

Investigating Laboratory-Generated Pyrobitumen Precursors for Unconventional Reservoir Characterization: A Geochemical and Petrographic Approach*

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Abstract

Analysis of pyrobitumen generated during the artificial maturation of source rock and oil-saturated core samples using geochemical and petrological techniques demonstrates a wide variation in many of the properties of pyrobitumen as a function of both the precursor oil composition and thermal maturity. It is believed that many of the properties of pyrobitumens deviate from those of kerogens at equivalent levels of maturity. The use of bulk parameters such as the Rock-Eval S2 curve to characterize organic matter in gas shales can lead to the misidentification of pyrobitumen as autochthonous kerogen (derived from sedimentary organic matter). This ongoing study aims to characterize some of these properties to provide tools to better identify pyrobitumen and its influence on shale gas reservoir properties.

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Speight, J.G., 2006, *The Chemistry and Technology of Petroleum*: Taylor & Francis, Boca Raton, FL, 984 p.



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Andy Mort, Hamed Sanei, Julito Reyes



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Preamble



Reply to comment on “Formation of nanoporous pyrobitumen residues during maturation of the Barnett Shale (Fort Worth Basin)”



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Shale gas systems serve as sources, reservoirs and seals to unconventional natural gas accumulations. These reservoirs are difficult for geologists and petroleum engineers to characterize most notably because of their tendency to be heterogeneous over several orders of magnitude of scale. Especially challenging is the micrometer to nanometer scale because these rocks are very fine grained and the pores are much smaller than those in conventional sandstone and carbonate reservoirs.

In a recent study published in *International Journal of Coal Geology* (Bernard et al., 2012a), we reported observations on PIR sections extracted from samples from the organic-rich Mississippian Barnett shale gas system (Fort Worth Basin, Texas, USA) at varying stages of thermal maturation. We documented the textural and chemical evolution of organics with increasing maturity using a combination of compositional organic geochemistry and spectromicroscopy techniques, including synchrotron-based scanning transmission X-ray microscopy (STXM), X-ray absorption near edge structure (XANES) spectroscopy and transmission electron microscopy (TEM), following the strategy introduced by Bernard et al. (2010).

In addition to the presence of bitumen in samples of oil window maturity, very likely genetically derived from thermally degraded kerogen, we evidenced the formation of nanoporous pyrobitumen in samples of gas window maturity, likely resulting from the formation of gaseous hydrocarbons by secondary cracking of bitumen compounds (Bernard et al., 2012a). This organic nanoporosity, which has been reported in most gas-mature gas shale systems worldwide since the pioneering study of Loucks et al. (2009), may likely have great influence on gas storage capacity and permeability of thermally mature gas shales (e.g., Bernard and Horsfield, in press).

The recent work performed by Reed et al. (2014–this volume) is important in the context of the present research effort to elucidate the better understanding of the gaseous hydrocarbon generation/retention processes occurring within these complex systems. Reed and co-authors report the characterization of Barnett shale samples coming from the same wells that our samples came from. In contrast to our approach, these authors chose to use the broad-beam Au-milling technique to prepare topography-free samples for fine scale characterization using FEG-SEM. This approach allowed them to evidence the occurrence of “nanoporous organic matter” in samples of oil window maturity, but, unfortunately, did not provide any molecular information which would have helped to identify these compounds. Nevertheless, Reed and co-authors raised several issues in their comment that require a response from us.

Reed and co-authors report the presence of “nanoporous organic matter” in samples of oil window maturity and state that “it is unfortunate that Bernard et al. (2012a, 2012b) did not see nanoporous organic matter in either of their oil-window-maturity samples as XANES could have identified the type of organic matter”. We indeed observed (and reported) organic compounds within Barnett shale samples of oil window maturity that might be described as nanoporous (see Fig. 5 of Bernard et al., 2012a) but which we identified based on their XANES signatures as bitumen compounds that do not completely fill interparticle pores. Thus, the observed pores are not organic pores *per se* but result from the incomplete filling of pre-existing pores by bitumen. The same observation has been made on Posidonia shale samples having reached a similar maturity level (Bernard et al., 2012b).

Reed and co-authors question our suggestion for the origin of bitumen-filled intra-mineral pores. We inferred that these bitumen-filled pores result from dissolution by organic acids produced during the thermal degradation of kerogen and suggested that these pores are, or were once, sufficiently interconnected to allow for bitumen to migrate (Bernard et al., 2012a). Loucks et al. (2012) have also suggested that such a process (i.e. dissolution by fluids associated with decarboxylation of kerogen) may impact the porosity network of a shale. Yet, Reed et al. (2014–this volume) refute this explanation by asking the question “Why would organic acids attack grain interiors but not the exterior?” highlighting that these authors have not fully considered how gas shales are structured in 3, not only 2, dimensions.

Although Reed and co-authors accept that some of the “nanoporous organics” they observe can be solid bitumen, they argue that “the patterned, perhaps even organized, appearance of the organic-matter pores” they observe allow these compounds to be identified as nanoporous kerogen. This is an interesting speculation, but a most probable

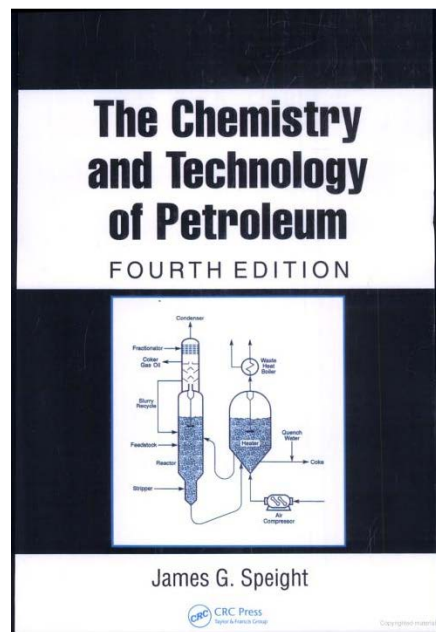
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Outline

- What is pyrobitumen?
 - Definition
 - Formation
 - Properties
- Why are we interested in pyrobitumen?
 - Significant part of the organic reservoir in mature shales
 - Φ_{org} usually increases with maturity but is still not reliably predictable
- How is it identified?
 - Organic Petrology
 - Geochemical: Rock-Eval
- What are the controls on pyrobitumen formation?



Pyrobitumen: definition



Pyrobitumen is a naturally occurring solid organic substance that is distinguishable from bitumen (q.v.) by being infusible and insoluble. When heated, pyrobitumen generates, or transforms into, bitumen-like liquid and gaseous hydrocarbon compounds. Pyrobitumen may be either asphaltic or non-asphaltic. The asphaltic pyrobitumen, derived from petroleum, is relatively hard, and has a specific gravity below 1.25. They do not melt when heated but swell and decompose (intumesce).

There is much confusion regarding the classification of asphaltoids, although four types are recognized: elaterite, wurtzilite, albertite, and impsonite—in the order of increasing density and fixed carbon content. In fact, it is doubtful that the asphaltoid group can ever be clearly differentiated from the asphaltites. It is even more doubtful that the present subdivisions will ever have any real meaning, nor is it clear that the materials have any necessary genetic connection. Again, caution should be exercised in the use of the names, and due care should be applied to the qualification of the particular sample.

Speight, J.G., (2006) *The Chemistry and Technology of Petroleum*. Taylor & Francis, Boca Raton, FL.



Origin of pyrobitumen

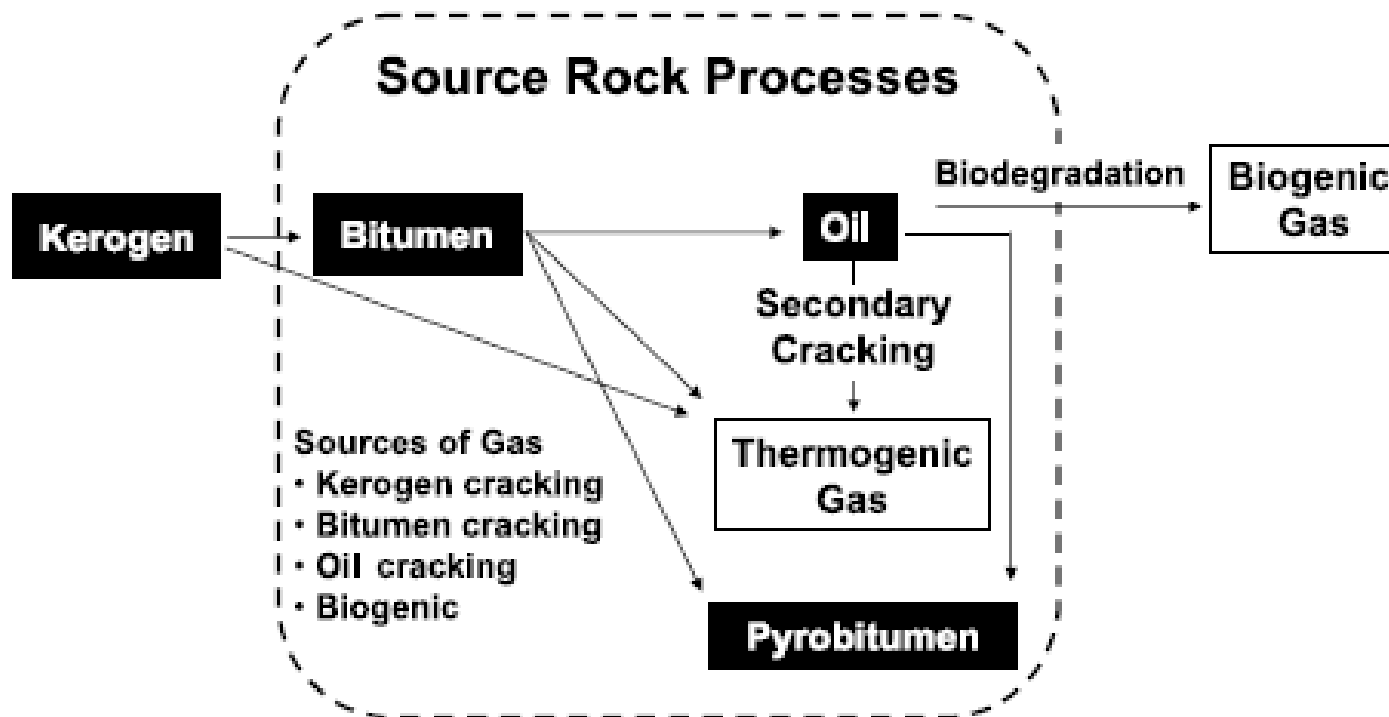
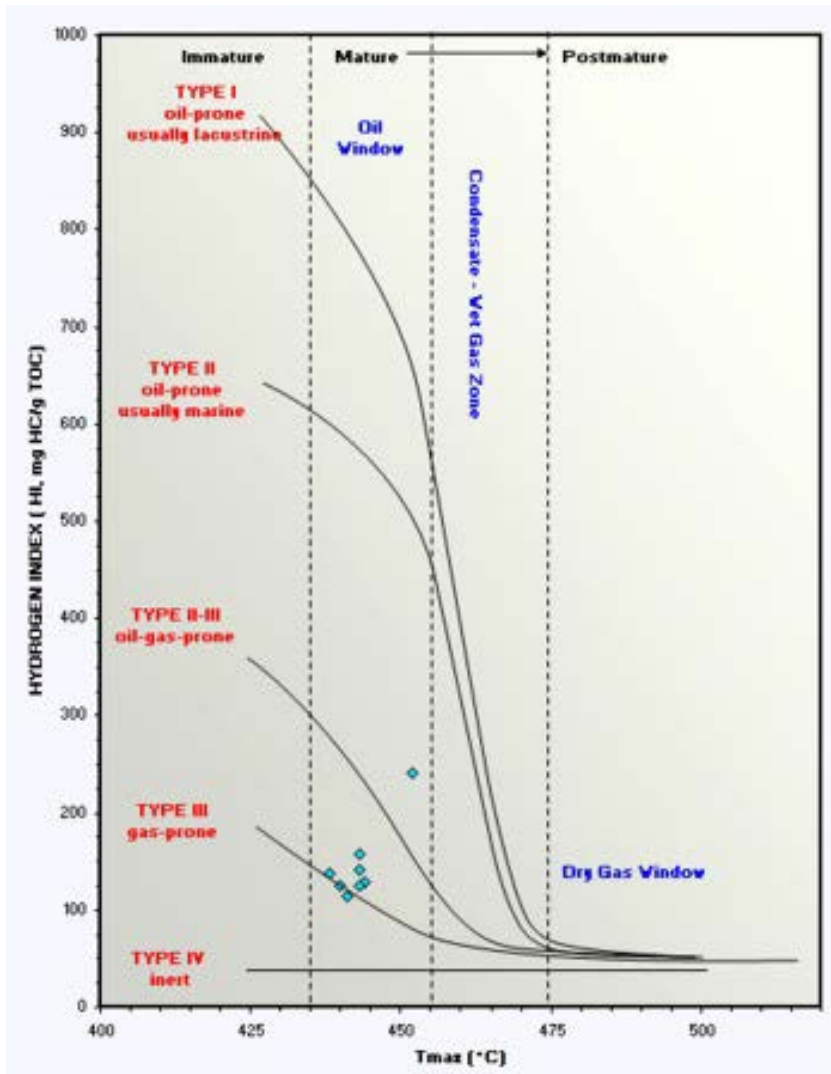


Figure 8. Processes in a source rock leading to oil, gas, and carbon-rich residue (pyrobitumen). High-maturity shale-gas systems derive high gas contents from the indigenous generation of gas from kerogen, bitumen, and oil cracking.

Jarvie, D.M., Hill, R.J., Ruble, T.E., Pollastro, R.M., (2007) Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. *American Association of Petroleum Geologists Bulletin*, 91(4), 475-499.

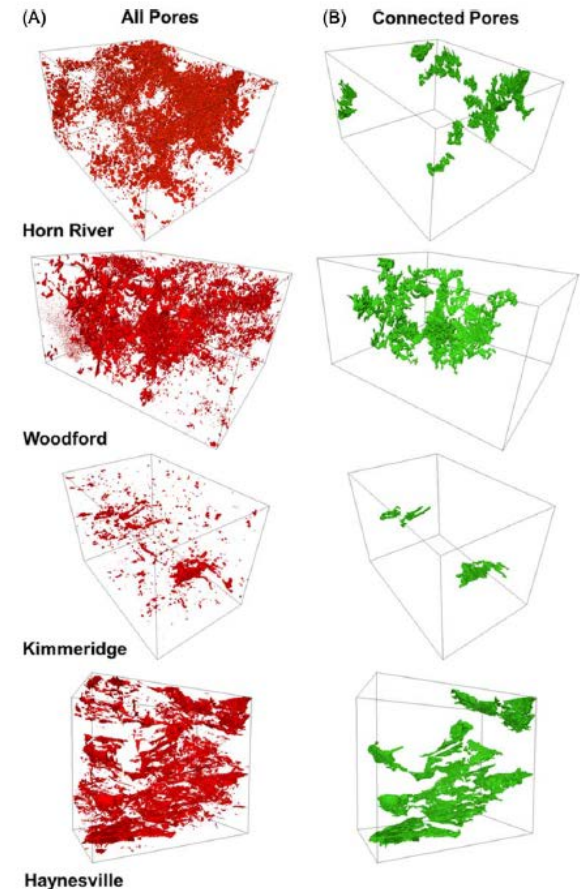
Petroleum generation 101



Kerogen Type	TOC Conversion
I	80%
II	50%
II-III	30%
III	20%

What has pyrobitumen got to do with unconventional shale plays?

- A significant proportion of gas is associated with porosity in the organic phase.
- Organic porosity is highly variable and effective permeability even more so
- Current understanding of the controls on organic porosity remains uncertain
- It is sometimes assumed that all organic matter in shales is kerogen.

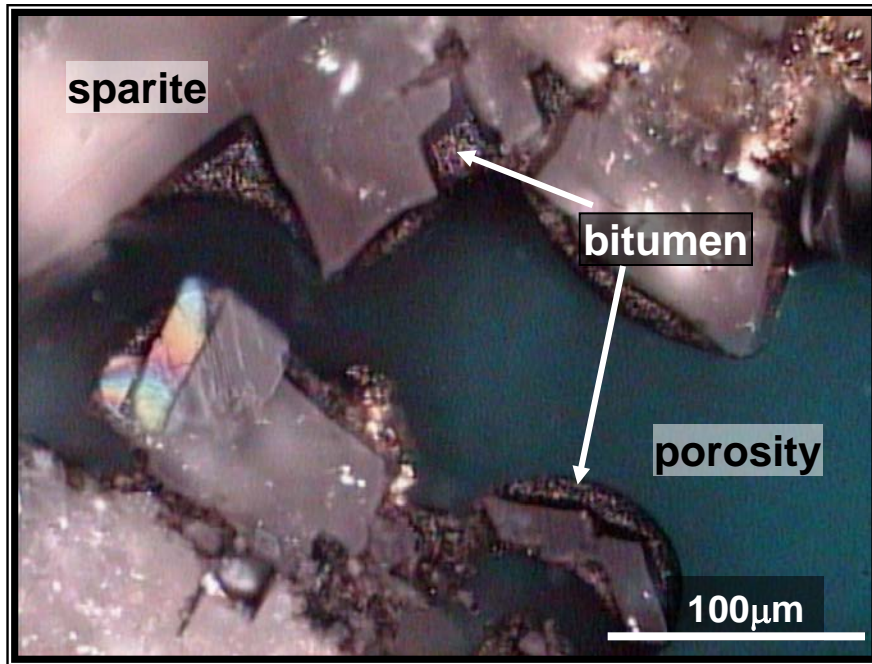


Curtis, M.E., Sondergeld, C.H., Ambrose, R.J., Rai, C.S., 2012. Microstructural investigation of gas shales in two and three dimensions using nanometer-scale resolution imaging. AAPG Bulletin 96, 665–677.

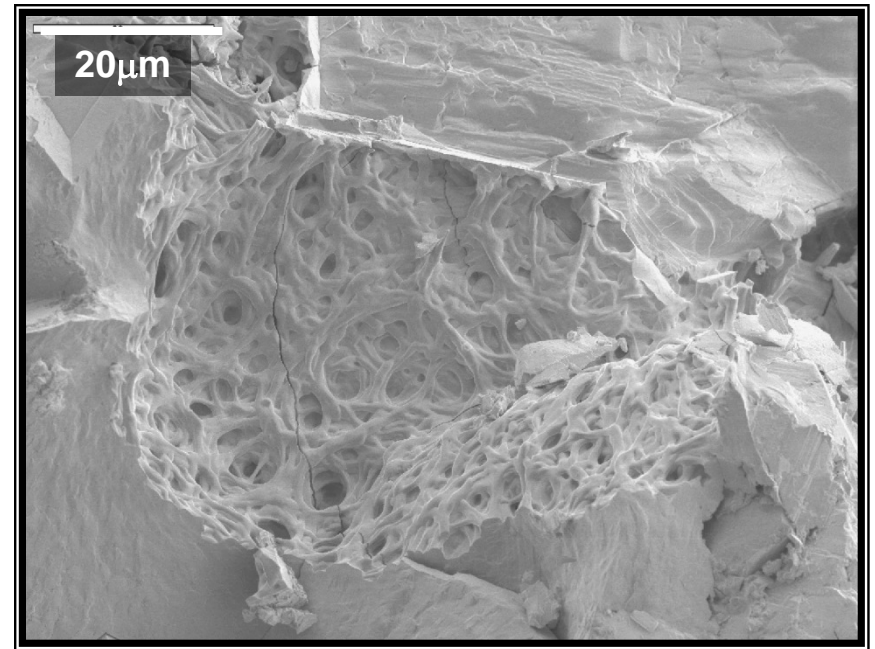


Pyrobitumen appearance

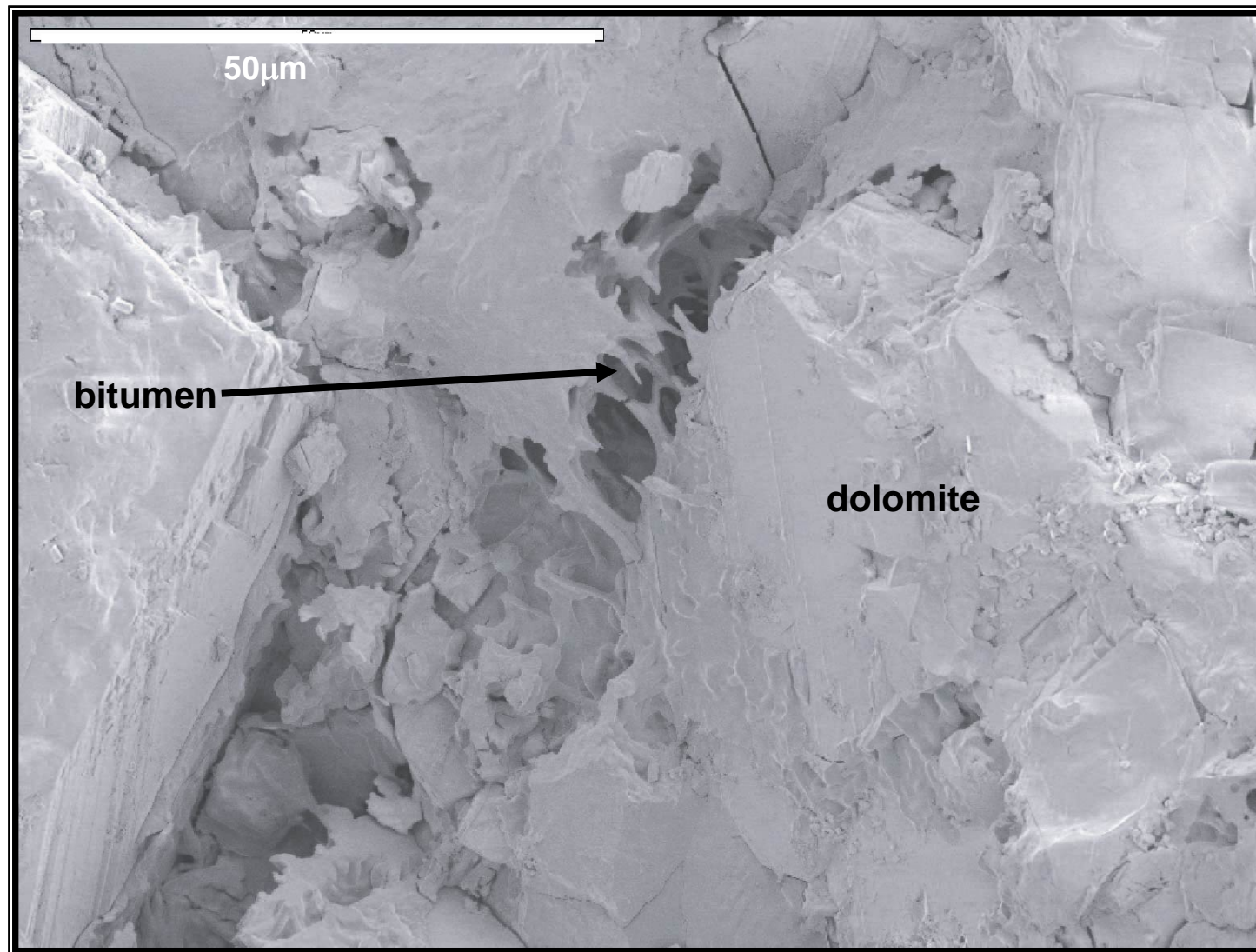
- Shares many characteristics with kerogen, particularly at high maturity
- Distinguished by morphology due to secondary emplacement
- Requires sample preparation which retains organic matter – lithology relationship



Thin section seen in transmitted white light

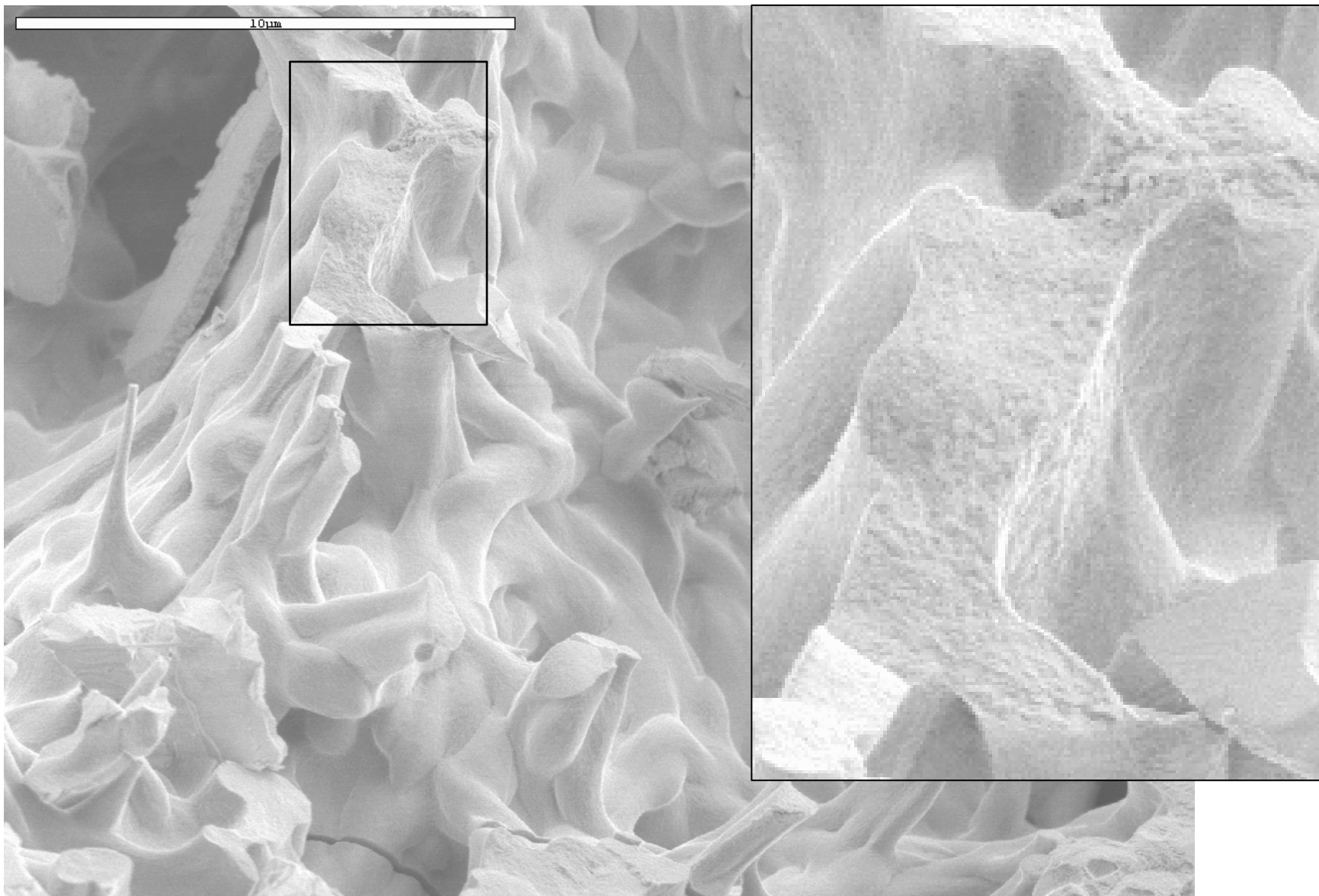


Uncoated core chip
(SEM secondary electron mode)



**Uncoated core chip
(SEM secondary electron mode)**





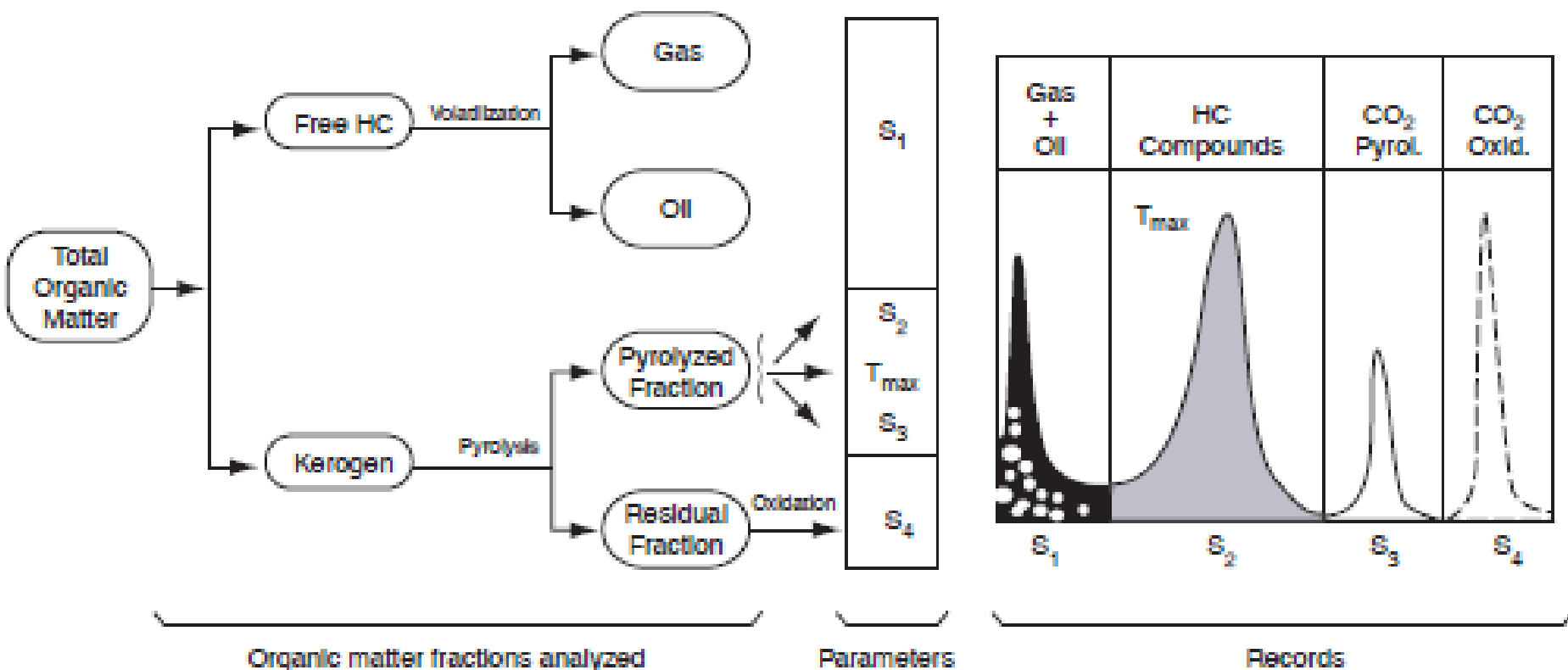
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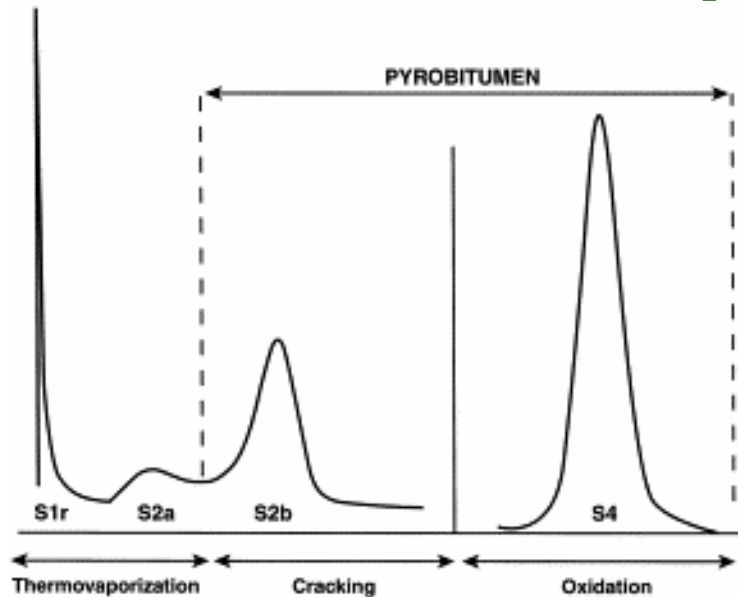
**Uncoated core chip
(SEM secondary electron mode)**

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Pyrobitumen ID using Rock-Eval

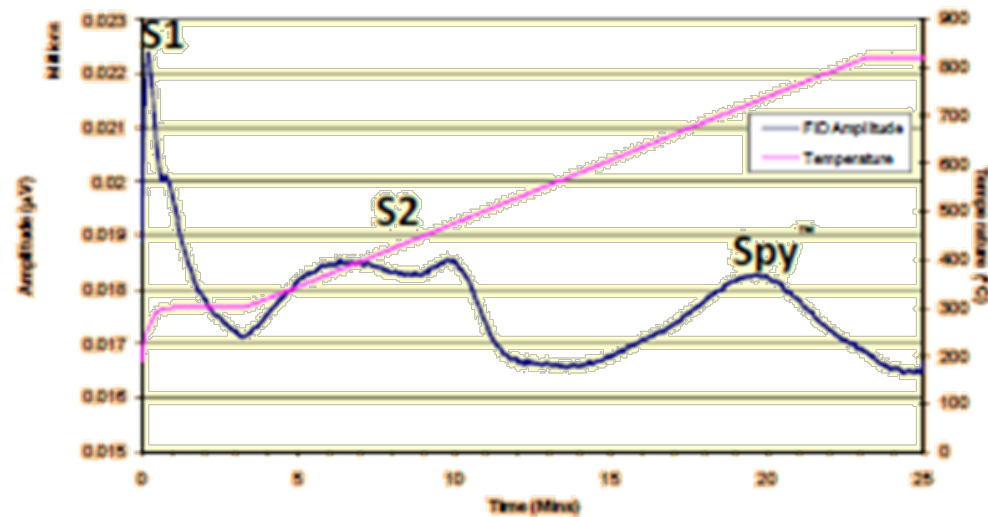


Rock-Eval S2 peak close up

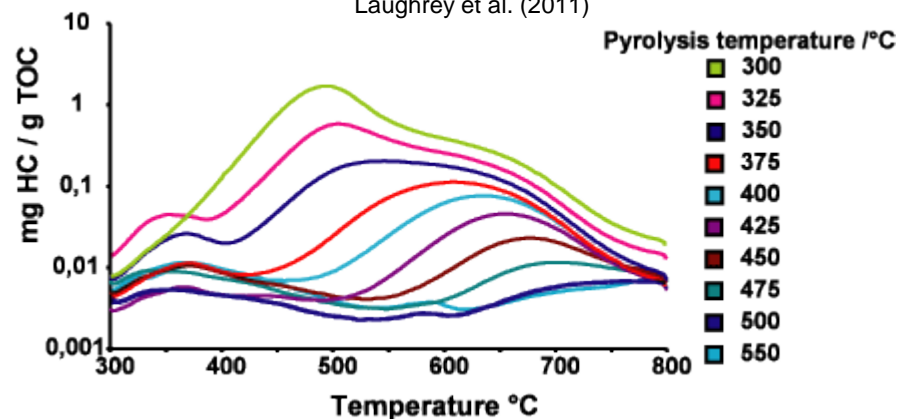


Trabelsi et al. (1994)

1. Low T_{max} hump visible in heavy oils or well-retained hydrocarbons
2. High temperature peak representative of



Laughrey et al. (2011)

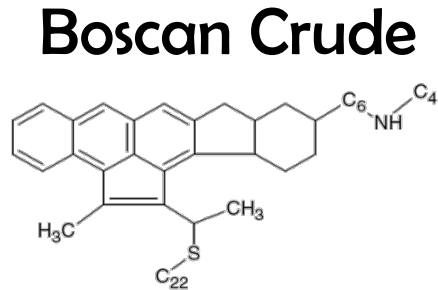


Experimental simulation of pyrobitumen formation and thermal evolution

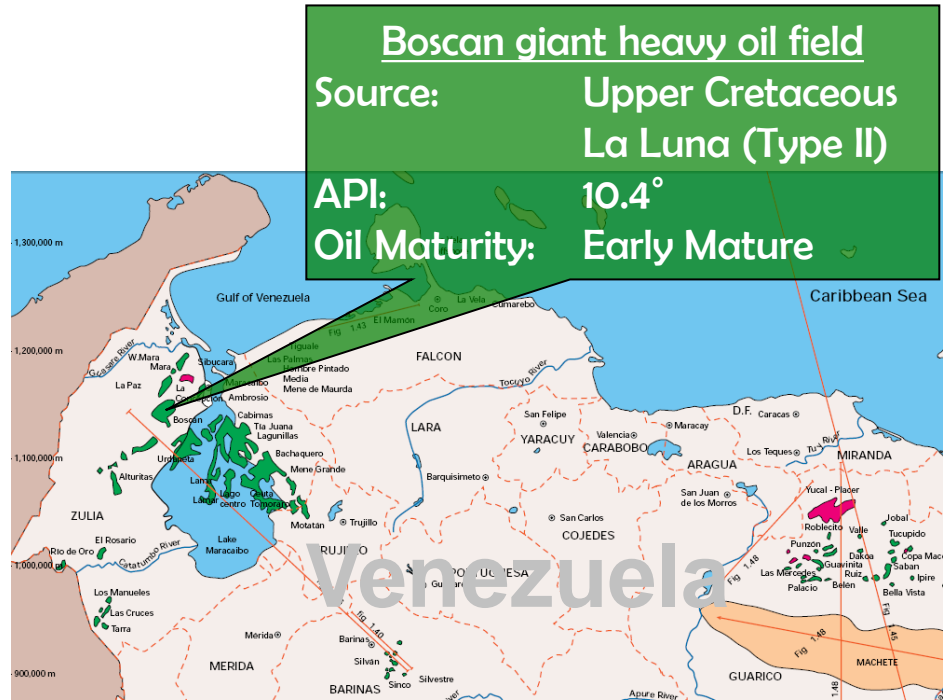
- Naturally occurring pyrobitumen
- Artificial maturation of different bulk chemical components of oil
- Synthesis of pyrobitumen from different oils
- Artificial maturation of natural pyrobitumen
- Hydrous pyrolysis of shale oil & conventional oil pairs (ongoing...)



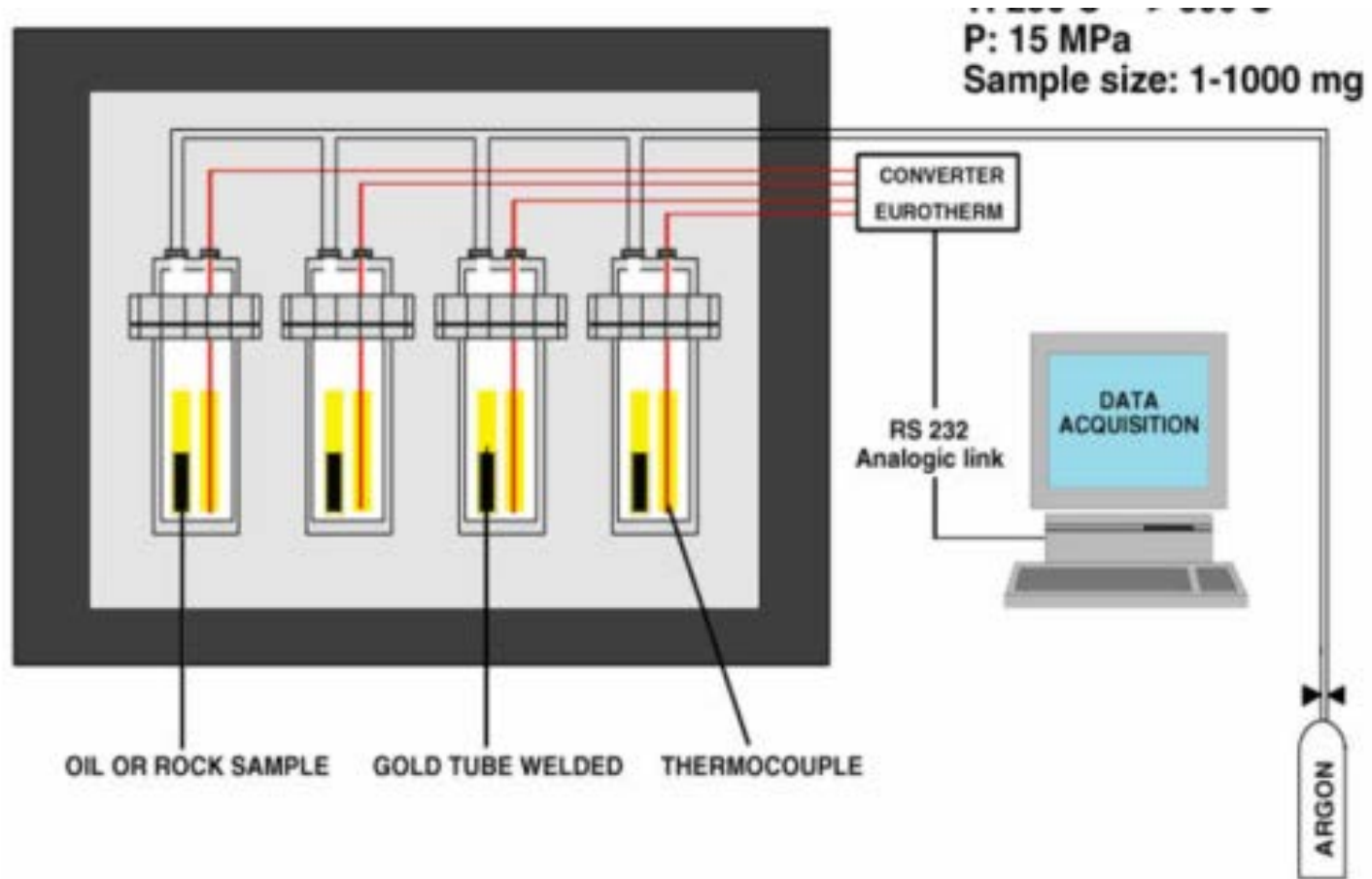
Artificial maturation of different bulk chemical components of oil



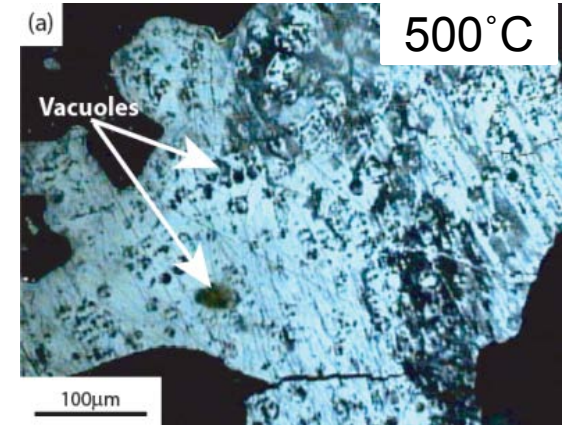
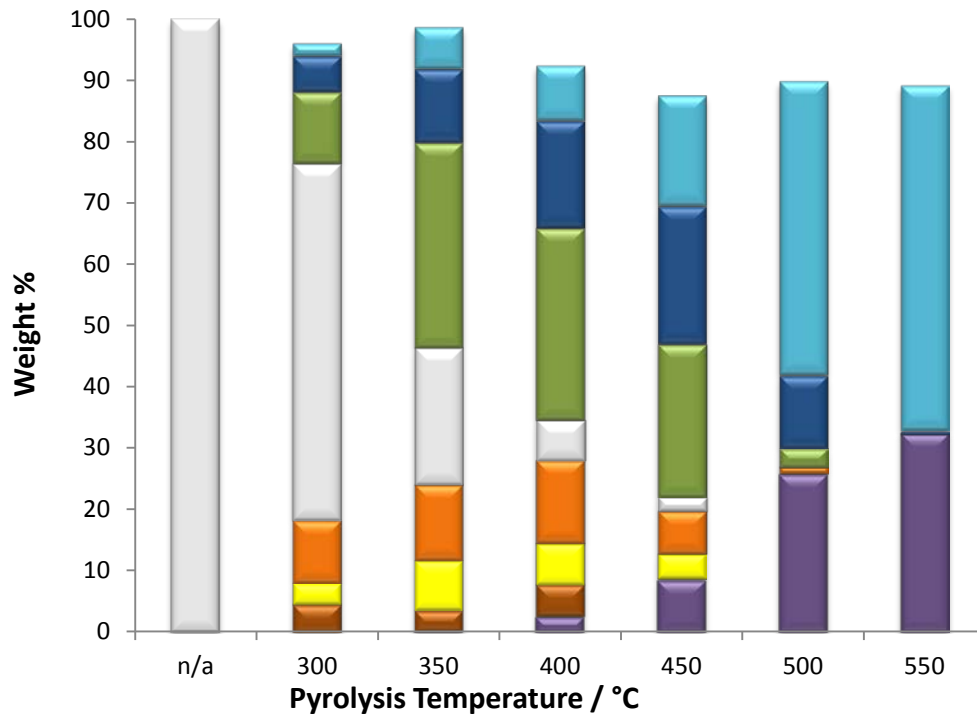
Average molecular structure of Boscan bitumen analysed by ^{13}C NMR (after Masson *et al.*, 2006)



Oil fractions: closed system pyrolysis – no added H₂O

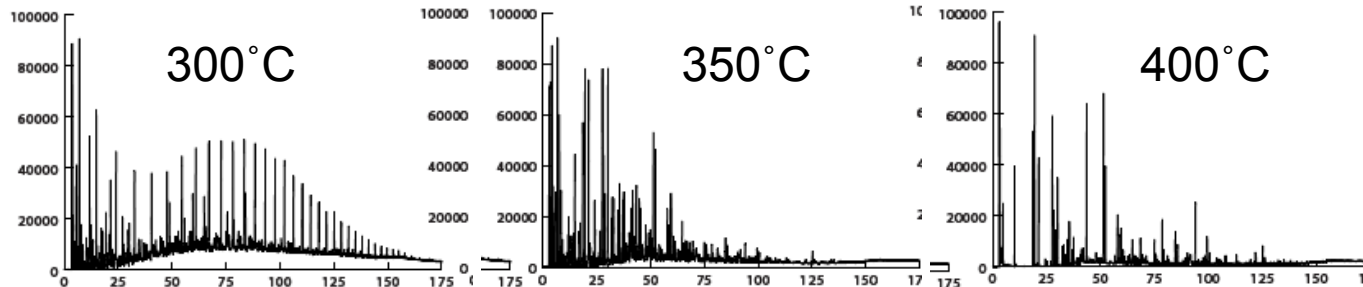


Saturate fraction

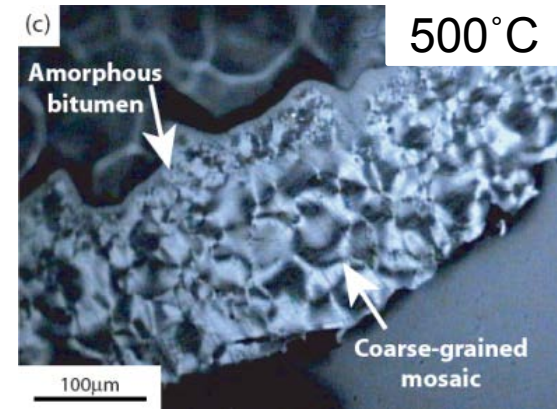
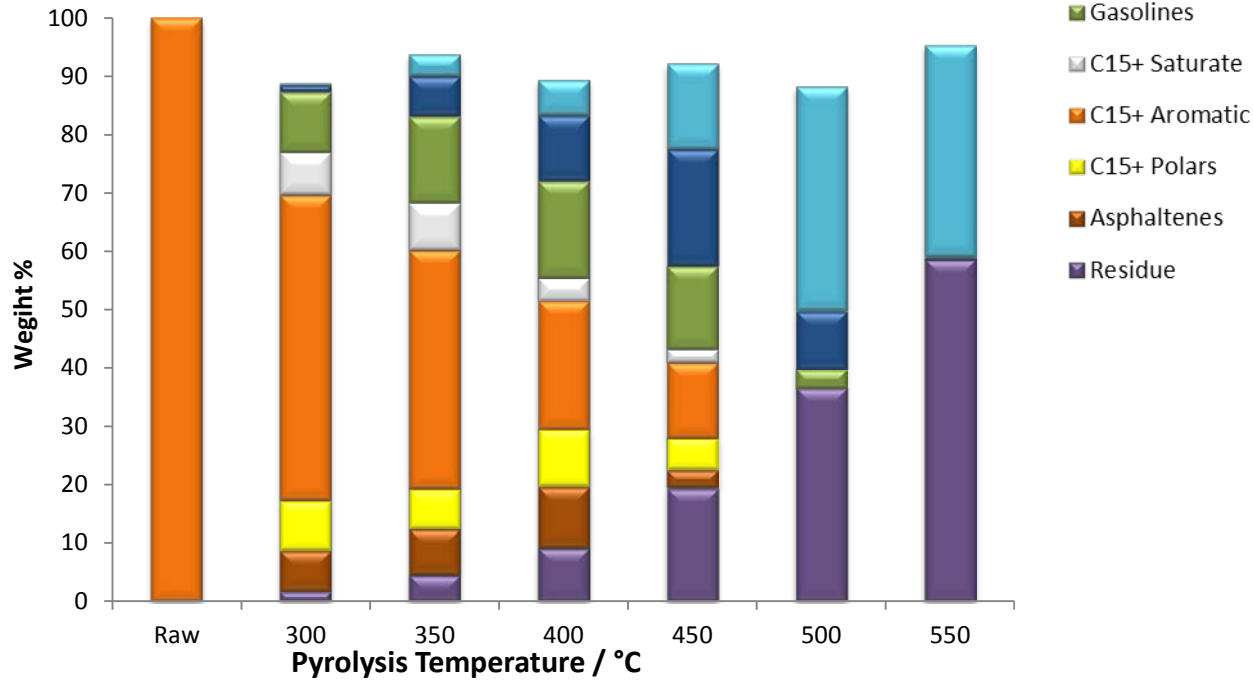


Saturates:

- Low yield of residue at
- Maximum residue yield = 32%wt fraction
- Rapid cracking of n-alkanes to gasolines + wet gas

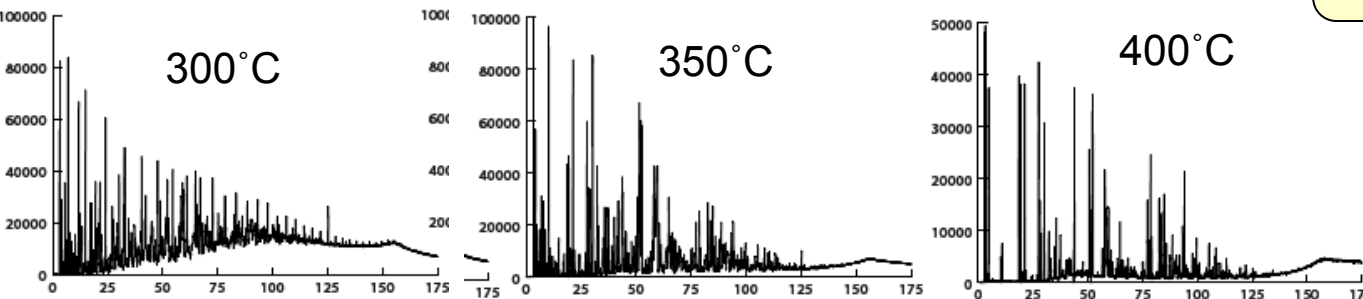


Aromatic fraction

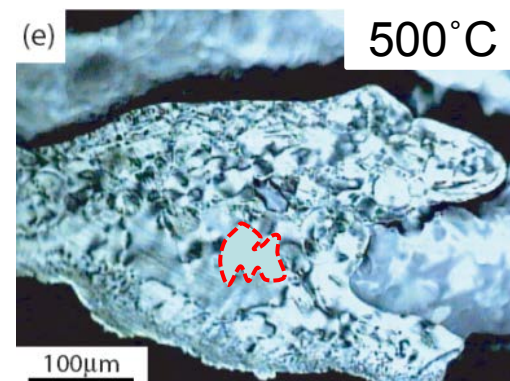
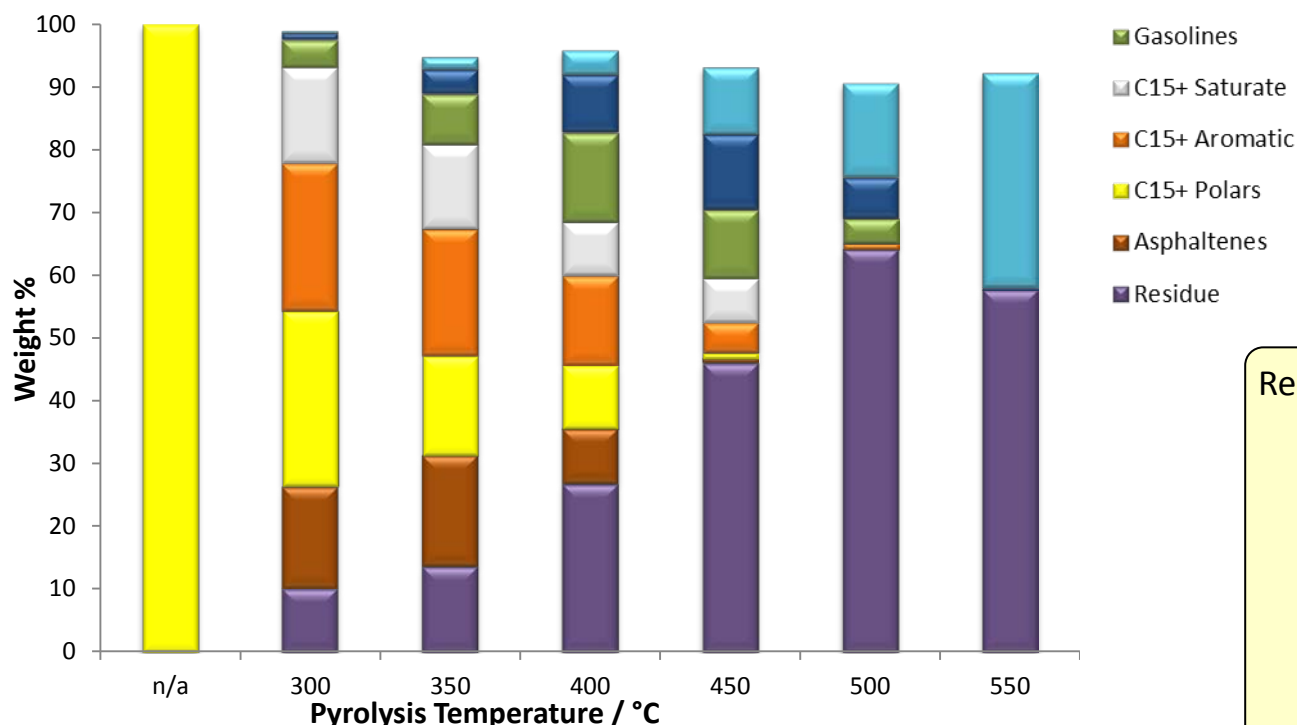


Aromatics:

- Low yield of insoluble residue at $T < 450^{\circ}\text{C}$
- Residue yield increases systematically with T to a maximum of 59% at $T = 550^{\circ}\text{C}$
- Aromatics are most stable fraction at intermediate temperatures (350-450°C)

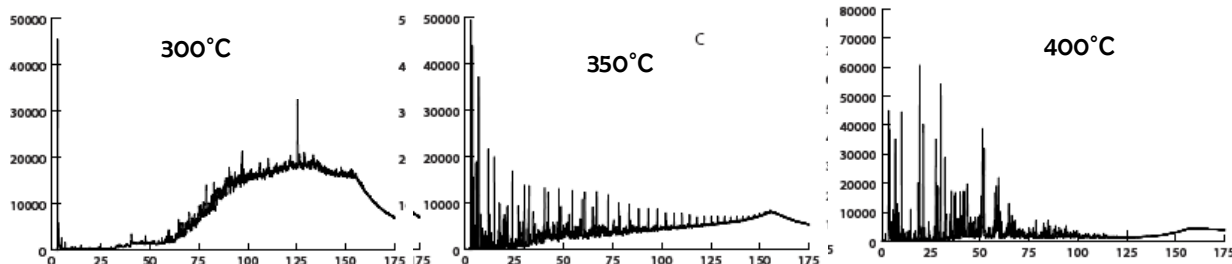


Polar (NSO) fraction

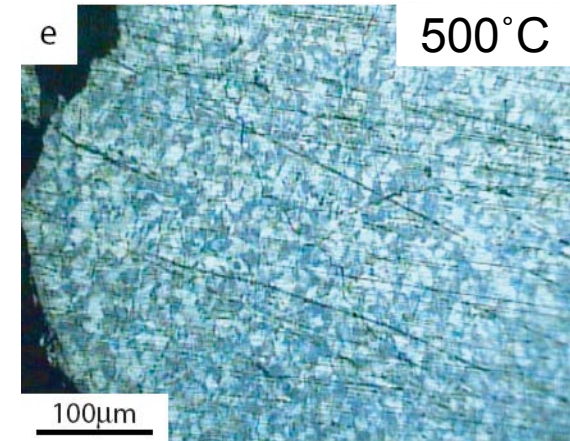
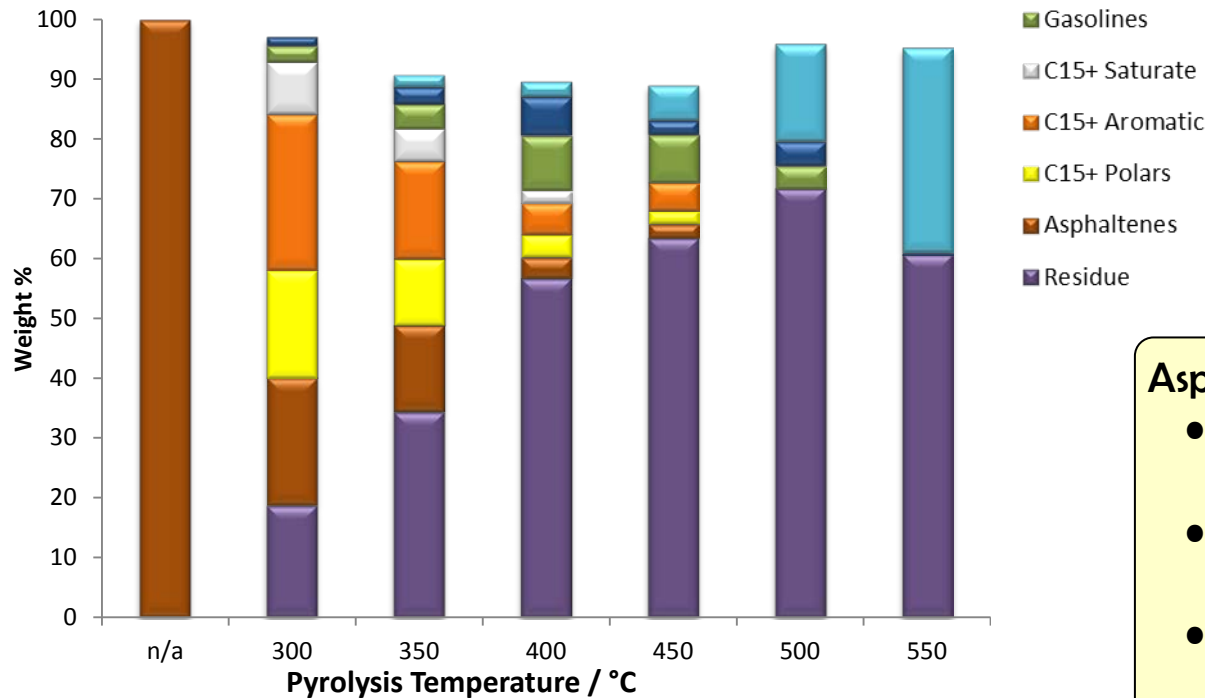


Resins:

- High yield of insoluble residue at $T < 450^{\circ}\text{C}$
- Residue yield reaches a maximum of 64% at $T = 500^{\circ}\text{C}$
- Neoformed residue undergoes polycondensation at $T = 550^{\circ}\text{C}$
- Significant metastable sats/aros produced at $T = 300\text{--}450^{\circ}\text{C}$

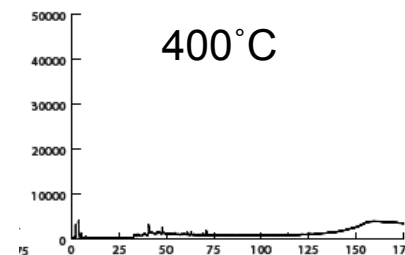
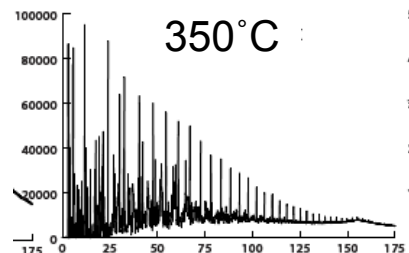
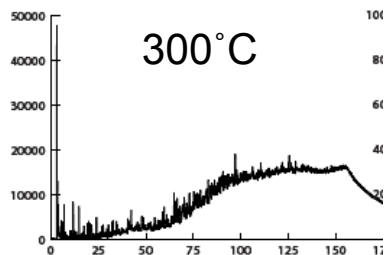


Asphaltene fraction



Asphaltenes:

- High yield of insoluble residue at $T < 400^{\circ}\text{C}$
- Residue yield reaches a maximum of 63% at $T = 500^{\circ}\text{C}$
- Tertiary cracking at $T = 550^{\circ}\text{C}$ to highly condensed aromatic residue and dry gas



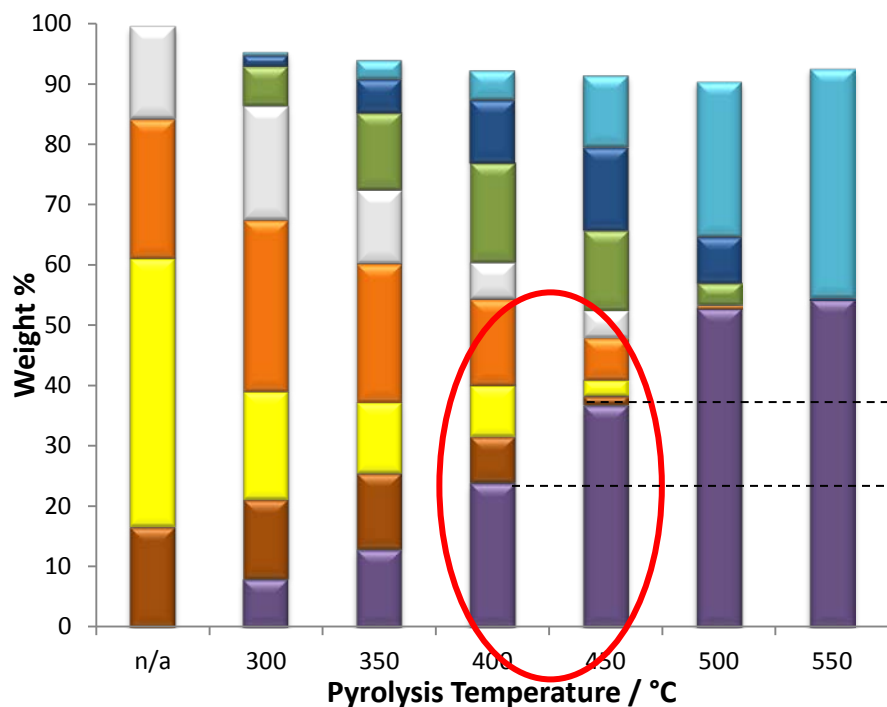
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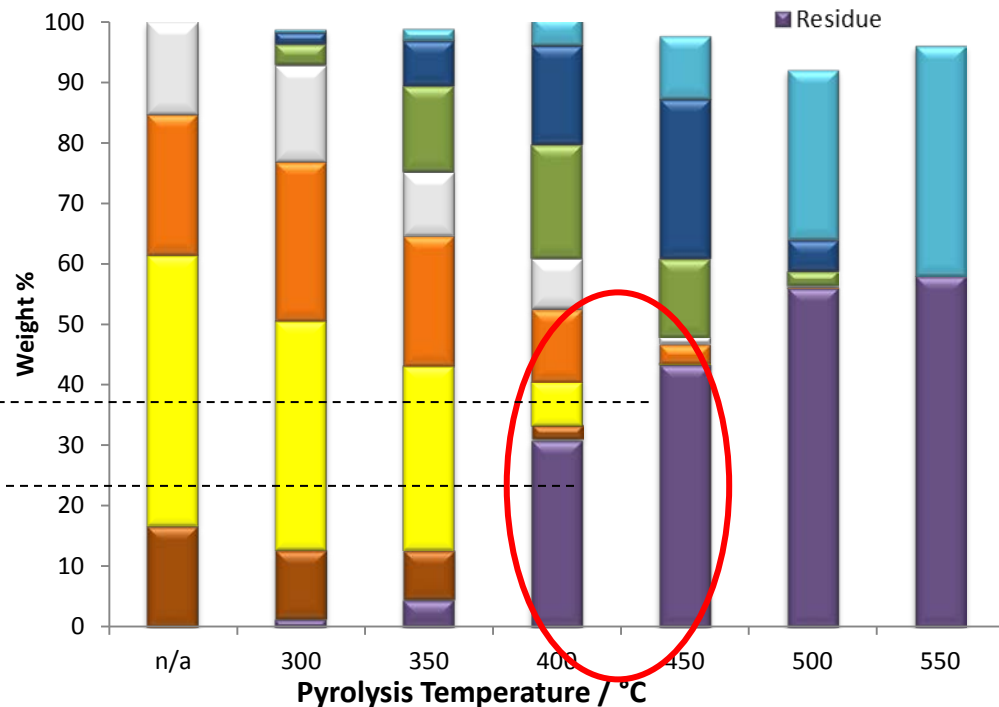
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Whole Oil

Calculated compositional maturation



Actual whole oil



Residue formation is greater than predicted at intermediate temperatures



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Key points

Formation of insoluble bitumen, although thermally driven, occurs at different temperatures and produces variable quantities depending on NSO content of the precursor oil.

Bulk oil composition moreover exerts a strong control on the optical, textural and structural properties of the bitumen formed.



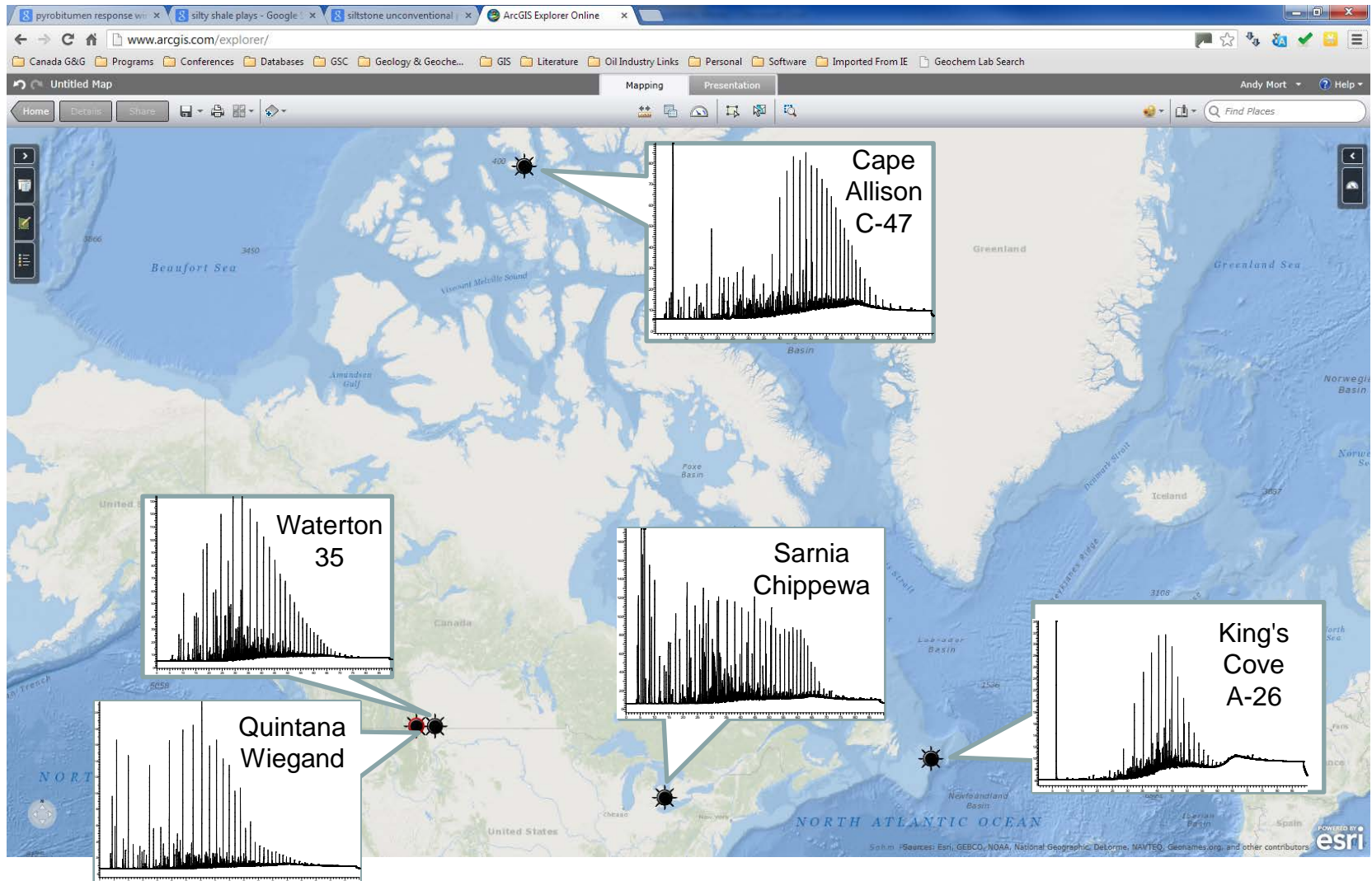
Key Questions

If molecular composition of precursors influences pyrobitumen formation and optical properties, does it also exert some control on pyrobitumen porosity evolution, pore size distribution, etc.?

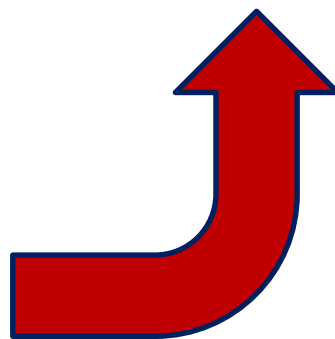
To what extent is the expulsion and retention of hydrocarbons by pyrobitumen governed by chemical structure versus nanostructure?



Open system maturation of oil samples



Reactant



Product



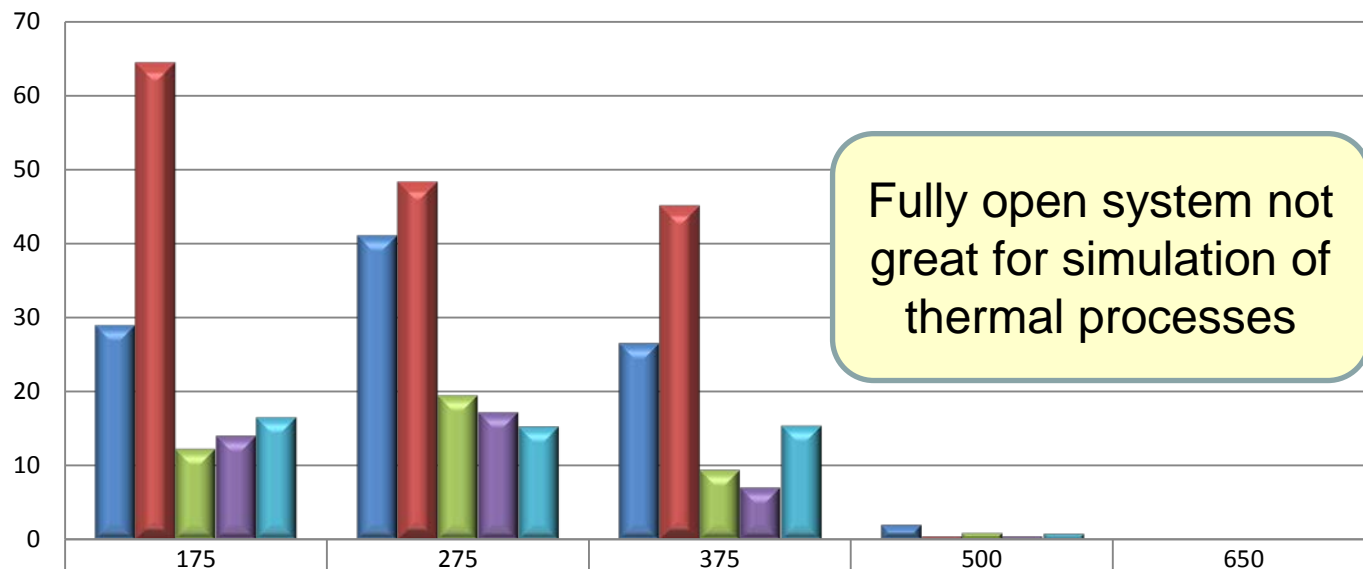
Extraction of pyrolyzates



Results: Generation Potential

Evolution of HC generation potential as a function of pyrolysis temperature

Rock-Eval S2



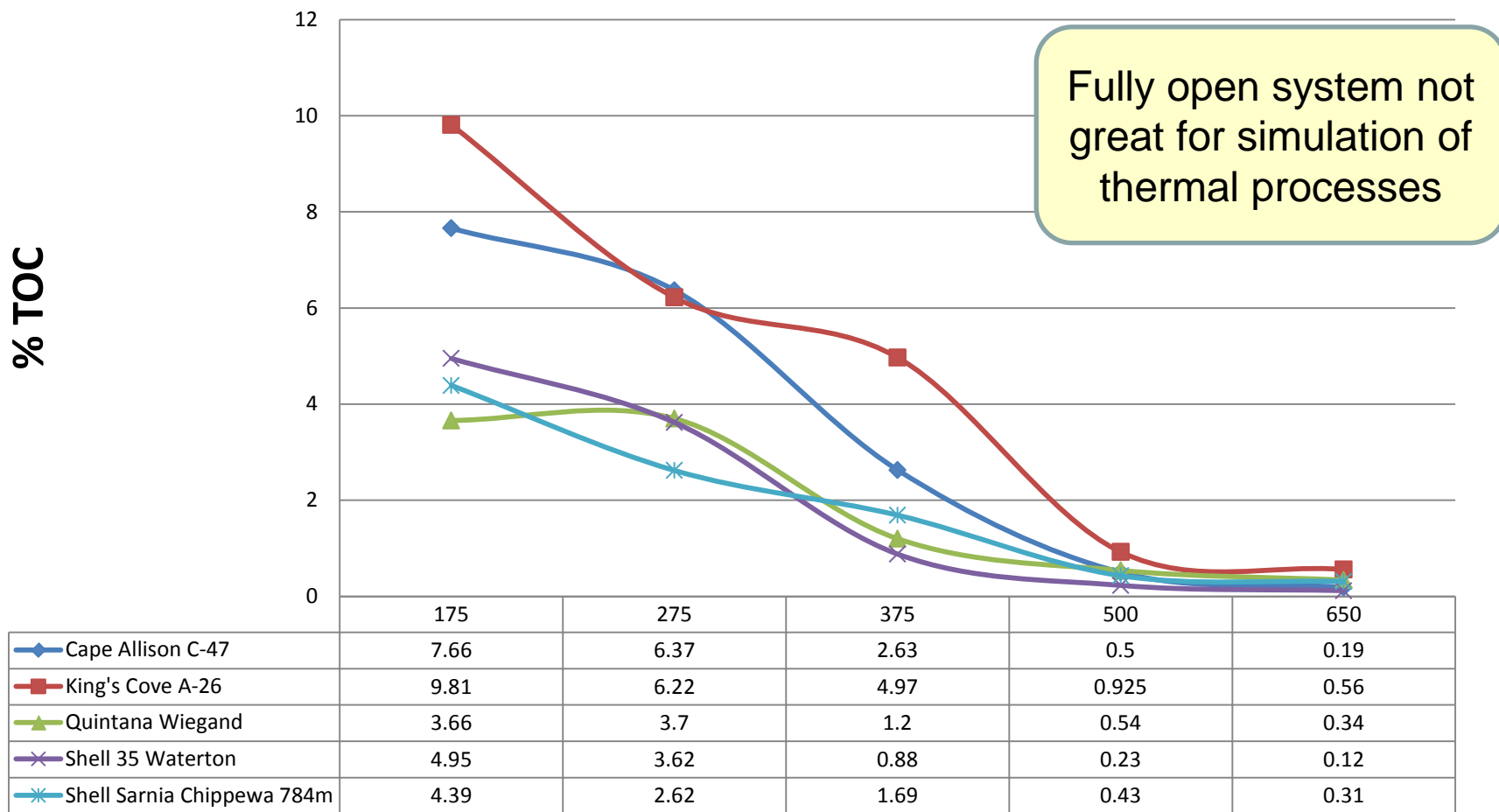
Fully open system not great for simulation of thermal processes

	175	275	375	500	650
■ Cape Allison C-47	29.05	41.16	26.57	2.01	0.04
■ King's Cove A-26	64.51	48.38	45.14	0.475	0.05
■ Quintana Wiegand	12.25	19.48	9.41	0.95	0.04
■ Shell 35 Waterton	13.95	17.08	7	0.46	0.08
■ Shell Sarnia Chippewa 784m	16.56	15.32	15.46	0.81	0.09

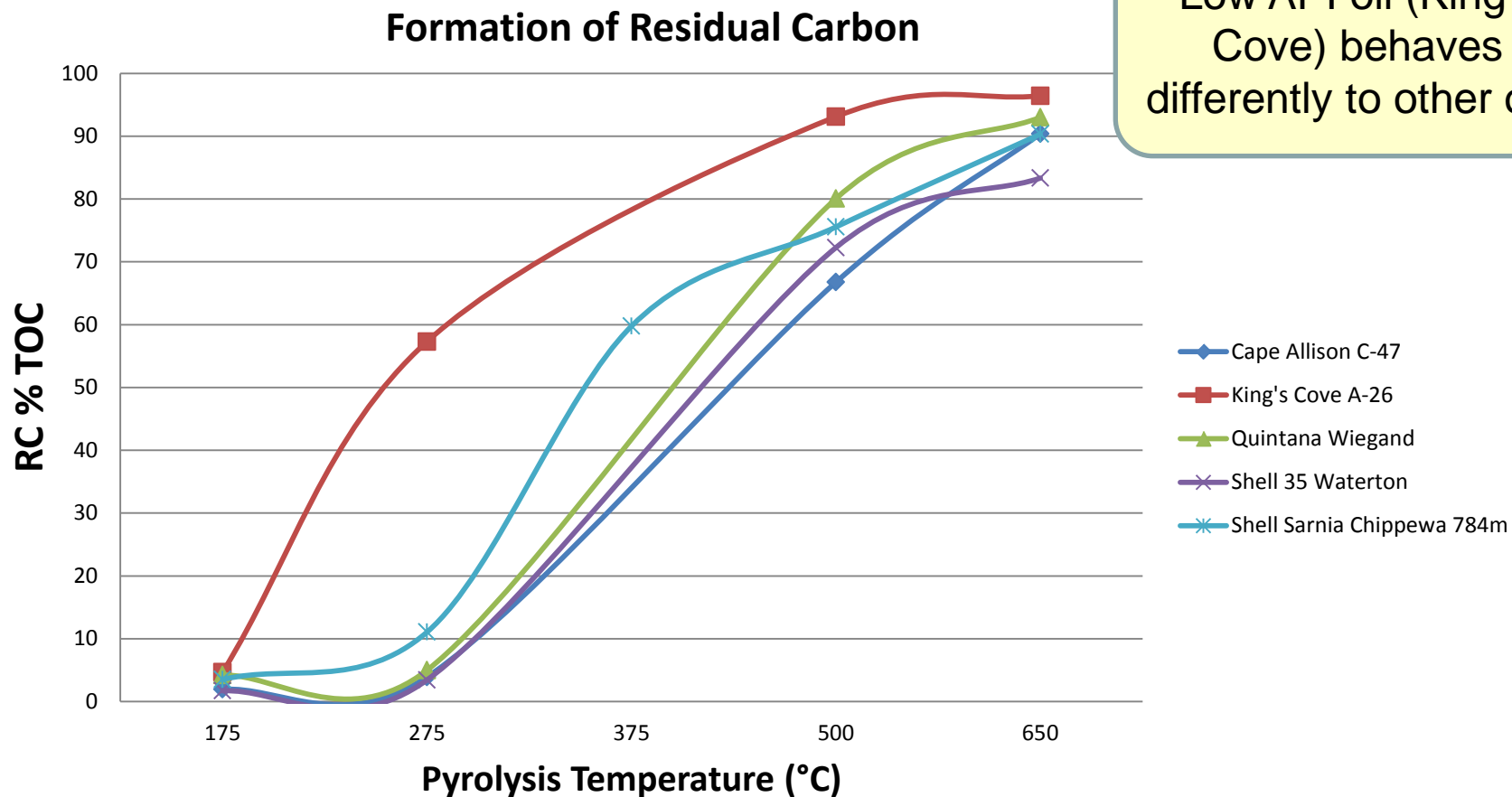


Results: TOC

TOC evolution with pyrolysis temperature



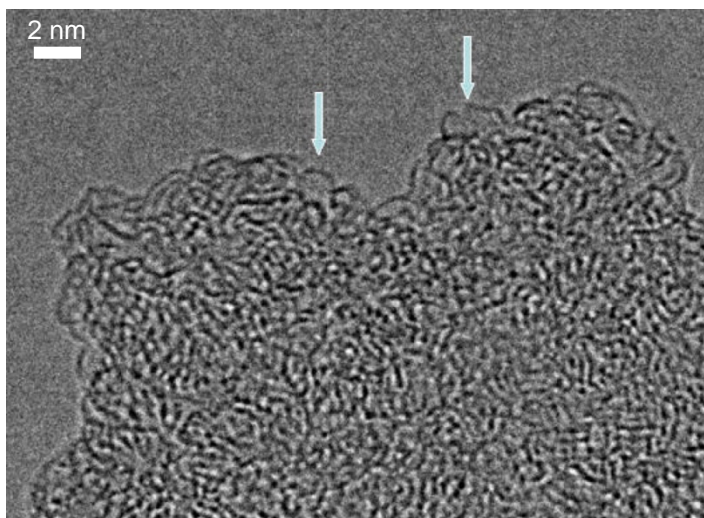
Residual (unreactive) carbon formation



Other evidence for pyrobitumen structure & composition

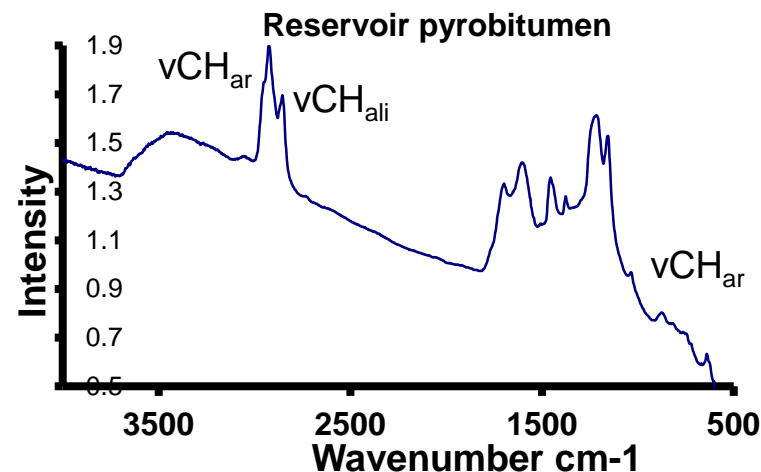
HRTEM and XRD can be useful techniques for studying nanostructure.

HRTEM

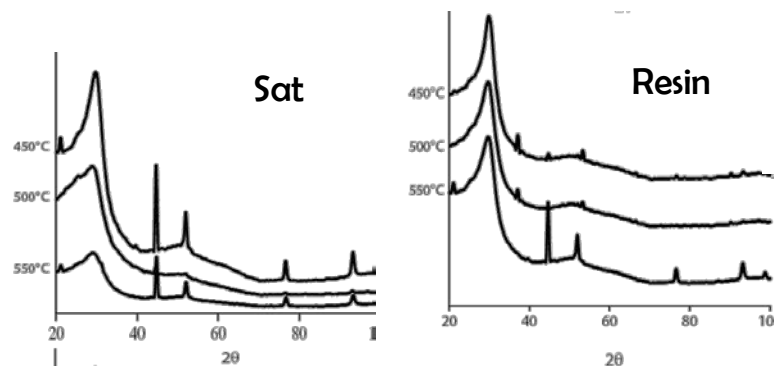


Romero-Sarmiento, M.-F., Rouzaud, J.-N., Bernard, S., Deldicque, D., Thomas, M., & Littke, R. (2014). Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation. *Organic Geochemistry*, 71, 7–16.

FTIR



XRD



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Ongoing work

- Artificial maturation of natural and oil-impregnated shales using hydrous pyrolysis
- Analysis of pyrolyzates & residues by TEM & Helium Ion Microscopy



Pyrobitumen: conclusions & ongoing musings

- Extent of pyrobitumen formation is dependent on precursor composition
- Properties vary with thermal evolution and precursor oil composition
- If precursor composition can be used to predict some properties of pyrobitumen it may be possible to incorporate these data into predictive models of hydrocarbon generation
- Pyrobitumen formation is likely to be dependent on bitumen retention as well as composition



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