# [PS]Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation*

**Lucy (Ting-Wei) Ko[1,2], Tongwei Zhang[1], Robert G. Loucks[1], Stephen C. Ruppel[1], Deyong Shao[3]**

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## Abstract

It is now well known that pore development in organic-rich mudrocks is associated with organic matter (OM) thermal maturation. Organic-rich mudrocks usually contain mixed types of kerogen. Therefore, routinely used vitrinite reflectance measurements cannot define exact OM transformation stages. Understanding the evolution of OM-hosted pores and mineral pores to well-defined oil and gas generation stage is essential to characterize mudrock reservoirs. Immature Barnett (quartz and clay mineral-rich), Woodford chert and mudstone (quartz and clay mineral-rich), and low-maturity Boquillas (carbonate-rich) core and outcrop samples were heated anhydrously in gold tubes to study the evolution of OM and OM pores during maturation. Geochemical characterization such as oil and gas yields, Rock-Eval, and Leco TOC analyses were used to characterize kerogen type and OM transformation stages. Samples were also prepared using Ar-ion milling to investigate pore development with field-emission scanning electron microscopy (FE-SEM). The OM in these immature and low-maturity mudrocks can be dominantly kerogen (Barnett) or bitumen (Boquillas) or a mixture. The difference between kerogen (insoluble, in-situ OM) and bitumen (soluble migrated OM) did not affect much of the pore evolution, even though theoretically kerogen contains more inert (dead) carbon than bitumen. In all samples, modified mineral pores are dominant during bitumen and oil generation, while during gas generation, nm-sized equant OM-hosted pores are dominant. The nanometer-sized equant OM-hosted pores observed during wet gas and dry gas window are interpreted to be related to gas generation. In the Barnett and Woodford mudstone, as maturation begins, OM first shrinks, forming artificial shrinkage pores. Later, the volume of OM significantly decreases. These pores continue to develop into the gas generation stage.

# Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation

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TEXAS Geosciences
The University of Texas at Austin
Jackson School of Geosciences

Mudrock Systems Research Laboratory MSRL

Bureau of Economic Geology

## Problem Statement and Objectives

It is well accepted that organic matter (OM) pores in mudrocks are predominantly formed by thermal maturation. We have demonstrated that the change of size and shape of OM pore is related to stepwise transformation of organic matter and can be associated with generated pre-oil bitumen, oil, gas, post-oil bitumen (pyrobitumen), char, and irreducible formation water by combined geochemical characterization, laboratory pyrolysis, and SEM petrography methods (Ko et al., 2014).

In this study, we investigate and compare the effects of bulk mineralogy, total organic content (TOC), and initial organic matter type (kerogen vs. bitumen) on the evolution of OM pores and mineral pores in mudrocks.

Immature Barnett siliceous mudrock (clay mineral-rich), Woodford chert and siliceous mudrock, and low-maturity Boquillas calcareous mudrock samples were artificially matured. OM pore evolution in each was investigated and compared.

**Specific research questions include:**

**1. Do differences in kerogen type affect OM pore development and evolution?**
**2. Does bulk mineralogy affect timing of OM transformation and thus pore evolution?**
**3. Does Woodford chert or mudstone develop better porosity?**
**4. Does pore evolution differ in kerogen and bitumen?**

## Flow Chart of Research Objectives

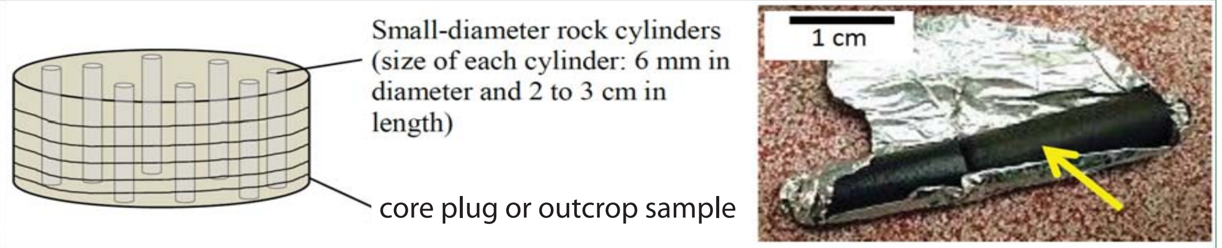
gaseous, liquid, and solid geochemical characterization → oil and gas generation stages

$N_2$ adsorption, SEM pore imaging for pore characterization (Zhang et al. 2014) → pore type, structure, distribution and PSD

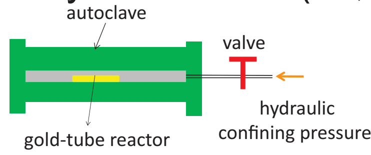
oil and gas generation stages ↔ pore evolution in OM thermal maturation ↔ pore type, structure, distribution and PSD

## Methods

1. Immature or low-maturity Barnett, Eagle Ford-equivalent Boquillas, and Woodford mudrocks were collected from cores and outcrops. For each sample, 8 small-diameter rock cylinders (6 mm diameter and 2-3 cm length) were drilled perpendicular to bedding planes.




2. The cylinders were pyrolyzed in sealed gold tubes that were placed in stainless steel autoclaves.
3. The pyrolysis experiments were conducted under isothermal conditions at temperatures of 130, 300, 310, 333, 367, 400, and 425°C for 72 hrs reaction time. A constant confining pressure was maintained at approximately 68.85 MPa (10,000 psi) during experiments.

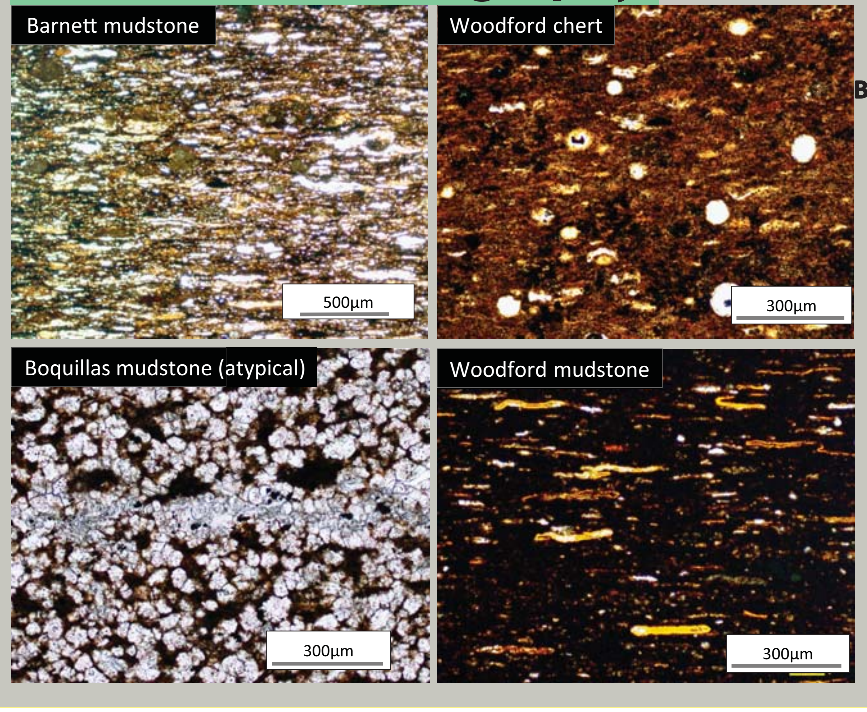



4. All generated petroleum (gas, liquid, and solid) were collected for compositional analyses. HC yield was determined by gas chromatography (GC). Saturate, aromatic, resins, and asphaltene (SARA) separation and quantification were done on each sample.
5. A flat surface was prepared by Ar-ion beam milling from post-pyrolysis rock cylinders (without solvent extraction) for SEM analysis. A FE-SEM was used to image pores and their association with OM and mineral grains.
6. The remaining sample was pulverized and analyzed for Rock-Eval and Leco TOC.

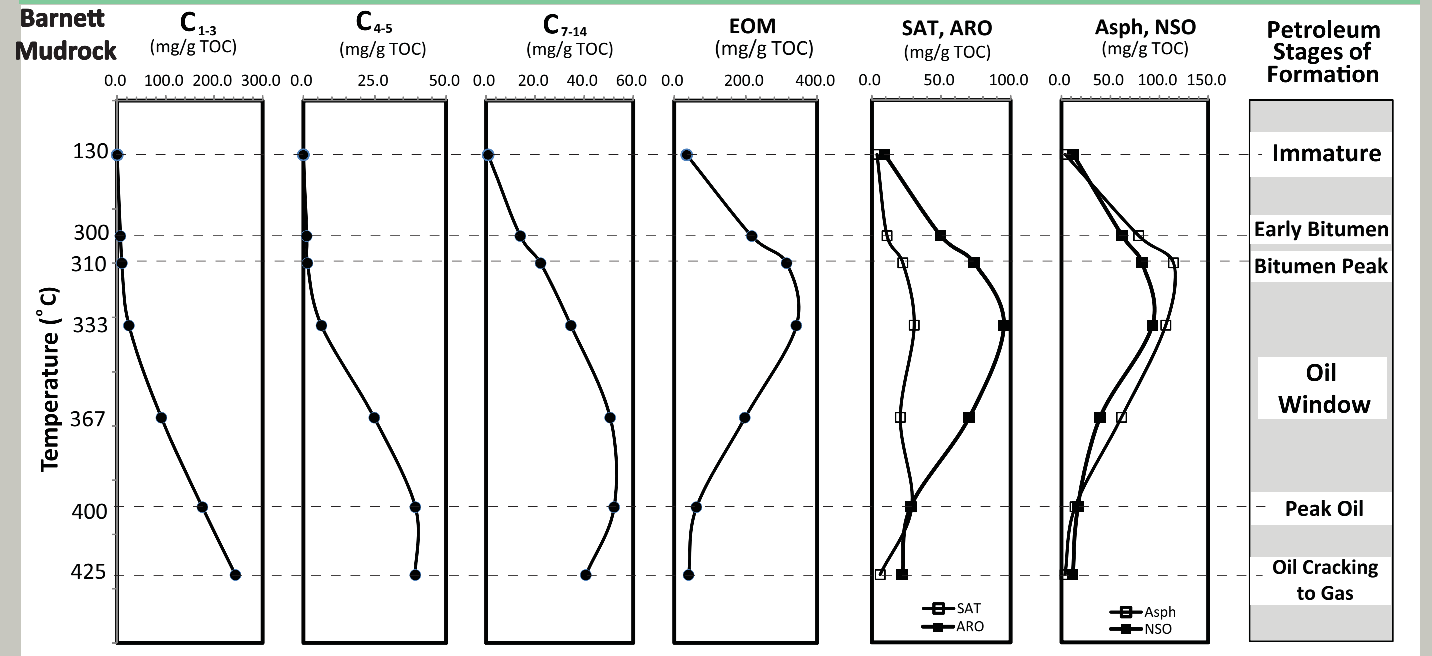
## Immature or Low-maturity Mudrock Properties

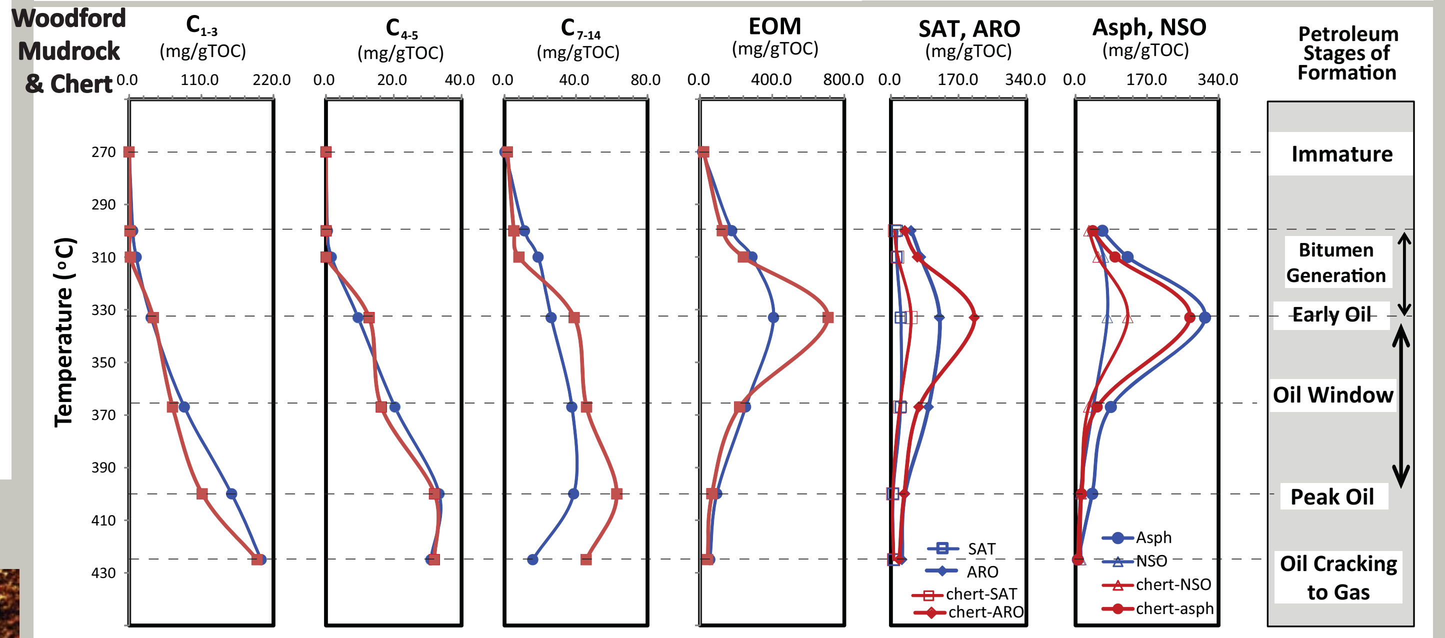
| Immature or low-maturity sample | Woodford chert | Woodford mudstone | Barnett mudstone | Boquillas mudstone |
|---|---|---|---|---|
| % carbonate | 3.33 | 4.25 | 11.43 | 89.61 |
| Leco TOC (wt %) | 6.20 | 16.7 | 9.70 | 1.48 |
| Rock-Eval $S_1$ (mg/gTOC) | 0.88 | 1.91 | 1.14 | 0.77 |
| Rock-Eval $S_2$ (mg/gTOC) | 37.69 | 90.56 | 53.72 | 9.53 |
| Rock-Eval Tmax (°C) | 432 | 425 | 420 | 437 |
| Calculated Ro (%) | 0.60 | 0.49 | 0.42 | 0.70 |
| Hydrogen Index (HI) | 610 | 542 | 554 | 644 |
| Oxygen Index (OI) | 6 | 4 | 15 | 30 |

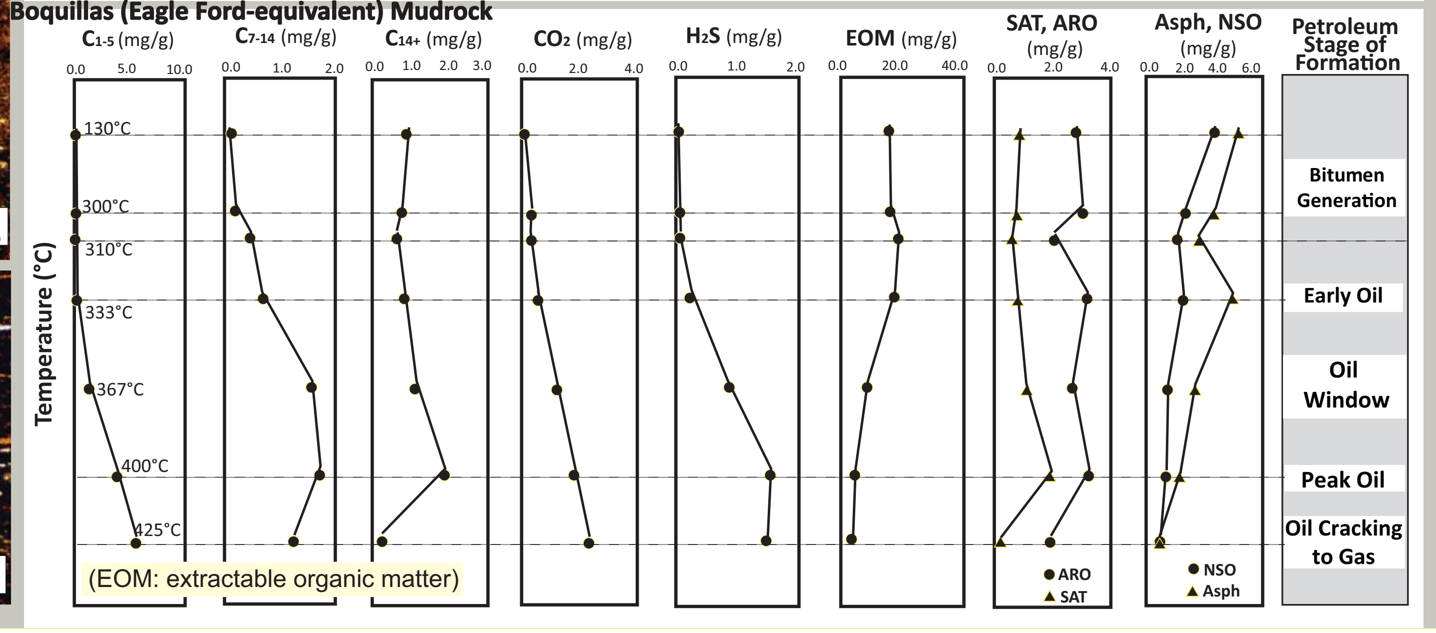
## Thin-section Petrography




## Geochemical Characterization of Generated Components




(EOM: extractable organic matter)

# Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation

## Types and Evolution of OM Pores and Mineral Pores

### Kerogen (solid) --> Bitumen (liquid) --> Oil (liquid)

**Organic matter (OM)**: a general term referring to any liquid or solid materials enriched in organic carbon. OM can have many forms, only some of which generate HCs and host pores.

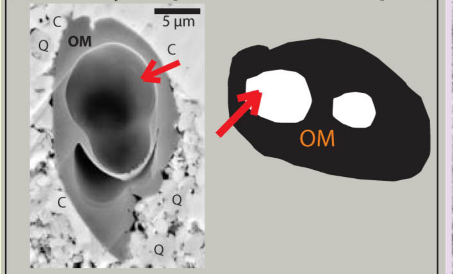
**Kerogen**: insoluble solid organic geopolymer. Kerogen can form pores by maturation and the pores are voids left behind by HCs that were generated and expelled or were original pores associated with plant material. Kerogen can contain (A) ***primary OM pores*** and (B) ***convoluted-OM pores***. The primary OM pores are present before any diagenesis begins.

**Bitumen**: soluble, viscous, liquid OM, from thermal cracking of kerogen under immature or low-maturity conditions. It can have a wide range of viscosities. This term is equivalent to "pre-oil bitumen" used by Curiale (1986) and Mastalerz and Glikson (2000). Bitumen is liquid and ***cannot host pores over long periods of time***.

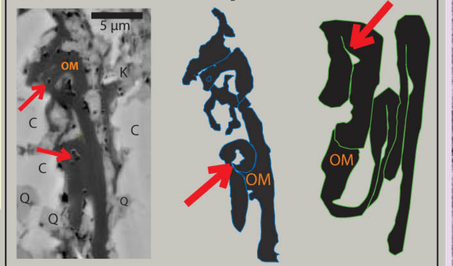
Q: quartz; C: calcite; OM: organic matter; K: kaolinite

Types of OM pore

(A) Primary OM pore (Inherited OM pore)



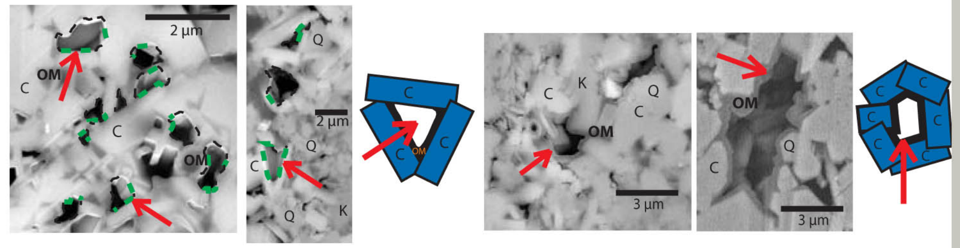

(B) Convoluted-OM pore




### Modified Mineral Pores (with Relic OM)

(A) Combination Mineral/OM pore

(B) Retention pore

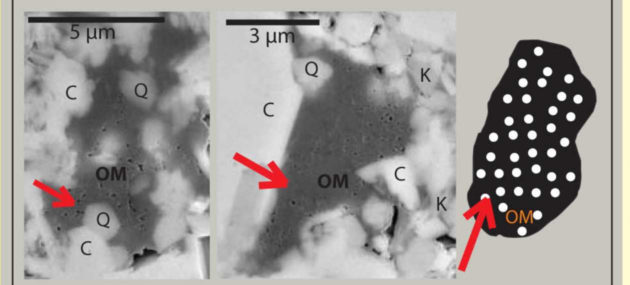



**Solid/solidified bitumen**: very viscous, difficult to dissolve in organic solvent, also equivalent to "pre-oil bitumen" but solidified in the subsurface, able to form ***combination OM/mineral pores***.

**Residual/retained oil**: the "liquid oil in subsurface but is solid or highly viscous at surface conditions resulted from expulsion of volatiles on the way up the wellbore and/or during handling and storage" (Bohacs et al., 2013), able to form ***retention pores***.

Types of OM pore

(C) Nanometer-sized OM spongy pore



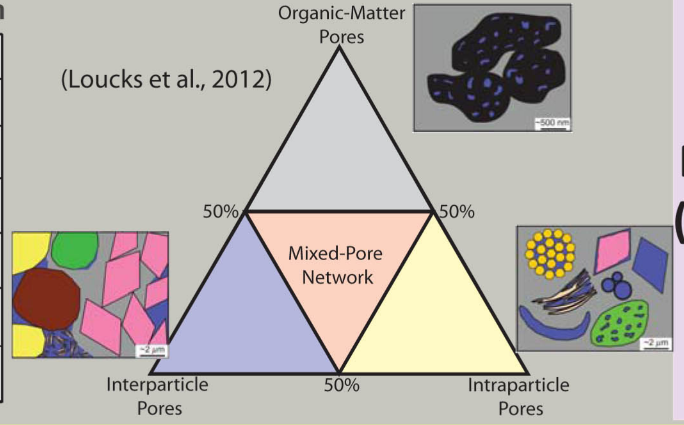

**Pyrobitumen**: secondary product from bitumen. Pyrobitumen consists of insoluble, nonvolatile, solid HC residues that "still retain some hydrocarbon generation capacity upon further heating" and can host pores (Bohacs et al., 2013). This term is equivalent to "post-oil bitumen" used by Mastalerz and Glikson (2000). Bernard et al. (2012) suggested pyrobitumen hosts (C) ***nanometer-sized spongy OM pores***.

**Char**: the "ultimate residue of HC generation with minimal H content and essentially no remaining potential for generating HCs, derived from further heating of pyrobitumen and bitumen." Char can also host (C) ***nanometer-sized spongy OM pores***.

### Summary of pore evolution associated with generated petroleum

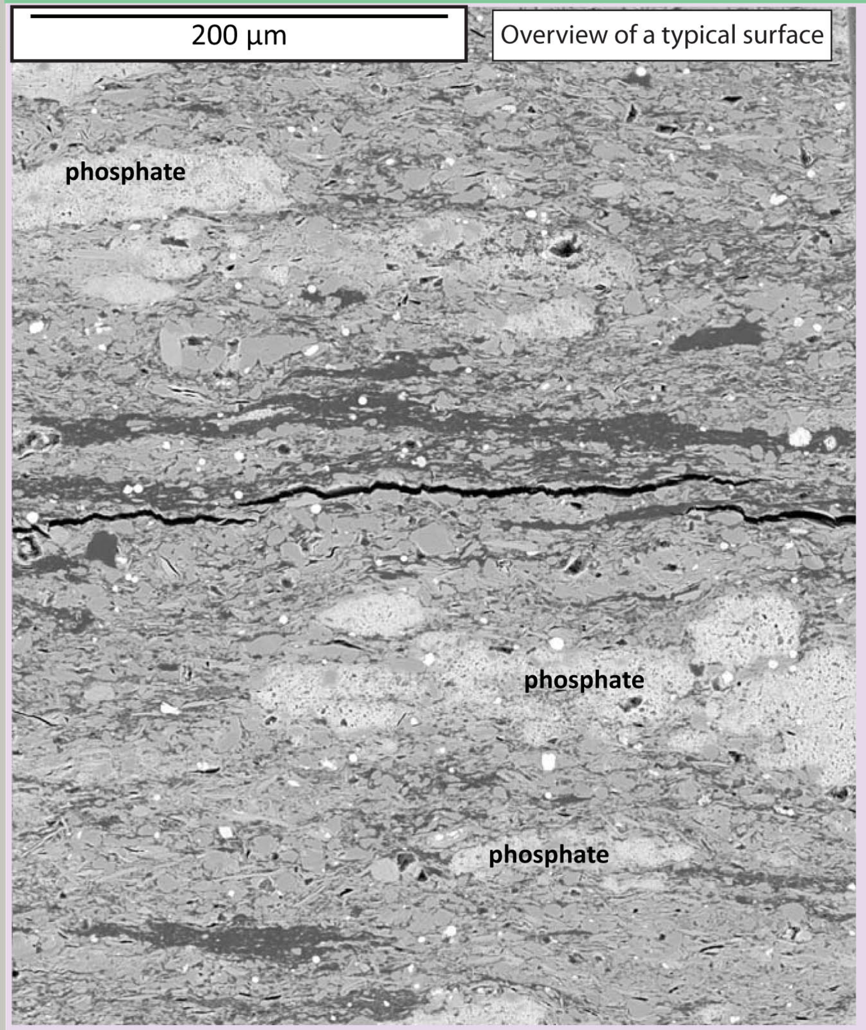
| HC generation stages | Chemical composition | | | | | | Pore type and pore evolution | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | NSO | SAT | ARO | $CO_2$ organic acid | $C_1$-$C_5$ | Pyro-bitumen | Most abundant pore type | 2nd abundant pore type | OM Pores | Mineral Pores |
| Bitumen | | | | | | | Modified mineral pore | Primary mineral pore | | |
| Early oil | | | | | | | Modified mineral pore | Primary mineral pore | | |
| Oil window | | | | | | | Modified mineral pore | nm-sized spongy OM pores | | |
| Peak oil | | | | | | | Modified mineral pore | nm-sized spongy OM pores | | |
| Early gas window | | | | | | | nm-sized spongy OM pores | Modified mineral pore | | |

(Loucks et al., 2012)

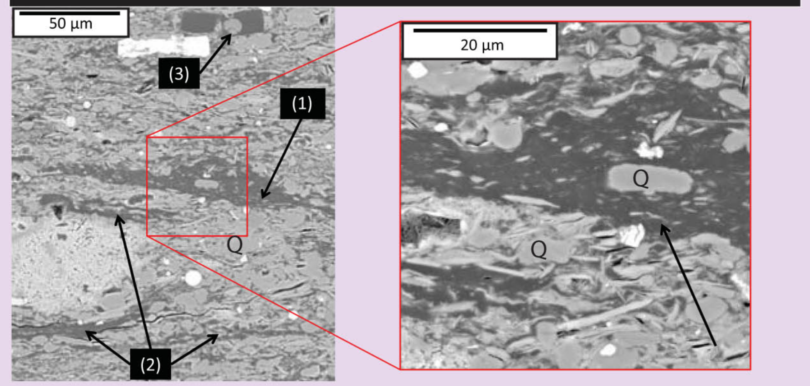



## Barnett Mudstone: Pore Types and Pore Evolution

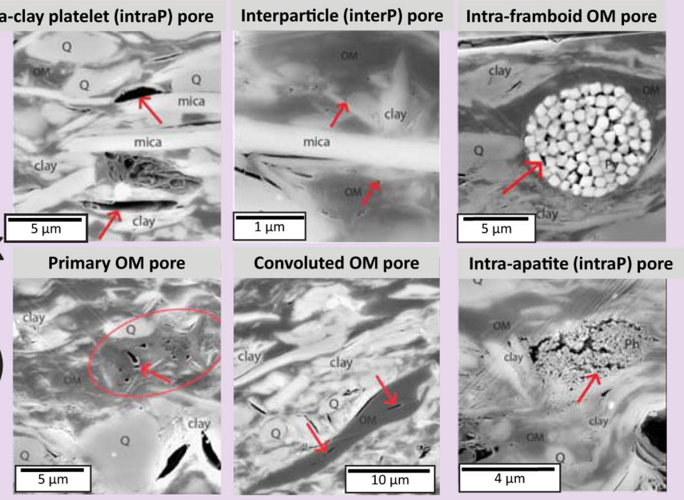
Overview of a typical surface



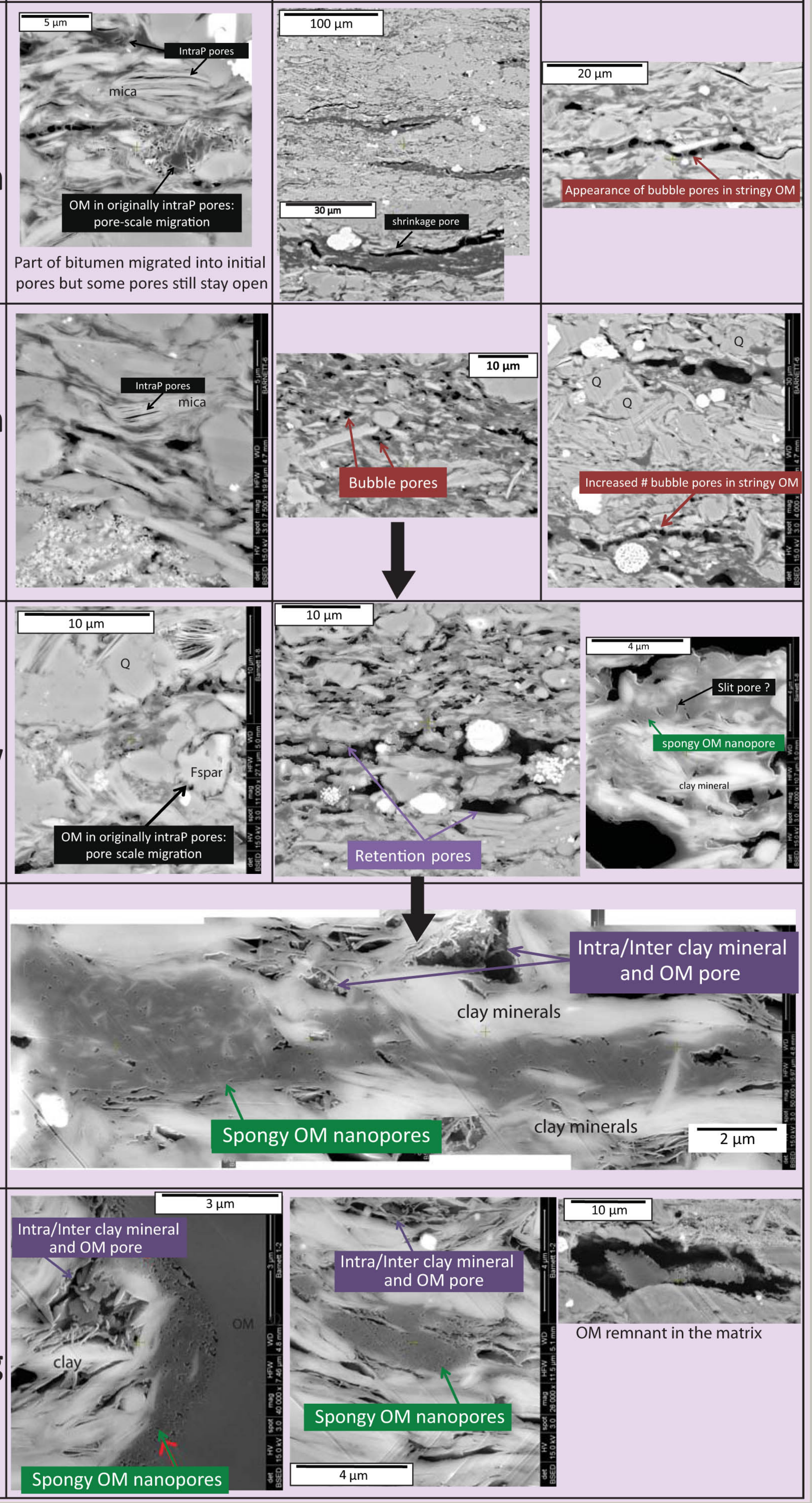

Types of OM in the Barnett Mudstone (photos below):
(1) OM-mineral admixtures: most commonly observed
(2) Stringy/flaky OM
(3) Brittle, structural, particulate OM (terrestrial kerogen)




Initial Pore Network (Ro = 0.4 to 0.5%)

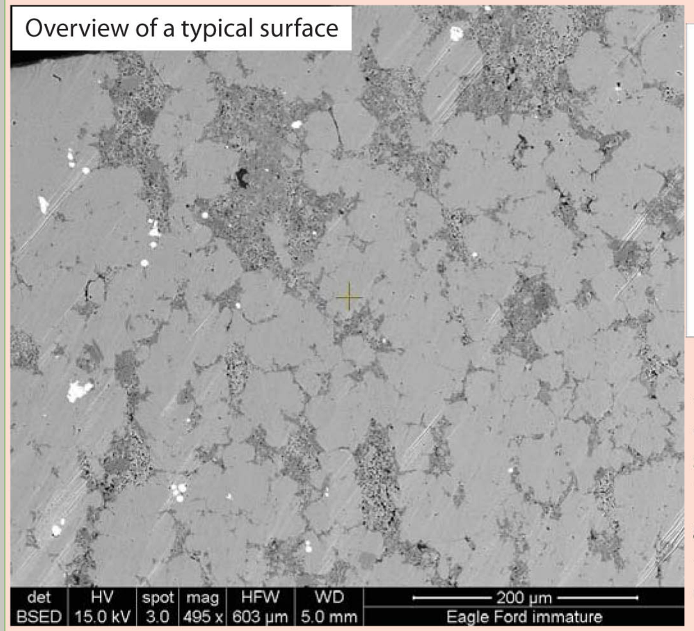


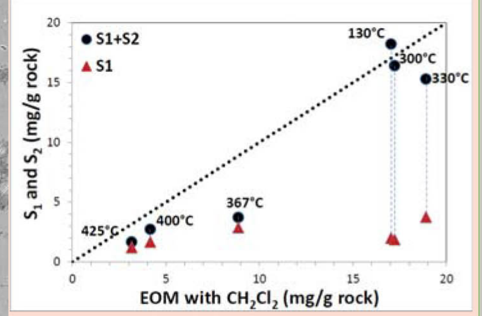

| HC Generation Stages | Pore Evolution and Pore Type Heterogeneity | | |
|---|---|---|---|
| | Mineral Pore | OM-Mineral Admixture | Stringy/flaky OM |
| Early Bitumen | | | |
| Bitumen Peak | | | |
| Oil Window | | | |
| Peak Oil | | | |
| Oil Cracking | | | |




## Boquillas Mudstone: Pore Types and Evolution

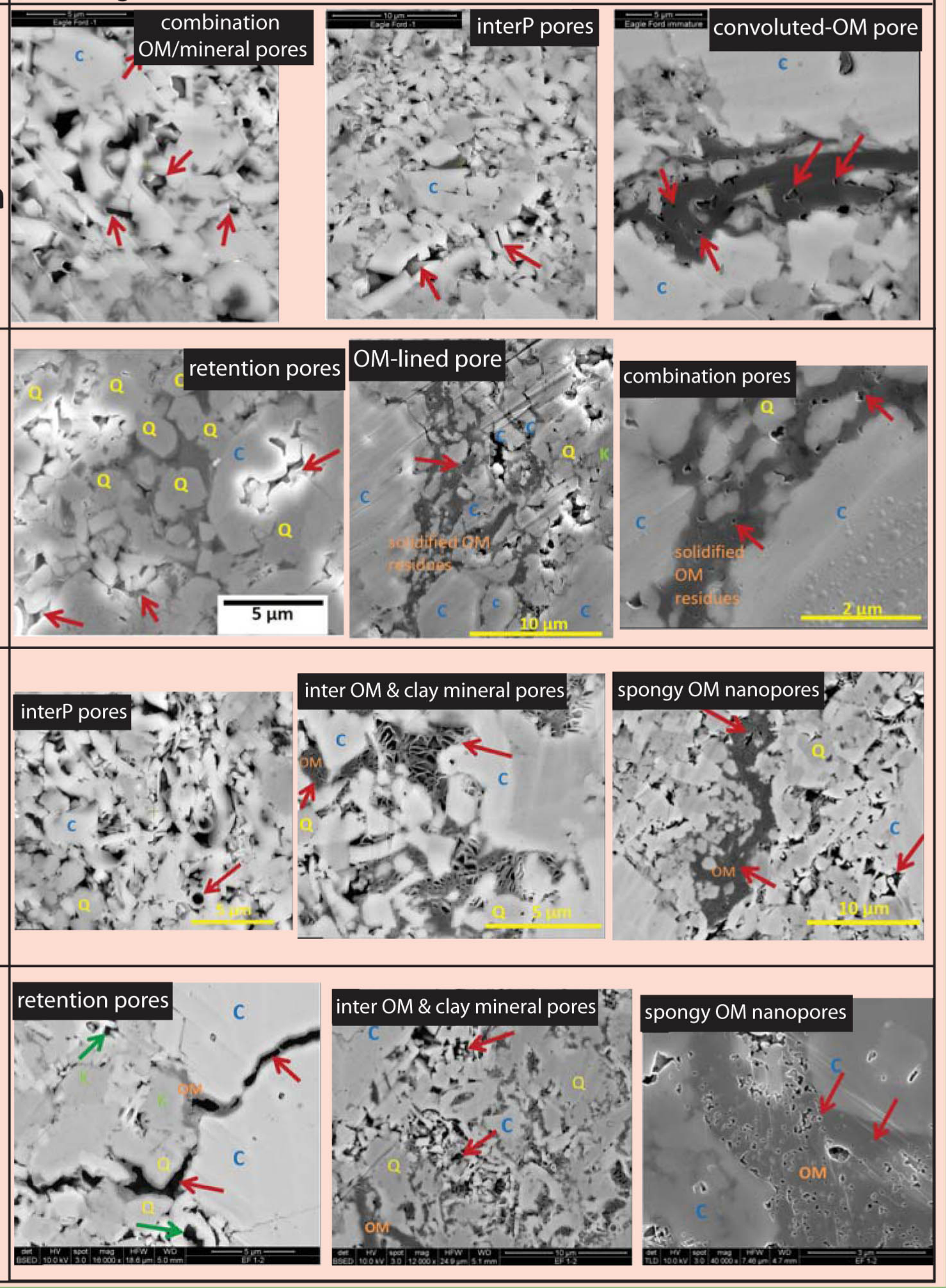
Overview of a typical surface




For low-maturity samples (130 and 300°C), EOM almost equals S1+S2 value and Rock-Eval S2 peak for these two samples is higher than S1 peak. This implies that HC that still has generation potential (S2) is mostly EOM (bitumen) instead of non-extractable OM (kerogen).

| HC Generation Stages | Pore Evolution and Pore Type Heterogeneity (left to right: most abundant to least abundant) |
|---|---|
| Bitumen Generation | |
| Oil Window | |
| Peak Oil | |
| Oil Cracking | |



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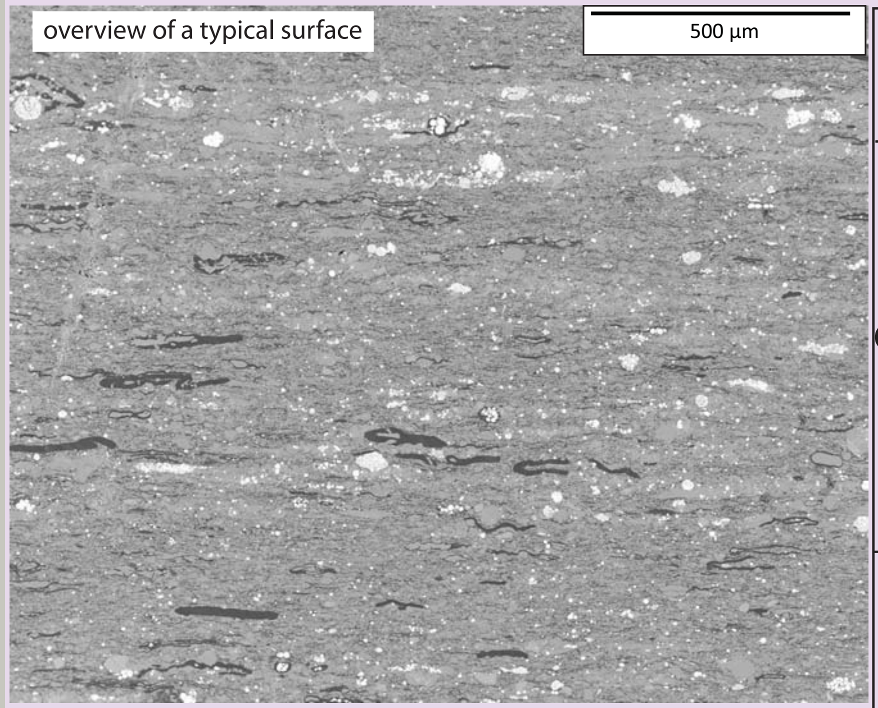
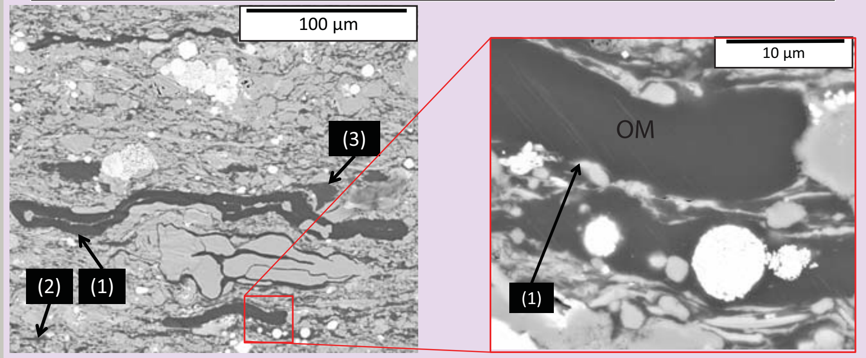
## Woodford Mudstone: Pore Types and Pore Evolution

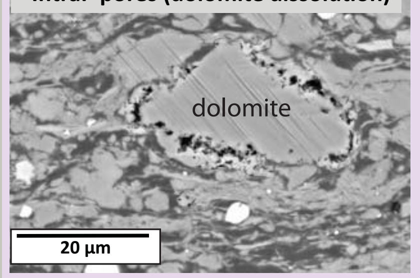



Types of OM in the Woodford Mudstone (photos below):
(1) *Tasmanites* remains
(2) Stringy/flaky OM?
(3) Brittle, structural, particulate OM (terrestrial kerogen)
(4) Other types of algae ?

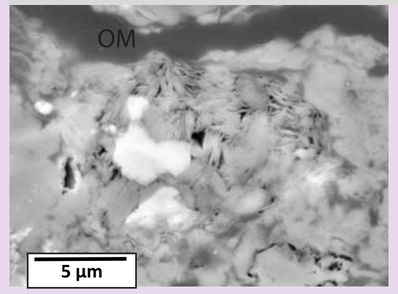



### Initial Pore Network (Ro = 0.5%)

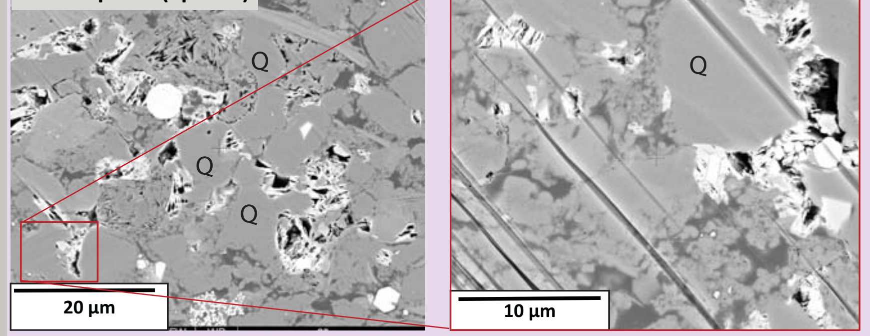
IntraP pores (dolomite dissolution)




IntraP pores (clay mineral platelets)



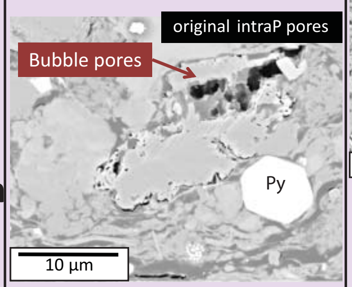

IntraP pores (apatite)



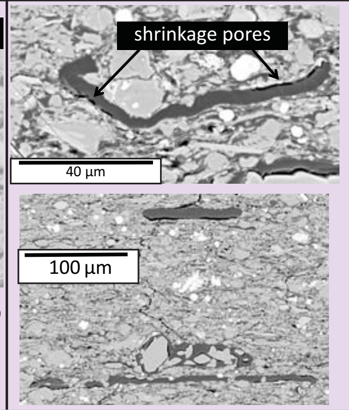

### Pore Evolution & Pore Type Heterogeneity

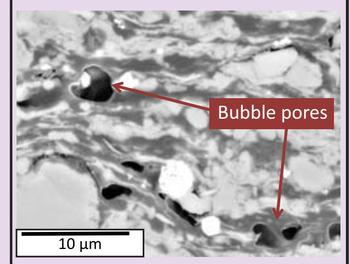
HC Generation Stages — Mineral Pore | *Tasmanites* Remains | Flaky OM in Matrix

**Bitumen Generation**

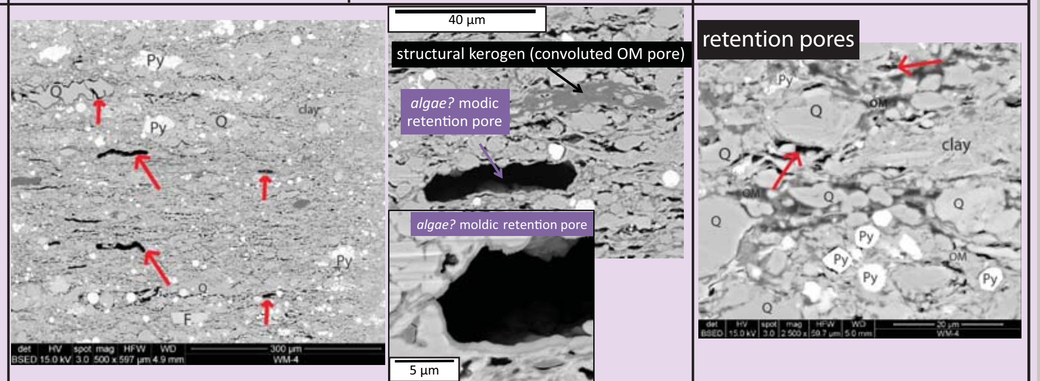



Part of bitumen migrated into original intraP pores, forming bubble pores.

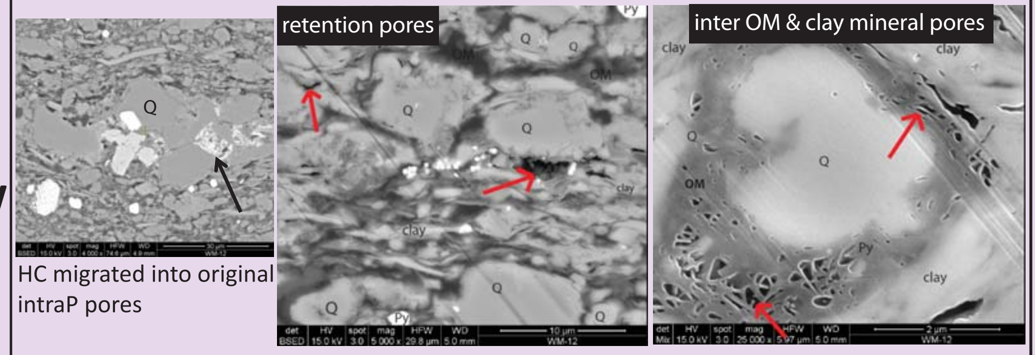



**Early Oil**

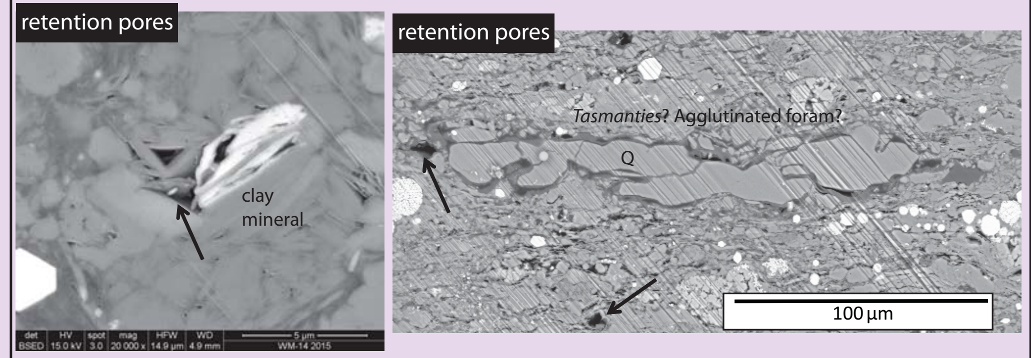



**Oil Window**

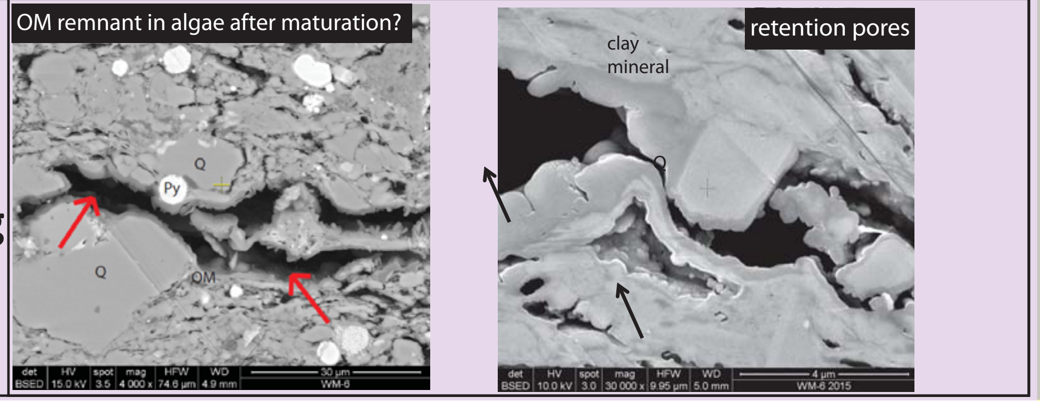



HC migrated into original intraP pores

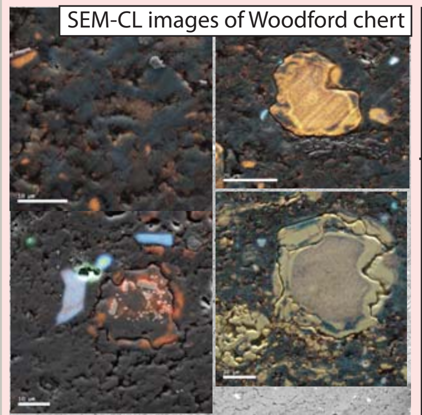
**Peak Oil**

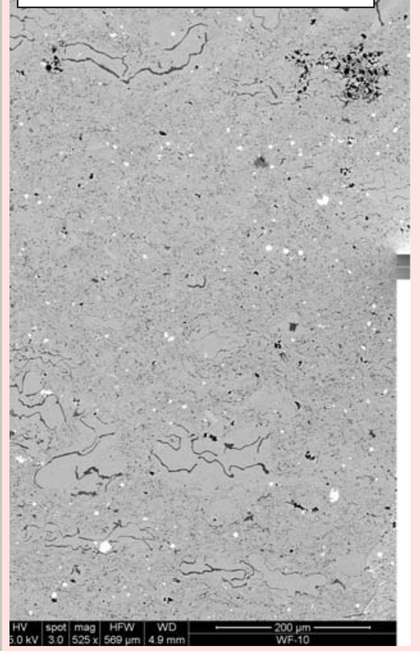



**Oil Cracking**

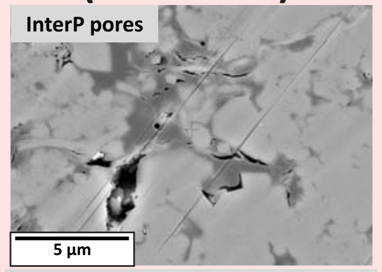


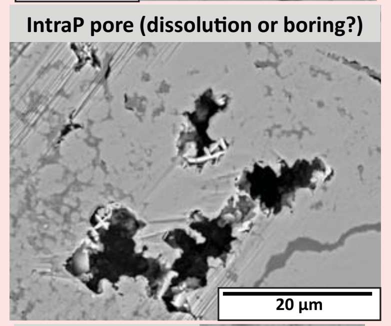

## Woodford Chert: Pore Types and Pore Evolution

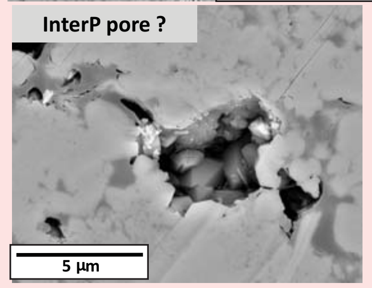



### Initial Pore Network (Ro = 0.6%)



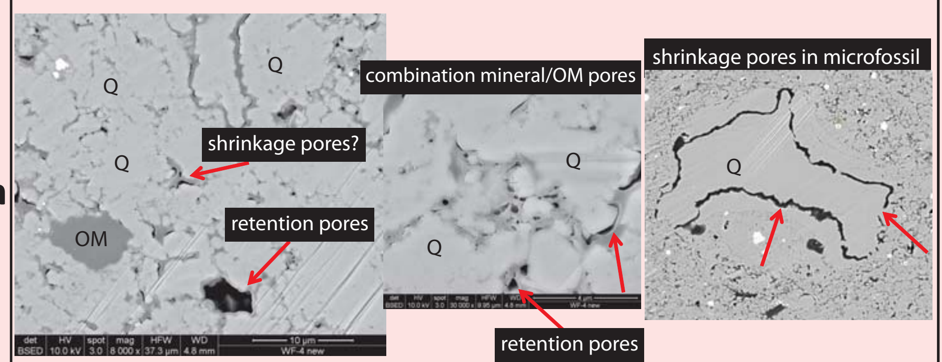




### Pore Evolution and Pore Type Heterogeneity

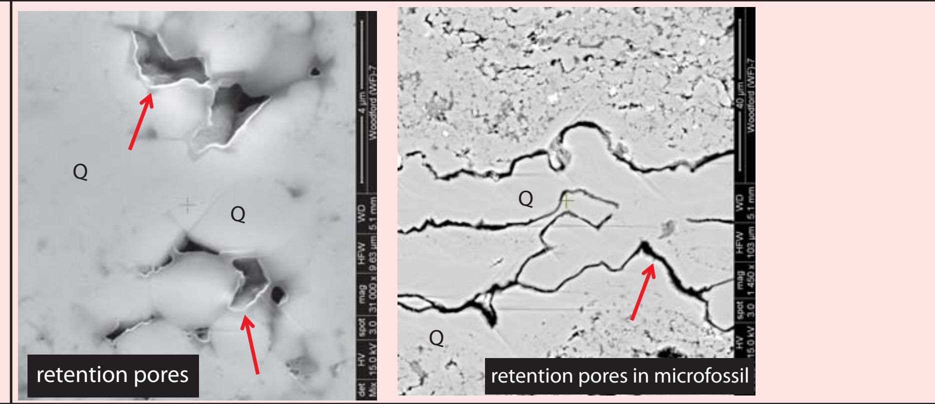
(left to right: most abundant to least abundant)

HC Generation Stages

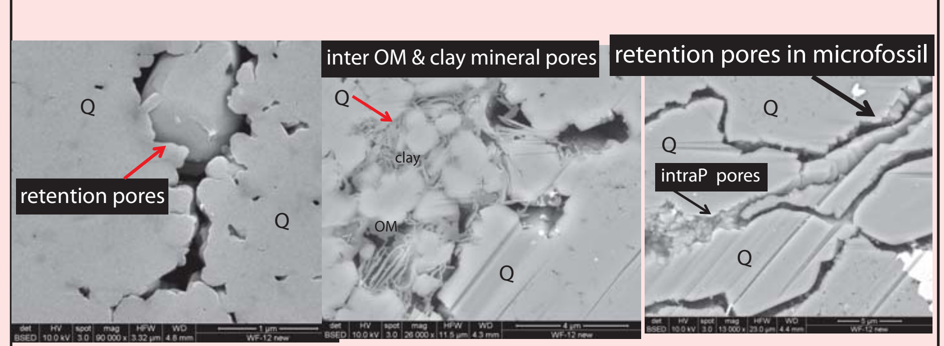
**Bitumen Generation**



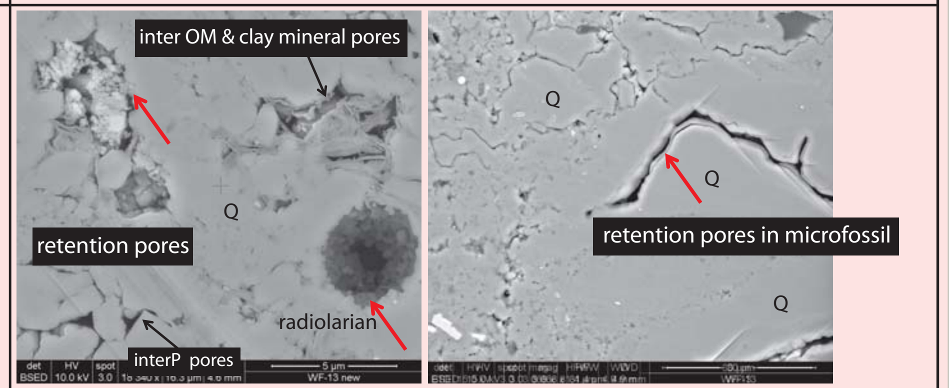

**Early Oil**



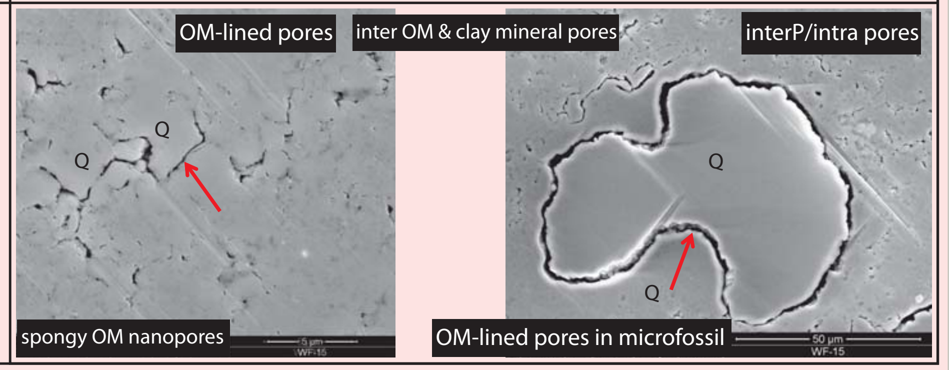

**Oil Window**




**Peak Oil**




**Oil Cracking**




## Barnett mudstone pore evolution summary:

(#: abundance)

| Stages | Dominant OM Pores | Mineral Pores |
|---|---|---|
| Immature | Primary, convoluted OM pores | IntraP pores |
| Bitumen generation | Bubble pores (shrinkage pores - artificial) | IntraP pores |
| Oil generation | Retention pores,slit pores, few spongy OM pores | IntraP pores |
| Cracking of oil to gas | Spongy OM pores | IntraP pores |

## Woodford mudstone pore evolution summary:

| Stages | Dominant OM Pores | Mineral Pores |
|---|---|---|
| Immature | Convoluted OM pore | IntraP pore |
| Bitumen generation | Bubble pore (shrinkage pore - artificial) | IntraP pore |
| Oil generation | *Algae?* moldic retention pore, retention pore | IntraP pore |
| Cracking of oil to gas | *Algae?* moldic retention pore, retention pore, some spongy pores | IntraP pore |

## Conclusions

1) Bulk mineralogy has relatively little impact on OM pore evolution
2) OM-pore evolution from bitumen decomposition (Boquillas) is similar to that from kerogen decomposition (Barnett & Woodford)
3) Initial pore networks are dominated by interP and intraP pores, which are a function of depositional and diagenetic processes
4) In general, dominant types of pores change from combination OM/mineral pores, bubble pores, retention pores, to nm-sized spongy OM pores with increasing thermal maturation.
5) Combination OM/mineral pores, bubble pores, retention pores, and OM-lined pores can be connected when OM (previously migrated bitumen or oil) becomes connected due to pore-scale migration. The connectivity depends on distance of migration.

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