Microstructural Analysis of the Transformation of Organic Matter During Artificial Thermal Maturation*

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Search and Discovery Article #42241 (2018)**
Posted July 30, 2018

*Adapted from oral presentation given at 2018 AAPG Annual Convention & Exhibition, Salt Lake City, Utah, May 20-23, 2018
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Abstract

A dynamic heating experiment using a field-emission environmental scanning electron microscope (FE-ESEM) equipped with a heating stage was designed to observe microstructural changes in a variety of organic macerals identified by optical organic petrology. The same region of interest was compared before and after heating by employing correlative optical and electron microscopy. An Ar-ion milled surface was prepared from a thermally immature (0.50 %Ro vitrinite reflectance), organic-rich (5-7 wt% TOC) outcrop sample of the Boquillas (Eagle Ford) Formation. A variety of organic macerals were identified by standard optical organic petrography including: (1) structured particles of vitrinite, inertinite, liptinite, and organo-mineral aggregates, 2) diffuse amorphous organic matter, and (3) solid bitumen.

The sample was heated in the FE-ESEM to 500°C at a rate of 1°C/min with a constant 2.0 Torr (266 Pa) vapor pressure. Static and video secondary electron images were captured using a heat compatible gaseous detector at 30 kV accelerating voltage. High resolution backscattered FE-SEM mosaics were also prepared before and after heating. The results of the experiment revealed that the alginitic macerals were the most altered by heating with elongate voids created presumably due to the transformation of kerogen to petroleum. Volumetric changes were also observed in solid bitumen and amorphous organic matter. As anticipated, no detectable changes were observed in the inertinite and gas-prone vitrinite macerals. The voids created within the alginitic macerals are atypical of the commonly observed organic pores in natural thermally mature subsurface samples. The slot-like voids associated with the alginitic macerals are thought to be unlikely preserved at reservoir conditions due to closure at overburden pressure. The processes governing the development of organic matter porosity remains poorly understood because the type of organic matter pores typically observed in organic-rich mudstone reservoirs have yet to be duplicated in the laboratory by the various artificial thermal maturation experiments published to date.
References Cited

https://www.youtube.com/watch?v=lISNwF5tMXM


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Outline

• Introduction
  – Previous studies
  – Study objectives

• Samples & Methodology
  – Optical organic petrology
  – FE-SEM characterization
  – Heating stage environmental SEM

• Results
  – Comparison before & after heating

• Conclusions
Introduction

- The *chemical* transformation of organic matter to oil & gas during heating is well understood from laboratory pyrolysis experiments.

- The *physical* changes of organic matter during thermal maturation are poorly understood:
  - including the development of pores in organic matter observed in unconventional shale (mudstone) reservoirs.
Research Questions

• What physical changes occur during transformation of kerogen to hydrocarbons?
  – Organic matter, rock, organic-mineral interactions?

• In what types of organic matter (macerals) do pores develop?

• What temperature do organic matter pores form?

• How do these changes correlate to pyrolysis (RockEval)?
  – S1, S2, S3, Tmax, etc.
Natural Porous Organic Matter (SEM)

Nanometer-scale pores (black) commonly observed in thermally mature shale reservoirs.
Previous Studies

- Dahl et al., 2015 demonstrated SEM images could be captured during artificial thermal maturation using an environmental SEM equipped with a heating stage element
  - Same sample, 25 °C/min to 550 °C (10 wt% TOC)
- Ko et al., 2016 compared SEM images of unheated samples with samples heating by gold-tube anhydrous pyrolysis
  - Different samples, constant temp 130-425 °C, 72 hrs (1.6 wt% TOC)
- Hooghan et al., 2017 compared the same sample before and after low temperature pyrolysis
  - 300-350 °C at 15 hrs, VR 0.5-1.2 %Ro
Study Objectives

- Observe the evolution of microstructural changes of a variety of types of organic matter (macerals) during heating of a thermally immature shale reservoir (Eagle Ford)
- Heating stage environmental SEM
  - Same sample
  - Same region of interest
  - Same macerals
  - Before, during, and after heating
Methodology

• Immature outcrop sample (VR 0.5 %Ro)
  – 1 in (25 mm) polished plug (Ar-ion mill)
  – XRD & geochemical analyses

• Maceral identification
  – Standard optical petrography (white & UV light)
  – ROI’s identified & optical image mosaics prepared

• SEM examination before, during, & after heating
  – 3 mm x 1.4 mm micro plug over ROI
  – Environmental SEM GSED
  – FE-SEM BSE image mosaics
Sample Analysis

SEM & EDX
3 mm x 1.4 mm micro plug

Optical Organic Petrology
25 mm diameter Ar-ion mill

XRD, TOC & Pyrolysis
25 mm diameter core plug

TOC: 5.2 wt%  HI: 603 mg HC/g TOC  VR: 0.50 %Ro  S2: 35.5 mg HC/g rock

Texas  Maverick Basin  Mexico

Eagle Ford Outcrop

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Organic Matter

- **Maceral** - microscopically identifiable organic component in sedimentary rocks
- **Liptinite** - (oil prone, type I, II kerogen)
- **Vitrinite** - (gas prone, type III kerogen)
- **Inertinite** - (non-generative, type IV kerogen)
- **Amorphous organic matter (AOM)** - unstructured macerals
- **Solid Bitumen** - secondary, void-filling AOM
Optical Organic Petrology

Polished Plug

Optical Mosaic

White Light

UV Light

100 µm

Alginite

Organomineral Aggregate

Matrix AOM

Foram w/ Bitumen

Alginite

Organomineral Aggregate

Foram w/ Bitumen

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Identified Macerals

- **Amorphous organic matter**
  - Dull fluorescent & micronized

- **Liptinite**
  - Lamalginate & telalginite

- **Vitrinite**

- **Inertinite**
  - Fusinite & semifusinite

- **Organo-mineral aggregate**

- **Solid bitumen**
  - foraminifera chamber fill
  - scattered lenses

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Comparative Microscopy

Reflected White Light

Arrows cut into sample for registration marks to aid in locating AOI between SEM microscopes

Backscattered Electron SEM

alginate

alginate
Heating Stage ESEM

- Sample heated 200-500 °C at 1 °C/min (5 hrs)
  - Constant vapor pressure (266 Pa)
- Static SE images captured every 10 °C
  - Gaseous SE detector, 30 kV
- Video images recorded throughout experiment
Time Lapse SE Imaging

Increasing electron charging with time noted along edge of alginate (white rim)

Presumably reflects kerogen transformation to oil
Results

Post Heating BSE Image Mosaic

- liptinite (alginate)
- organo-mineral aggregate
- AOM
- solid bitumen

Scale: 50 µm
Liptinite (Alginite)

Before

After

Residual optical oil

40 µm
Liptinite (Alginitite)

Before

After

void (generated oil)

residual alginate

partially converted kerogen?

alginitite

crack (artifact)

10 µm

10 µm
O-M Aggregate

Before

After

no apparent change
Matrix AOM

Before

- coccolith fragments & mineral grains
- AOM
- pyrite

10 µm

After

- coccolith fragments & mineral grains
- no apparent change
- pyrite

10 µm
Matrix AOM

Before

After

coccolith fragments & mineral grains

AOM

15 μm

coccolith fragments & mineral grains

AOM

cracks & voids developed

15 μm
Solid Bitumen

Before

- Residual optical oil
- foraminifera
- SB

15 µm

After

- foraminifera
- void
- SB
- crack
- mineral exposed

15 µm
Conclusions

- Most significant changes observed in oil prone macerals liptinite (alginate) & AOM, and secondary solid bitumen
  - Solid organic matter presumably transformed to oil
- No significant changes observed in gas prone and inert macerals vitrinite & inertinite as anticipated
- SEM gray scale contrast observed in artificially matured alginate may reflect compositional changes during the transformation of kerogen to oil
Final Thought

Heating experiments to date have produced relatively large kerogen moldic pores and cracks, but have failed to replicate natural organic matter pores observed in shale reservoirs.
Acknowledgements

• Organic Petrology: Wayne Knowles
• Geochemistry: Tim Ruble
• SEM Imagery: Kultaransingh (“Bobby”) Hooghan
• Heating Stage ESEM: Ken Mossman (ASU)