular lipids. Nonlinear responses occur when very intense optical fields interact with materials and two or more photons combine to produce another photon at a different frequency. Contrast and spectra from NLO effects include two-photon excitation fluorescence (TPEF), second harmonic generation (SHG), and coherent Raman scattering (CRS, including coherent anti-Stokes Raman scattering, CARS, and stimulated Raman scattering, SRS). CRS responses are important because they are orders of magnitude more intense than conventional Raman scattering and spatially coherent, allowing separation of the vibrational Raman response from fluorescence. For the first time, we have imaged fluorescent, hydrogen-rich Tasmanites algal cysts based on C-H vibrational motions using CRS methods. NLO microscopes can simultaneously produce image contrast from TPEF, CRS, and SHG,

thereby opening the possibility of simultaneous non-destructive 3D imaging of OM and diagenetic minerals. CRS can image minerals directly with Raman scattering. SHG contrast occurs only in non-centrosymmetric minerals, most commonly quartz. For example, in OM-rich mudrocks we have observed the 3D distribution of detrital and diagenetic quartz down to sub-micrometer (clay size) particles and diagenetic quartz in-filling microporosity in Tasmanites. The crystal structures of a number of clay minerals are non-centrosymmetric, opening the possibility of non-destructive 3D imaging of alteration of OM and minerals in samples across the thermal maturation range of oil generation and expulsion.

At higher levels of thermal maturity (Ro > 0.8%), fluorescence intensity of organic matter decreases and maximum intensity shifts to the red, allowing observation of the weak spontaneous (incoherent) Raman scattering signal. The "graphitic" D and GRaman bands "ride" on top of the spectrally broad background of fluorescence emission. The D and G bands change systematically with increasing maturity and the fluorescence background changes in both the wavelength and intensity of maximum emission. Both changes reflect cracking and reorganization of complex kerogen and bitumen macromolecular complexes into planar polynuclear aromatic structures and ultimately graphite at very high maturities. However, published correlations of systematic shifts in Raman spectra with increasing maturity require subtraction of the fluorescence background, eliminating a possible source of additional information on transformations of OM. Analysis of variations in both fluorescence and Raman scattering in OM particles in gas-rich mudrocks should allow us to distinguish residual kerogen from bitumen and pyrobitumen, thus providing better understanding of gas generation at high thermal maturity.

By integrating laser imaging and spectroscopy methods with conventional wide-field reflectance and fluorescence microscopy for organic petrology, we are attempting to extract as much information as possible about the in situ variations in composition of organic matter within petroleum source rocks. Nonlinear optical methods show potential for chemically differentiating types of fluorescent organic matter within the oil window, but will require additional work to identify the most useful spectroscopic responses. Although optical methods will never achieve the spatial resolution of FIB-SEM, we are convinced that LSCM methods can provide an important bridge between SEM scale observations and traditional wide-field microscopy methods of organic petrology. To that end, we are beginning to explore correlative microscopy methods that will allow us to integrate optical responses with SEM images to better understand organic matter transformations at all scales relevant to oil and gas generation and expulsion.

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