Determining Quantity and Quality of Retained Oil in Mature Marly Chalk and Marlstone of the Cretaceous Niobrara Formation by Low-Temperature Hydrous Pyrolysis

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Issues

How can we best determine the quantity and quality of retained oil in a mature source (TRA, Dean Stark, Rock-Eval)?

Can low temperature hydrous pyrolysis (LTHP) provide quantity and quality of retained oil?

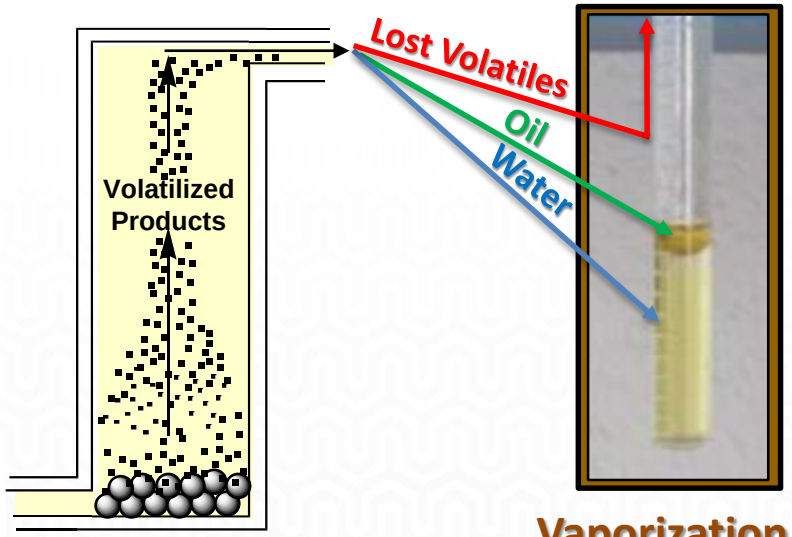
Can LTHP differentiate between bitumen and retained oil?

Can LTHP provide a better measure of production allocations from different lithologies?

Objective

Address these issues in a comparative study of TRA and LTHP on mature Niobrara Chalk and Marlstone cores.

Tight Rock Analysis (TRA) is an Anhydrous Open System



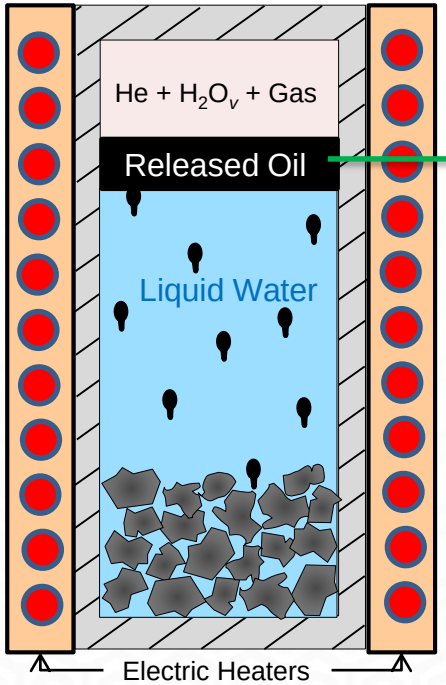
Conditions

~27gram of 12/20 mesh rock is heated at 316°C (600°F) in an open system at near atmospheric pressure for an hour or more until oil yield ceases.

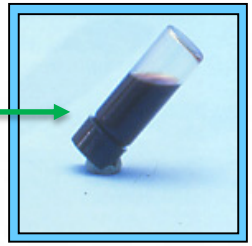
Products

Condensable Retained Oil
Pore Water

Low-Temperature Hydrous Pyrolysis (LTHP) is a hydrous closed system



Oil



Thermal Expansion & Buoyancy

Conditions

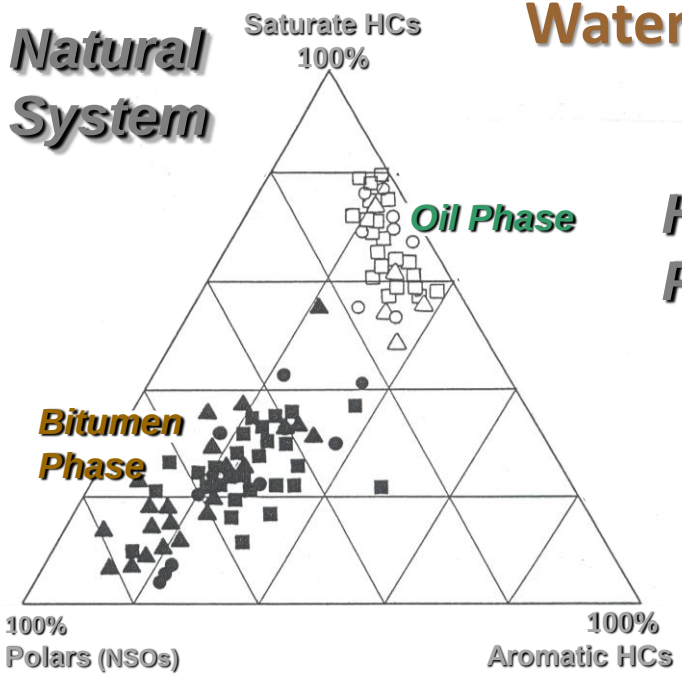
~500 gram of 12/20 mesh rock is heated at 300°C (572°F)in 1-liter reactor in the presence of liquid water for 24h at 9 MPa (1300 psi) for 24 hours.

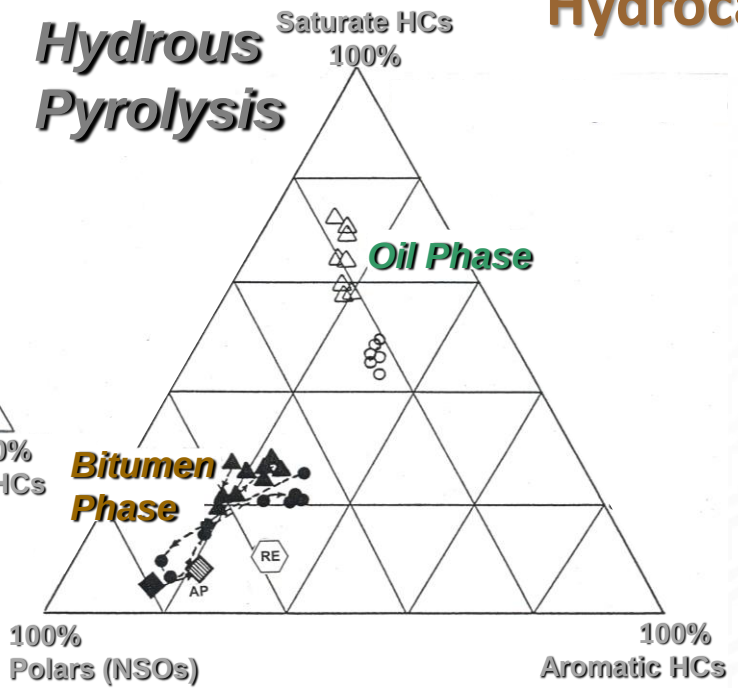
Products

Retained Oil
Water
Gas

RATIONALE

Water Dissolved in Polar-rich Bitumen results in phase separation of immiscible Hydrocarbon-rich Oil





Components:
Saturates & Aromatics = hydrocarbons
Polars (NSOs) = nonhydrocarbons

SAMPLES

Niobrara cores from "B" Horizon, Smoky Hill Member, in Horsetail well (between 5,500 and 5,784 ft)

Marly Chalk core

TOC = 2.38 wt %

S_1 = 8.1 mg/g Rock

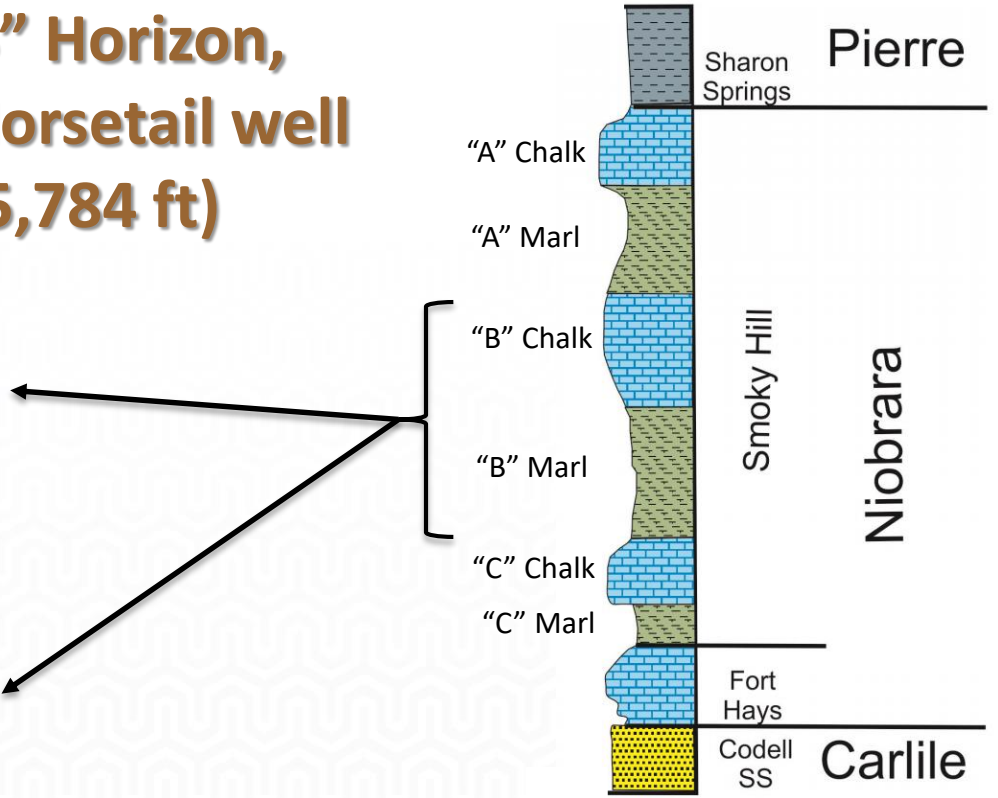
T_{max} = 442 °C

Marlstone core

TOC = 3.06 wt %

S_1 = 2.3 mg/g Rock

T_{max} = 447 °C

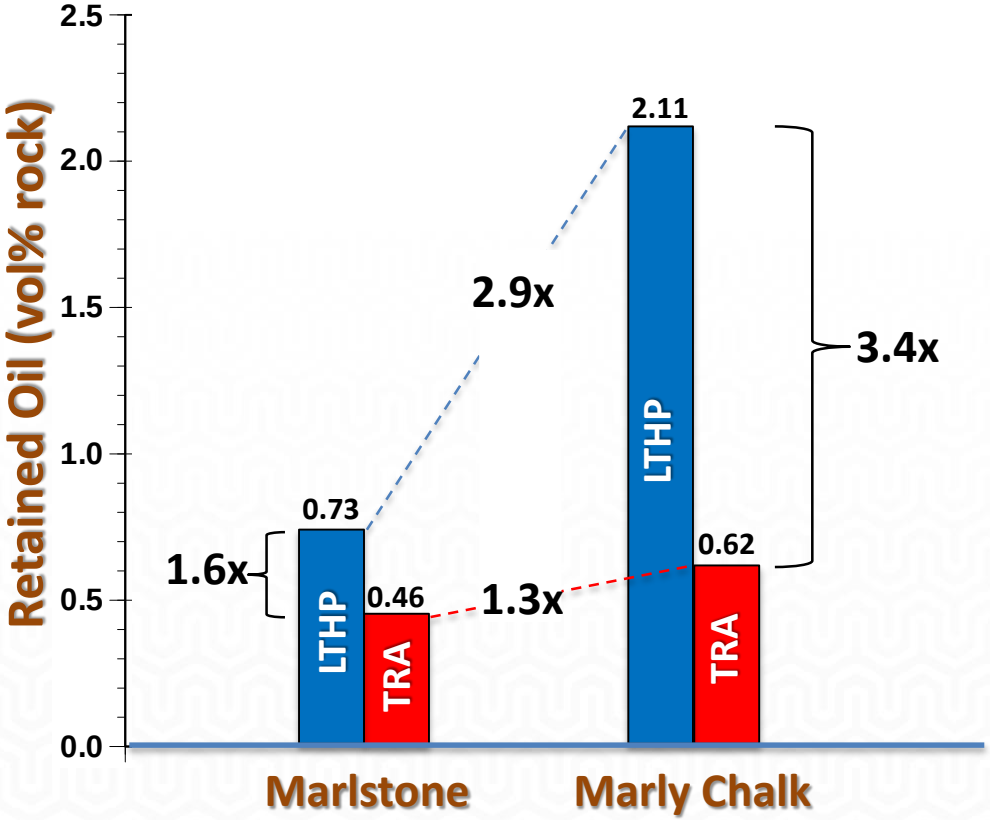


Modified after Sonnenberg (2012)

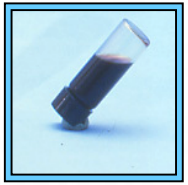
Retained Oil Released Yields by LTHP and TRA

LTHP yields 1.6 to 3.4 x more released oil than TRA.

Proportions of released retained oil between Marlstone and Marly Chalk are 2.9 x for LTHP and 1.3 x for TRA.

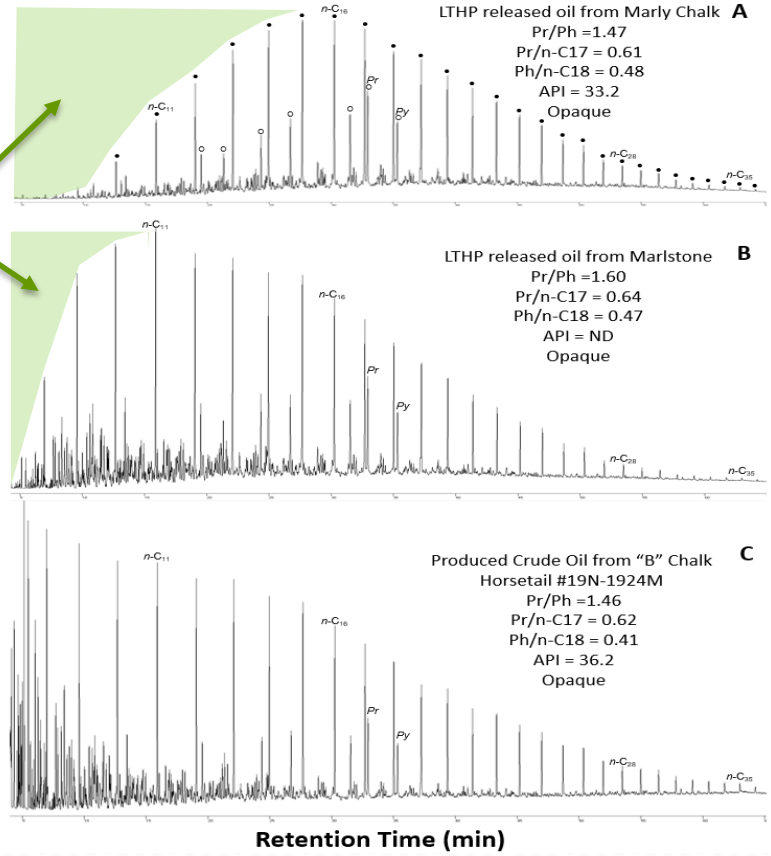


Composition of Retained Oil Released by LTHP and Produced Oil



Opaque black oil with GC characteristics similar to produced oil

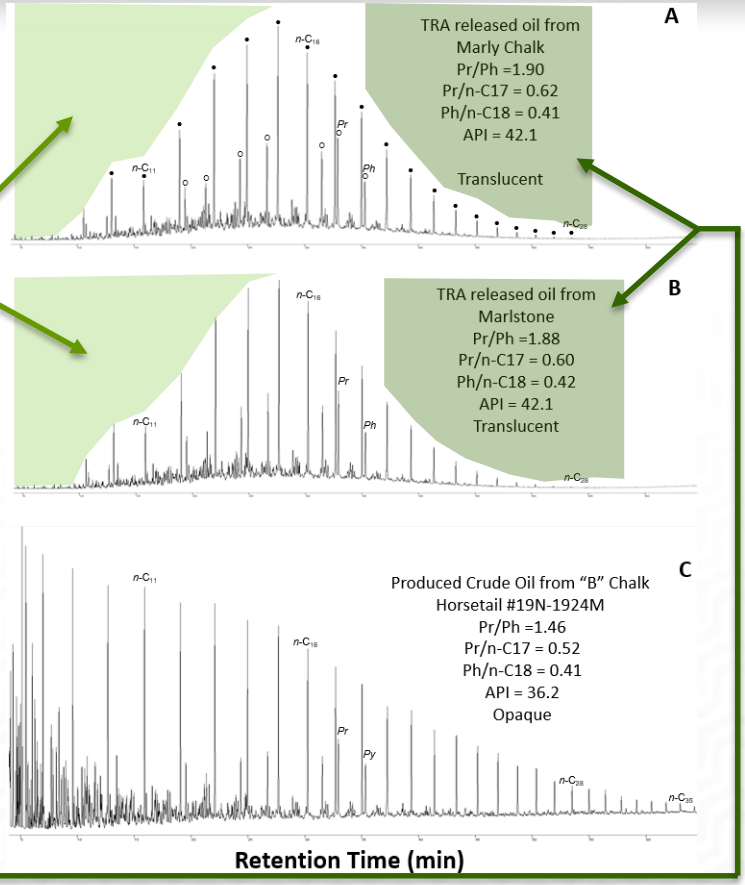
Light-hydrocarbon volatile losses from core prior to LTPH



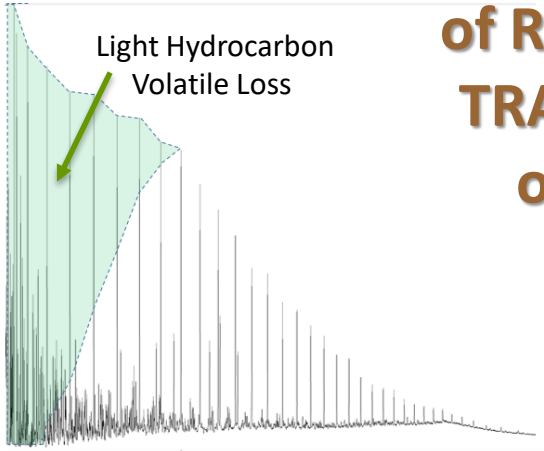
Composition of Retained Oil Released by TRA and Produced Oil

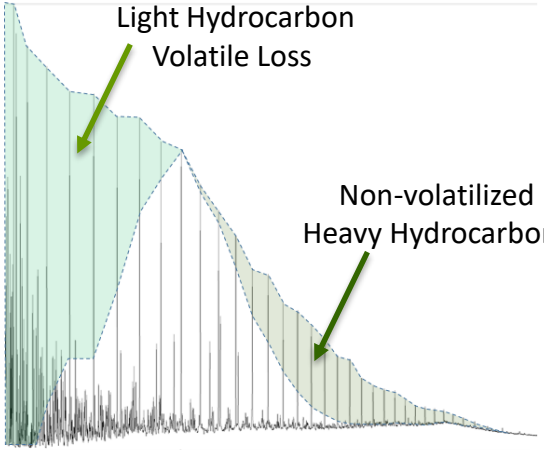
Translucent oil with GC characteristics different than produced oil

Light-hydrocarbon volatile losses and non-volatized heavy hydrocarbons from core prior to and during TRA



Differences in quantities and quality of Retained Oil released by TRA and LTHP are a result of collection methods

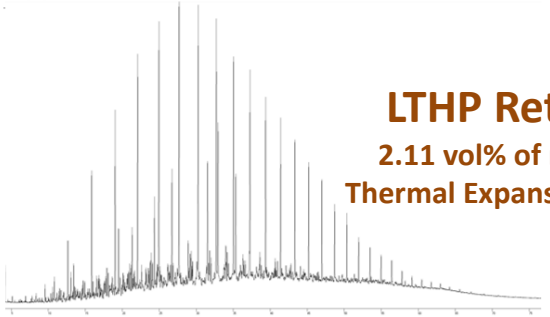




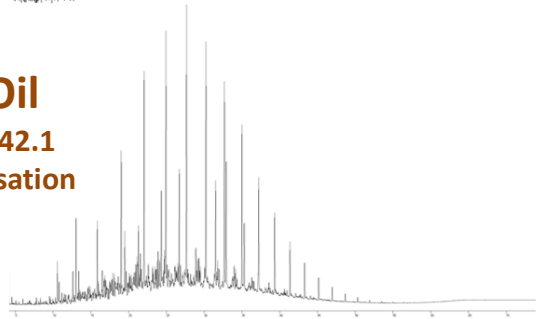
Horsetail Produced Oil
(API 36.2)

Marly Chalk Oil

LTHP Retailed Oil
2.11 vol% of rock; API 33.2
Thermal Expansion & Buoyancy

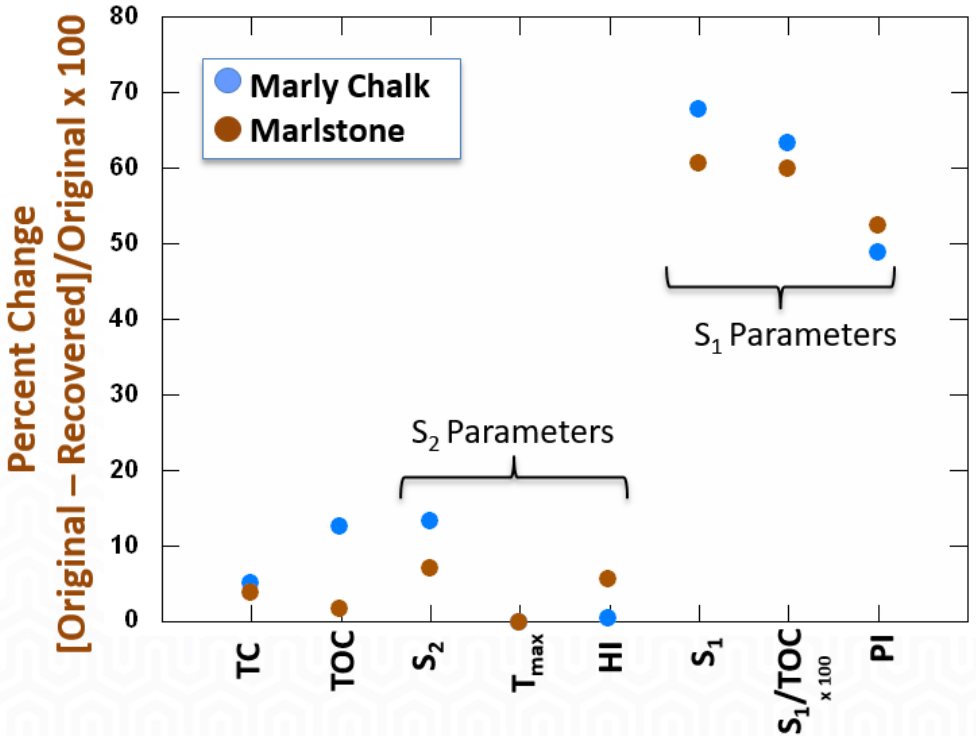


TRA Retailed Oil
0.62 vol% of rock; API 42.1
Volatilization & Condensation



RESULTS

Characterization of the rocks before and after LTHP by HAWK pyrolysis indicate no significant oil is generated and only preexisting retained oil is released.



Summary

Low-temperature hydrous pyrolysis (LTHP) released retained oils from mature Niobrara marly chalk and marlstone cores.

Released oil accumulates on the water surface in the reactor, and is compositionally similar to oil produced from the same well.

Quantities of oil released from the marly chalk and marlstone by LTHP are respectively 3.4 and 1.6 times greater than those determined by TRA.

Gas chromatograms indicated this difference is a result of TRA oils losing more volatiles and volatilizing less heavy hydrocarbons during collection than LTHP oils.

Characterization of the rocks before and after LTHP by HAWK pyrolysis indicate that under LTHP conditions no significant oil is generated and only preexisting retained oil is released.

Although LTHP appears to provide better predictions of quantity and quality of retained oil in a mature source rock, it is not expected to replace the more time and sample-size efficacy of TRA.

However, LTHP can be applied to composited samples from key intervals or lithologies originally recognized by TRA. Additional studies on duration, temperature, and sample size used in LTHP may further optimize its utility.

Acknowledgements

Whiting Petroleum Corporation: making cores available

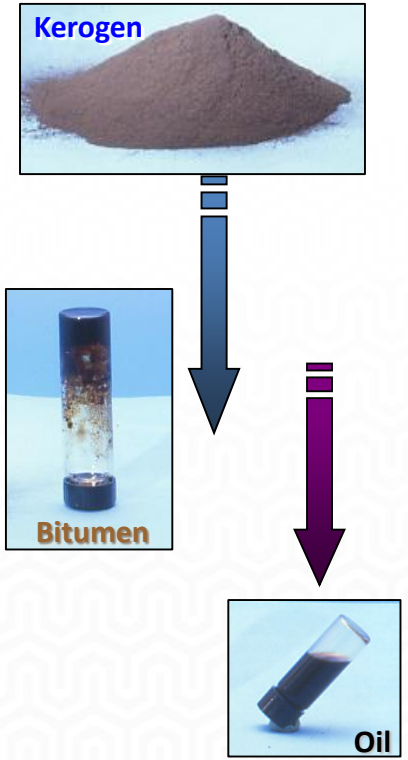
USGS analytical work: Augusta Warden, Zach Lowry, Mark Dreier

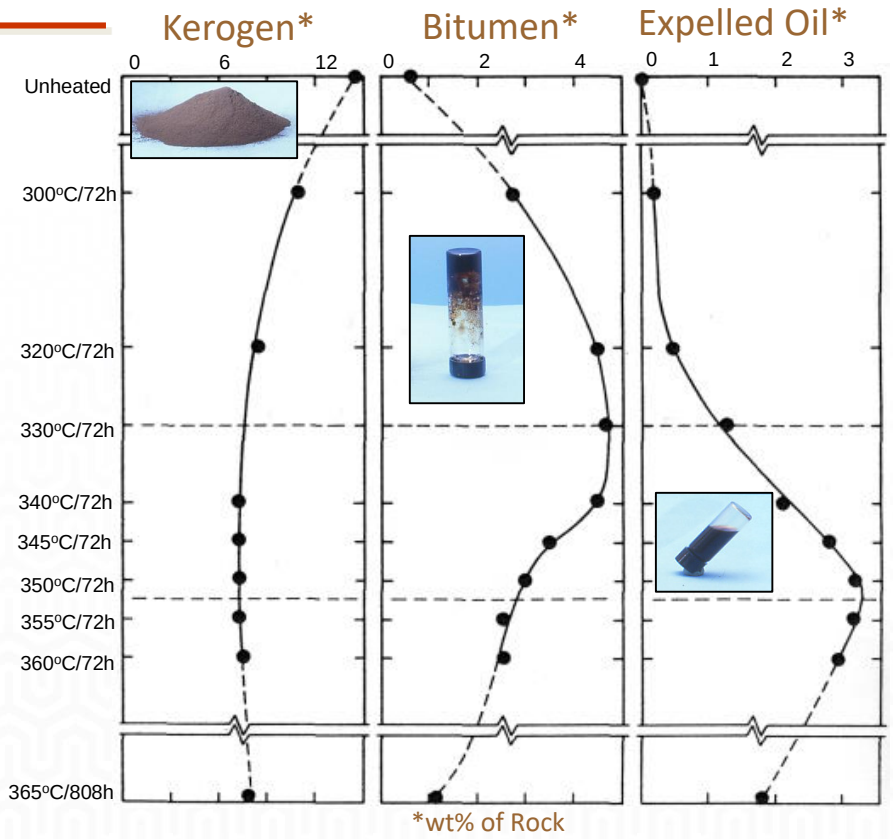
TerraTek Schlumberger Reservoir Lab: Discussions on TRA results

EXTRA BACK UP Slides

RATIONALE

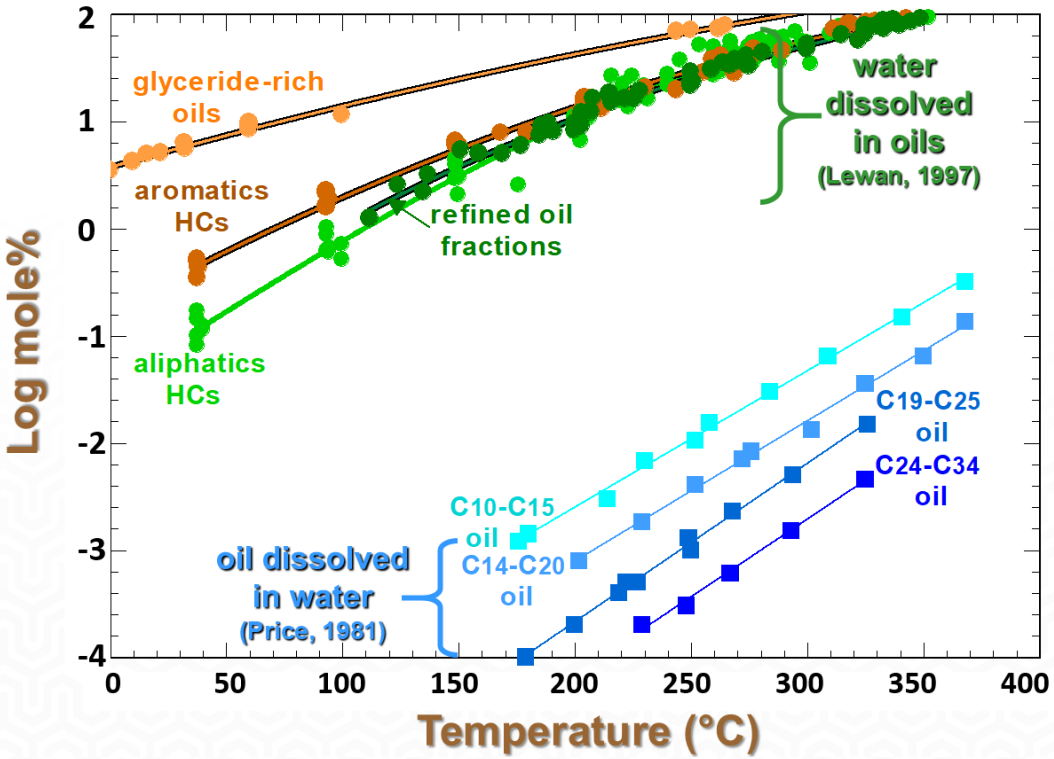
Kerogen → Bitumen → Oil





(Lewan, 1985)

RATIONALE



Immiscibility of Hydrocarbon-rich Oil in Polar-rich, dissolved-water-bearing Bitumen

Kerogen experiment
(Lewan, 1997)

Ga-In experiment
(Lewan, 1997)

Bio-oils and Petroleum
(Mohan et al., 2006)

Oil-Bitumen Mixtures
(Cruse, 2005)