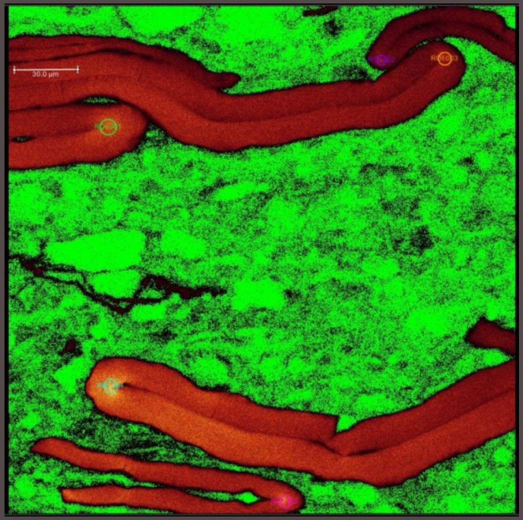
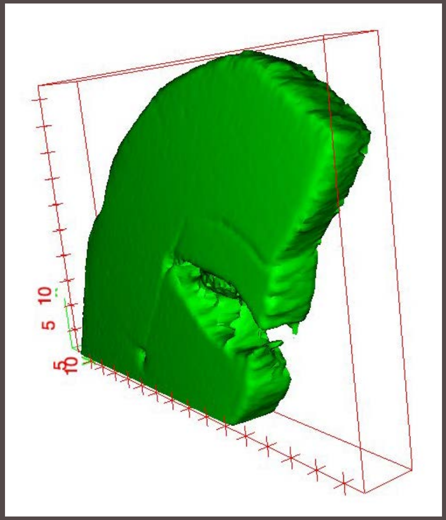
FLUORESCENCE SPECTROSCOPY OF SEDIMENTARY ORGANIC MATTER VIA CONFOCAL LASER SCANNING MICROSCOPY

Presented for TSOP, September 9, 2019





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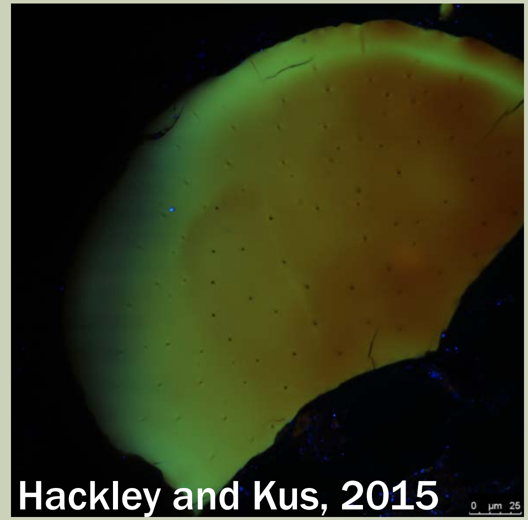
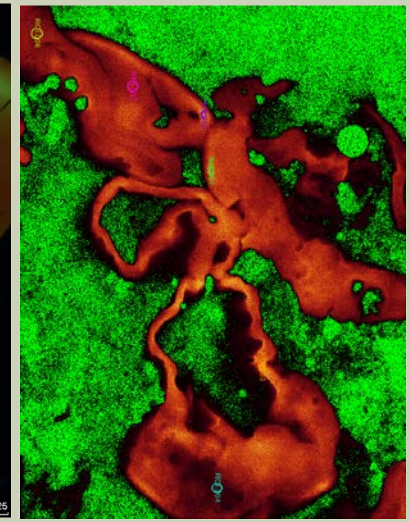
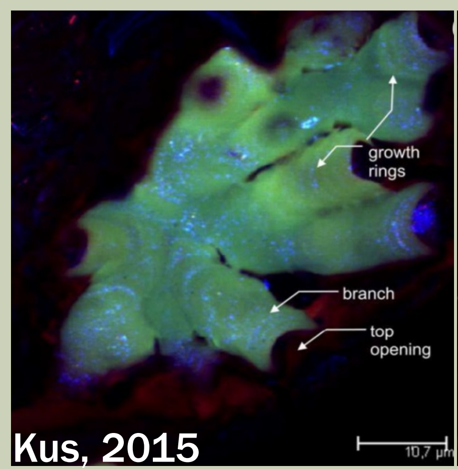
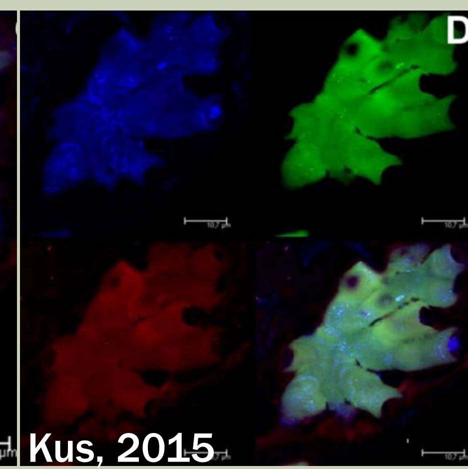
OUTLINE OF THIS TALK

- Why do this?
- What is *Tasmanites*?
- What is *G. Prisca*?
- How fluorescence works
- Samples and geology
- Conventional fluorescence compared to confocal laser scanning (CLSM)
- CLSM spectroscopy results
- Summary/future directions



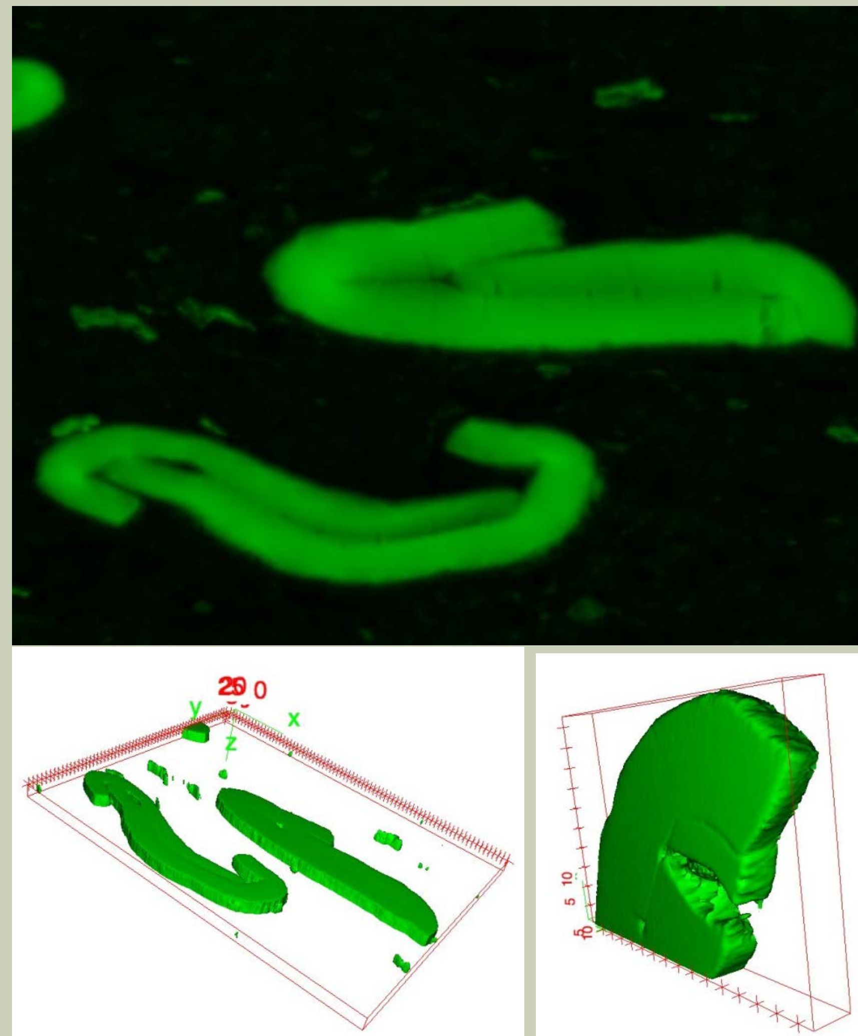






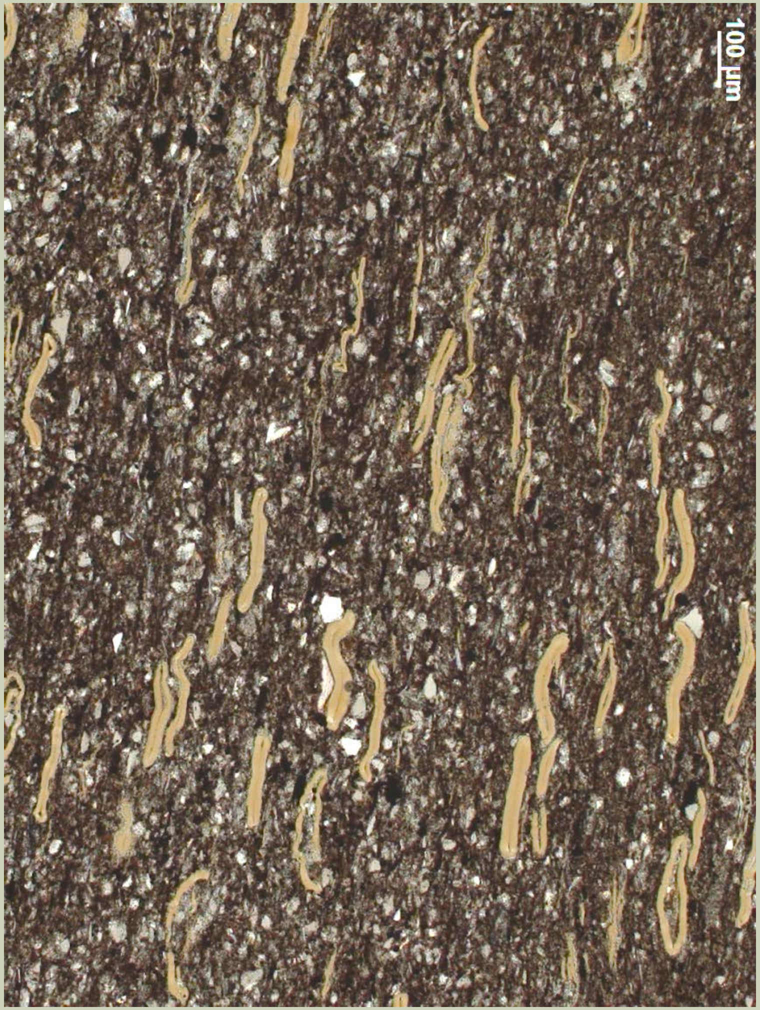
WHY DO THIS?

- May help answer questions about kerogen compositional evolution with thermal stress
- CLSM application is broadly underutilized
- High resolution (~200 nm)
- 3-D reconstructions, video
- Non-destructive
- Can be applied to thermal maturity of SOM, oils, fluid inclusions



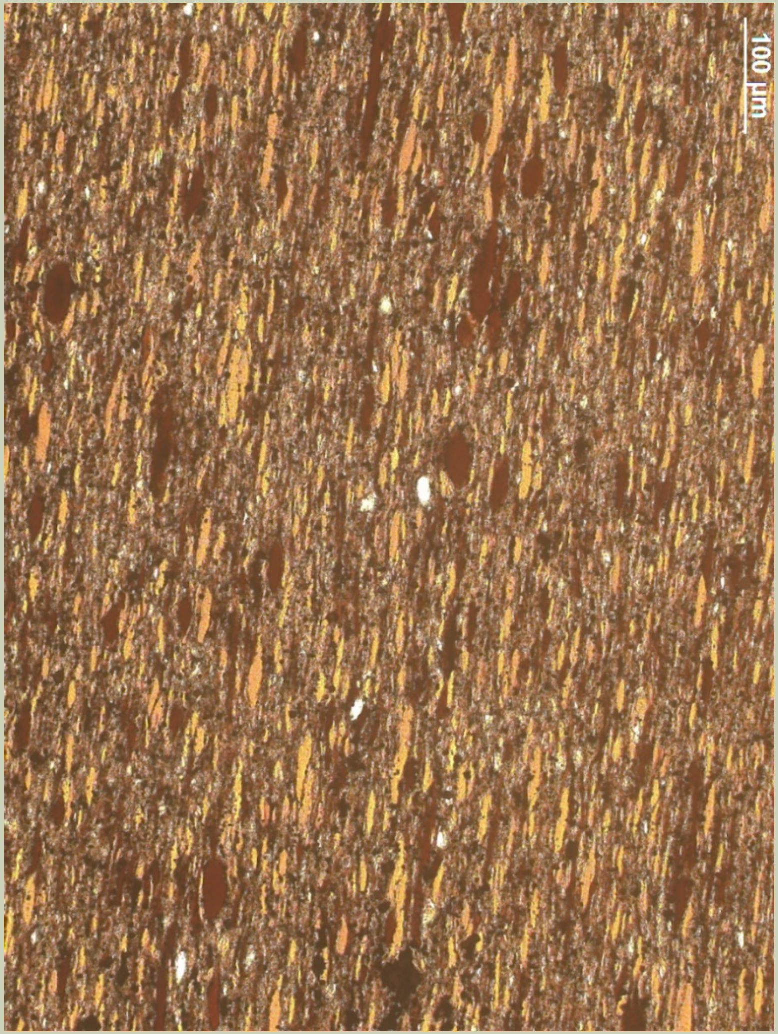
WHAT IS *TASMANITES*?

- Unicellular planktonic marine alga
- Simple spherical shells, some ornamentation
- Large stratigraphic range (Neoproterozoic to Holocene)
- Sometimes visible with bare eye (100-500 μm diameter)
- Easy to find and image
- Made of algaenan - unsaturated aliphatic aldehydes and hydrocarbons

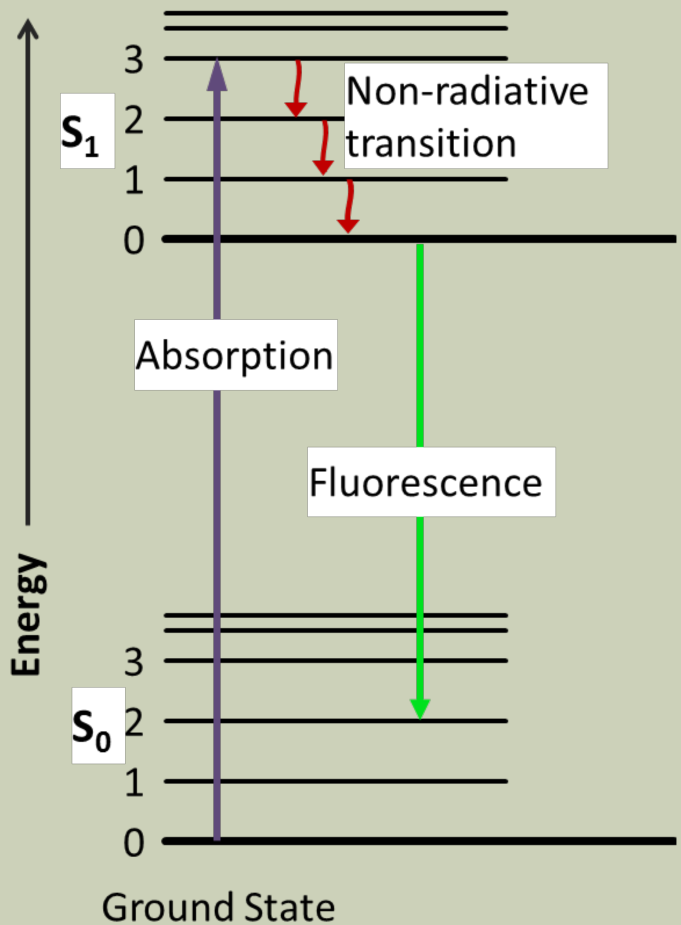


WHAT IS *G. PRISCA*?

- Planktonic/benthic marine alga
- Simple ovoid forms
- Disseminated or stromatolitic
- Limited stratigraphic range (Cambrian to Devonian, mostly Ordovician)
- Microscopic (100 µm diameter)
- Also made of algaenan - unsaturated aliphatic aldehydes and hydrocarbons, mainly *n*-C_{21} and *n*-C_{23}
- Contains wide range of carbonyl and carboxyl moieties



HOW FLUORESCENCE WORKS



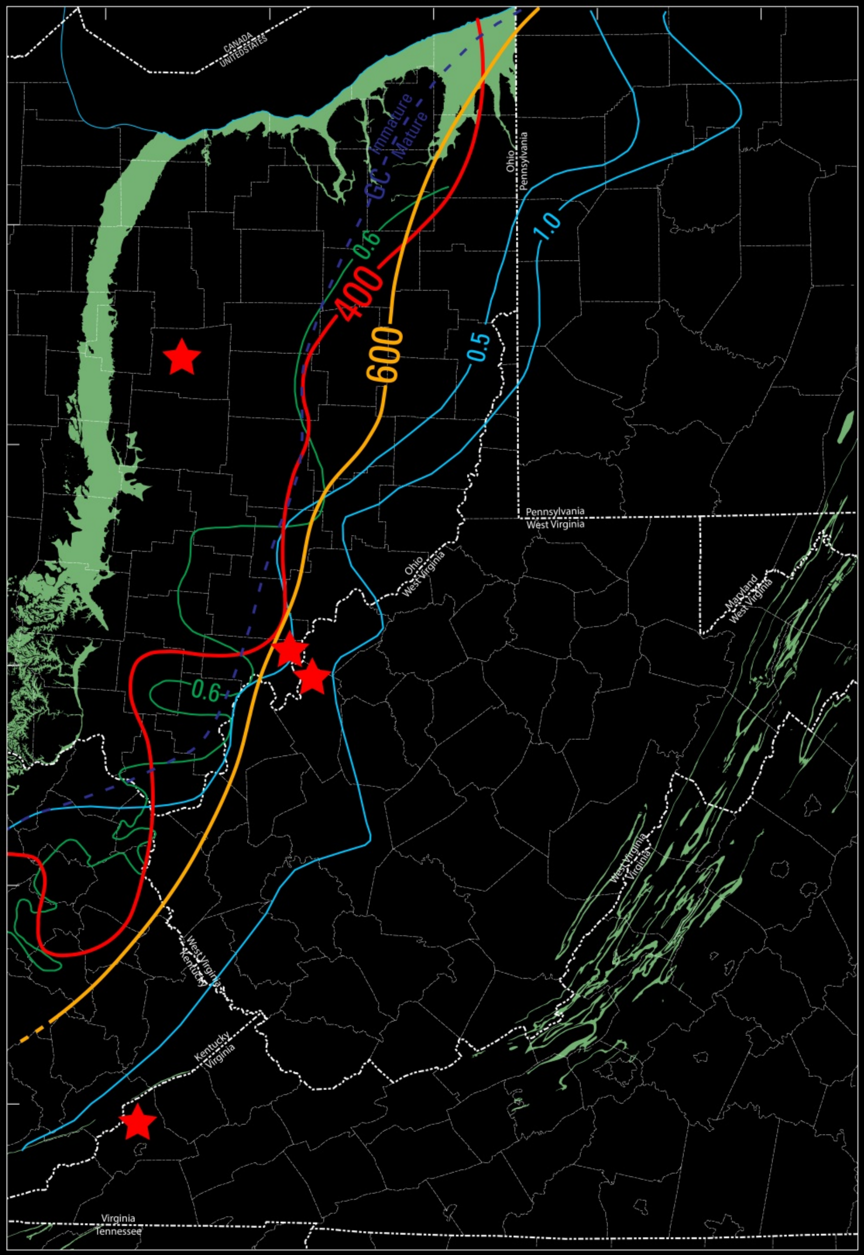
https://en.wikipedia.org/

$S_0 + \mathbf{hv}_{ex} \rightarrow S_1$

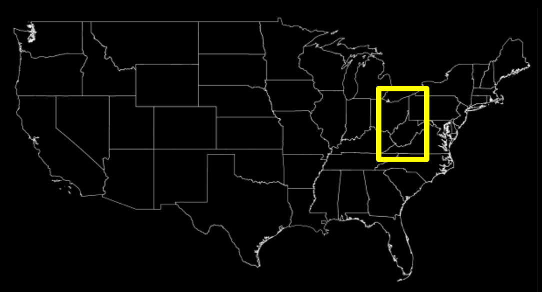
$S_1 \rightarrow S_0 + \mathbf{hv}_{em} + \text{heat}$

$\mathbf{hv}_{ex} - \mathbf{hv}_{em} \approx \text{Stokes Shift}$

- Fluorescence of organic matter mostly from conjugation of C bonds: polyunsaturated molecule
- Diminishes at higher thermal maturity of geologic samples (R_o>1.0%) due to non-radiative transitions



Objective: how does the composition and structure of *Tasmanites* change with increasing thermal maturity?



Explanation

- Sample location
- Devonian R_o isograd
- Pennsylvanian $R_{o(max)}$ isograd
- GC Mature/Immature boundary line
- Spectral Fluorescence 600 isograd
- HI 400 isograd
- Outcrop areas of Devonian black shales

50 25 0 50 100 Miles

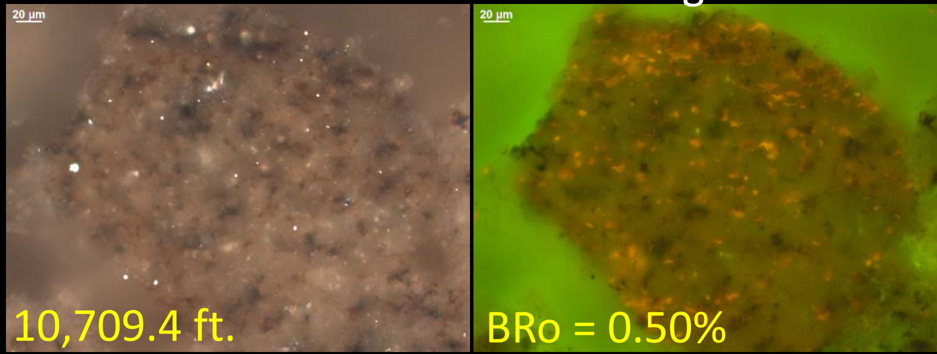
Ryder et al. 2013, AAPG S&D; Hackley et al. 2013, Fuel; Araujo et al. 2014, IJCG; Hackley and Kus, 2015, Fuel; Hackley et al. 2017, OG

- **Objective**: how does petroleum fractionate during expulsion and primary migration?

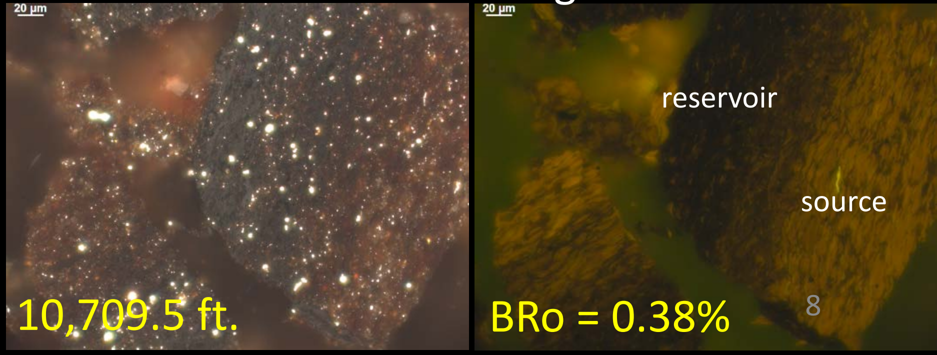
10,709.4 ft.
TOC: 1.14%
S2: 4.93
Tmax: 444

10,709.5 ft.
TOC: 21.60%
S2: 136.48
Tmax: 444

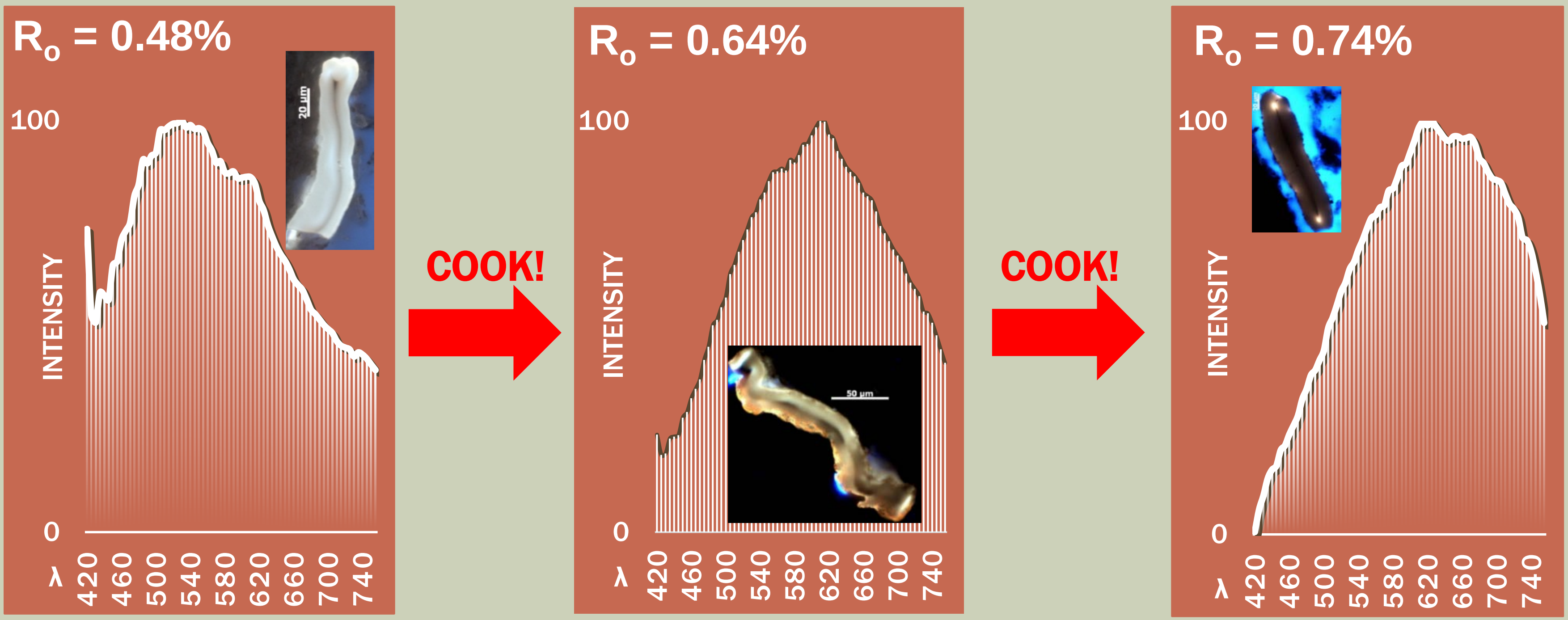
carbonate reservoir rock – no kerogen

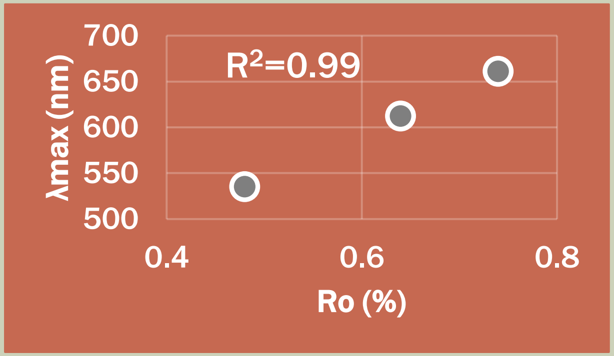


kukersite source rock – kerogen



CONVENTIONAL FLUORESCENCE SPECTROSCOPY

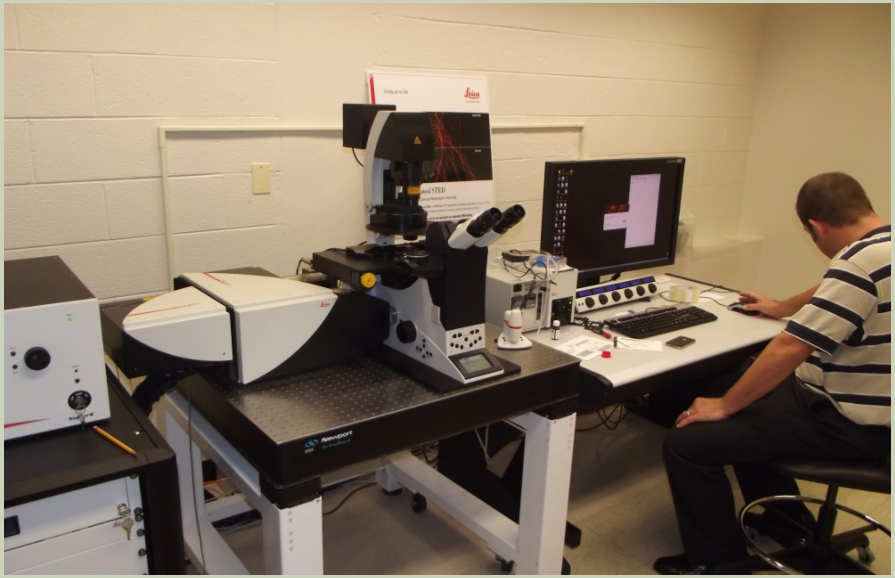


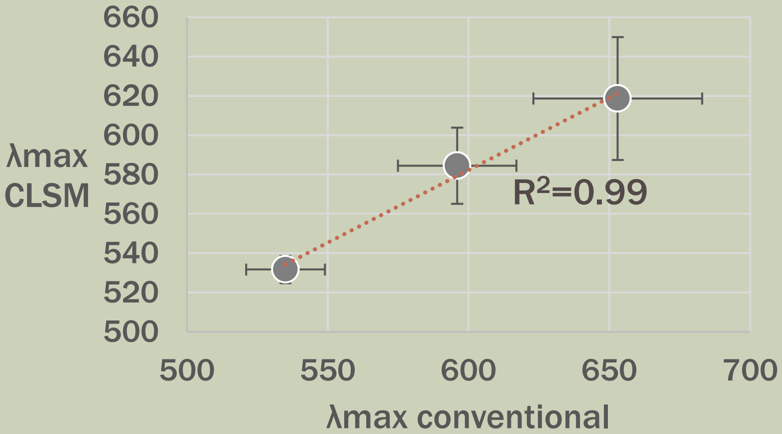


- Spectra red shift with increasing thermal stress – cross-linking condensation
- Fluorescence intensity decreases – increasing fluorophore density, non-radiative energy loss

CONFOCAL LASER SCANNING MICROSCOPY (CLSM)

- Laser or diode illumination
- Continuous excitation white light laser (470-670 nm)
- Light is rastered (scanned)
- Very narrow focal plane
- CLSM spectroscopy within analytical uncertainty to conventional spectroscopy (Hackley & Kus, 2015)

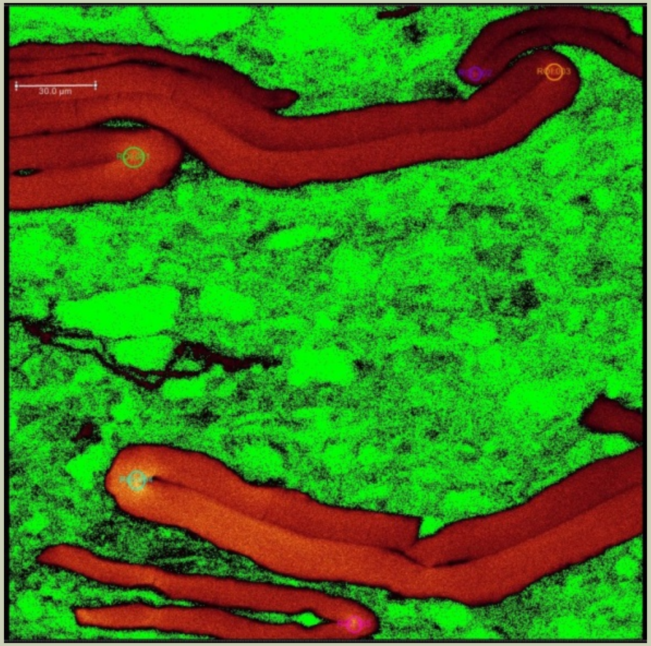


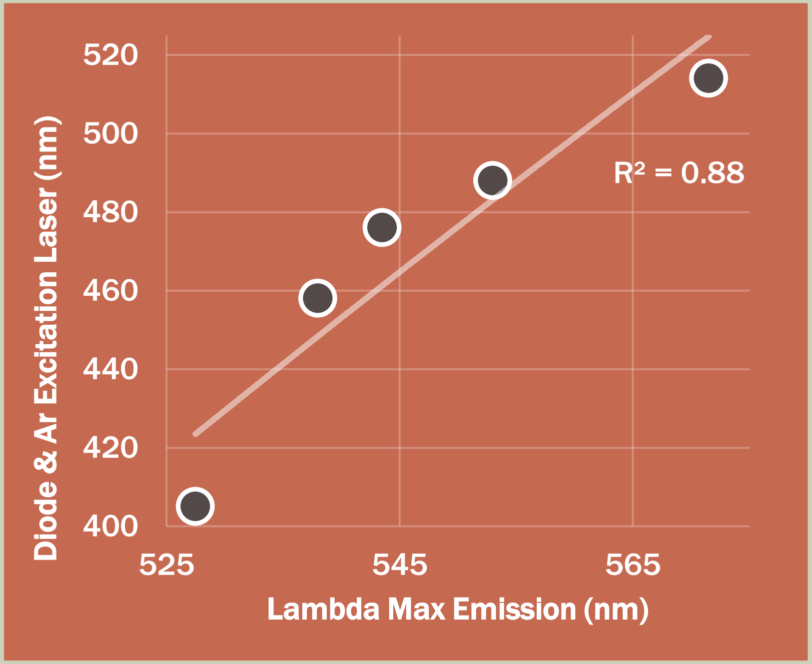


CLSM SPECTROSCOPY RESULTS

- Are multiple distinct fluorophore functions located in same region of *Tasmanites* molecule?

- Yes! seen using different diode and Ar laser excitation wavelengths

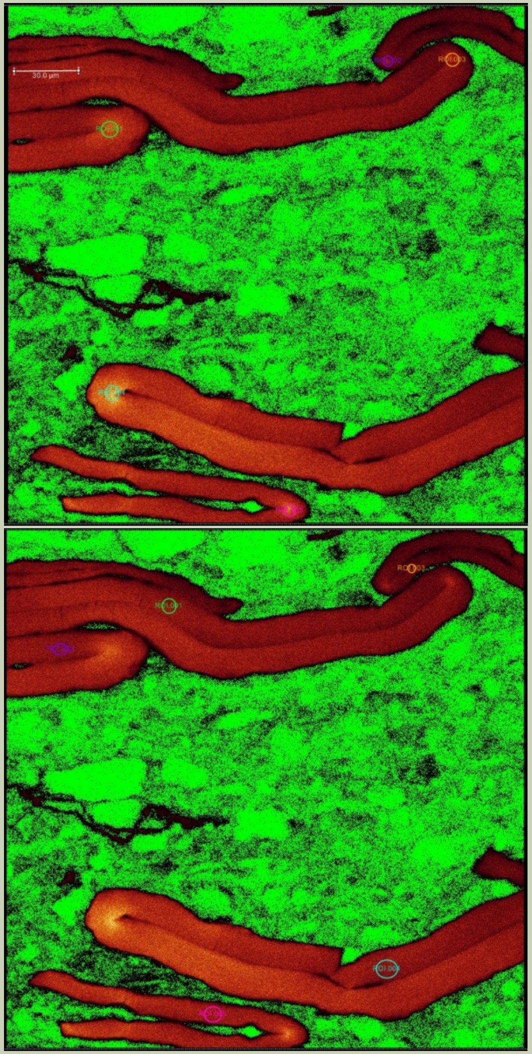


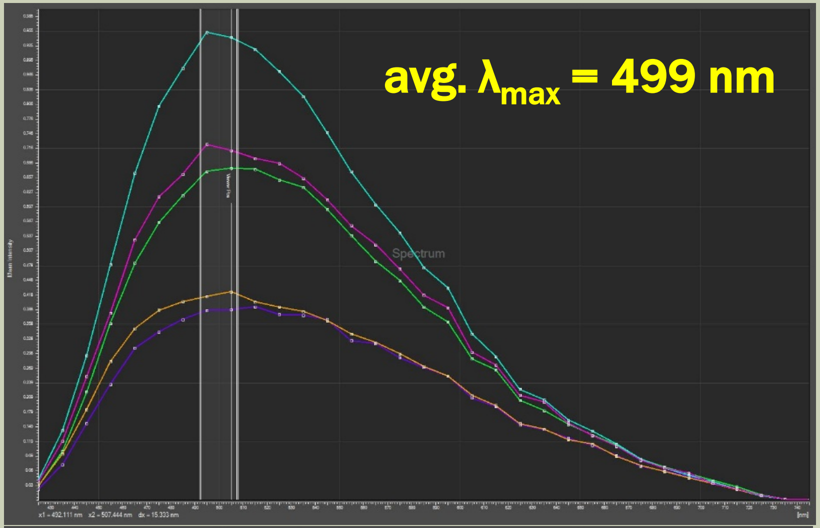


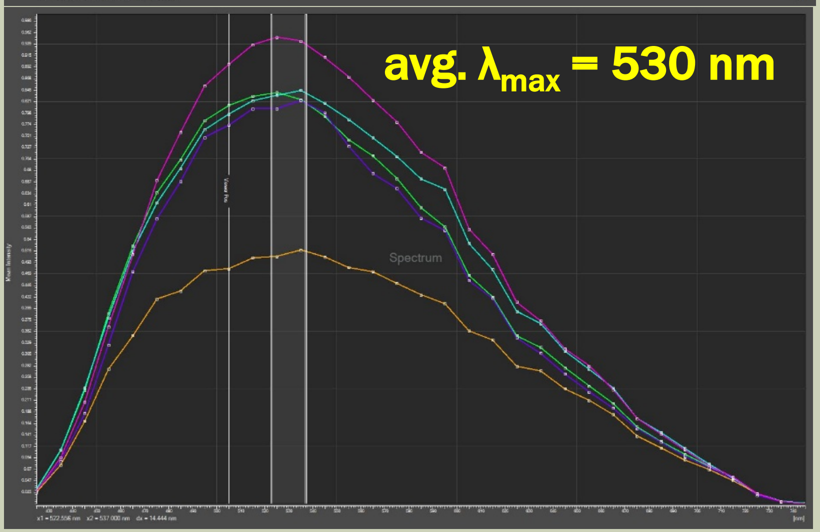
CLSM SPECTROSCOPY RESULTS

- Can we tell what fluorophores are present by varying the excitation wavelength?
- Stokes shift decreases with increasing excitation wavelength
- Multiple fluorophores present in same region with different $S_1 \rightarrow S_0$ energies
- At higher excitation wavelengths, less absorbed light energy is dissipated via non-radiative transitions

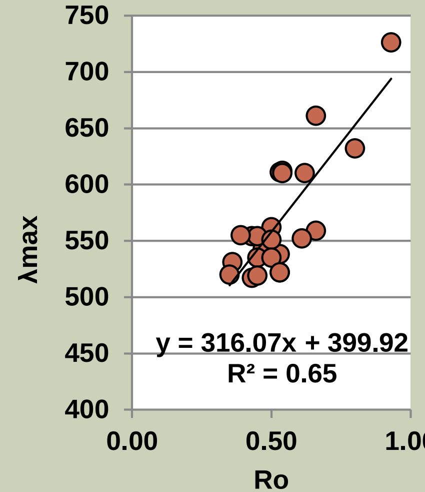
CLSM SPECTROSCOPY RESULTS







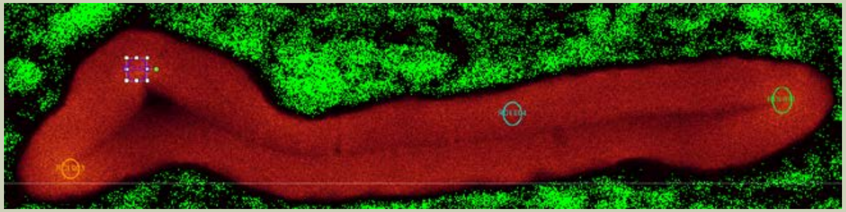
- what about internal variations in emission?

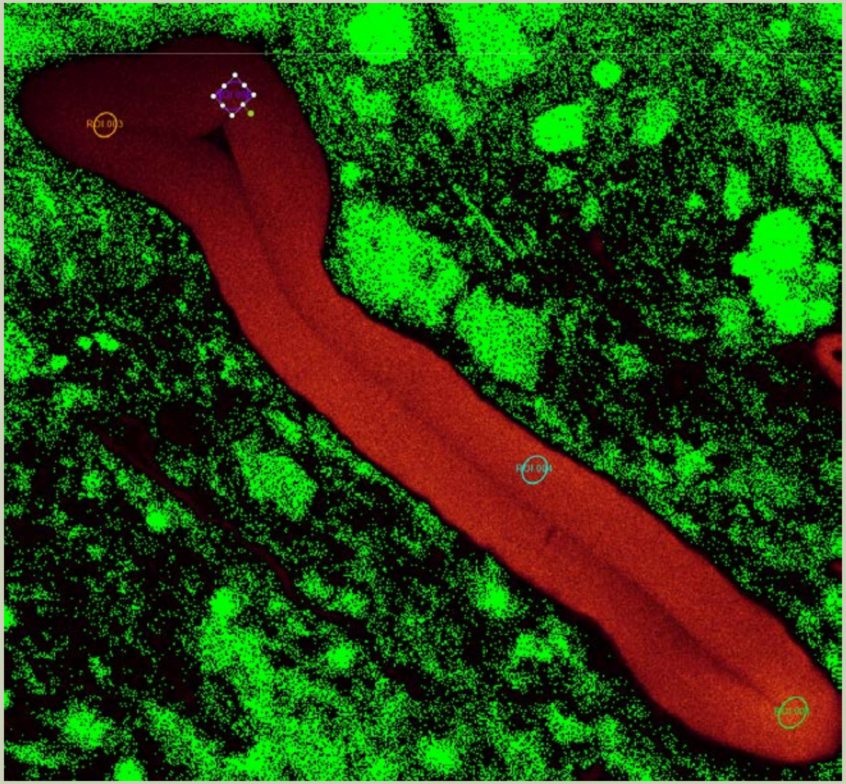


499 vs. 530nm = 0.1% R_o

- Quenching?
- Polarity?

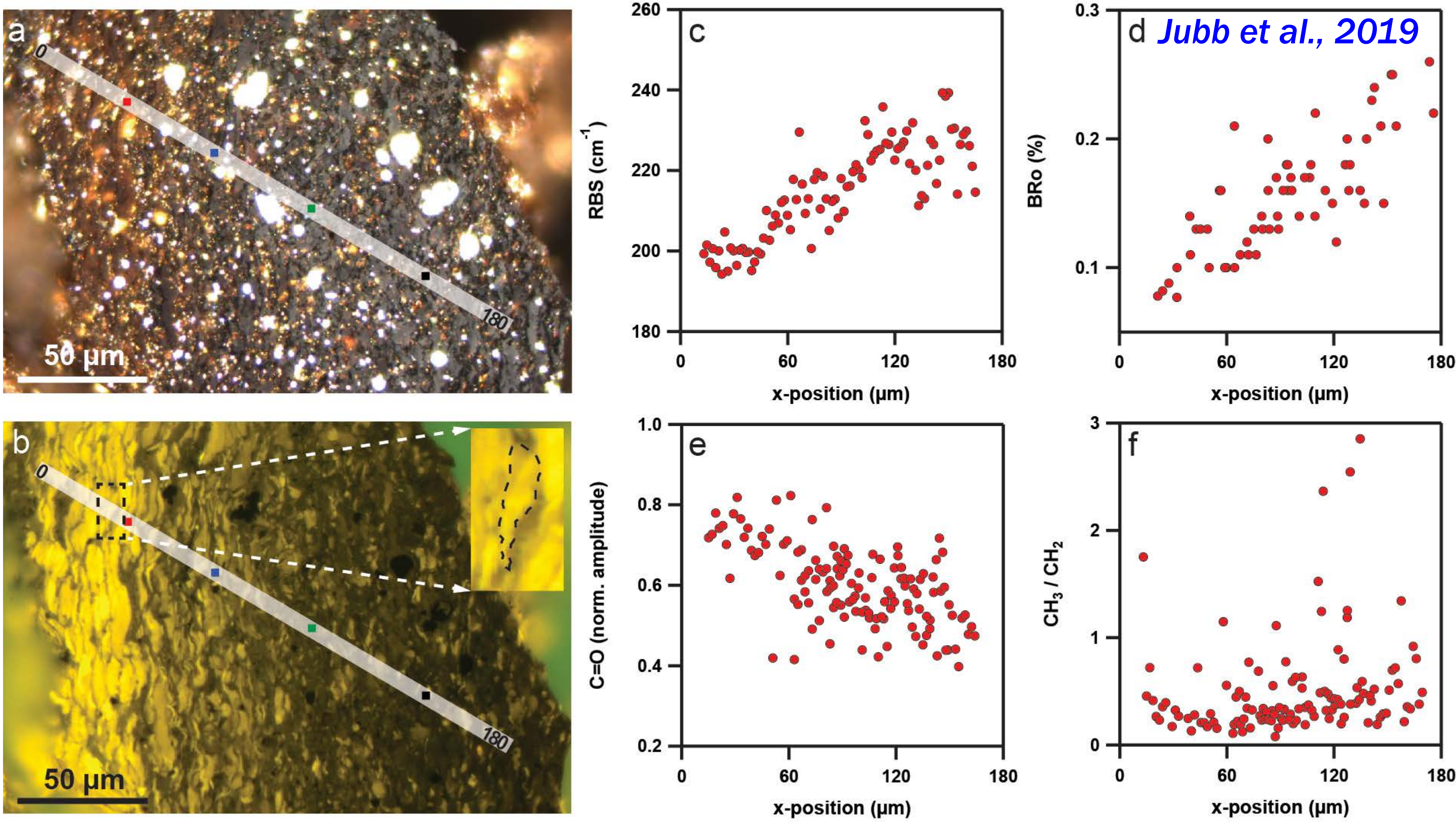
FLUORESCENCE ANISOTROPY



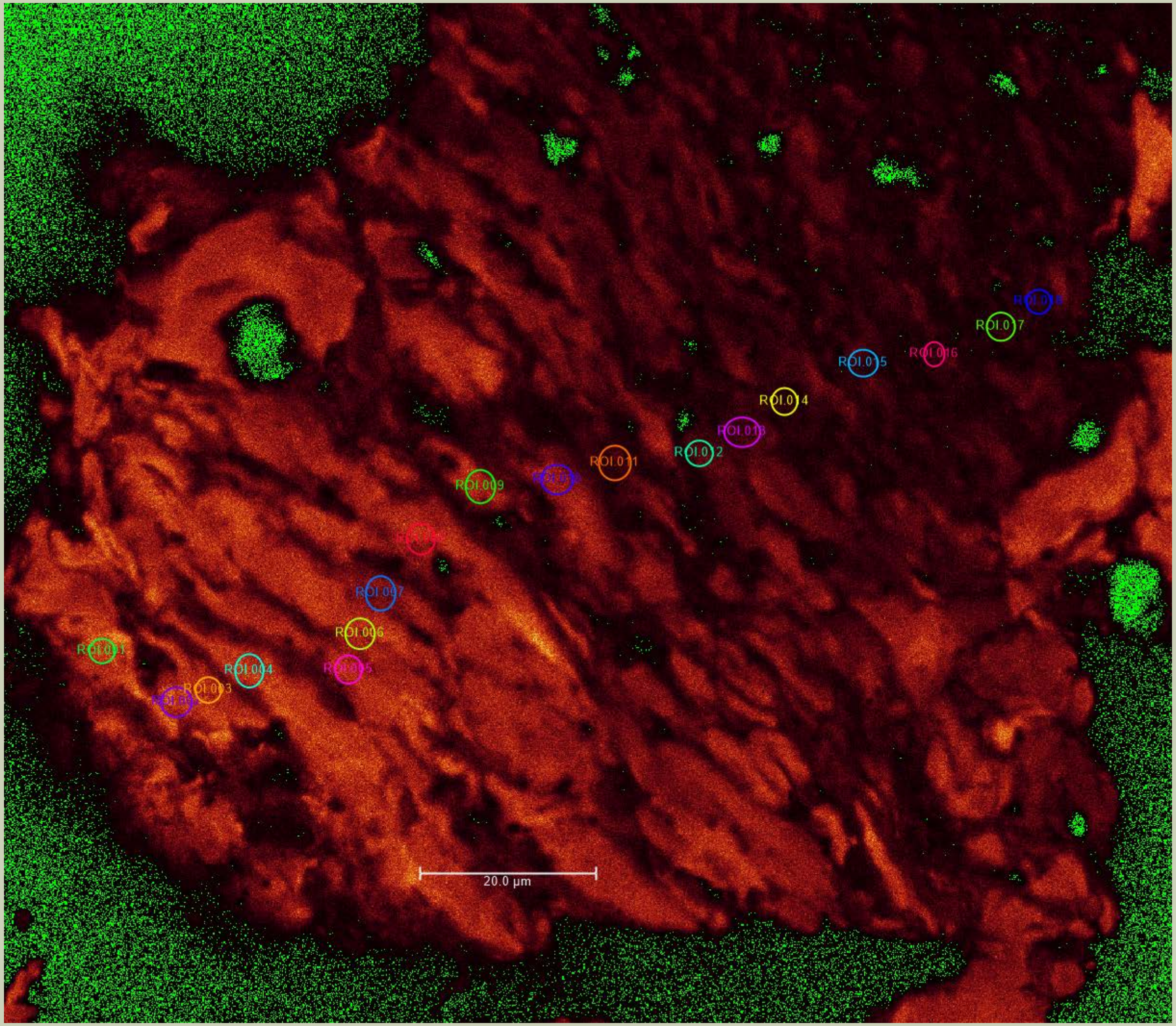


- *Tasmanites* is anisotropic, shows parallel extinction, positive elongation in bedding parallel view
- CLSM is polarized, so fluorescence anisotropy is present
- Spectra are blue-shifted in 45° position, λmax position, center of mass
- No shifts observed for bedding normal view

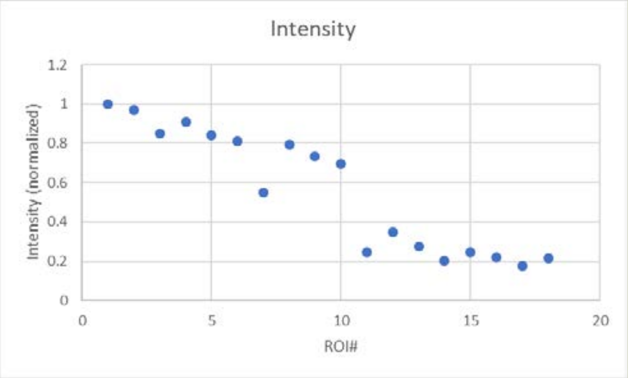
G. PRISCA IN KUKERSITE



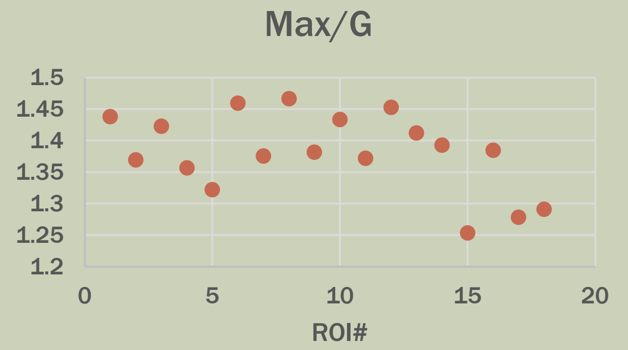
G. PRISCA CLSM RESULTS



- Decrease in intensity

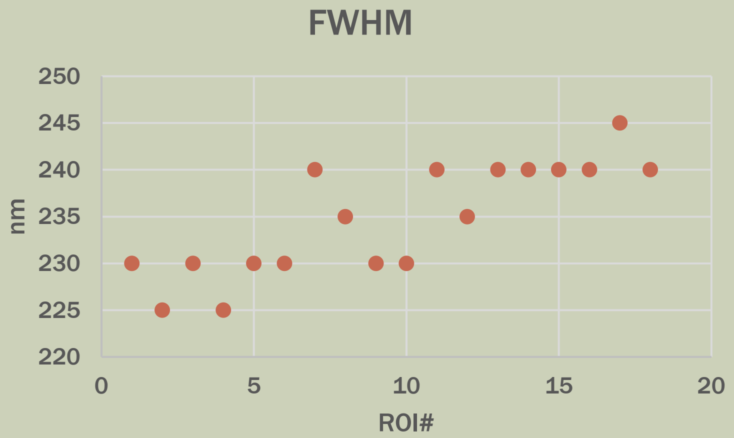


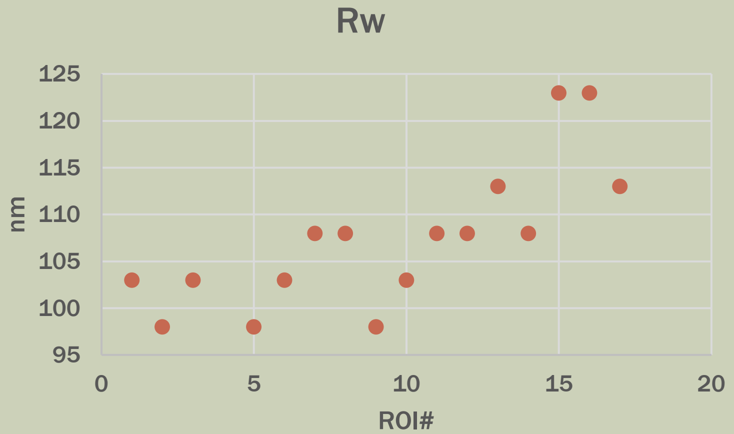
- Decrease in Max/G



G. PRISCA CLSM RESULTS

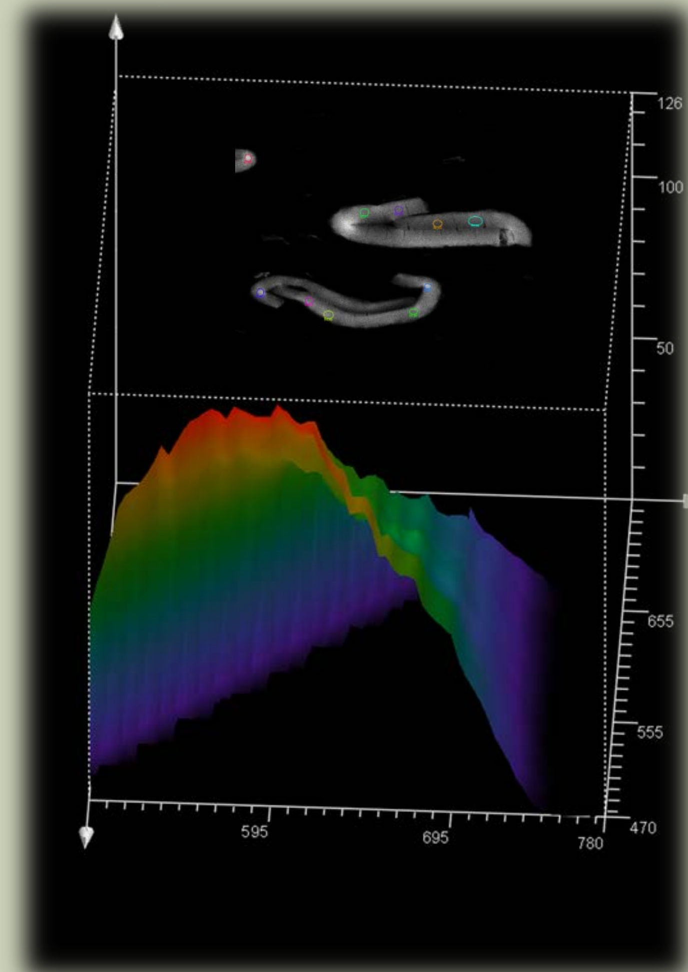
- On transect from *G. Prisca*-rich source layer to solid-bitumen rich reservoir layer:
- Fluorescence intensity decreases
- Spectral color is red-shifted, per decreasing λmax/G, increasing FWHM with increasing Rw
- Indicates increase in maturity (aromaticity) of OM from source to reservoir layer





SUMMARY AND FUTURE DIRECTIONS

- CLSM spectroscopy reveals compositional information about sedimentary organic matter and its evolution with thermal maturity
- CLSM spectroscopy has been successfully applied to thermal maturity determination
- CLSM experiments show internal variations, polarization effects
- CLSM indicates increase in maturity (aromaticity) of OM from source to reservoir layer
- Further application of white light lasers and evaluation of excitation-emission matrices (3-D spectroscopy)
- New ICCP working group to apply CLSM to sedimentary organic matter (using KCF)




Thank You!

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