Sub-micron chemically-specific 3D imaging and spectroscopy of geologic materials with multimodal, nonlinear optical microscopy

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The intensity of tightly focussed, near infrared, ultrafast (750-1040 nm, ~150 fs) laser pulses can create nonlinear optical responses at low pulse energy due to the 2nd and 3rd order polarizability of molecular structures. The response is a nonlinear function of the intensity at the focus, generating image contrast only within the focal spot. Therefore, imaging is intrinsically confocal, allowing depth sectioning and creation of 3D image volumes with diffraction-limited resolution. Image contrast can arise from second harmonic generation (SHG), two-photon excitation fluorescence (TPEF), third harmonic generation (THG), coherent anti-Stokes Raman scattering (CARS), and stimulated Raman scattering (SRS). Spectral analysis of the Raman responses creates chemically-specific hyperspectral data volumes. Following on our proof-of-concept application of multimodal CARS microscopy to fluid inclusion analysis [1], we are exploring more general geoscience applications, initially imaging minerals and organic matter in sedimentary rocks. SHG is a unique response non-centrosymmetric minerals. Quartz is the most common example. In mudrocks SHG reveals the 3D distribution of quartz silt and clay size (<1 μm) detrital and diagenetic grains. CARS and SRS allow rapid vibrational imaging and spectroscopy of fluorescent organic matter (algal microfossils, kerogen, bitumen) in petroleum source rocks that is impossible with conventional confocal Raman imaging due to intense fluorescence at visible wavelengths. Depth-sectioning with multimodal imaging creates 3D images of organic matter and minerals with contrast from aromatic fluorophores (TPEF) and C-C and C-H vibrational frequencies (CARS, SRS) and mineral vibration modes from 400 to 4000 cm^{-1} (SRS). The wide spectral range of SRS allows imaging of minerals (quartz, carbonates, sulfates) as well as organic matter in 3D to depths of ~ 70 μm [2]. For the first time, we successfully imaged Devonian age *Tasmanites* algal cysts and the intergranular organic matter network of a petroleum source rock using CARS and SRS while simultaneously imaging quartz in the matrix. We believe the non-destructive multiple imaging modes possible with nonlinear optical methods have broad application in 3D chemical characterization of geologic materials.

[1] Burruss *et al*. (2012) Geology, v. 40, pp. 1063-1066. [2] Houle, *et al*. (2016, in review), J. Raman Spectroscopy