How Mobile is your Total Oil Saturation? SARA Analysis Implications for Bitumen Viscosity and UV Fluorescence in Niobrara Marl and Bakken Shale, Supported by FIB-SEM Observations of Kerogen, Bitumen and Residual Oil Saturations within Niobrara Marls and Chalks*

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Search and Discovery Article #41903 (2016)**
Posted October 10, 2016

*Adapted from oral presentation given at AAPG Annual Convention & Exhibition, Calgary, Alberta, Canada, June 19-22, 2016

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Abstract

Variations in UV fluorescence among a continuum of rock types from clean Niobrara Chalk through black Niobrara Marl led us to investigate the role of asphaltenes percent not only on quenching of UV fluorescence but, more importantly, on hydrocarbon viscosity. Stepwise reintroduction of separated asphaltenes into an asphaltene-free extract of Niobrara Marl demonstrates asphaltene quenching of UV fluorescence and associated progressive increases in viscosity, even when measured at full bottom-hole temperatures. This simple study raises questions about the validity of log and core-derived (solvent-based) So, is it mobile oil or highly viscous bitumen? Parallel nano-scale FIB-SEM investigations of depressurized/degassed core samples suggest that contextual and morphologic distinctions are possible among kerogen, bitumen, and residual oil saturations (Sor).

Our earlier SARA extraction work on the Bakken Shales demonstrates extreme differentiation in asphaltene percent between extracts from Upper and Lower Bakken shales versus from the intervening Middle Bakken reservoir cores as well as from produced fluids, to the point that we began to strongly question the relevance of source rock “So” derived from log and core analyses because its producibility was highly questionable due to high viscosity. The Niobrara, by contrast, shows a complete continuum between clean chalk and source rock “marl”, also expressed by gradational attributes such as gray-scale (% carbonate and %TOC), UV fluorescence, and asphaltene percent. This led us to pursue more involved extraction experiments to determine whether asphaltenes percent impacts viscosity to the degree that we must ask what percent of OOIP is really Mobile Oil in Place

within Niobrara Marls? SEM imaging suggests that kerogen, bitumen, and residual (mobile) oil saturation ("Sor") can and should be differentiated. Not only does this have implications for flow capacity from source rocks in the oil window, but it has important implications for "Mobile" Original Oil in Place (OOIP) Calculations, which in turn impact expected and observed Recovery Factors. We need to understand bitumen evolution every bit as much as kerogen evolution when exploring for and exploiting tight oil plays. At reservoir conditions, is produced oil in full solution with the bitumen we extract from source rocks and hybrid reservoir/source rocks or are they two distinct phases in the reservoir, with bitumen behaving more as an obstruction to flow that inconveniently calculates as So?

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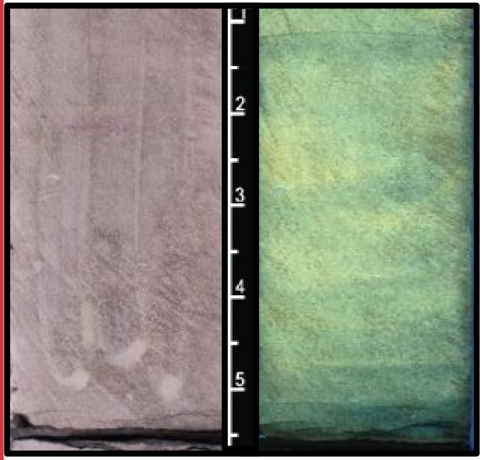
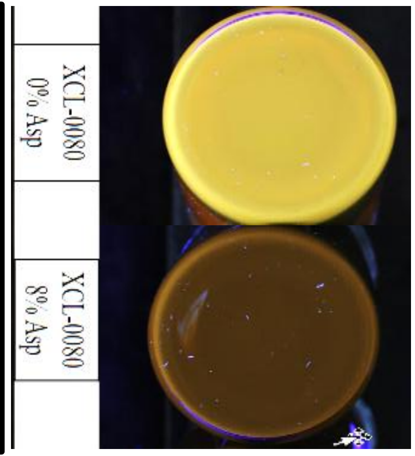
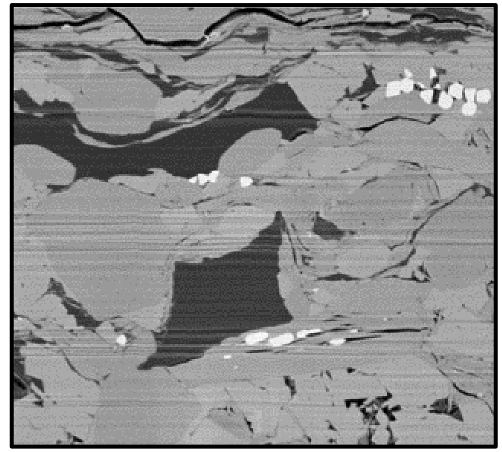
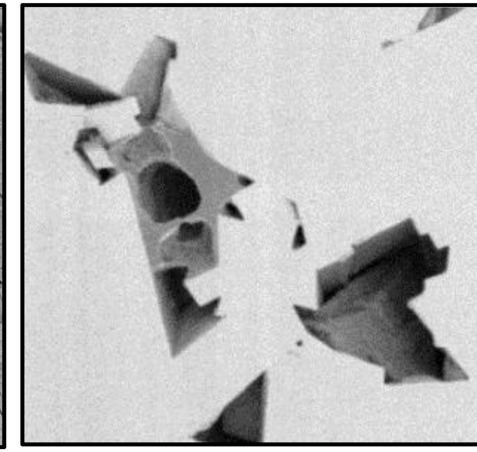








How Mobile is Your Total Oil Saturation?

SARA Analysis Implications for Bitumen Viscosity and UV Fluorescence in Niobrara Marl and Bakken Shale, Supported by FIB-SEM Observations of Kerogen, Bitumen, & Residual Oil Saturations within Niobrara Marls & Chalks

Mark D. Sonnenfeld and K. Lyn Canter

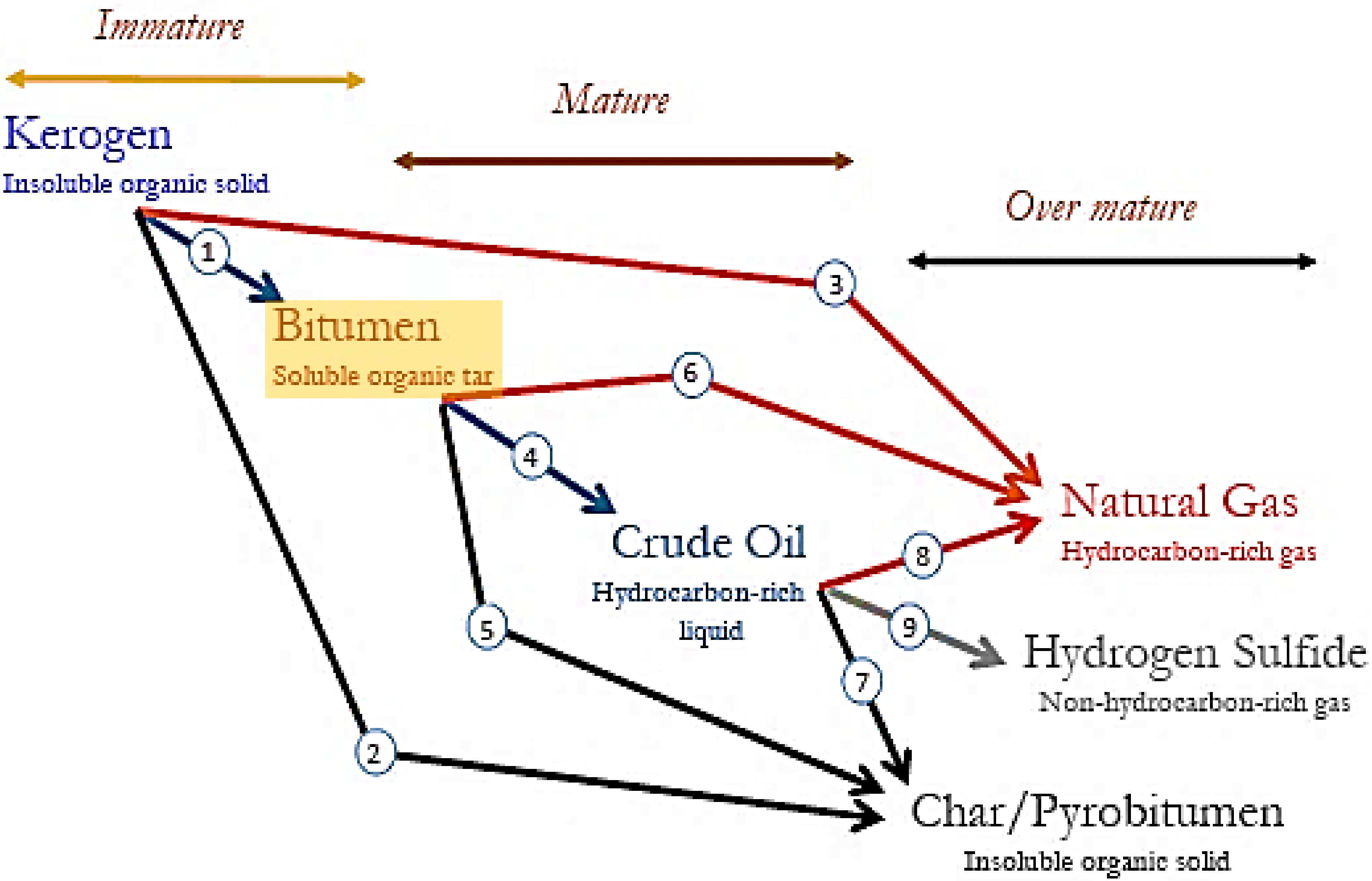
Whiting Petroleum Corp.

AAPG Calgary, January 21, 2016

Outline:

1. The *Underemphasized* Relevance of Bitumen
2. Hydrocarbon Composition Impacts on Viscosity
3. SARA Fractionation for Hydrocarbon Characterization
4. Primary Expulsion Fractionation:
    - Global Data
    - Bakken and Niobrara SARA Extraction Experiments
5. SEM Images of Kerogen, Bitumen, & Sor
6. Implications for *Mobile* Oil-in-Place

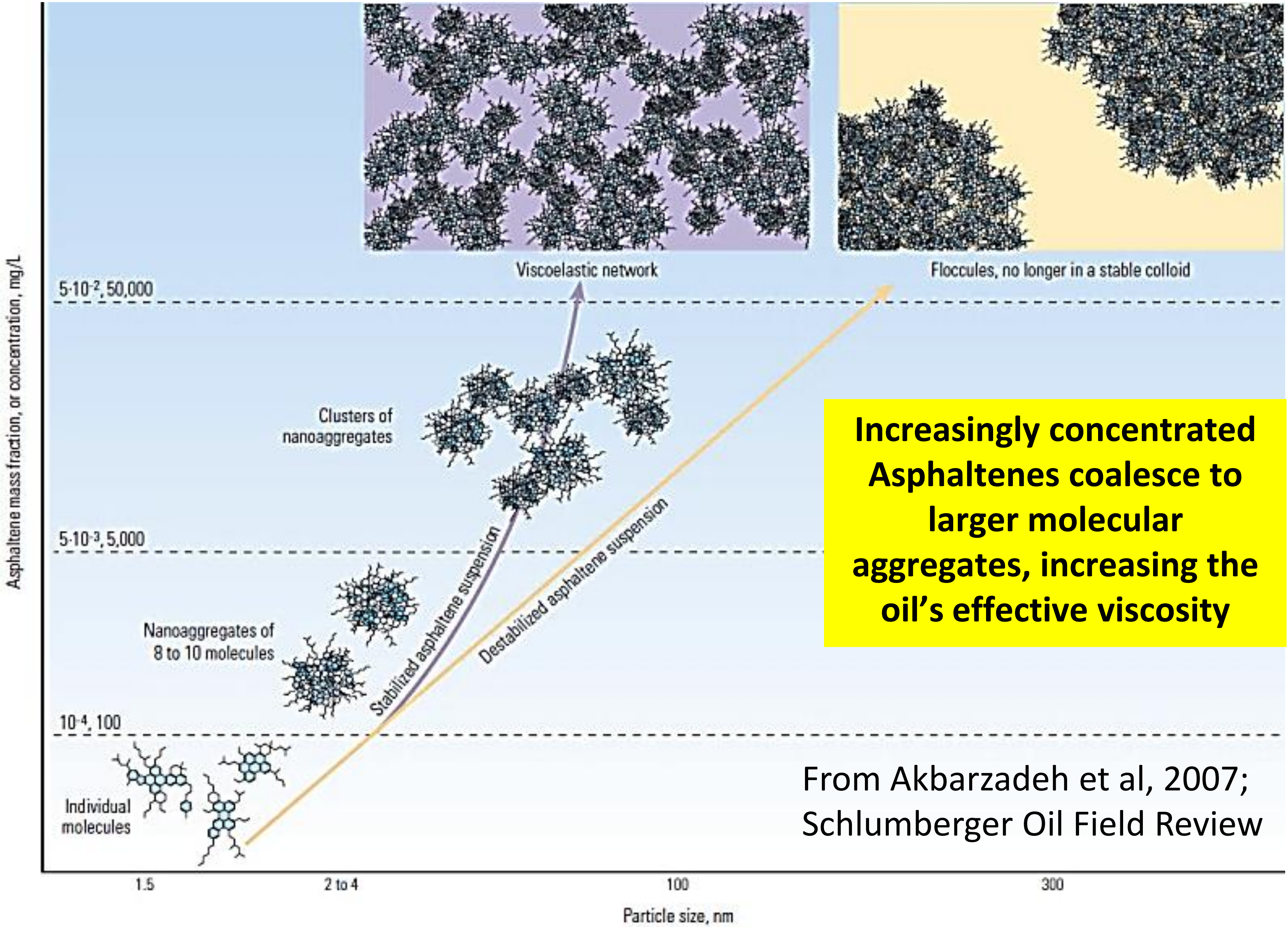
Petroleum Generation



Courtesy Michael Lewan, USGS

Historical Recognition of Bitumen

- Oil-shale retort studies in the early 1900s recognized bitumen as an intermediate between Kerogen and light oil (Engler, 1913; McKee and Lyder, 1921; Franks and Goodier, 1922).
- Louis and Tissot (1967), reiterated the concept of bitumen as an intermediate in natural petroleum generation.
- However, open system <u>anhydrous</u> pyrolysis *de-emphasizes* intermediate bitumen because all hydrocarbon products are volatilized.

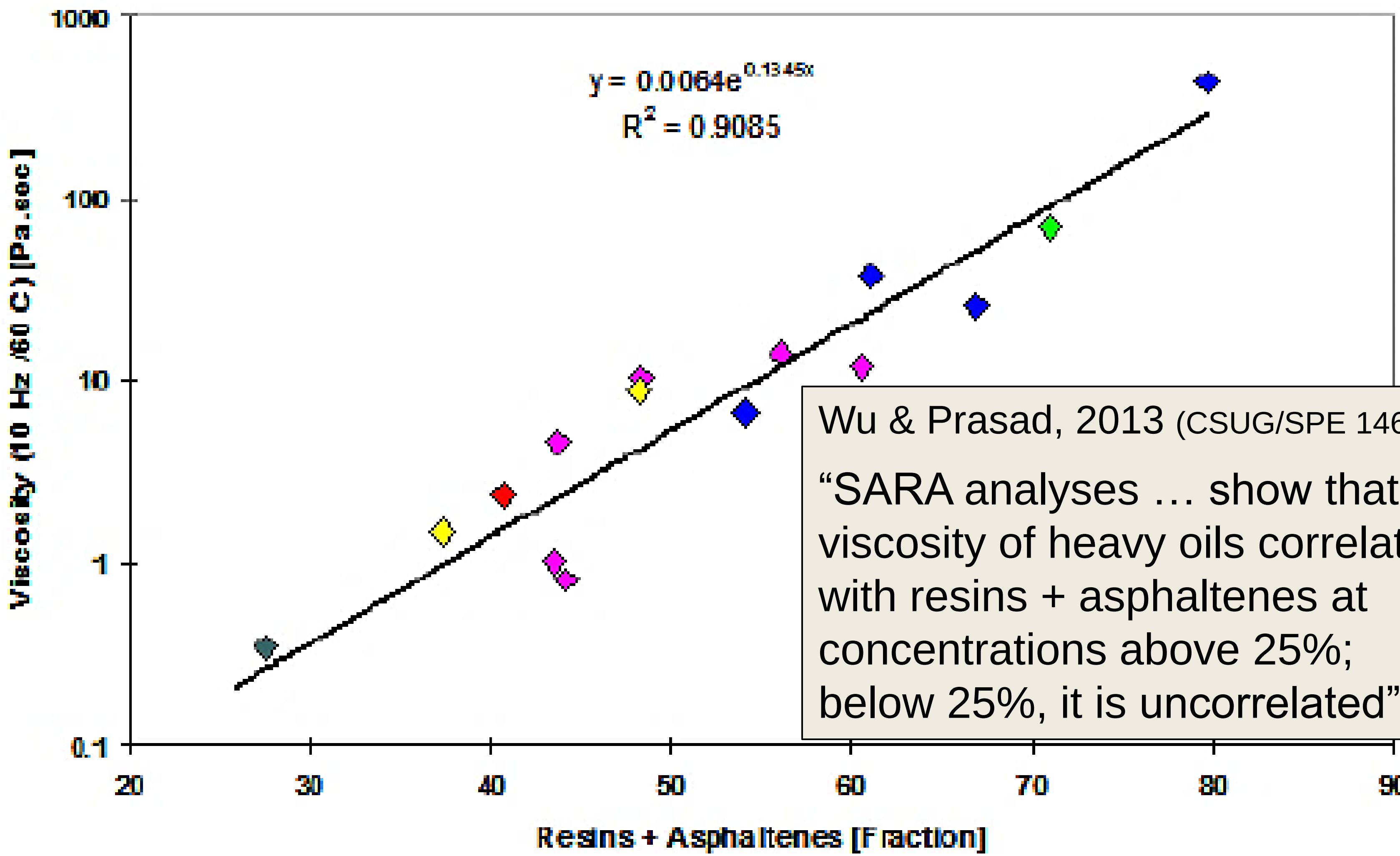


Increasingly concentrated Asphaltenes coalesce to larger molecular aggregates, increasing the oil's effective viscosity

From Akbarzadeh et al, 2007; Schlumberger Oil Field Review

NYSE: WLL

Viscosity vs. %(Resins + Asphaltenes)



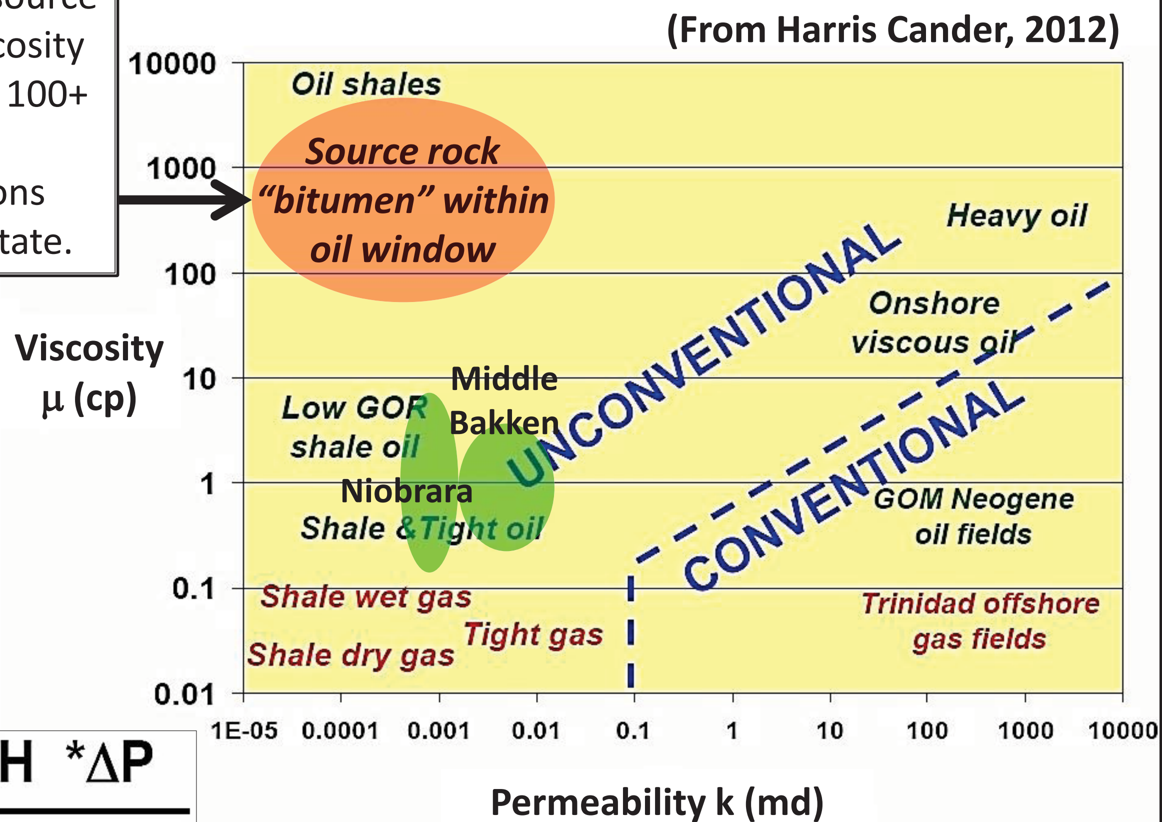
Wu & Prasad, 2013 (CSUG/SPE 146107):

"SARA analyses … show that viscosity of heavy oils correlates with resins + asphaltenes at concentrations above 25%; below 25%, it is uncorrelated"

NYSE: WLL

Viscosity Matters for Darcy Flow…

Our contention: source rock bitumen viscosity varies from 10 to 100+ cp, depending on reservoir conditions and maturation state.



$$Q = \frac{k * H * \Delta P}{\mu}$$

NYSE: WLL

Presenter's notes: Cander emphasizes the role of perm and viscosity in defining "problematic" hydrocarbon accumulations than can be viewed as "unconventional"… Production solutions either increase surface area through hydraulic stimulation, or reduce viscosity through application of heat…

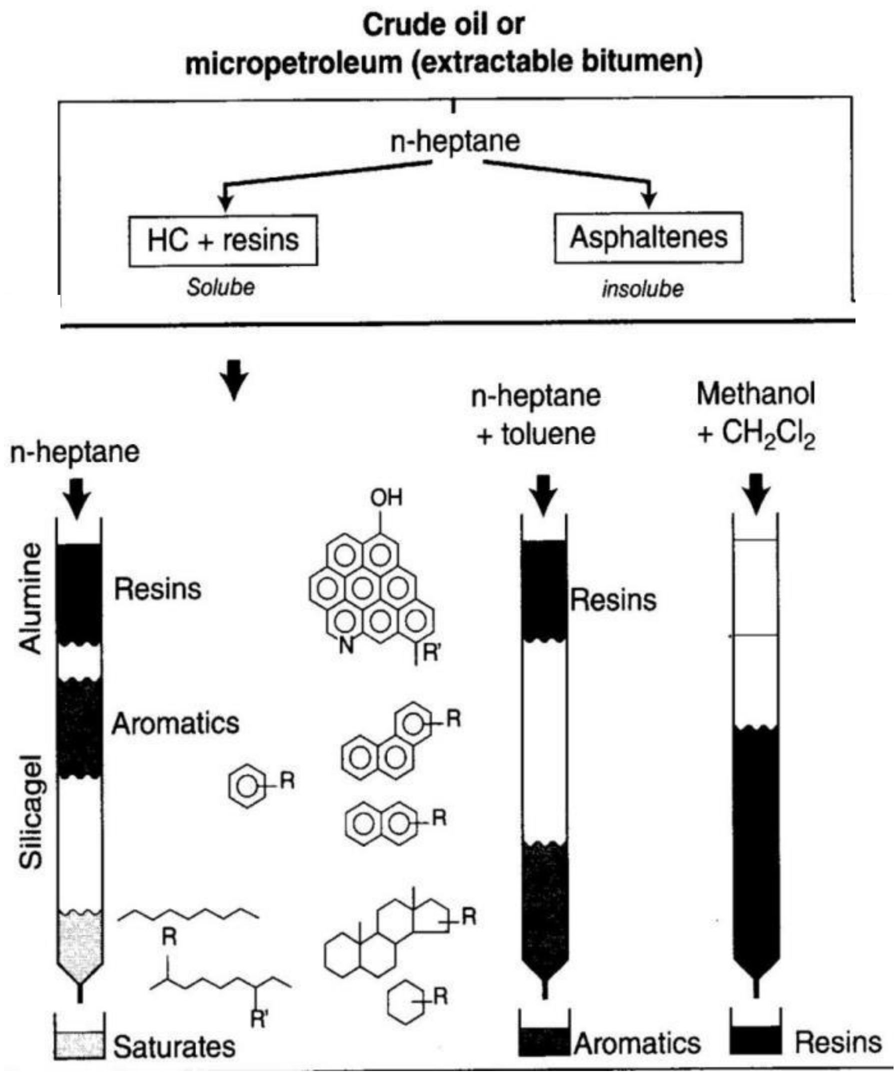
SARA Column Chromatography:

First: Methylene Chloride extraction of **Bitumen**;

Then, **Asphaltene fraction** removed by adding n-heptane to destabilize Asphaltene-Resin aggregates and induce Asphaltene precipitation for simple filtration.

Remaining **SAR (="Maltene"=HC + resins)** is added to a column filled with adsorbent silica gel and/or alumina suspended in n-hexane solvent.

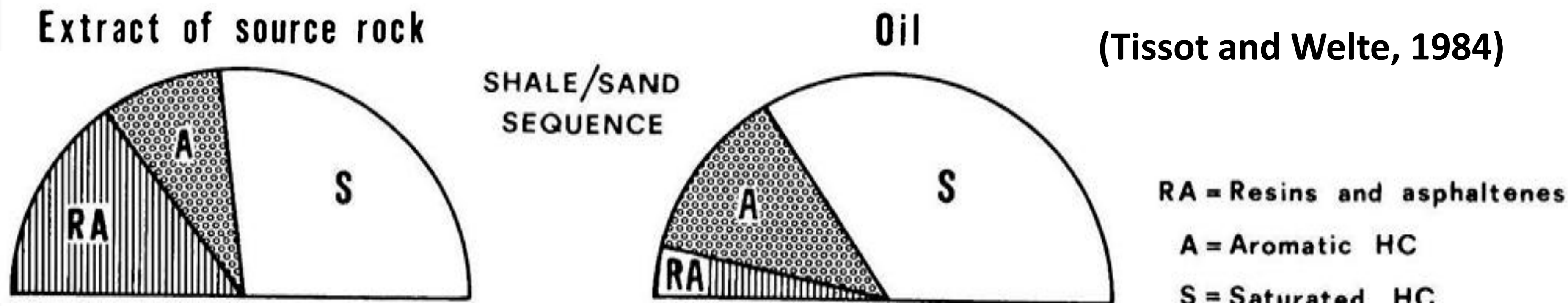
- Dissolved **Saturates** elute first (run through column) with *least polar* solvent (n-hexane)
- **Aromatics** elute second with stronger (*more polar*) benzene solvent.
- **NSO's ("resins")** remain nearly stationary until eluted with *most polar*, chlorethane methanol solvent



From Huc, 2013

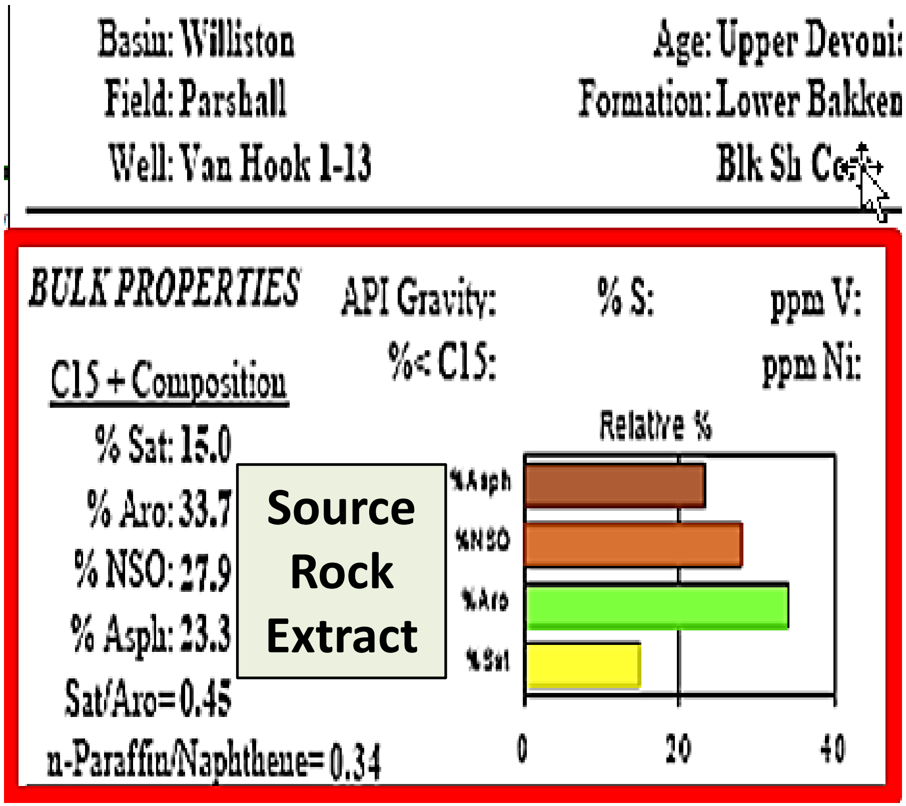
Oil vs. Source Rock Bitumen—Global Database

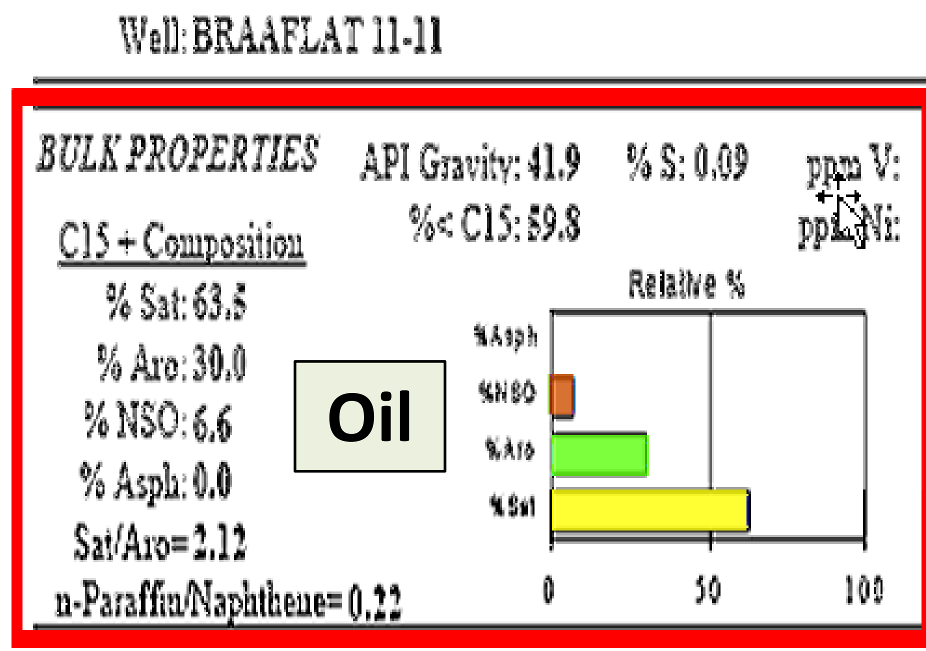
(Tissot and Welte, 1984)



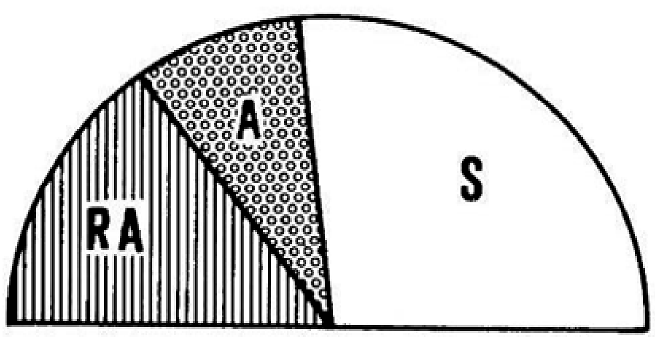
only a small amount of the total dispersed bitumen is mobilized and transferred into carrier or reservoir rocks, and an even smaller amount is accumulated in oil fields. The heaviest and most polar molecules, like asphaltenes, are strongly adsorbed on the source rock and can hardly be expelled into the reservoir. Therefore, the common distribution of petroleum constituents in crude oil parallels the adsorptive behavior of these constituents, i.e., the least polar saturated hydrocarbons are most frequent, then follow aromatics and benzothiophenes, and least abundant are the most polar and most easily adsorbed resins and the least soluble asphaltenes.

From Geomark “O.I.L.S.” database





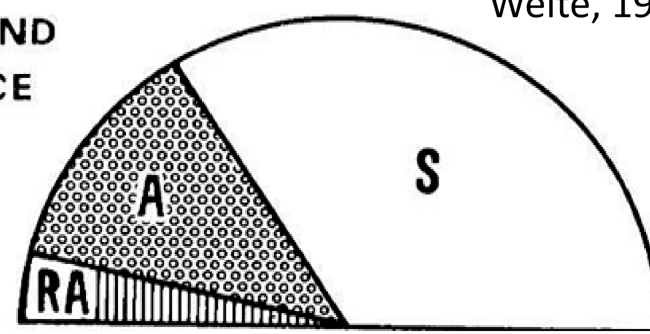
Extract of source rock



SHALE/SAND SEQUENCE

Oil

(Tissot and Welte, 1984)



Chromatographic Separation during Primary Migration

“Principles of column chromatography … are essentially the same as for chromatographic separation of compounds during (primary) migration.”

(D. Waples, 1985)

… geochromatographic effect must be associated with expulsion in order to explain the preferential expulsion of saturated hydrocarbons over NSO-compounds.

From “Recognition and quantification of the effects of primary migration in a Jurassic clastic source-rock from the Norwegian continental shelf”

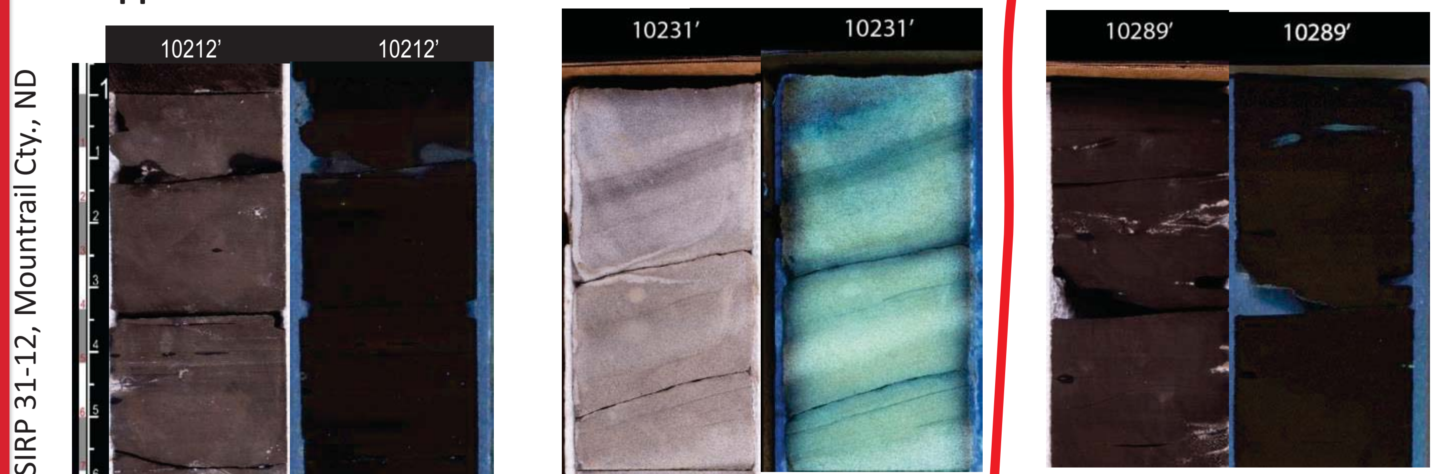
A. Wilhelms, S.R. Larter, D. Leythaeuser, and H. Dypvik, *Advances in Organic Geochem*, 1990

Bakken Produced Oil vs Extracts:

58.6%<C15 (Locken 11-22h):

%Sat: 50.1, %Aro: 44.0, %R:5.9, %**Asph: 0.0**

Upper Bakken Sh | Middle Bakken "B" | Lower Bakken Sh



% Sat: 10.6 % Res: 18.2
% Aro: 37.3 % Asph: 34.0

%Sat: 40.3% %Res: 35.6%
%Aro: 15.8% %Asph: 8.4%

% Sat: 11.1 % Res: 17.4
% Aro: 36.3 % Asph: 35.3

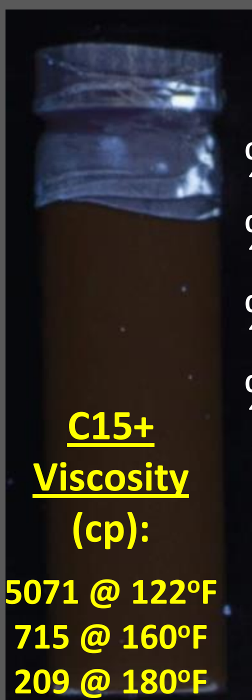
NYSE: WLL

Presenter's notes: Note molecular fractionation from source rock to adjacent reservoir (primary migration effect); later on there is also production fractionation between produced oil and Sor.

- Experiment shows QUENCHING effect of Asphaltenes on UV, from bright yellow toward dull gold-brown to no UV (365nm excitation wavelength)
- Presence of polar Asphaltenes INCREASES VISCOSITY & tendency toward oil-wet condition.

Upper Bk Sh

API=7.9



% Sat: 10.6

% Aro: 37.3

% NSO: 18.2

% Asph: 34.0

Methylene Chloride extraction

Lower Bk Sh

API=5.4

% Sat: 11.1

% Aro: 36.3

% NSO: 17.4

% Asph: 35.3

Methylene Chloride extraction

Lower Bk Sh

API=16.9

% Sat: 29.6

% Aro: 48.3

% NSO: 22.2

% Asph: 0.0

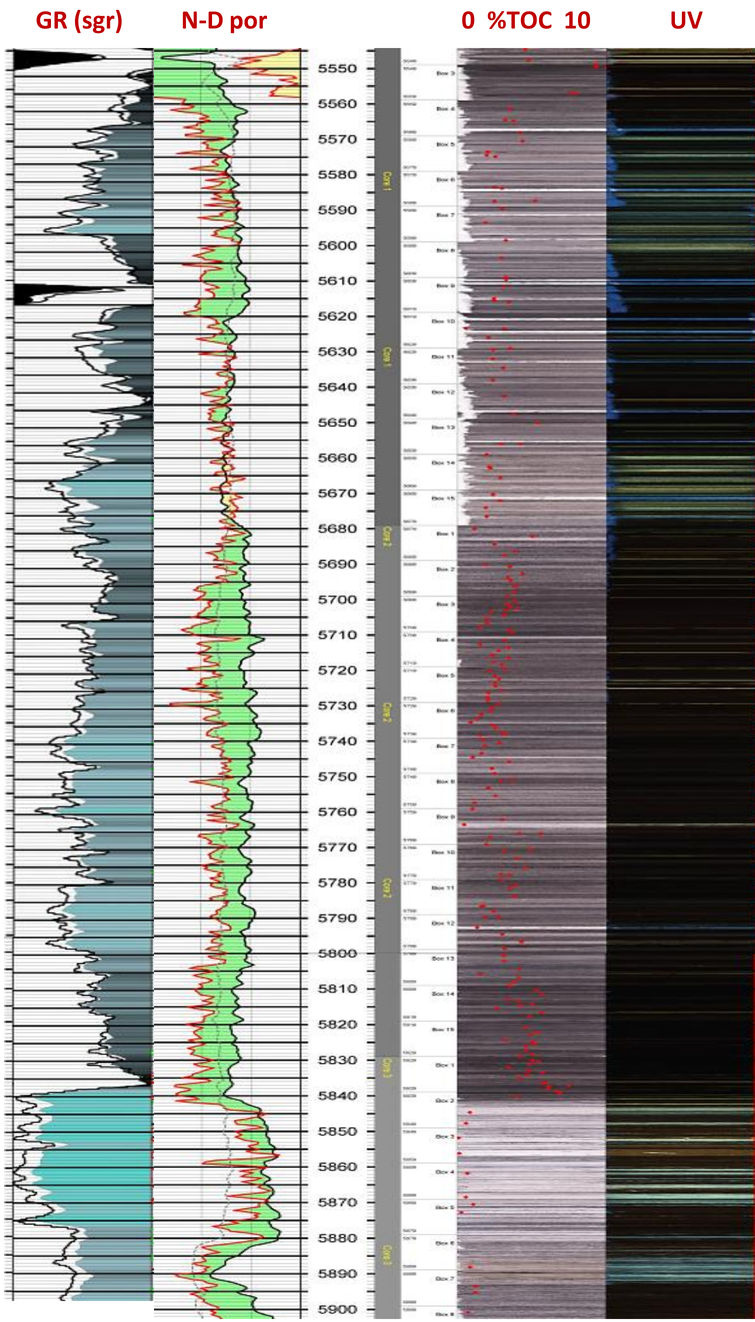
n-Hexane extraction

Bakken vs. Niobrara:

- SARA extraction work on Bakken Shales demonstrated extreme differentiation in Asphaltene% between extracts from Bakken shales *versus* extracts from the intervening Middle Bakken reservoir.
- We tend to question the relevance of Bakken *source rock* “So” derived from log and solvent-based core analyses because liquids producibility is plagued by high bitumen viscosities.

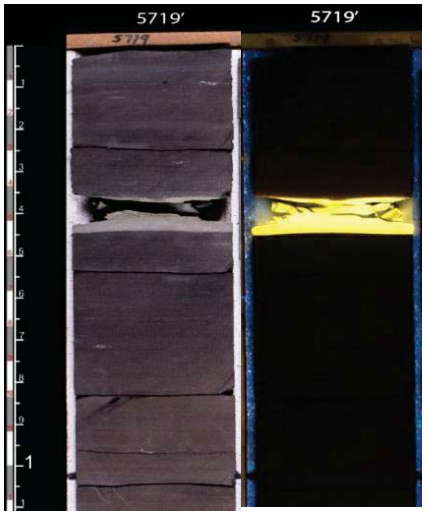
Bakken vs. Niobrara:

- Niobrara, by contrast, contains a continuum between clean chalk and source rock "marl"
- Expressed by gradational attributes:
  - gray-scale (f: % carbonate, % clays, %OM, [U]),
  - UV fluorescence
- Pursued more involved extraction experiments to further assess %Asphaltene impact on viscosity and UV



Whiting Oil and Gas Razor 25-2514

Niobrara "B marl"



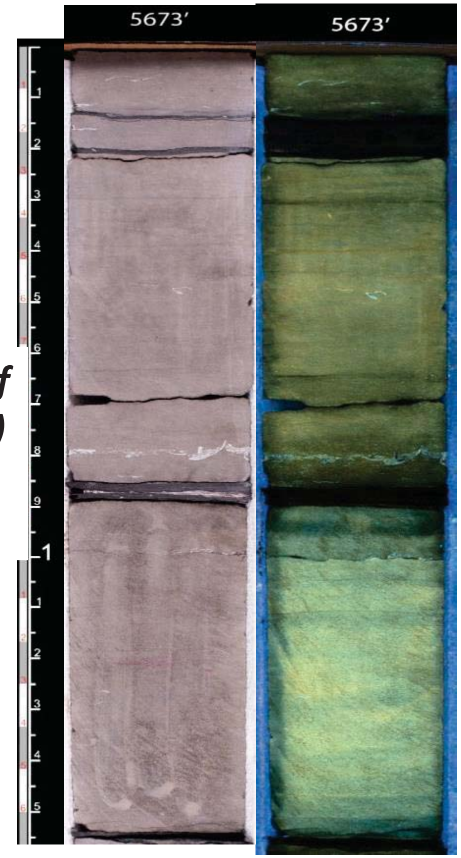
% Sat: 36.4
% Aro: 34.6
% Res: 15.2
% Asph: 13.9

More polars: Bitumen and mobile oil (but how viscous?)

Niobrara B Chalk "bench"

%Sat: 48.1%
%Aro: 28.3%
%Res: 14.5%
%Asph: 9.2%

Combination of mobile oil (Sor) and minor bitumen.



Razor 26-3524H **Produced 36.3 API oil**
(*50.4%<C15*)
%Sat: 57.8, %Aro: 26.1, %R:15.8, %**Asph: 0.4**

NYSE: WLL

Presenter's notes: Note molecular fractionation from source rock to adjacent reservoir (primary migration effect); later on there is also production fractionation between produced oil and Sor.

Stepwise Asphaltene Reintroduction Experiments:

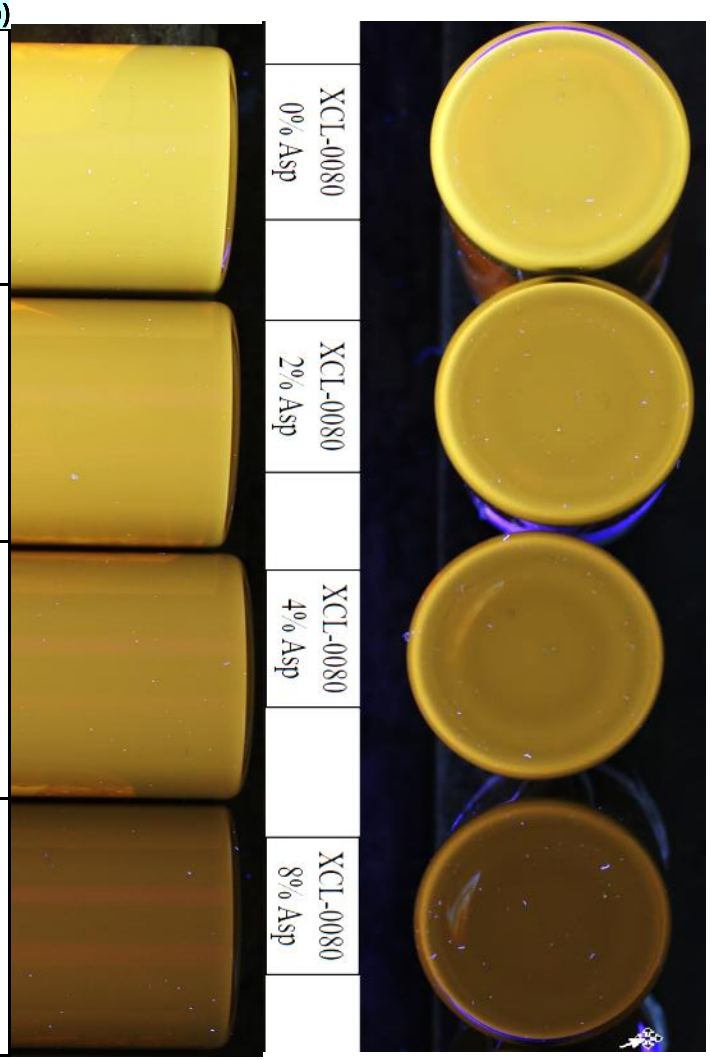
Niobrara Marl solvent-extractions with stepwise asphaltene reintroduction performed with Geomark Research:

- Perform separate n-Hexane and Dichloromethane extracts on Nio. B marls to yield 1-2ml each.
- Precipitate out Asphaltenes from DCM extract.
- Incrementally add Asphaltenes (now a black powder) back to the Asphaltene-free n-Hexane extracts to create separate 2-4-6-8% admixtures.
- Measure API gravity and viscosity (Core Lab Bakersfield).
- Viscosity measured at 122, 160, 180, 200, & 220 degrees F.

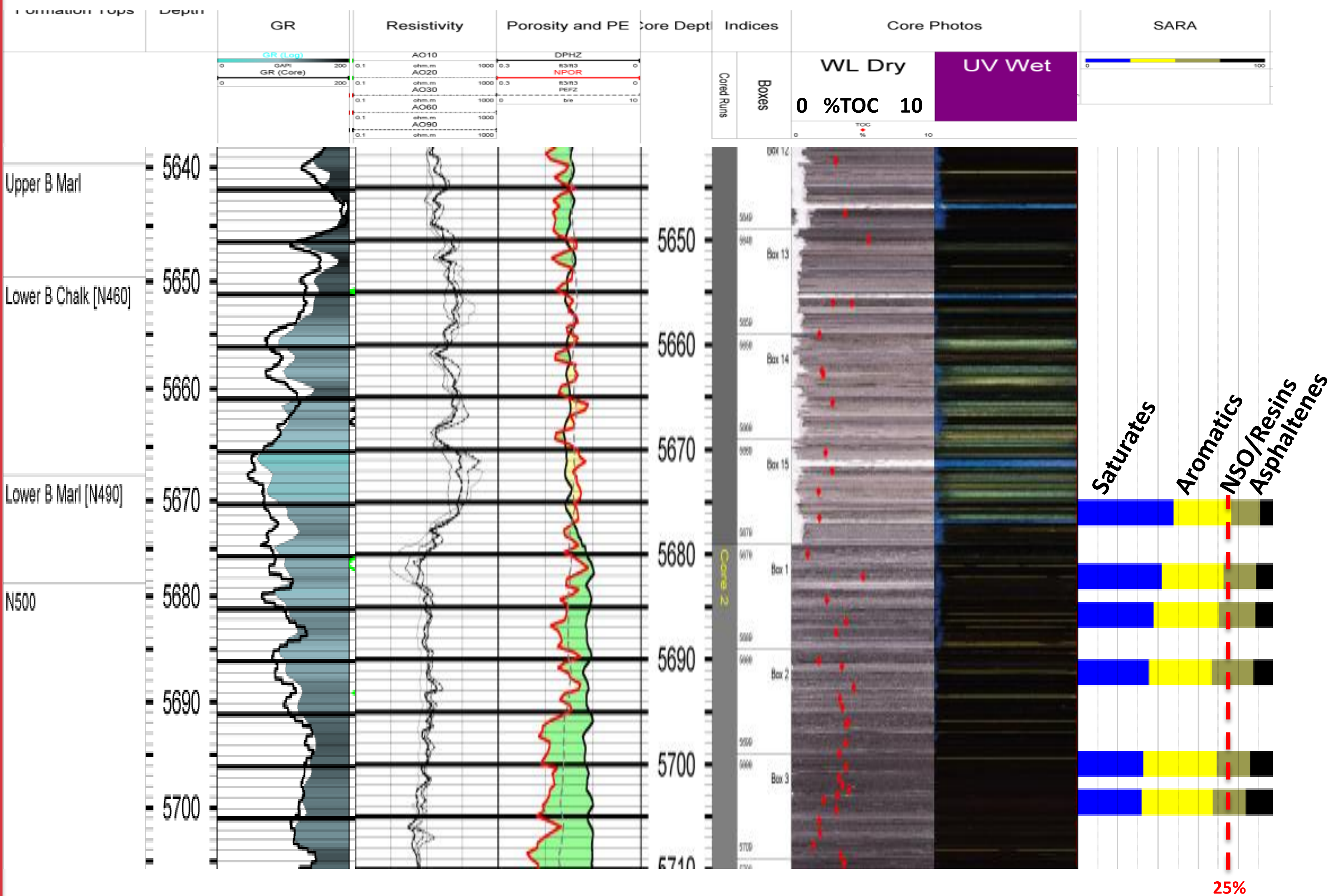
Stepwise Asphaltene Re-introduction:

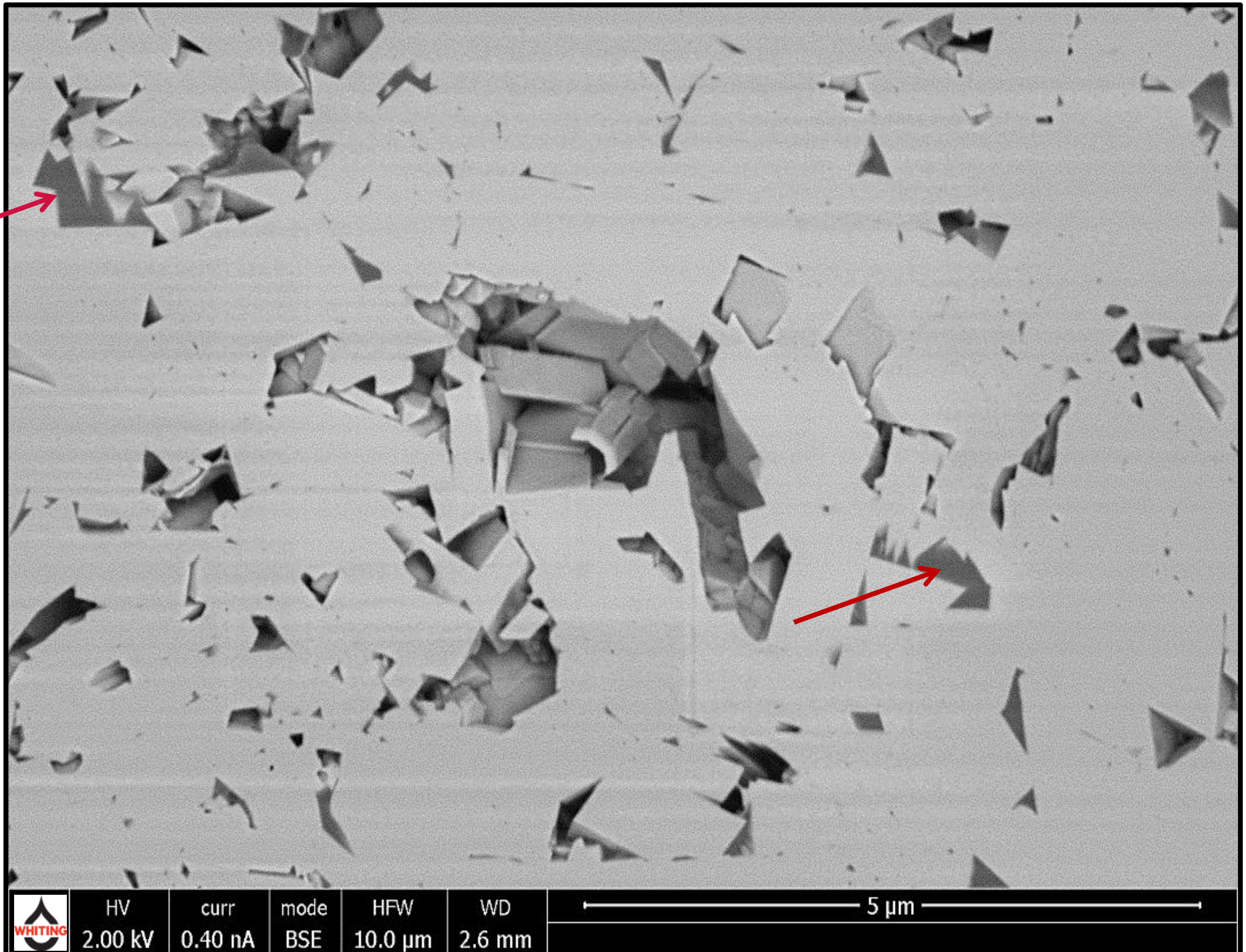
Sample ID	Temp °F	°API	Viscosity (cp)
0% Asp	60	15.0	---
	122		170
	160		54.0
	180		34.0
	200		23.0
	220		14.9
2% Asp	60	14.2	---
	122		220
	160		67.5
	180		41.6
	200		28.4
	220		19.4
4% Asp	60	13.7	---
	122		270
	160		80.5
	180		48.4
	200		32.8
	220		19.8
8% Asp	60	12.8	---
	122		429
	160		118
	180		67.1
	200		34.2
	220		28.8

Core Lab RESERVOIR OPTIMIZATION

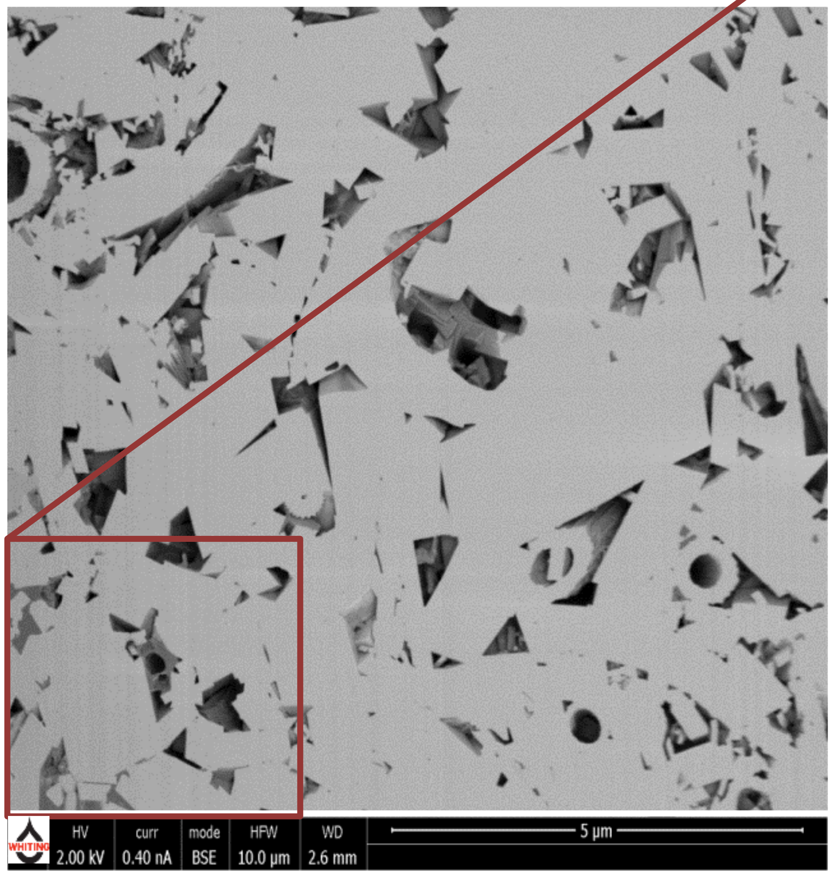


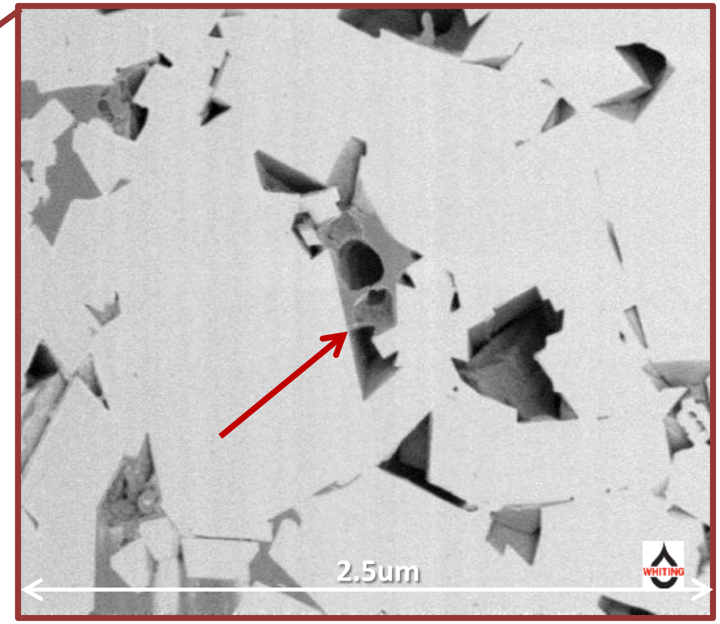
- **Asphaltene % impacts viscosity and therefore producibility, especially in tight oil plays.**
- **Pitfalls to simplistic UV interpretation:**
  - ***Asphaltene quenching is as or more important than Aromatic concentration***

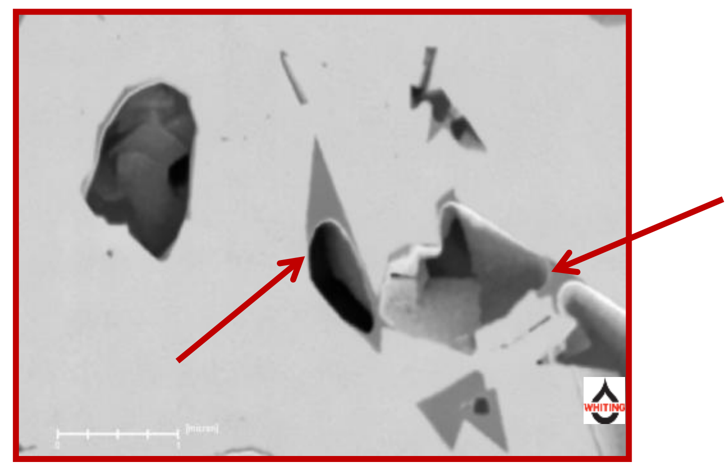

GR
Resistivity
Porosity and PE
Indices
Core Photos
SARA
GR (Log)
GR (Core)
AO10
AO20
AO30
AO60
AO90
DPHZ
NPOR
PEFZ
Cored Runs
Boxes
WL Dry
0 %TOC 10
UV Wet
Upper B Marl
Lower B Chalk [N460]
Lower B Marl [N490]
N500
5640
5650
5660
5670
5680
5690
5700
5710
Core 2
Saturates
Aromatics
NSO/Resins
Asphaltenes
25%



- **Niobrara Chalk: Residual hydrocarbon fills euhedral crystal lined pores (arrows). TOC is very low in the chalks. Minor OM_S in small pores (OM_S = secondary / migrated OM).**

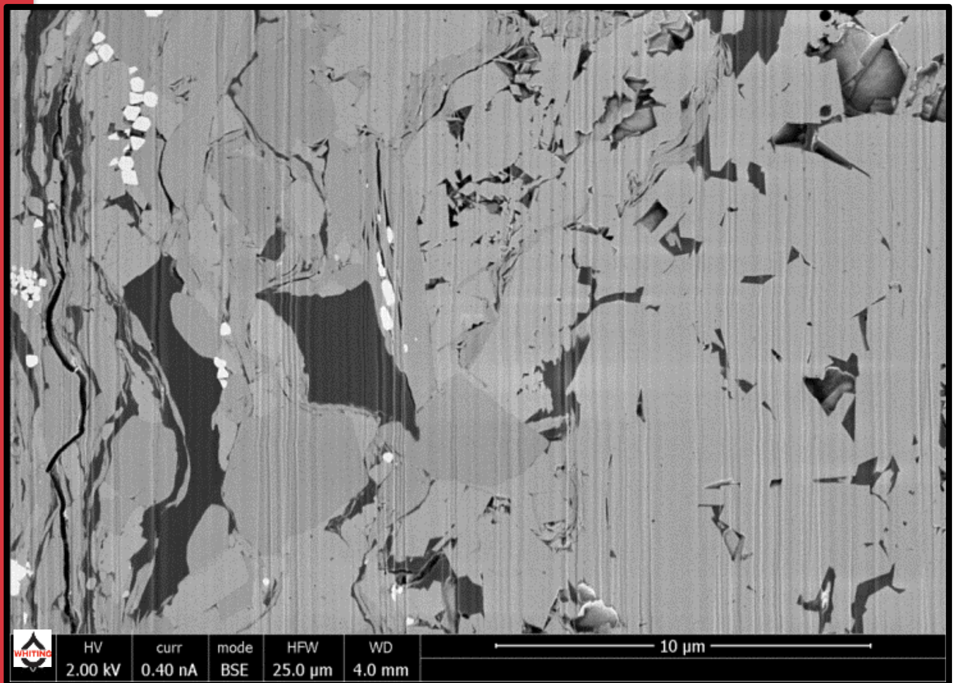






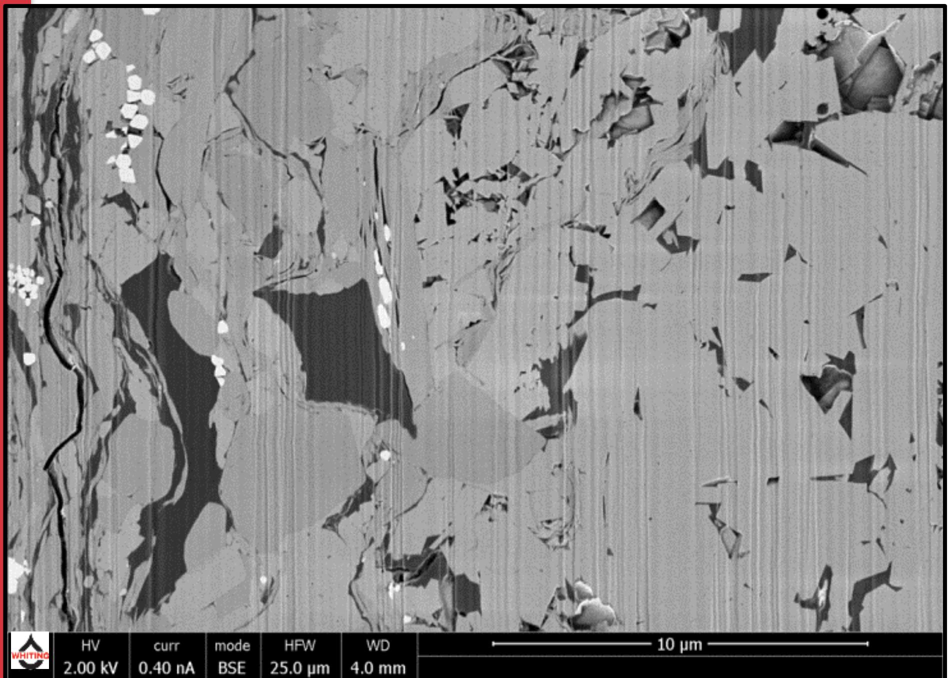
- **All of the OM is in euhedral crystal lined pores, therefore it represents migrated oil (OM_S).**
- **Obvious "meniscus" habit suggestive of fluid, residual oil (Sor) in a partially oil-wet system (arrows)**

Before Toluene

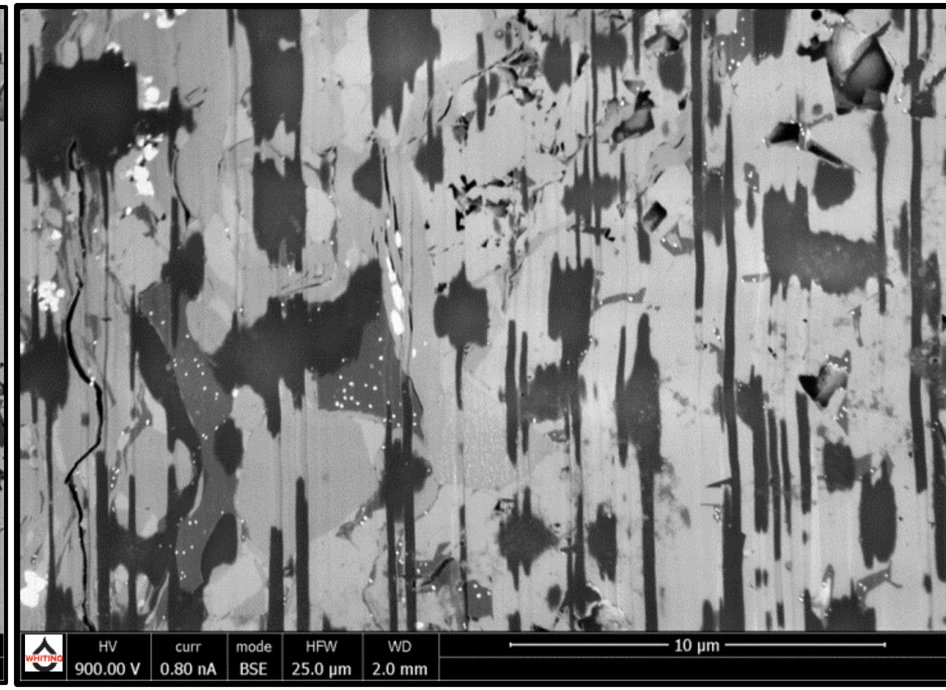


- Niobrara Chalk Example
- Kerogen lamination at left (vertical, but originally horizontal) is partially converted to bitumen based on sporadic solvent dissolution (Kerogen is NOT soluble in organic solvents; but bitumen is).

Before Toluene

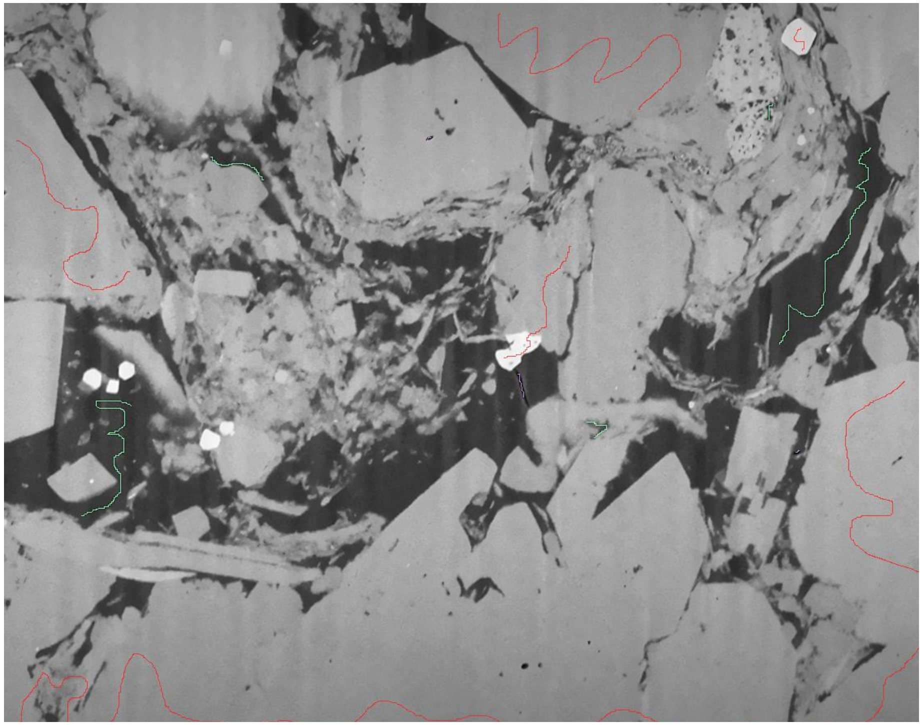


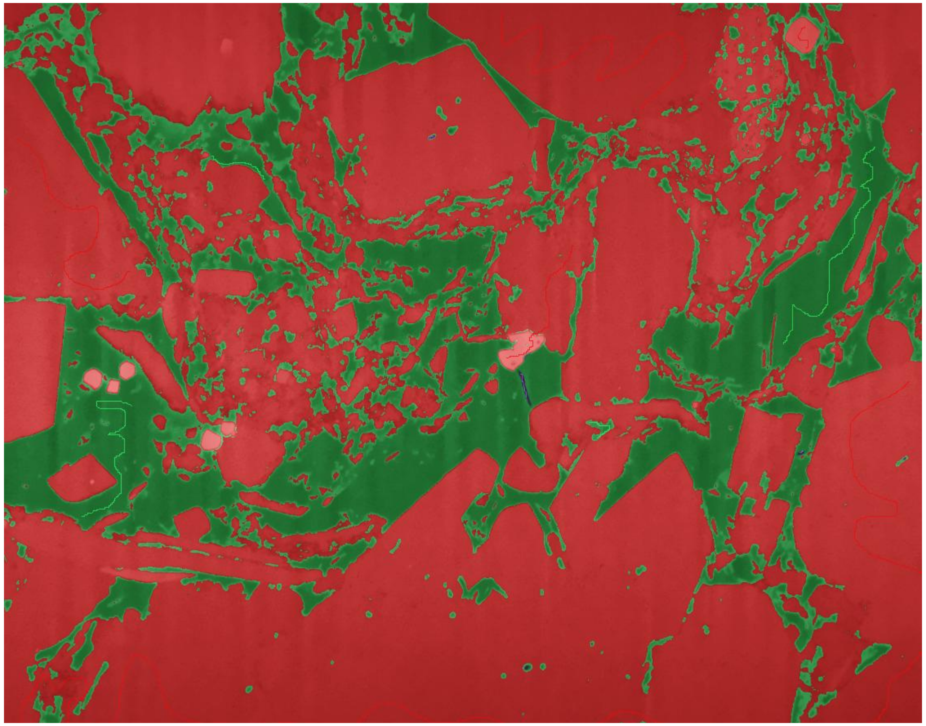
After
Toluene-soak (partial extraction)



- *"poor-girl" Toluene extraction* of marly chalk (at ambient temp.)
- More complete dissolution of hydrocarbons filling of euhedral pores at right—this is probably ALL bitumen. Open pores at upper center and far right represent voided pores, probably originally filled with mobile oil. ALL THREE EXIST IN COMPLEX MARLY FABRICS — this is a true hybrid source rock / lower grade reservoir.

Digital Dissolution within a Nio Marl:



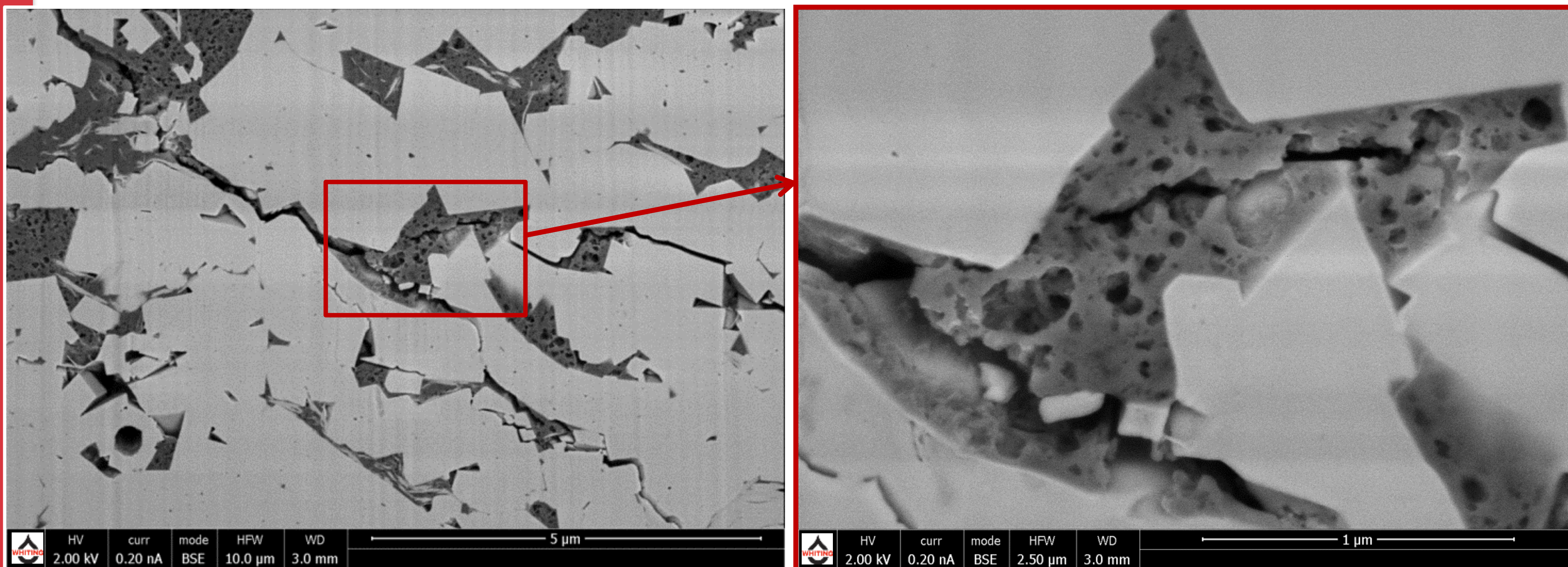


- Nio Marl with significant bitumen-filled porosity
- Negligible "voided" pore space which would be expected had these pores been filled with light oil…

- Green represents "digital dissolution" of all bitumen (and any Sor).
- A grossly *over-optimistic* portrayal of mobile oil that is equivalent to what Dean Stark analyses would portray…

Wattenberg Niobrara – Gas condensate window:

Well-developed pores predominantly within bitumen (gas escape) pores in bitumen …



<u>Interpretation</u>: This is NOT kerogen nanoporosity.

- Pores are a result of more advanced bitumen cracking than at Redtail (oil window)

Material density

Conclusions:

- Closely consider whether your log and core-derived So is *mobile* oil or highly viscous bitumen… Solvent-based extraction techniques, at least as conventionally implemented, extract both.
- We recognize that SARA extractions lack the C1-C14 fraction (lost with solute evaporation), so exact property measurements, especially viscosity, will not truly mimic subsurface conditions--but comparative high vs. low viscosity trends between bitumen and migrated oil remain meaningful.
- We need to consider bitumen evolution every bit as much as kerogen evolution when exploring for and exploiting tight oil plays.

Implications:

- At reservoir conditions, is produced oil fully miscible with the bitumen (as it is with Sor) that we extract from source rocks and from hybrid reservoir/source rocks??
- Or, are they two distinct phases in the reservoir, with bitumen behaving more as an obstruction to Darcy flow that inconveniently calculates (and extracts) as So?
- Not only does this have exploration implications for flow capacity from source rocks in the oil window (is it all bitumen or is mobile oil “blocked” by bitumen?), but it has important exploitation implications for “Mobile” Oil in Place (MOIP) Calculations, which in turn impact expected and observed Recovery Factors.

Next Steps:

Developing multiple independent approaches to determining bitumen vs. mobile oil ratios:

- SARA analyses
- NMR (wireline and core)
- Quantitative UV fluorescence analyses of extracts and oils
- Extracted vs. UN-extracted Pyrolysis pairs (S2 vs. S2*)
- Alternate Pyrolysis temp. schedules emphasize S2a peak
- Dean Stark vs. Retort Analyses
- Cap Pressure and Oil Flow experiments at reservoir temperature with UNcleaned samples (retaining bitumen).
- Ongoing SEM and Digital Rock Physics investigations