Organic Diagenesis: Artificial Thermal Maturation studies: Pyrolysis with SEM observations

Kultaransingh (Bobby) Hooghan* Lori Hathon; Mike Myers****

*Independent Imaging/Characterization consultant, **University of Houston

OUTLINE

- Prime interest: Organic Matter Characterization
- Sample selection
- Design of Experiments
- Empirical details
  - Imaging modalities etc.
- Observations
- Summary/Conclusions
- Q & A

SAMPLE SELECTION

- 3 samples from Eagle Ford formation
- One sample from the Barnett formation
- One sample from an unknown formation (clay rich)
- Maturities range: 0.5-1.2% RO
- Classified as low, medium, and high maturity
- Above samples to be studied to cover a variety of mudrock compositions (calcareous, siliceous and clay rich)

DESIGN OF EXPERIMENTS

- Micro-CT scan horizontal 1” core plugs
- From end trims
  - Take mirror surfaces for Thin Section prep(TS) and Argon Ion Milling (AIM)
- Crush carcass material for TOC, XRD etc.
- Two large pcs subjected to : Notch AIM (A & B)
- A & B subjected to native state imaging (Low mag mosaics)
  - Hi resolution images of selected areas on the AIM surface
- Barnett formation: 1’ end trim Ion Milled
- A : extract/image; retort (300° C..) etc.
- B : retort only (300°/350°/400° C)

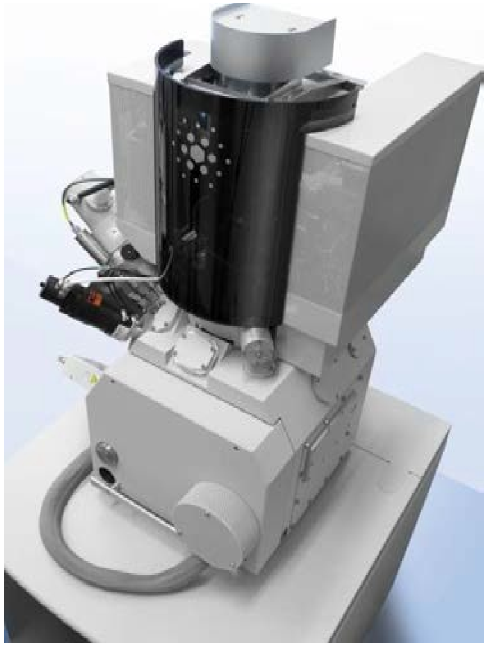
EMPIRICAL DETAILS

- Retort:
- Imaging modalities utilized
  - Optical mosaics (100X reflected white /UV light) on end trims
    - SEM higher magnification mosaics
  - Notch mosaics (low magnification) native state/ post retort
  - Hi magnification images (native state/post retort)
  - Barnett: locations 1-5 on vertical plug end trim, mosaics: native state and post retort

EMPIRICAL DETAILS

- Apparatus used for this experiment

Heating oven

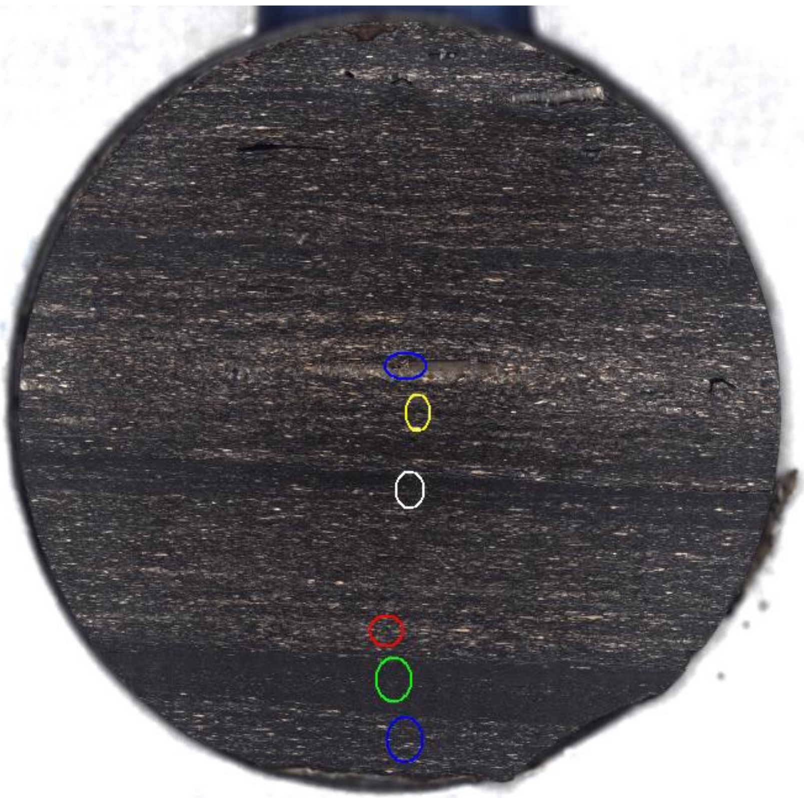


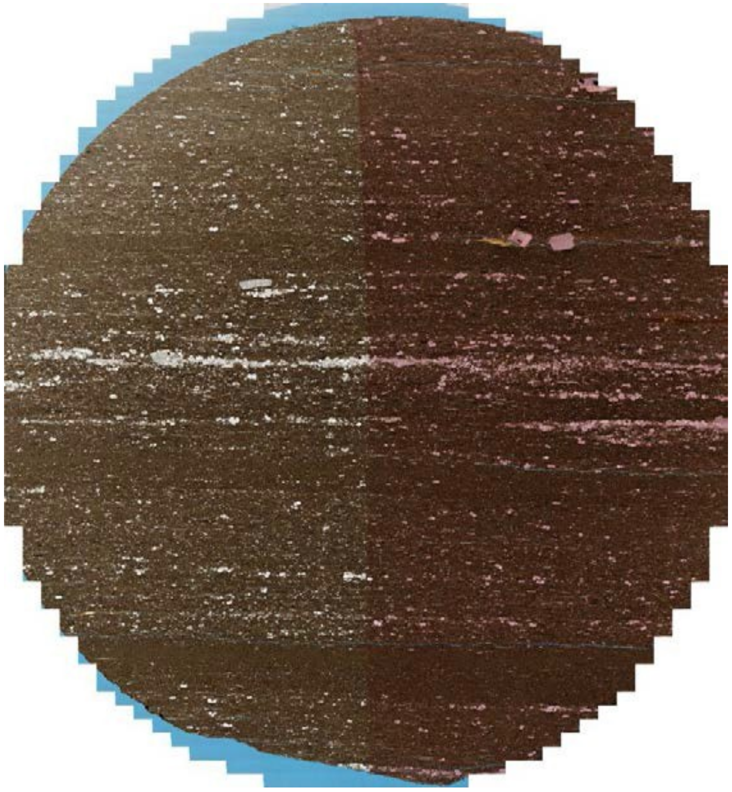
Helios 650 Dual Beam System

EAGLE FORD FORMATION

- Low, medium, and high maturity samples

Reflected and Transmitted Light Imaging

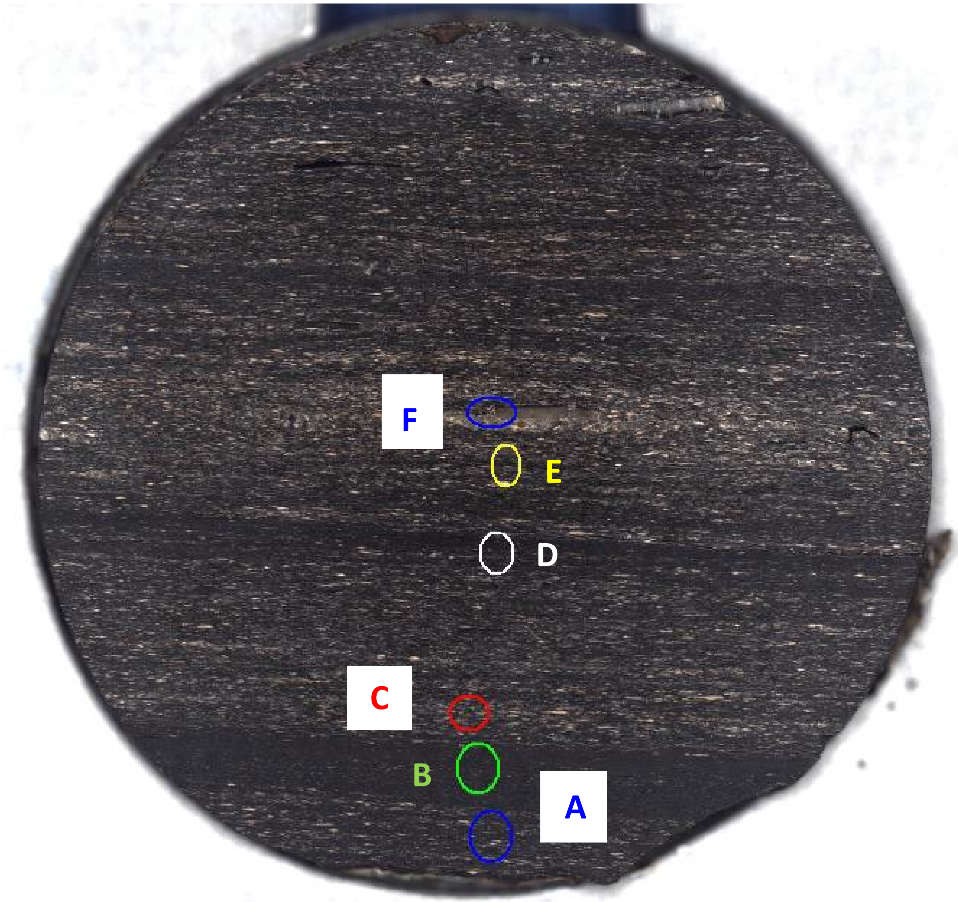




The reflected light image of the ion milled surface illustrates porosity, mineralogy, and TOC differences and enables ROI selection

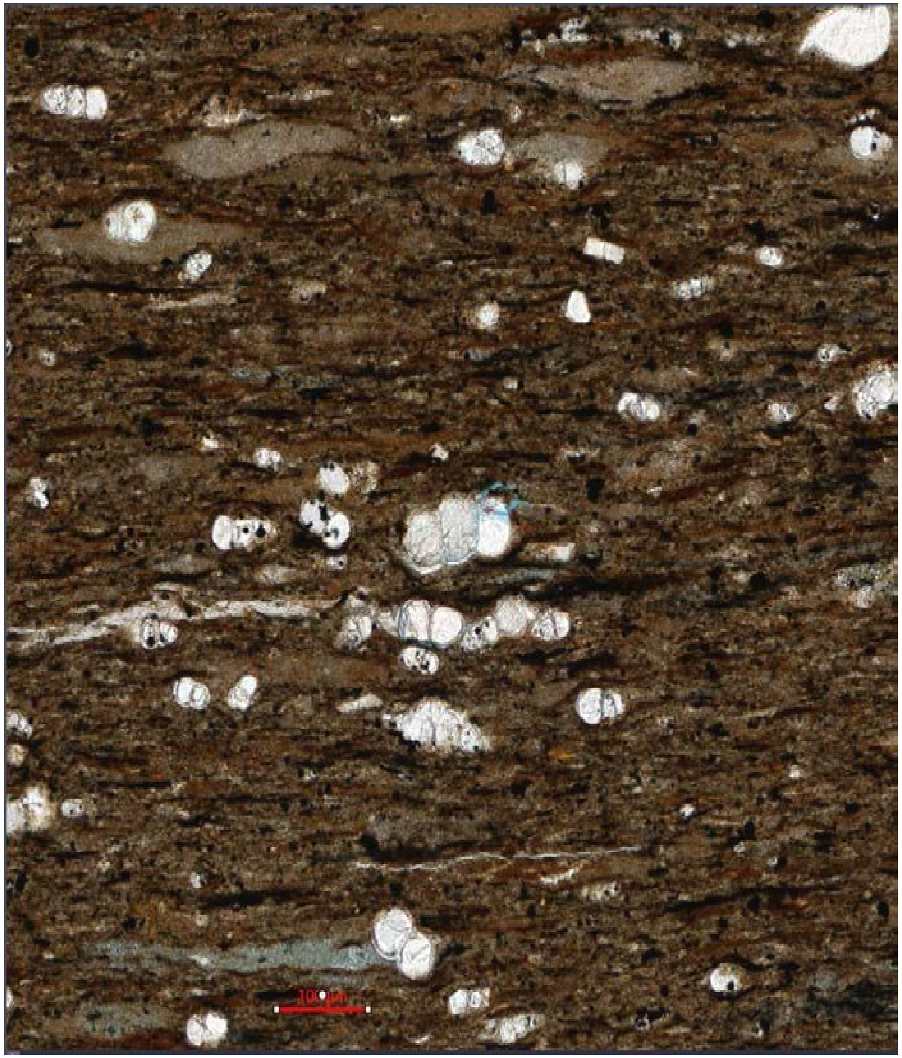
The transmitted light image of the twin thin section surface allows inferences regarding depositional setting to be made.

Low Resolution Reflected Light Imaging



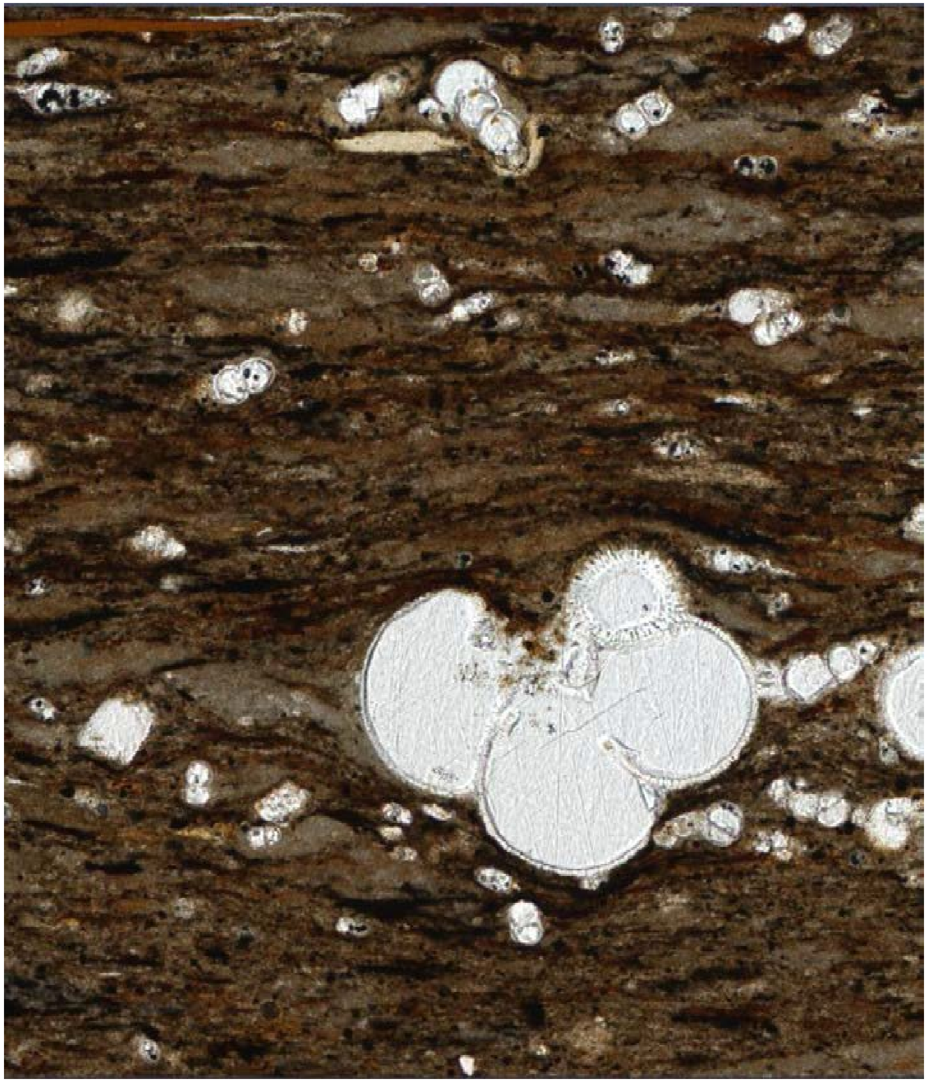
- Effectively highlights different lamina types present within a one inch end trim.
- Relative volumes of each lamina type can be estimated.
- Bright (reflective) regions/layers indicate carbonate content and porosity
- Dark regions/layers indicate lamina higher in TOC
- Regions of interest for further investigation can be highlighted.
- Image is used to guide navigation around the sample in the SEM.

Transmitted Light Imaging



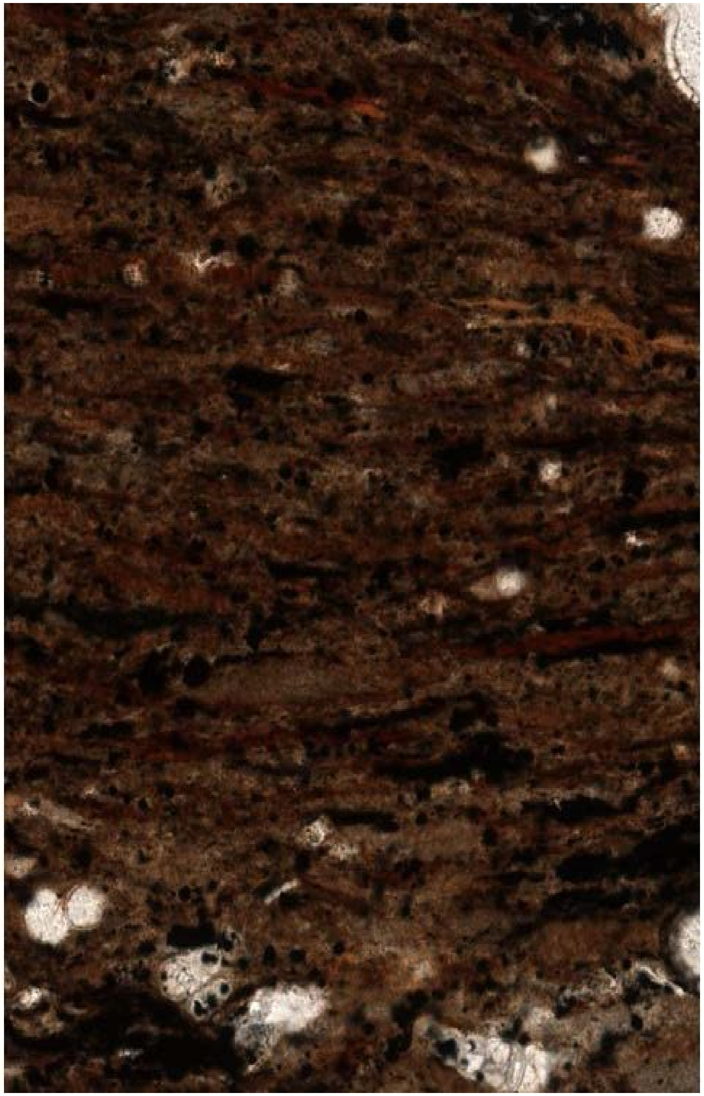
- Region of Interest A
- Moderately peloidal (bright regions)
- In general peloidal regions are quite large and large forams are observed locally.
- Size and abundance of peloids are indicative of oxygen levels in the water column.
- In low maturity samples the majority of the visible pore space in SEM images is associated with peloids.

Transmitted Light Imaging



- Region of Interest C
- Highly peloidal lamina
- In general peloidal regions are quite large and large forams are observed locally.
- Size and abundance of peloids are indicative of higher oxygen levels in the water column.
- This lamina type displays the highest porosity

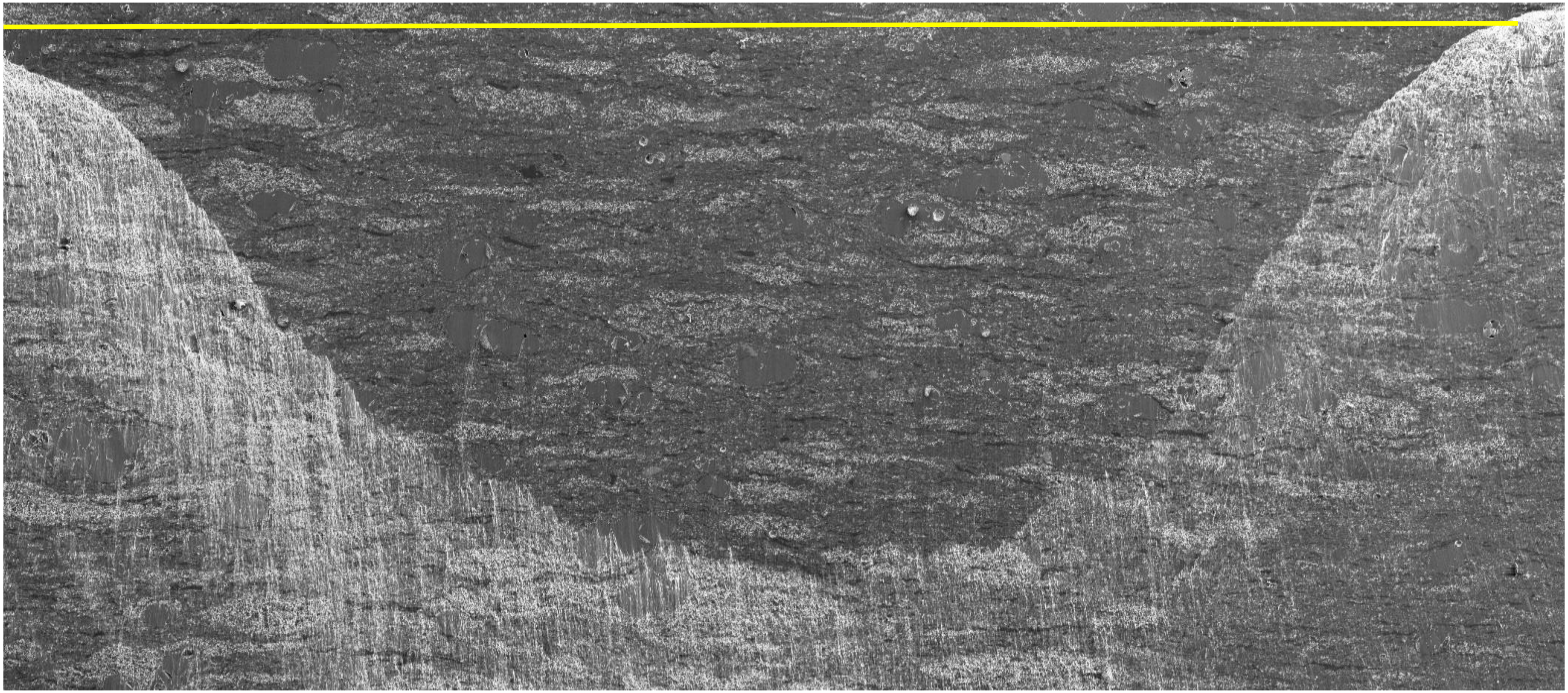
Transmitted Light Imaging



- Region of Interest B
- Sparsely peloidal lamina
- Peloids are small and relatively rare indicating lower levels of oxygen in the water column do
- Dwarf faunal forms observed
- This lamina type displays the highest TOC content and the lowest porosity in low maturity samples

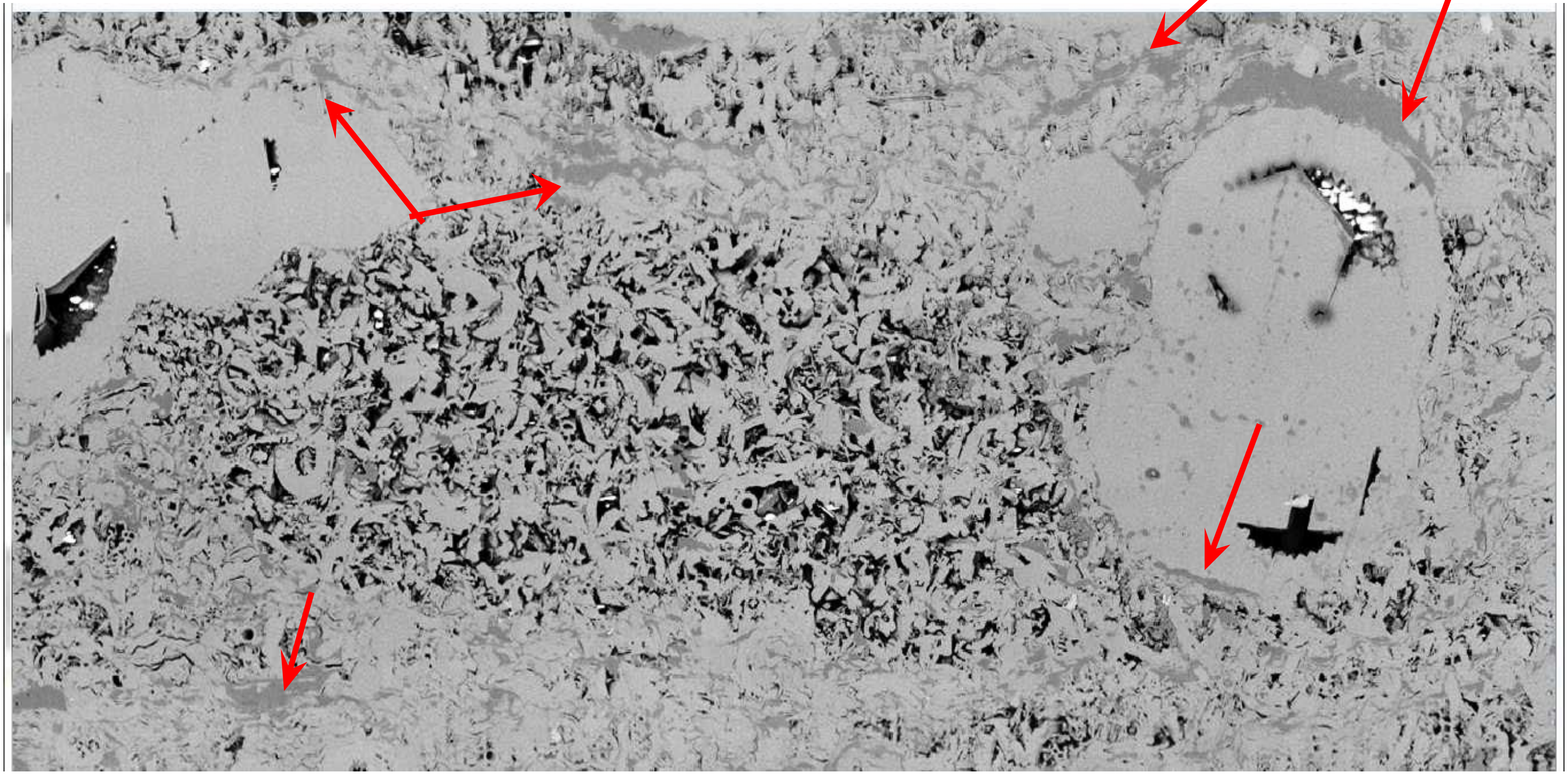
Low Resolution SEM Imaging (Low Maturity)

Ion milled notch on low maturity Eagle Ford sample. Comparison with the ion milled end trim image suggests this sample is from an "A" type lamination (moderately peloidal) as described previously. Field of view is approximately 2mm wide.



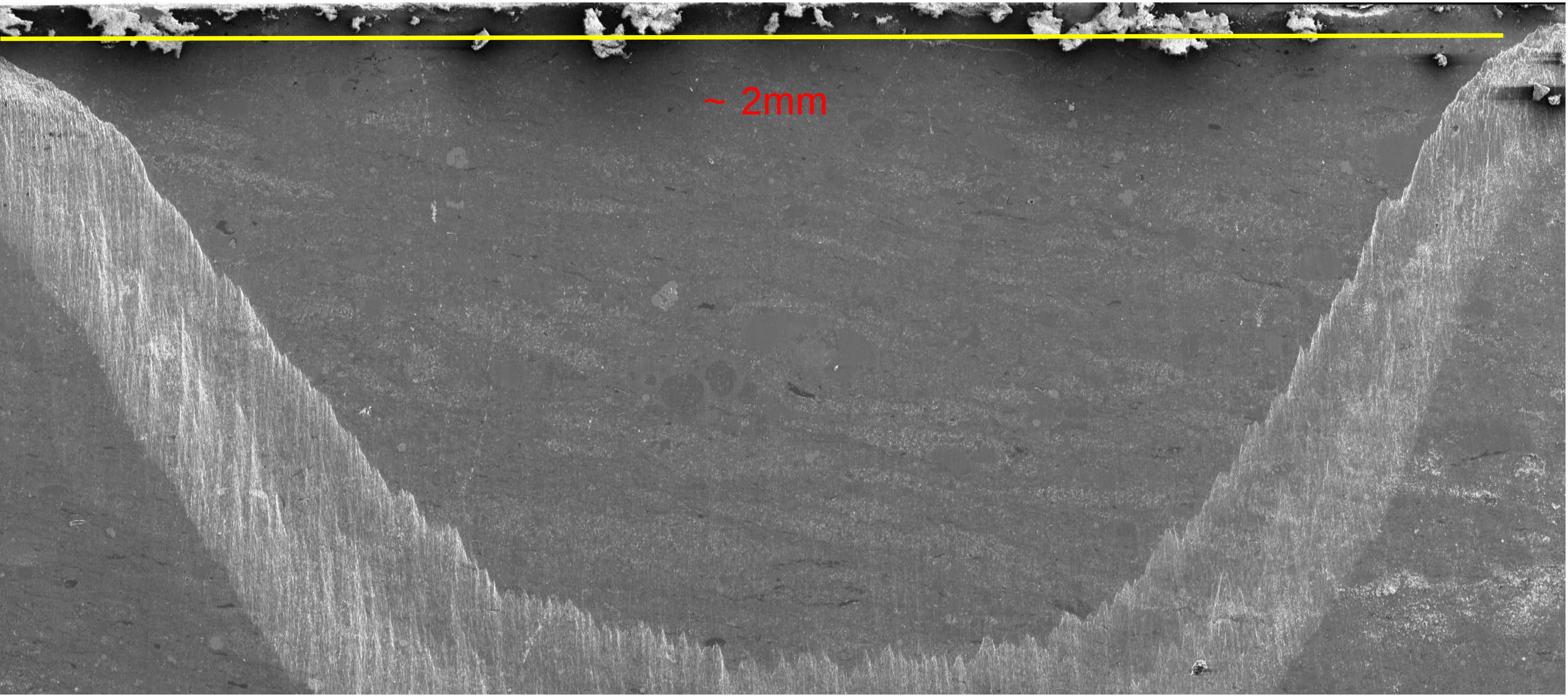
High Resolution SEM Imaging

Ion milled notch on low maturity Eagle Ford sample. Note that most of the pores in the peloid are open, although locally they are partially filled with bitumen indicating some HC generation even at low maturity. Majority of OM in field of view is bedding plane parallel sedimentary marine organic material (amorphous; red arrows). Magnification is ~1000x.



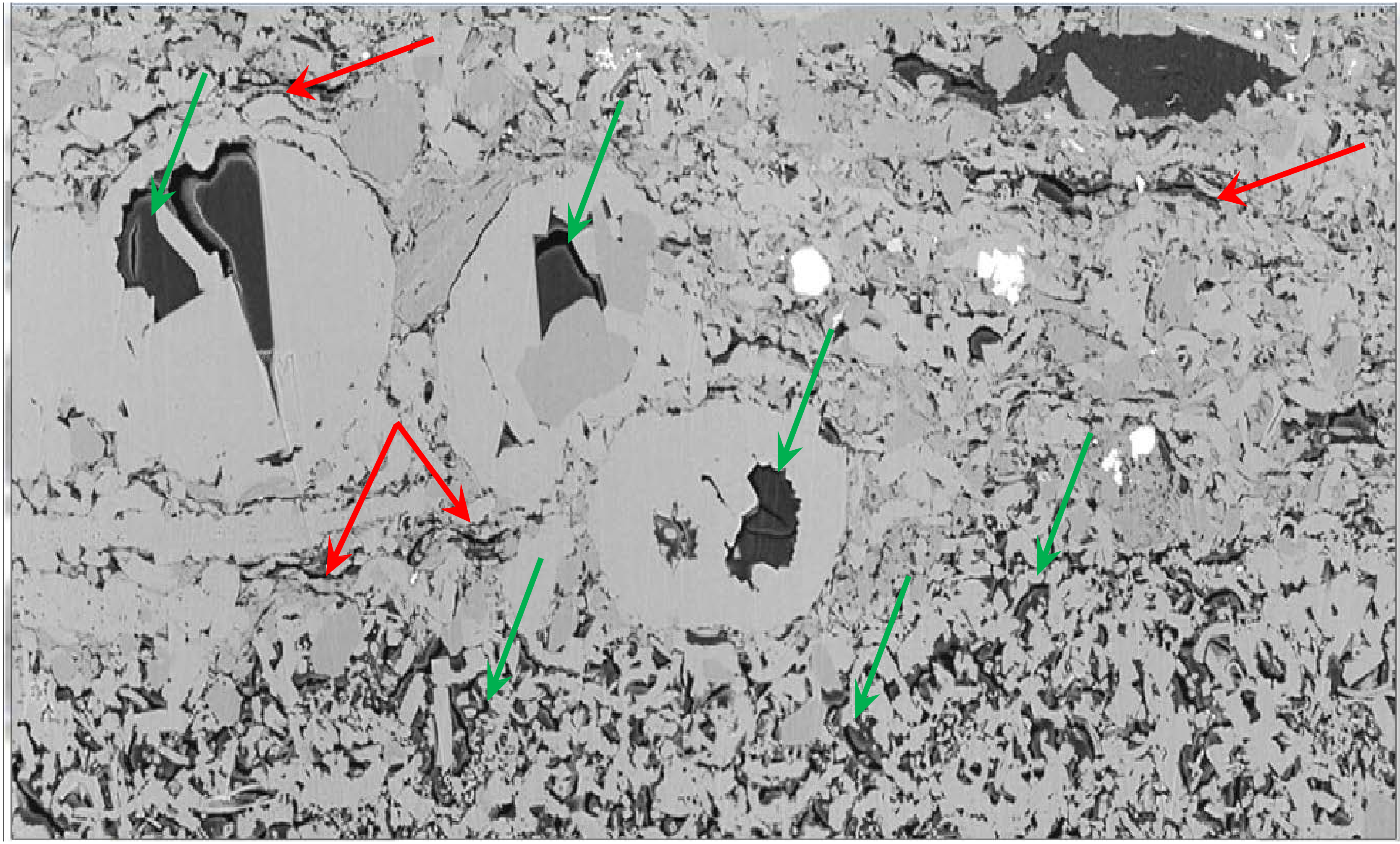
Low mag SEM Imaging (medium maturity)

Ion milled notch on medium maturity Eagle Ford sample. Similar to the low maturity notch image, this sample is from an “A” type lamination (moderately peloidal) as described above. Total porosity is lower because pore space in peloids is largely filled with bitumen.



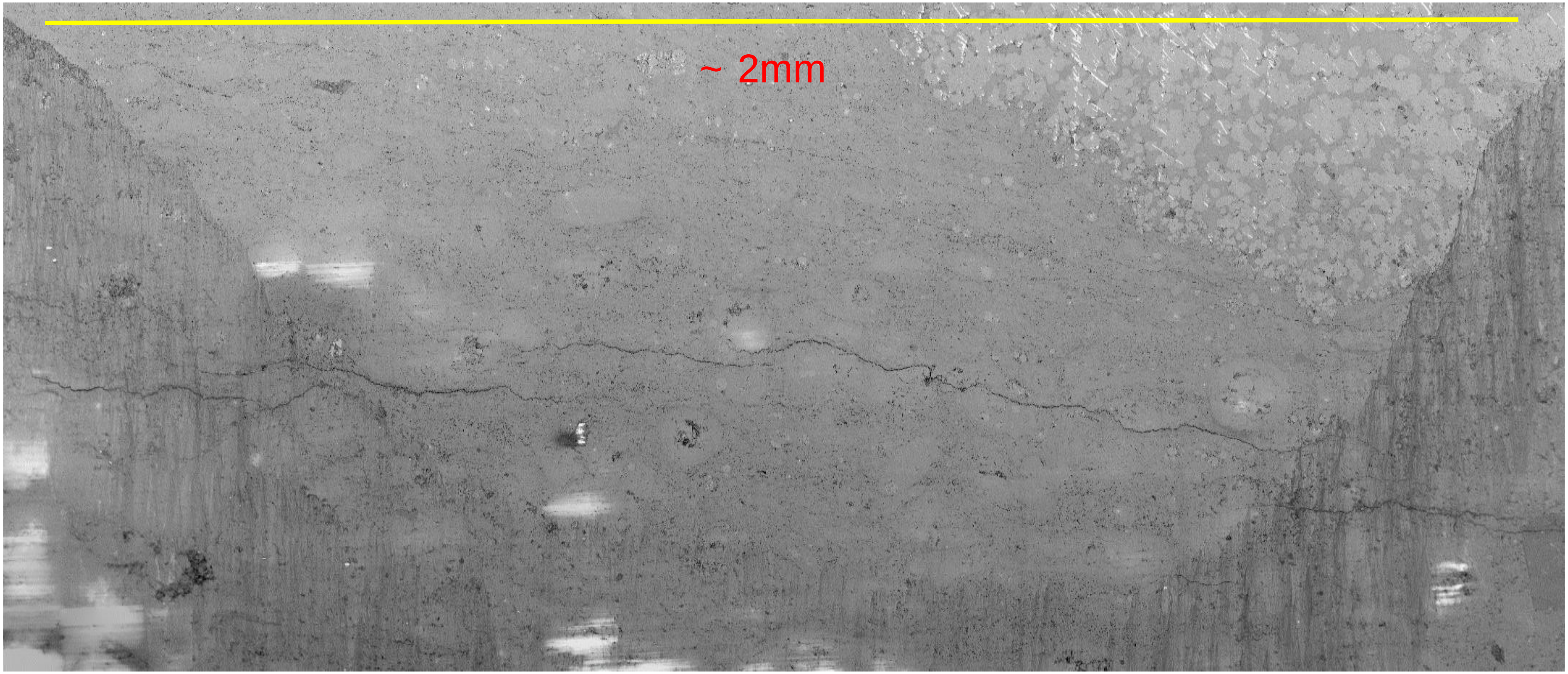
High Resolution SEM Imaging

Ion milled notch on medium maturity Eagle Ford sample. Note that most of the pores in the peloid filled with bitumen. Majority of OM in field of view is migrated bitumen (green arrows) with rare bedding plane parallel sedimentary marine organic material (amorphous; red arrows)



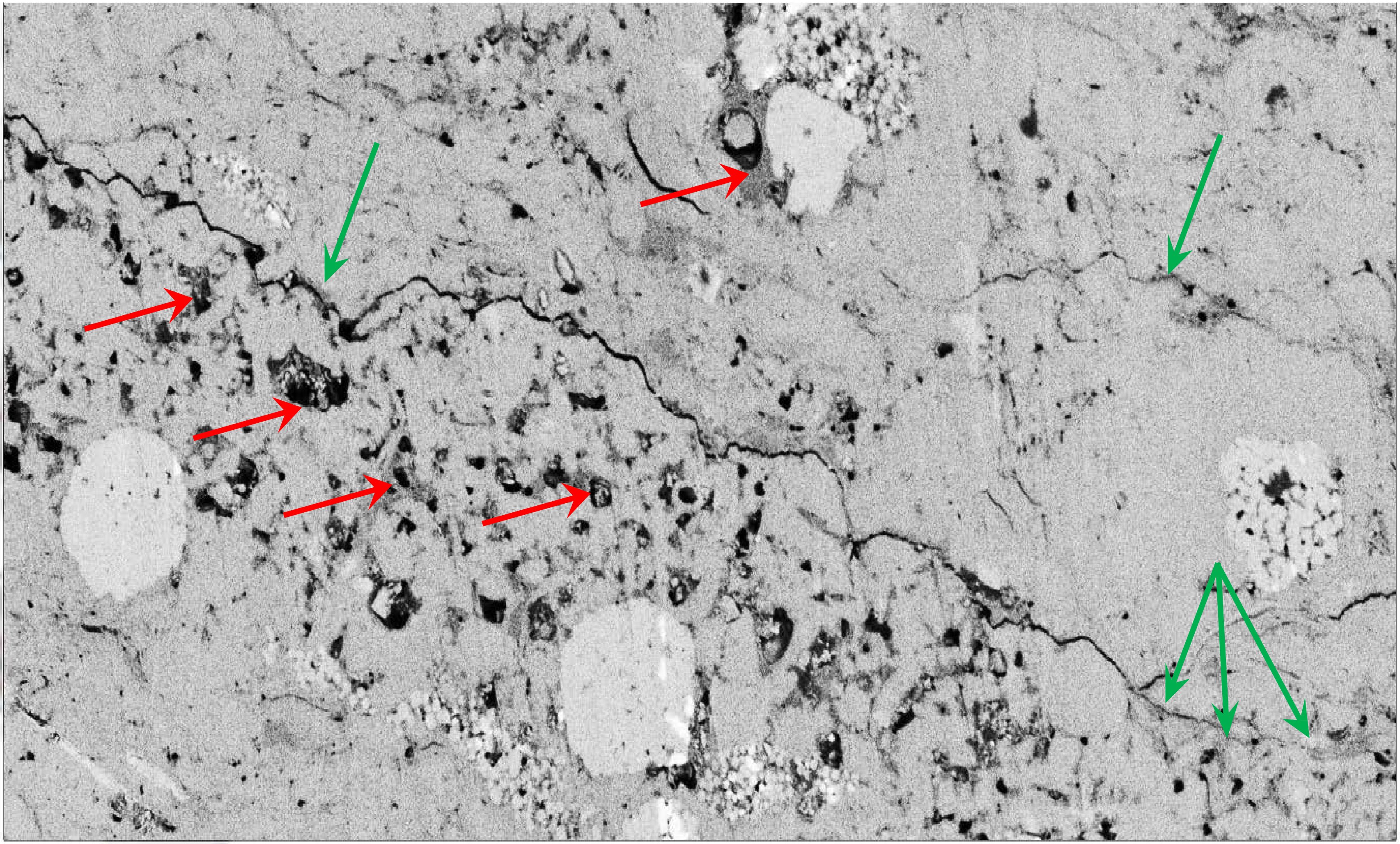
Low Resolution SEM Imaging

Ion milled notch on high maturity Eagle Ford sample. Similar to the low maturity notch image, this sample is from an “A” type lamina (moderately peloidal) as described above. Total porosity is somewhat higher than for middle maturity sample due to cracking of bitumen and formation of OM hosted porosity in pyrobitumen.

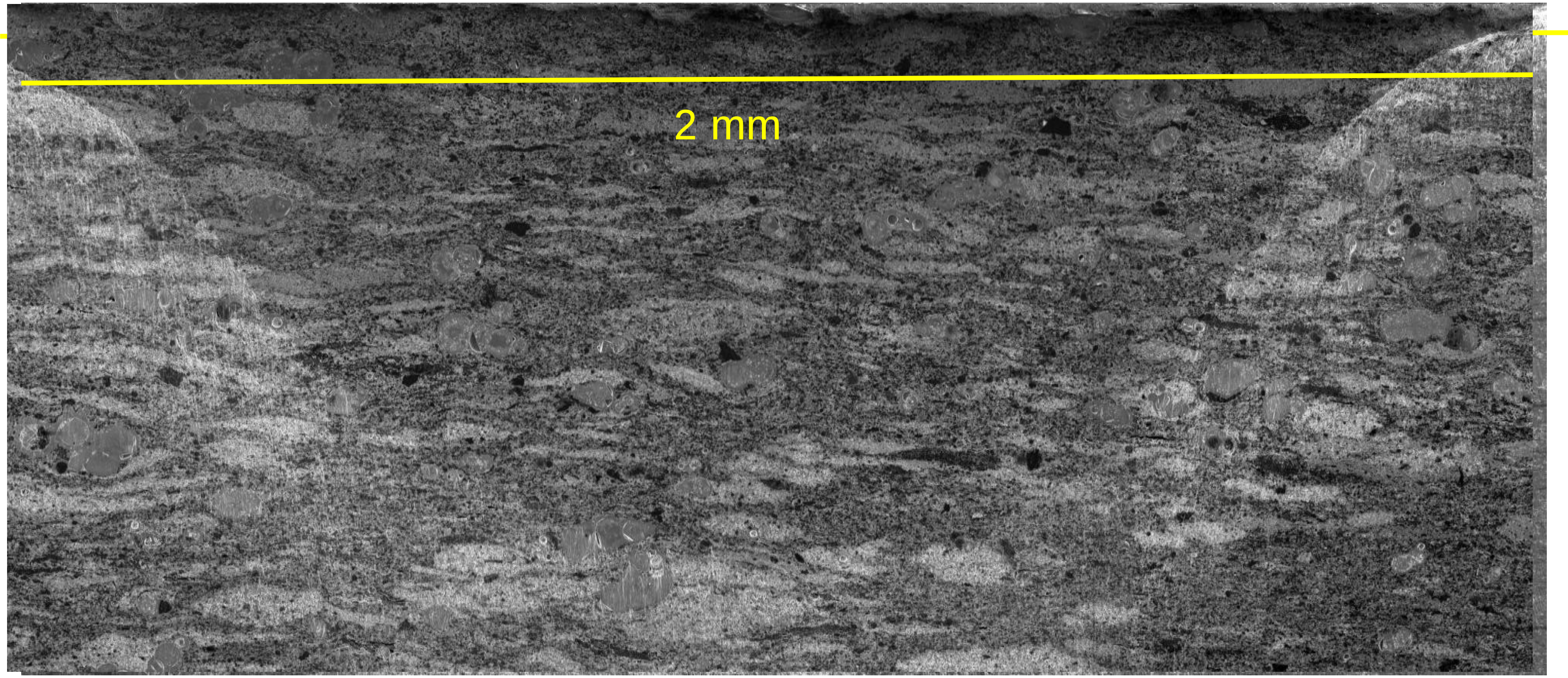


High Resolution SEM Imaging

Ion milled notch on high maturity Eagle Ford sample. Similar to previous notch images, this sample is from an "A" type lamina (moderately peloidal) as described above. Note pores developed in pyrobitumen (red arrows) and trace remnants of bedding plane parallel sedimentary OM (green arrows).



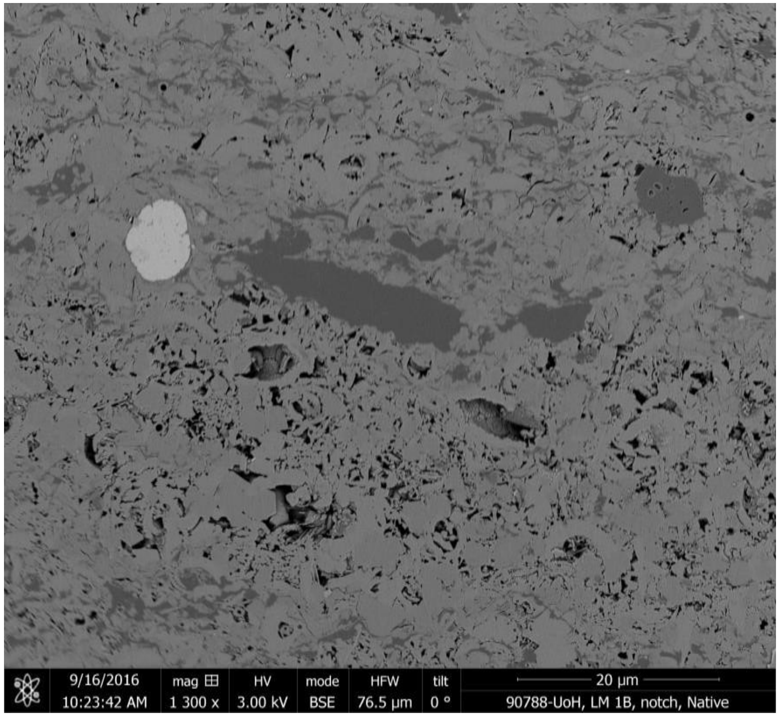
LOW MATURITY MOSAIC (NATIVE STATE) and post retort

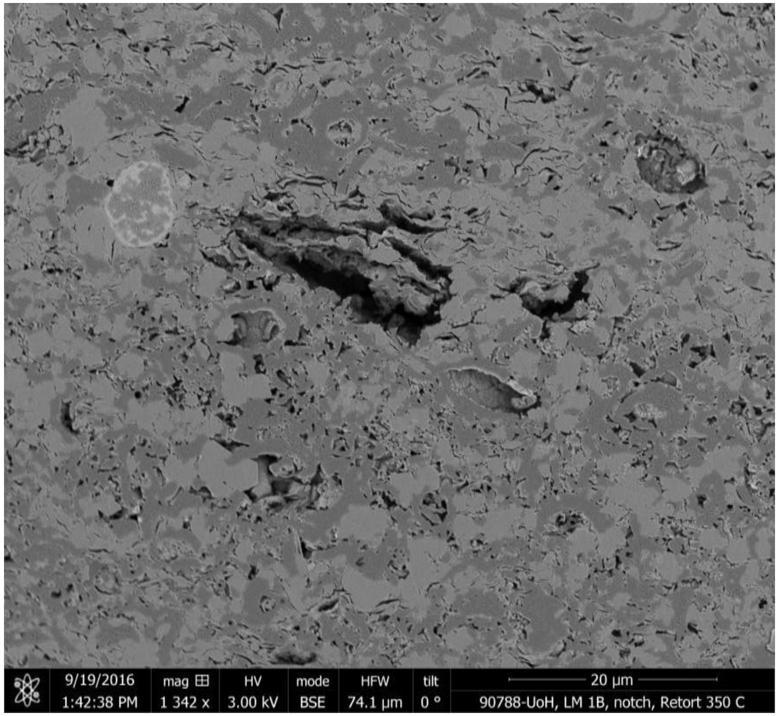


HI MAGNIFICATION/RESOLUTION COMPARISONS

Native state	Post retort

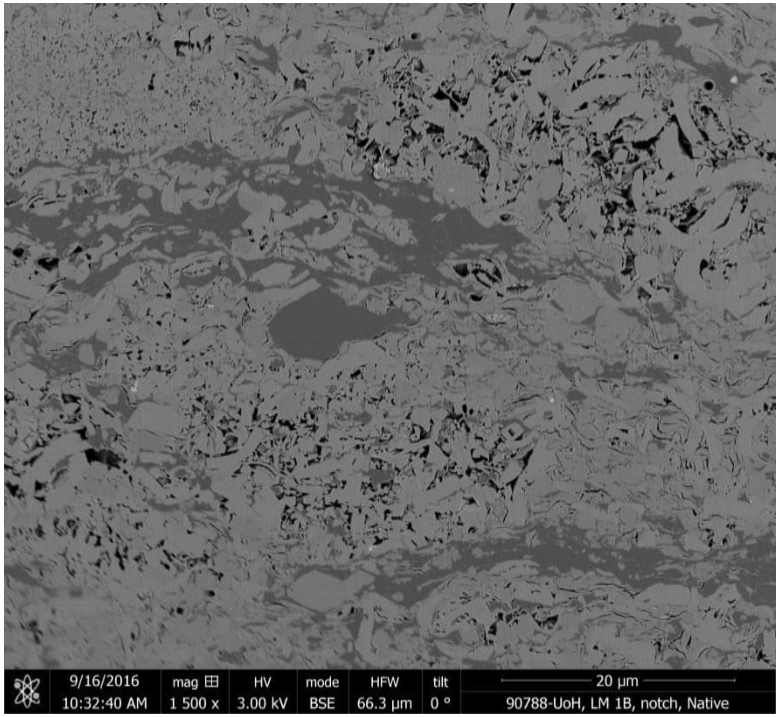
- Note complete removal of organic material at 350C.

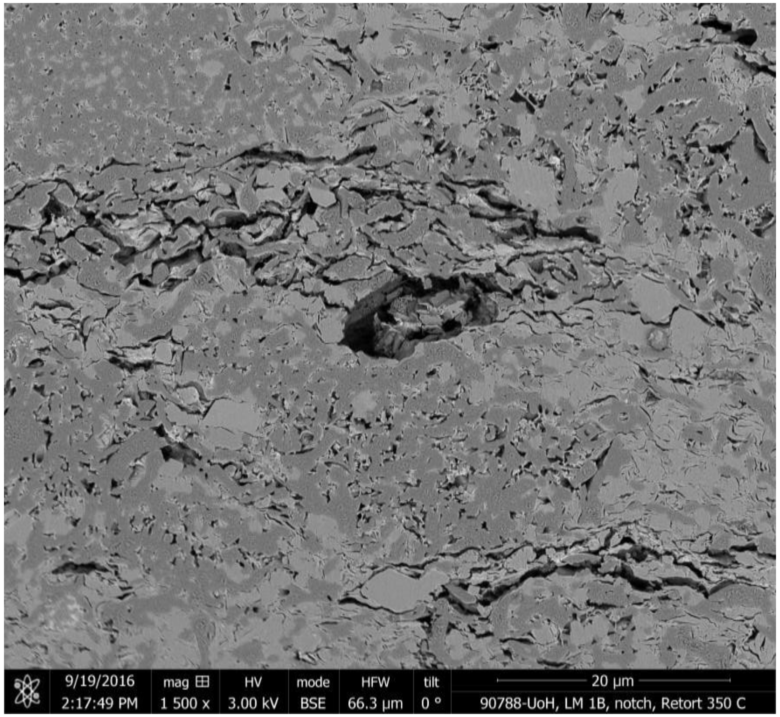




HI MAGNIFICATION/RESOLUTION COMPARISONS: LOW MATURITY SAMPLE 1B

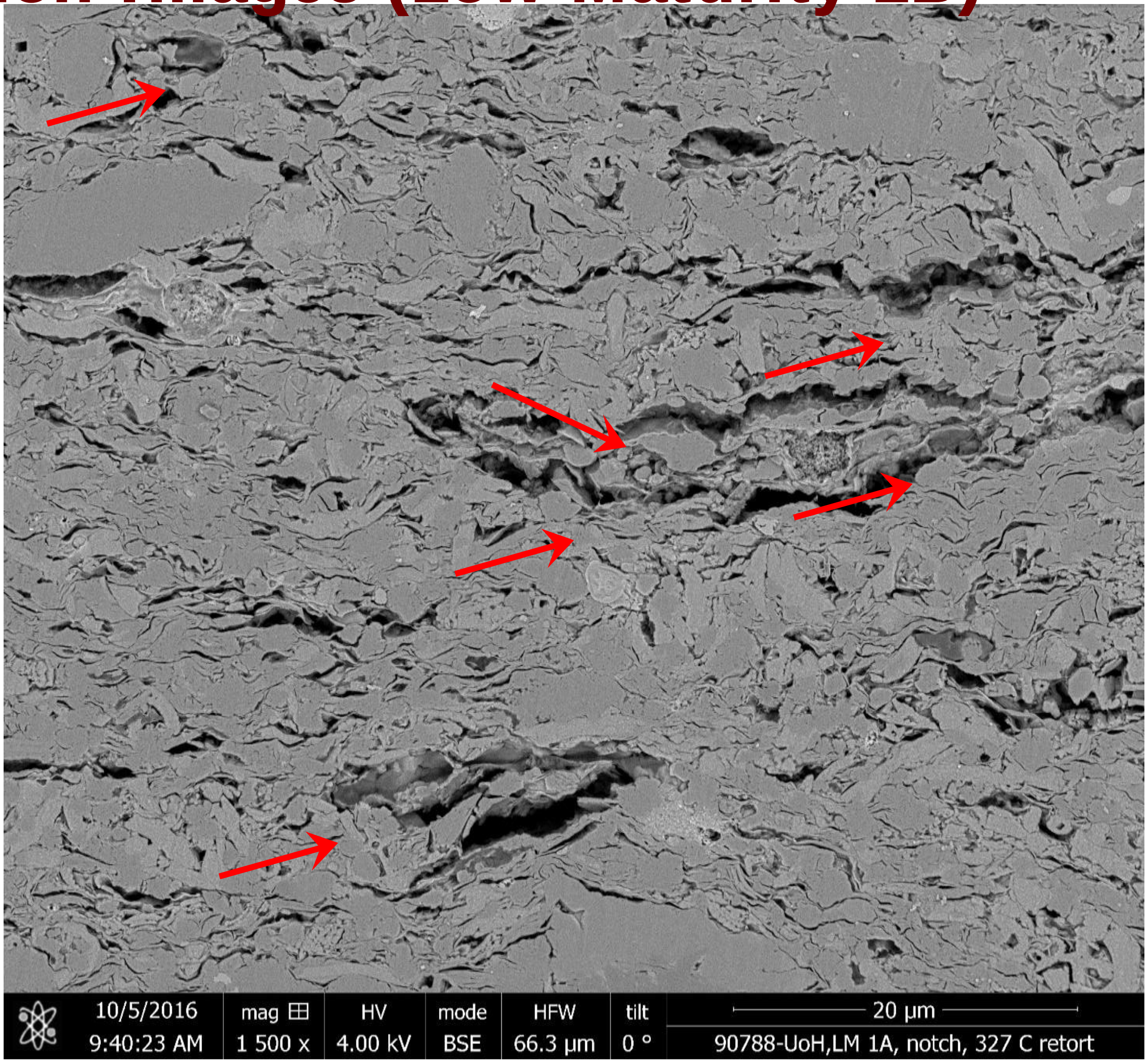
Native state	Post retort





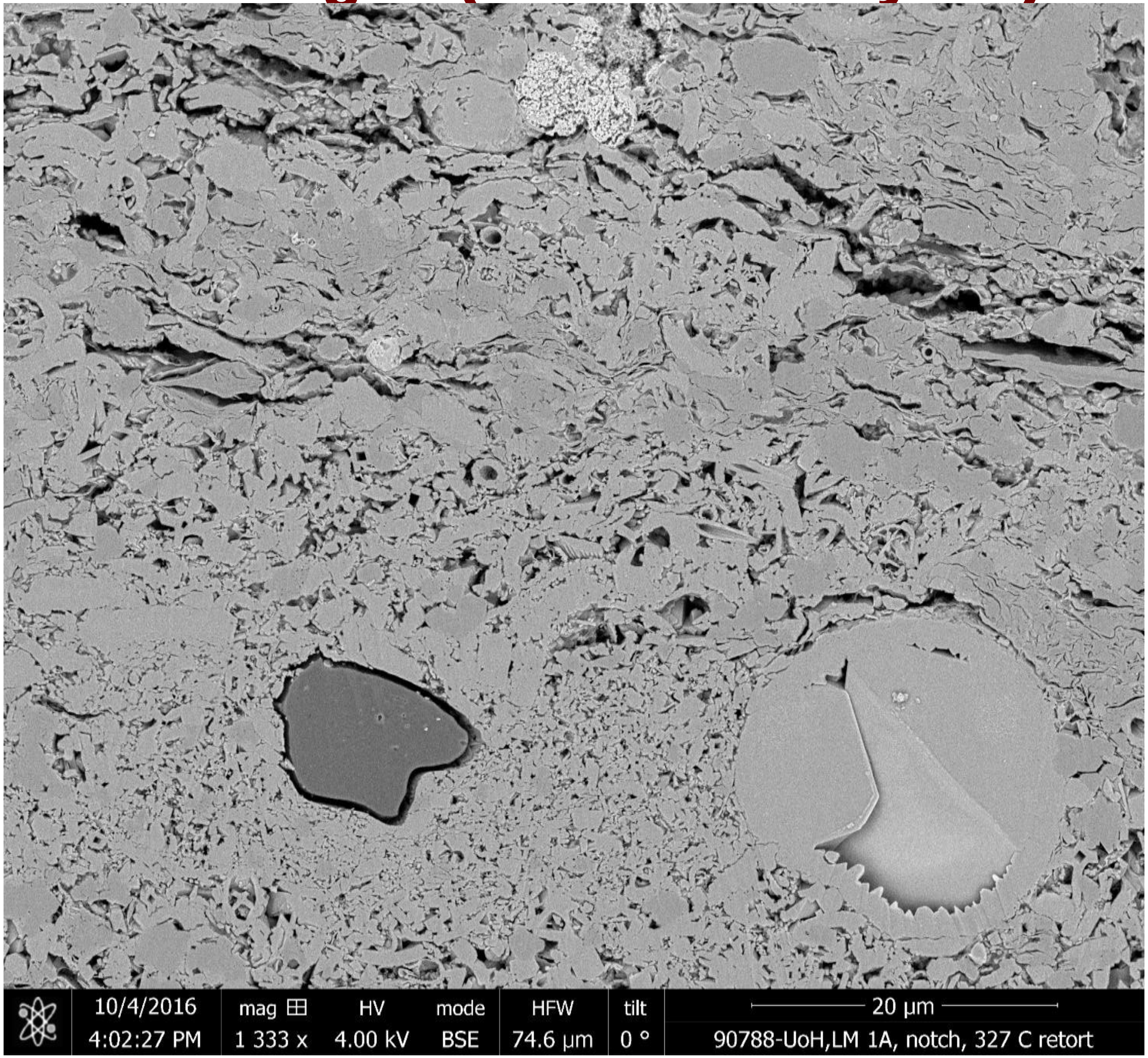
High Resolution Images (Low Maturity 1B)

Post 300^{o}C bedding plane parallel (BPP) oriented, sedimentary organic material has responded to heating by shrinkage. OM films line regions where BPP OM was originally present (red arrows). Post 327^{o}C retort BPP OM is nearly entirely removed.



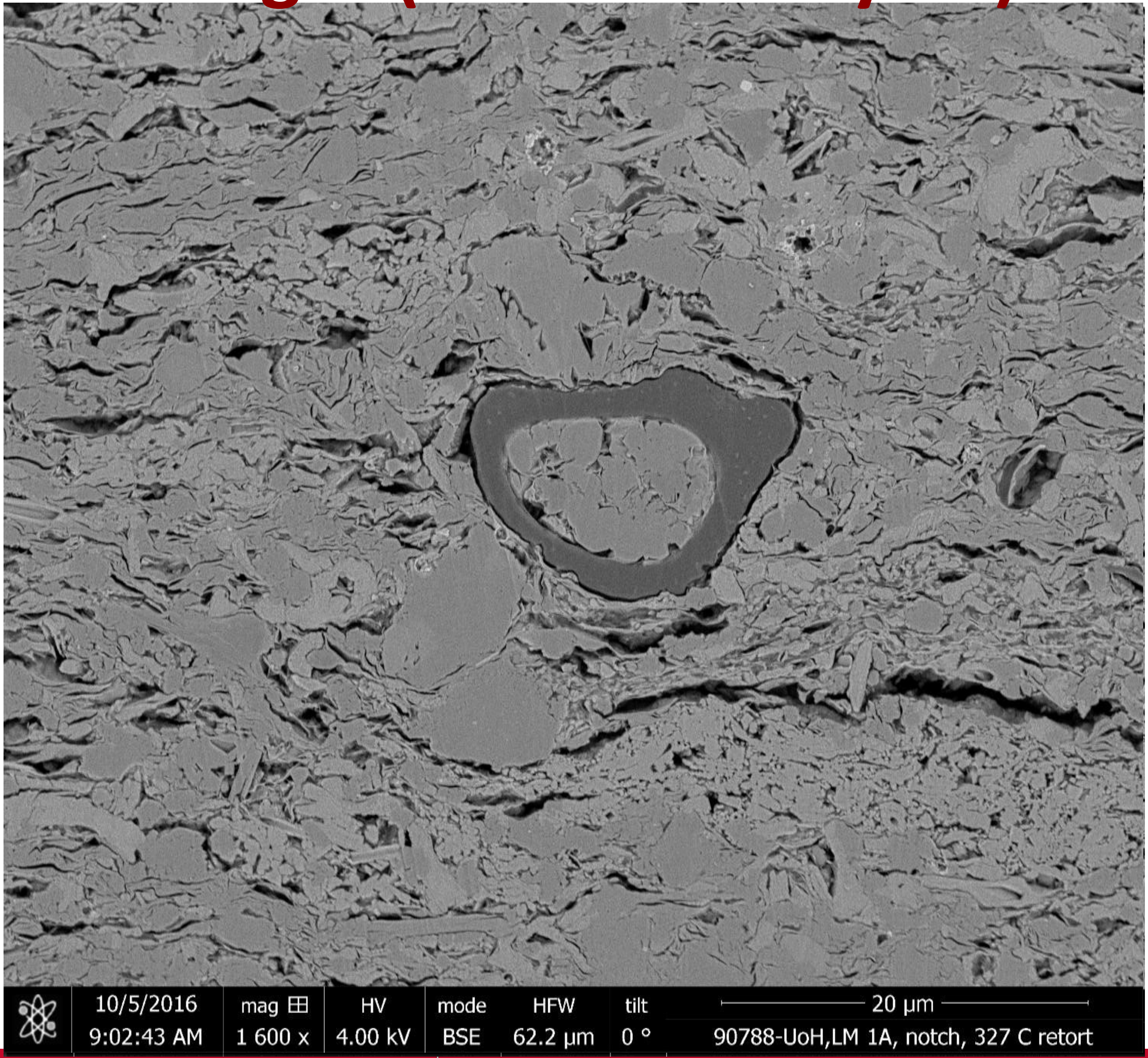
High Resolution Images (Low Maturity 1B)

Post 327^{o}C retort, note that minor early generated bitumen has been completely removed, bedding plane parallel, marine sedimentary OM (amorphous) has undergone shrinkage, and terrestrial OM has not changed.



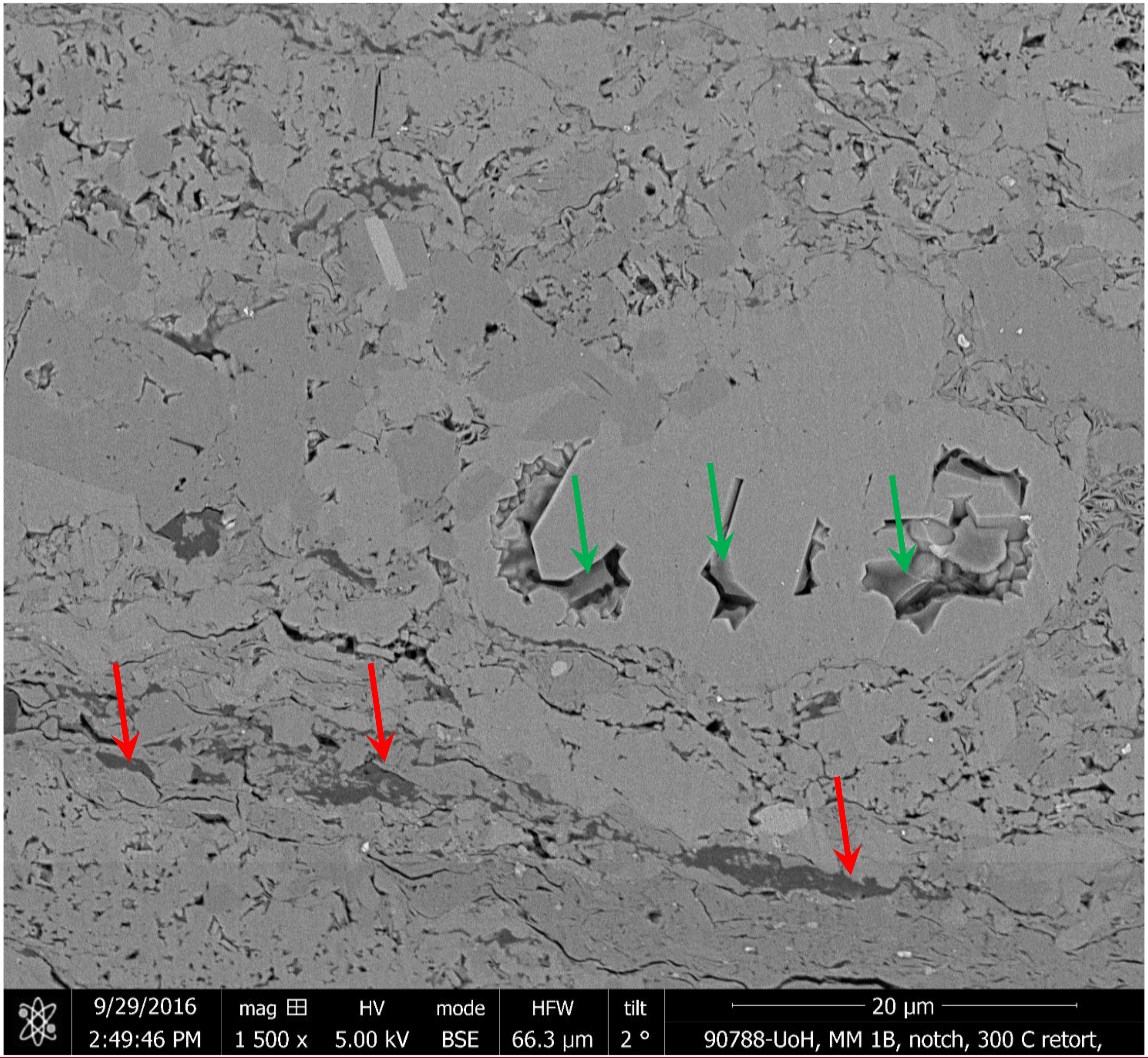
High Resolution Images (Low Maturity 1B)

Post 327°C retort, only remnant thin films of bedding plane parallel, marine sedimentary OM (amorphous) remain, together with terrestrial OM does not exhibit shrinkage.



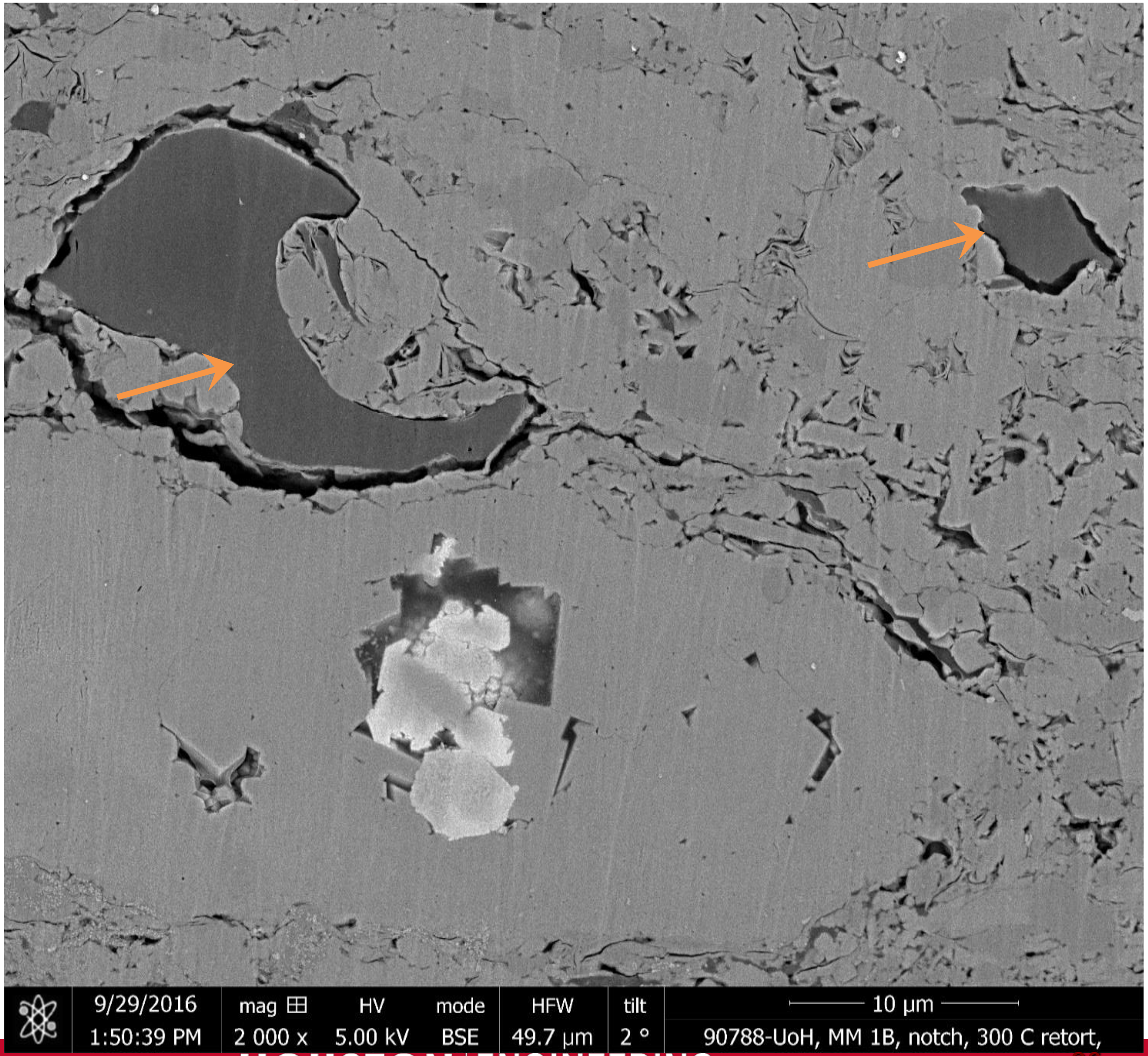
High Resolution Images (Medium Maturity 1B)

Note that pore filling bitumen (previously present in large pores in foram, green arrows) is nearly completely removed by heating to 300C. Also note that residual bedding plan parallel OM (naturally matured to Ro~0.9; red arrows) is stable to retort at 300C.



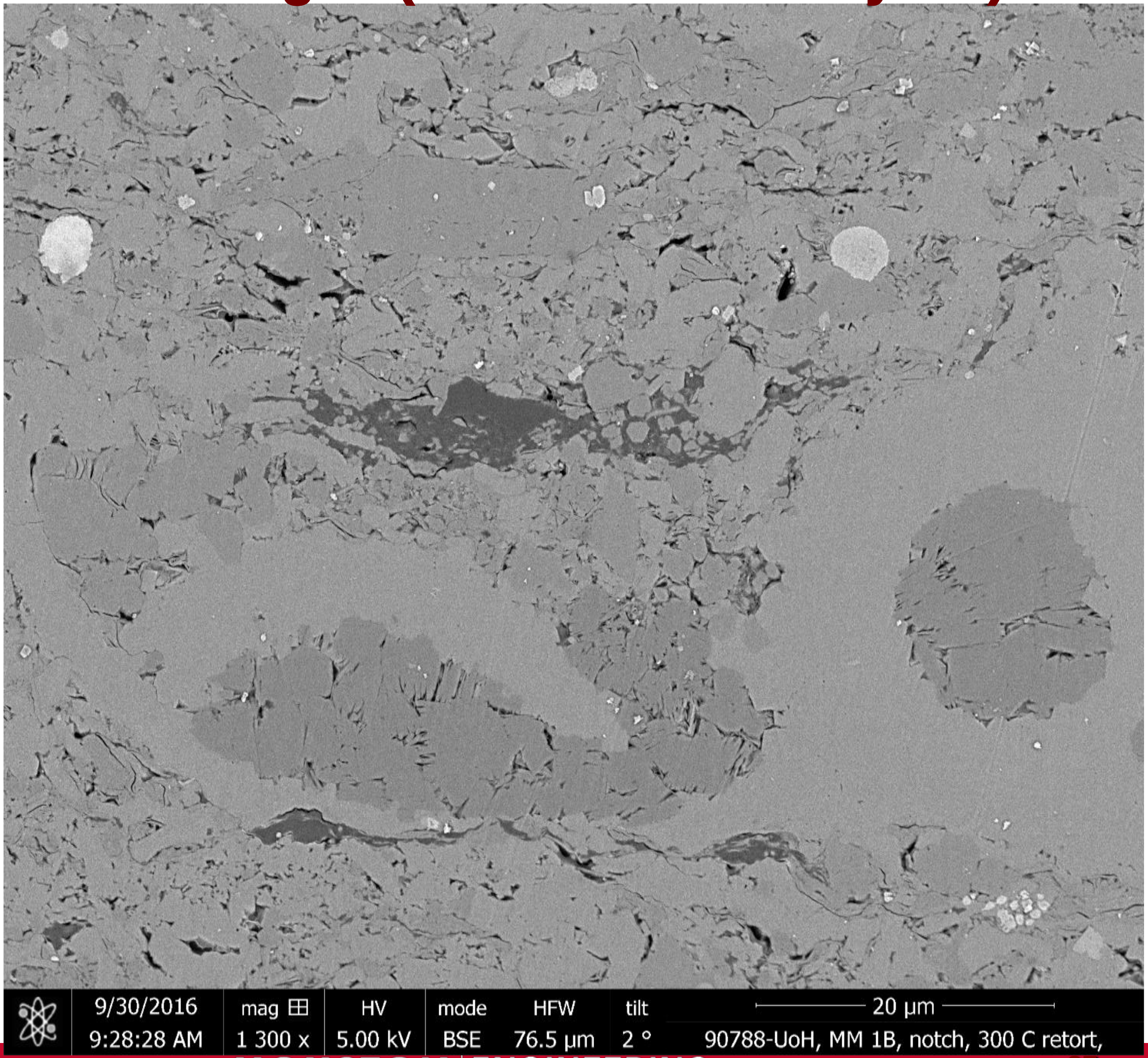
High Resolution Images (Medium Maturity 1B)

As expected terrestrial OM (orange arrows) appears to be stable during retort.



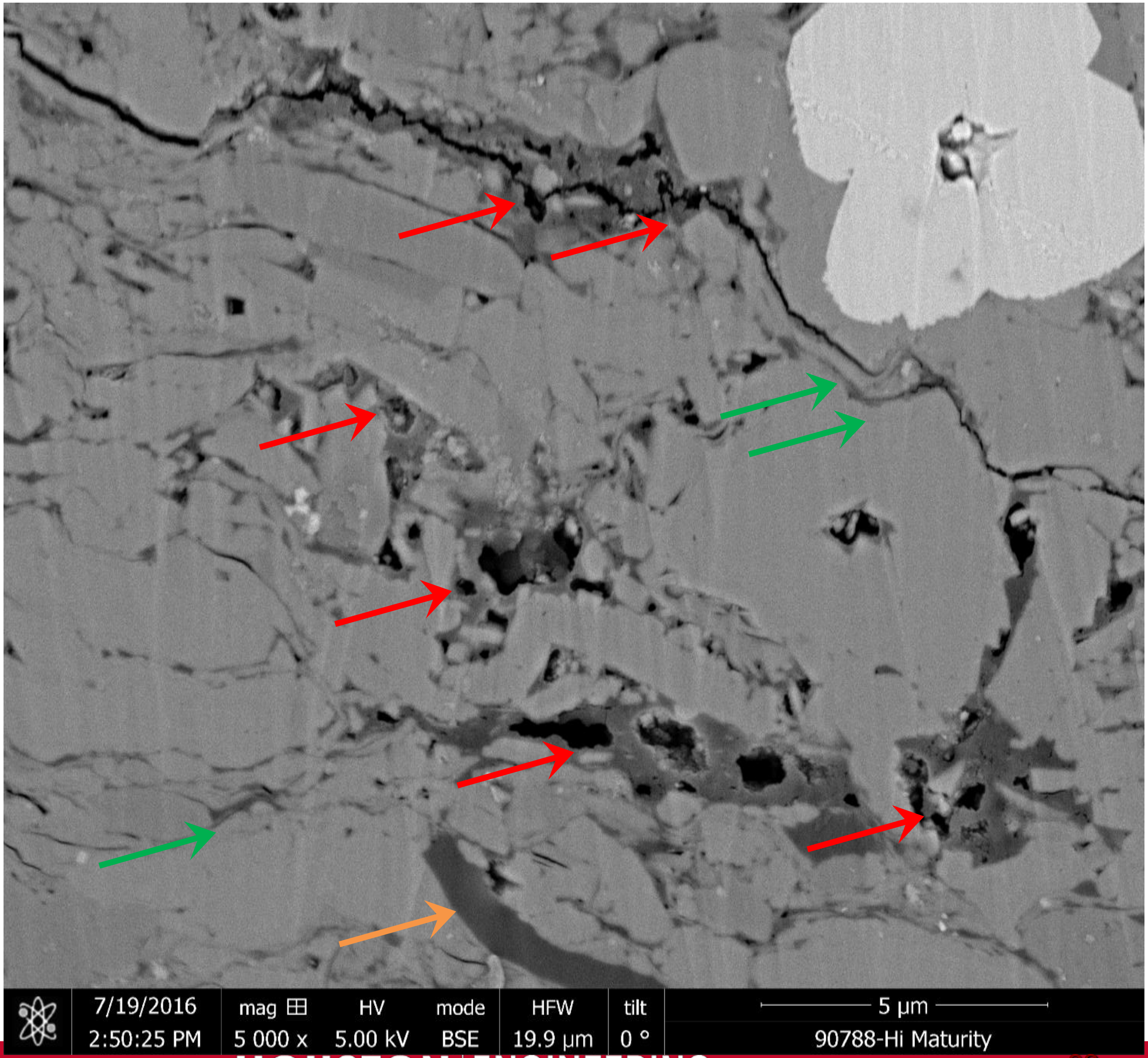
High Resolution Images (Medium Maturity 1B)

Residual marine sedimentary OM appears stable (no shrinkage observed), as does terrestrial organic material. This is in contrast to post retort images of low maturity samples showing significant shrinkage in marine sedimentary OM.

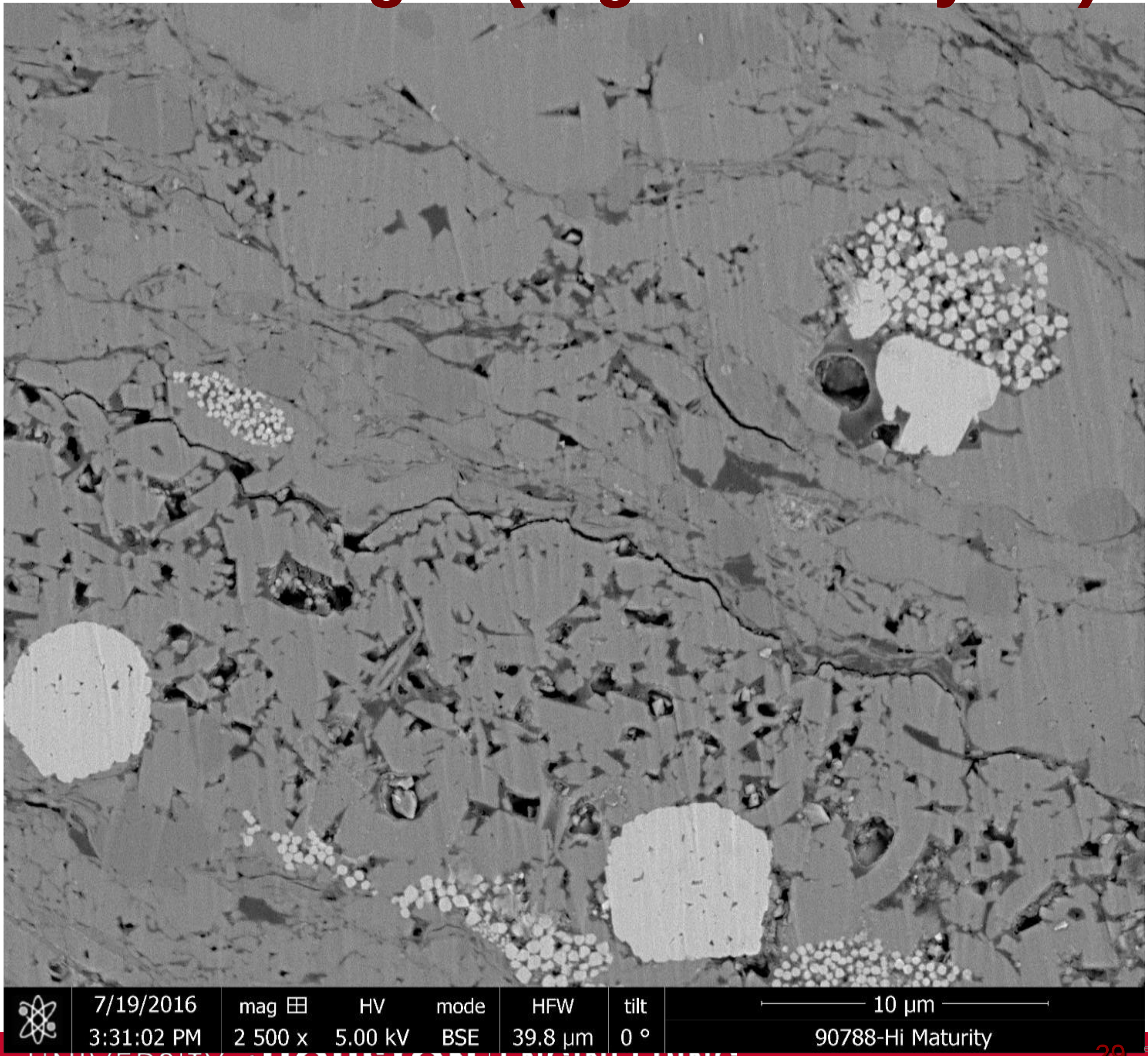


High Resolution Images (High Maturity 1B)

Note porosity developed in bitumen (pre retort; red arrows), rare remnant BPP OM (green arrows), and stable terrestrial OM (orange arrow). Common bedding plane parallel cracks with residual organic material may result from nearly complete removal of primary OM during maturation.



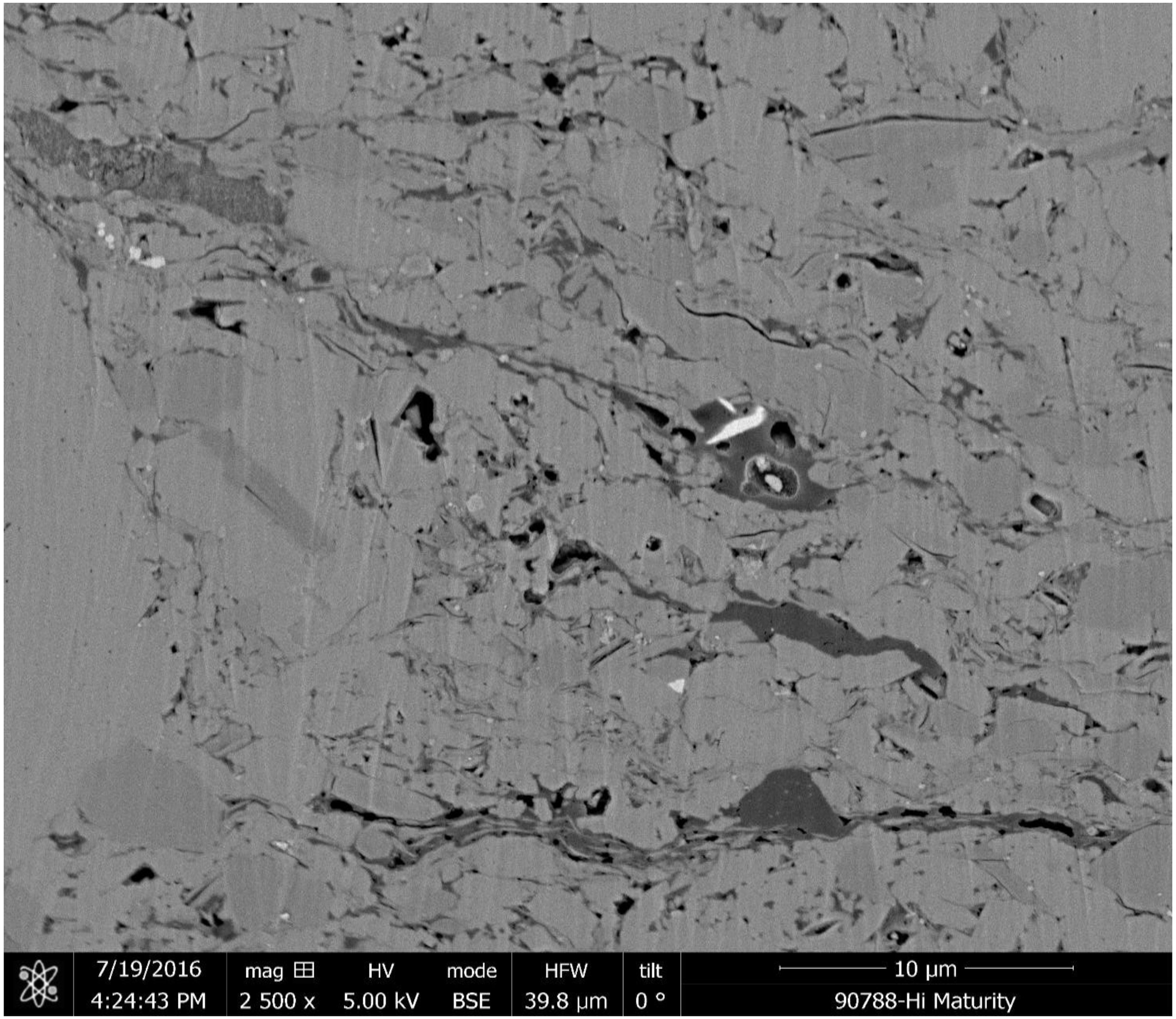
High Resolution Images (High Maturity 1B)



Bedding plane parallel cracks may provide migration pathways for generated hydrocarbons. Naturally matured OM at Ro~1.2-1.4% is stable to retort to 350C.

High Resolution Images (High Maturity 1B)

Residual pyrobitumen displays typical spherical micro- and nano-pores, whereas residual primary kerogen (both terrestrial and marine) appears non porous. Naturally matured OM at Ro~1.2-1.4% is stable to retort to 350C.

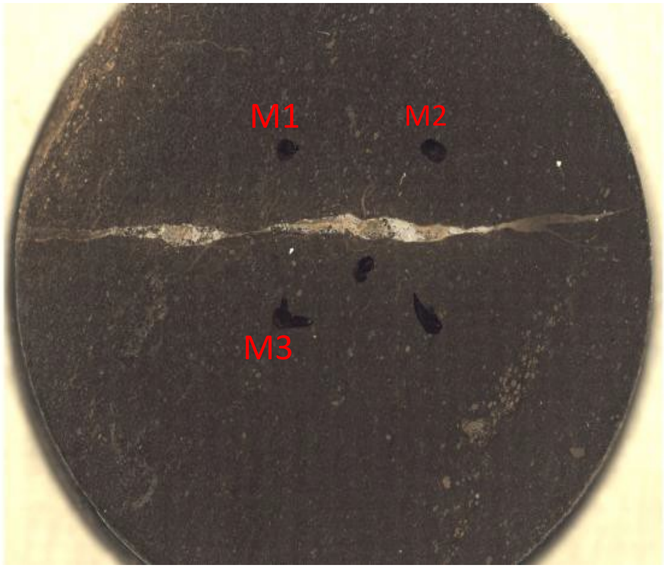


BARNETTE FORMATION

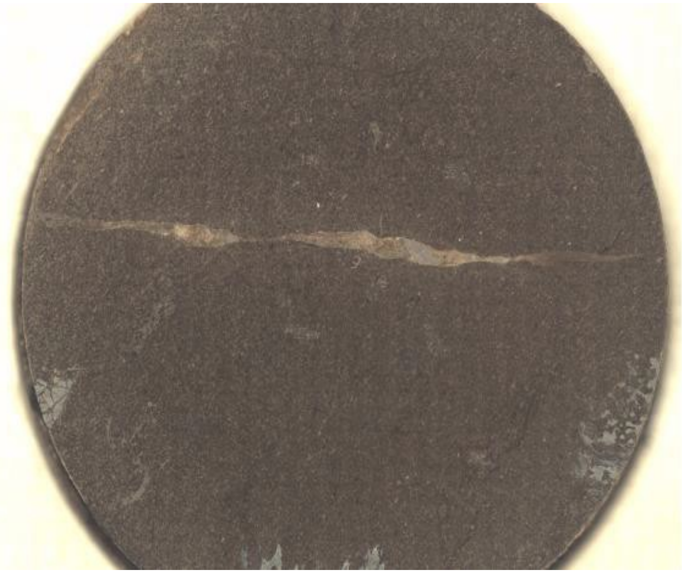
- 1” end trim
  - Argon Ion Milled
  - Marked with felt pen dots for navigation
  - Optical mosaics (100X) native state and Post retort
- Mosaics 1-5 native state and post retort,
  - Individual images

BARNETTE SAMPLES (OPTICAL MOSAICS: 100X; 1"DIA END TRIM)

- Native state



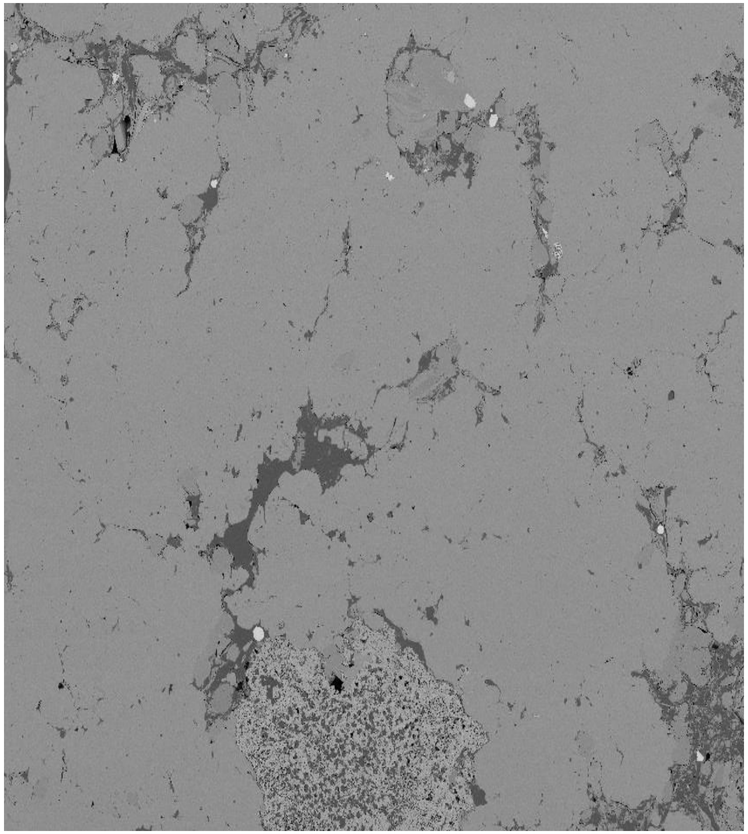
- Post 300 C retort

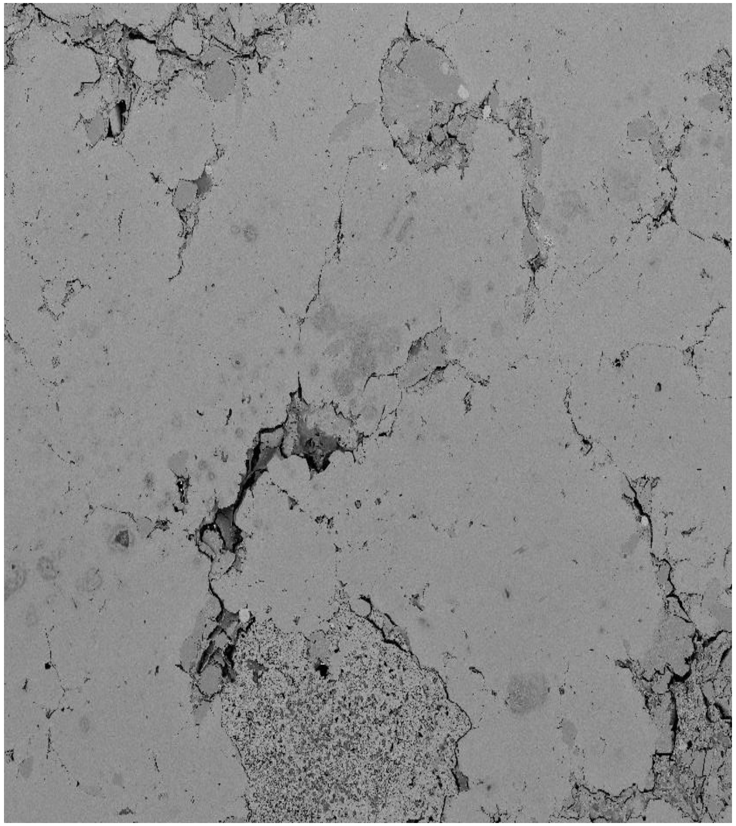


BARNETTE SAMPLE: MOSAIC

Pre and post-retort images of Barnett Formation at "middle" maturity (~0.9% Ro). Distribution and morphology of OM were used to infer that majority of OM in field of view is migrated bitumen. Nearly complete removal of OM during retort to 300C supports this inference.

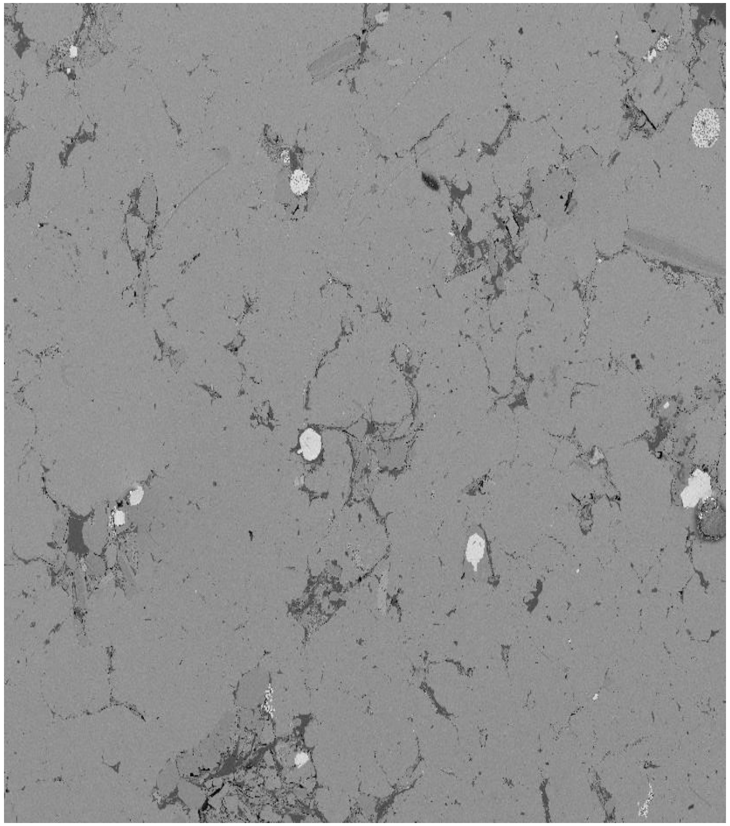
- M1 :Native state: HFW~169µ
- M1 :Post 300° C retort HFW~169µ



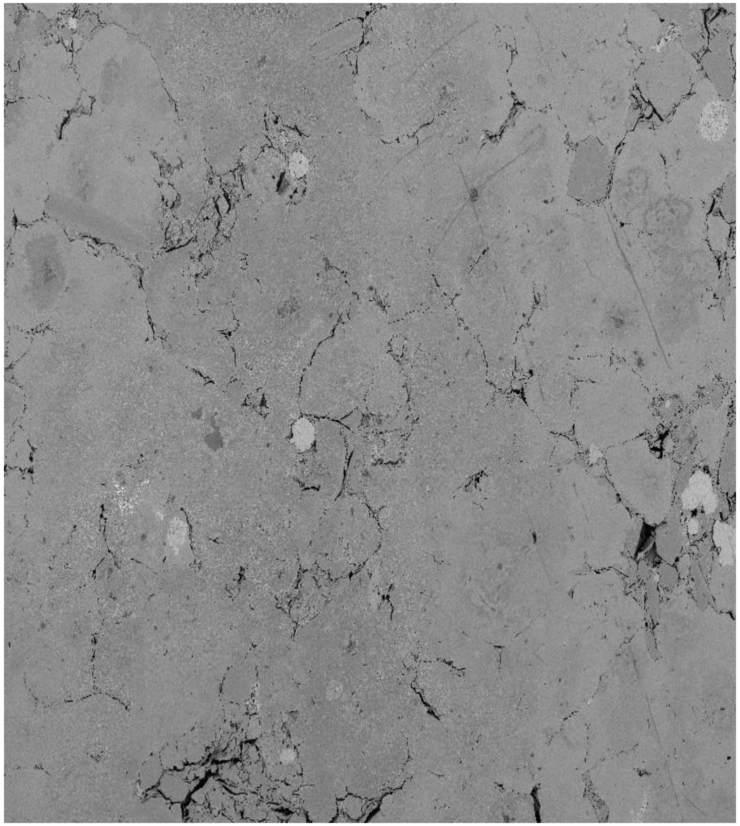


BARNETTE SAMPLE: MOSAIC

- M2: Native state: HFW~169µ

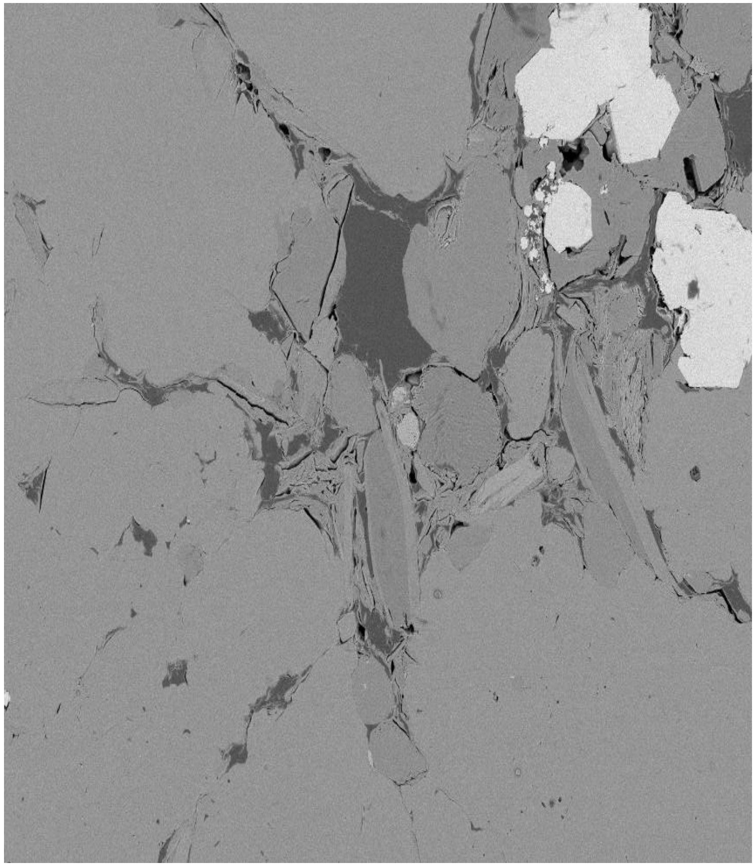


- M2: Post 300^{o}C retort :HFW~169µ

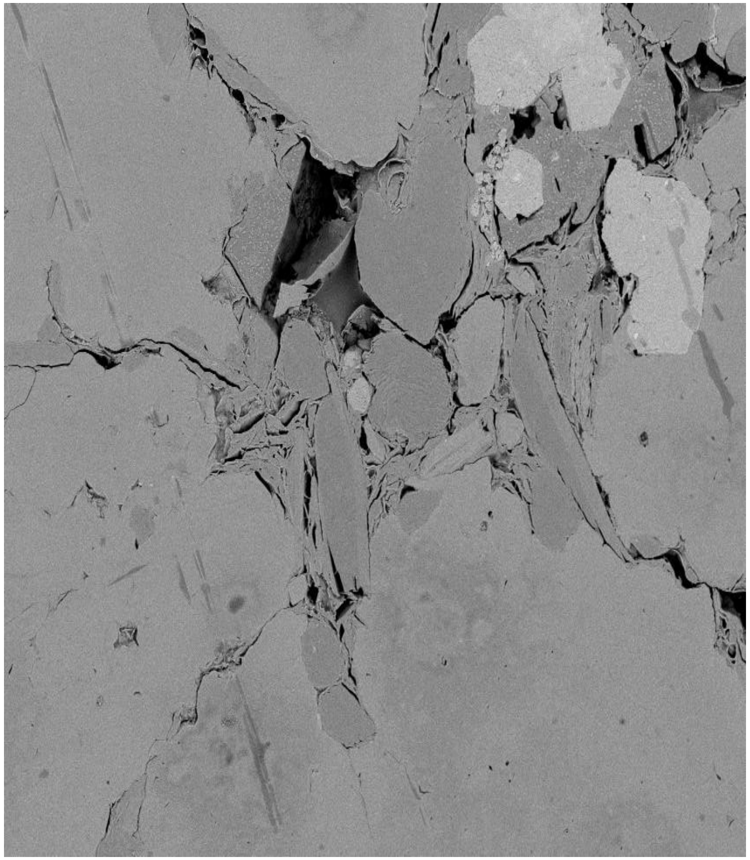


BARNETTE SAMPLE: MOSAIC

- Native state: HFW~39.8µ



- Post 300^{o}C retort : HFW~39.8µ



Conclusions

- "Conventional wisdom" holds that retort to 300C will remove any previously generated oil from organic rich reservoirs. Extraction post retort to 300C will remove bitumen.

- Our findings suggest that in low maturity samples, exhibiting only minor, early bitumen in native state samples (e.g. low maturity Eagle Ford samples in this study), retort to 300 C results in significant conversion of primary sedimentary OM.
    - This is suggested by significant reduction in observed TOC post retort, and "softening/shrinkage" exhibited by residual marine sedimentary OM.
    - Bitumen present in native state sample (migrated product occupying residual primary pores) is removed by retort to 300C, although stable during extraction experiments (in this case).

Conclusions

- Residual marine sedimentary organic material in medium maturity samples is stable during retort to 300 C.
- Medium and high maturity Eagle Ford samples exhibit common bedding plane parallel cracks with residual organic material along their length.
- These features may result from nearly complete removal of primary OM during maturation, similar to that observed in progressive retort of low maturity Eagle Ford samples.
- Bedding plane parallel cracks may provide migration pathways for generated hydrocarbons.
- Residual bitumen in high maturity Eagle Ford samples displays typical spherical micro- and nano-pores, whereas residual primary kerogen appears non porous.

Conclusions

- Mutli-modal imaging and image analysis enables upscaling of image data and places imaging studies into a broader geologic context.

- Low resolution reflected and fluorescent light imaging can be used to select rock types and regions of interest for high resolution work. When crushed material is analyzed, reflected light imaging of the intact sample can be used to place the crushed sample into the larger context. This has been more successful than low resolution SEM imaging of the 1” end trim in rapidly
identifying variations in lamina types within the samples.

- SEM imaging has been linked to high resolution reflected light imaging and Raman Spectroscopy of various organic matter types in a companion study.

Future Work

- Expand to additional reservoirs.
- Perform SEM/nano-indentation studies on existing Eagle Ford samples to estimate strength properties of organic matter types as a function of maturity.
- Acoustic microscopy of end trims prior to SEM imaging and image analysis, will allow us to measure acoustic properties of finely laminated samples at a 50 micron resolution. Acoustic properties will be linked to porosity/TOC/mineralogy of individual lamina as a function of thermal maturity.

QUESTIONS??