

Low-Temperature Hydrous Pyrolysis (LTHP) on Oil-Field Core Samples for Estimating Original In-Place Retained oil in Mature Source Rocks and Tight-oil Reservoirs**

V. S. Nowaczewski¹, J. Barton¹, B. Lagues¹, A. Tang¹, and M. D. Lewan²

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¹Chesapeake Energy, 6015 N. Classen BLVD, Oklahoma City, OK 73118 (ysnowaczewski@gmail.com)

²GeoConsulting Corp, 6785 W. Yale Ave, Lakewood, CO 80227 (mlewan1@comcast.net)

Abstract

The amount of original-oil-in-place (OOIP) is routinely estimated by conventional core analysis techniques and geochemical tests such as programmed non-isothermal pyrolysis. A relatively new method is low-temperature hydrous pyrolysis (LTHP) that was introduced by Lewan and Sonnenfeld (2017). As they described for mature Niobrara cores, LTHP releases retained oil that is similar to unconventionally produce oil. Quantities of LTHP released oils are not a product of high temperature volatilization or solvent extraction, which includes polar-rich bitumen that is not mobile producible retained oil. LTHP used crushed mature source rock core isothermally heated at 300⁰C for 24 to 72 hours. These conditions allow hydrocarbon-rich oils to be released from the mature source rock by thermal expansion and water displacement and its dramatic difference in miscibility with polar-rich bitumen in the presence of water (Lewan, 1997), but are not sufficient to generate oil. Chesapeake Energy has been applying the LTHP method in their Reservoir Technology Center hydrous-pyrolysis laboratory with favorable results. The method has also been extended to determine quality and quantities of retained oil in nonsource-rock tight oil reservoirs. Quantities of released oil typically are sufficient to determine API gravities, gas chromatography and biomarker signatures, Examples of LTHP within this presentation include a series of samples that illustrate changes in quantity and quality of retained oil with increasing thermal maturation and the importance of volatile losses from cores. LTHP provides quantities and quality of retained producible oil in maturing source rocks that other methods do not.

References cited:

Lewan, M. D., and M. D. Sonnenfeld, 2017, Determining quantity and quality of retained oil in 811 mature marly chalk and marlstone of the Cretaceous Niobrara Formation by low-812 temperature hydrous pyrolysis (abs): Unconventional Resources Technology Conference, 813 Austin, Texas, July 24-26, doi:10.15530/urtec-2017-2670700.

Lewan, M.D., 1997, Experiments on the role of water in Petroleum Formation, *Geochimica et Cosmochimica Acta*, v. 61, pp. 3691-3723.



V.S. Nowaczewski¹, J. Barton¹, B. Lagunes¹, A. Tang¹ & M.D. Lewan²

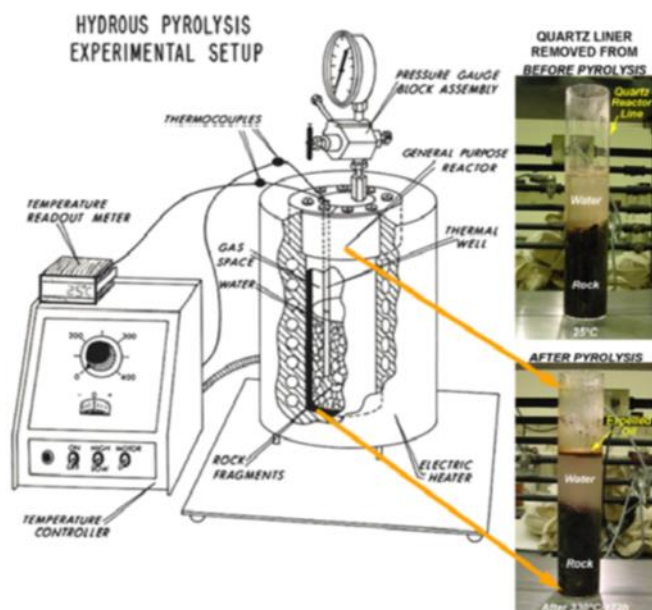
LOW-TEMPERATURE HYDROUS PYROLYSIS (LTHP) ON OIL-FIELD CORE SAMPLES FOR ESTIMATING ORIGINAL IN-PLACE RETAINED OIL IN MATURE SOURCE ROCKS AND TIGHT RESERVOIRS

ACKNOWLEDGMENTS

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- ▶ David Mohrbacher and Steve Chipera for insightful suggestions on the presentation.
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- ▶ Uzzie Fierro, Kyle Bradford and Don Harville of the Chesapeake Reservoir-Technology-Center Lab (RTC-Lab) for support in isolating samples from core.
- ▶ Kim Nguyen for excellent work in the pyrolysis lab.
- ▶ Lesley Evans for good suggestions on expanding LTHP into non-source-rock intervals.

PURPOSE

Show the utility of Low-Temperature Hydrous Pyrolysis (LTHP) in determining retained oil in mature source rocks and tight reservoirs (sandstones and carbonates).



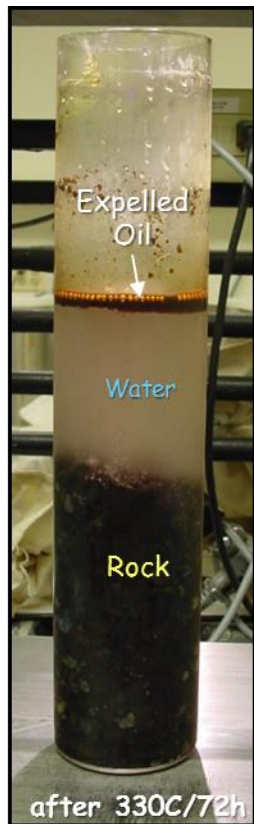
It has previously been shown that LTHP at 300°C for 24 h released retained oil in mature Niobrara cores that was similar in composition and API-gravity to produced oil. (Lewan and Sonnenfeld, 2017)

Other methods currently in use (TRA, Dean Stark, Rock-Eval, and solvent extraction) are problematic in providing products that do not include light and heavy ends of a retained oil, do not differentiate retained oil from polar-rich bitumen, or only produce an electric signal.

PRESENTATION OUTLINE

- ▶ **Rationale and Methodology of Low-Temperature Hydrous Pyrolysis (LTHP)**
- ▶ **Examples of LTHP yields from different rock types (mature source rocks and tight reservoirs)**
- ▶ **Sample considerations and precautions prior to LTHP**
- ▶ **Conclusions**

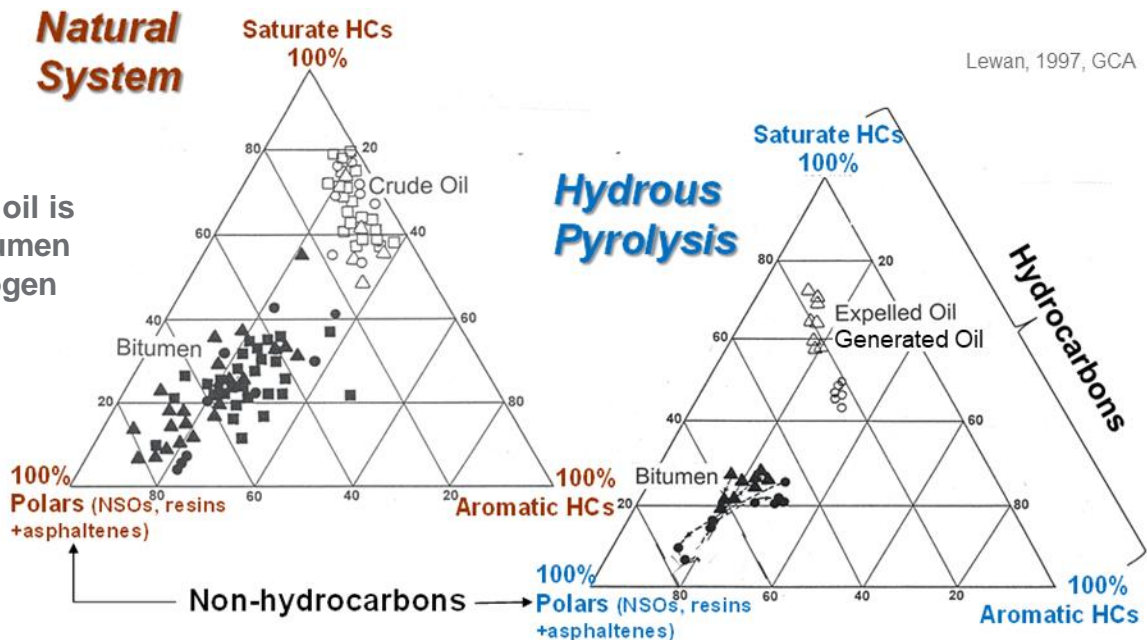
RATIONALE OF LTHP



It has been shown that hydrous pyrolysis of immature source rocks at high temperatures ($>320^{\circ}\text{C}$ for 72h) generates an oil phase that is immiscible in the polar-rich bitumen phase of a source rock.

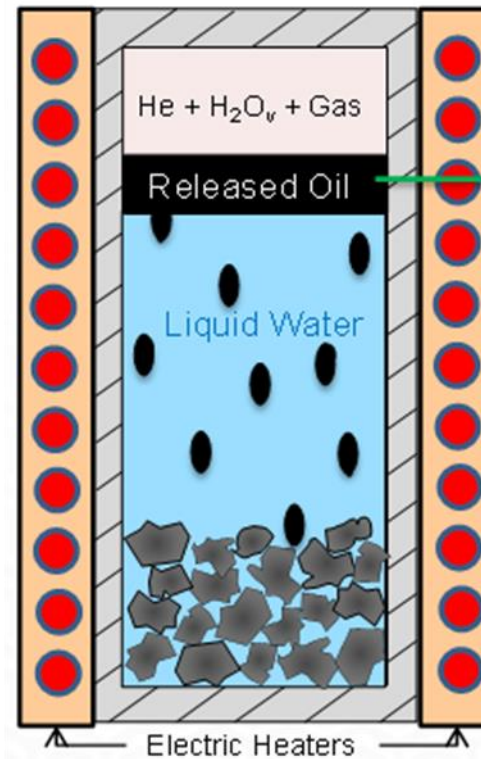
Rationale of LTHP at $300^{\circ}\text{C}/24$ or 72h was to use this immiscibility to differentiate retained oil from the polar-rich bitumen within a mature source rock, which Lewan & Sonnenfeld (2017) showed was possible with mature Niobrara cores.

Generated expelled oil is immiscible with bitumen in the rock or kerogen

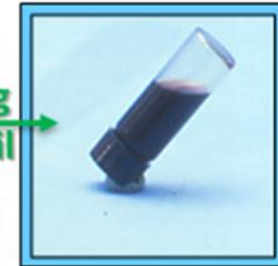


CHESAPEAKE LTHP METHODOLOGY

500g of rushed core (0.5 to 2.0 cm) placed in 1-liter stainless-steel (316) reactor with sufficient water to maintain a submerged rock before, during, and after heating isothermally at 300°C for 72 hours.



Pre-existing
Retained Oil

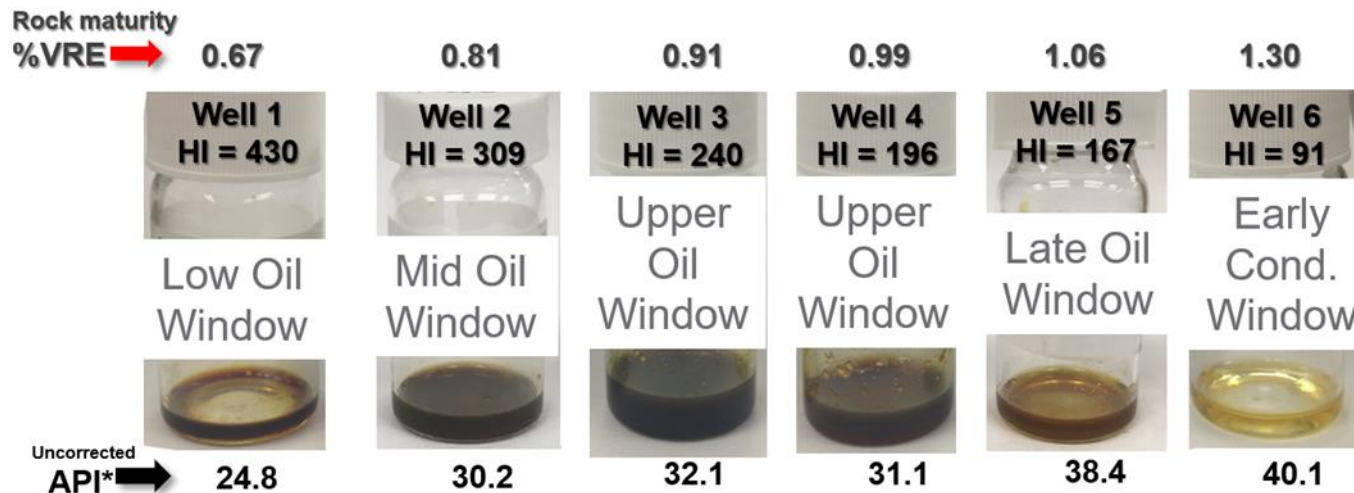


Water dissolved in the polar-rich bitumen phase of the rock assists in separating the retained oil from the solid or highly-viscous organic phases. The density differences force released petroleum to collect upon the water-columns surface

The RTC-Lab has all of the capabilities described in this presentation for characterizing retained oils within oil-field core-samples.

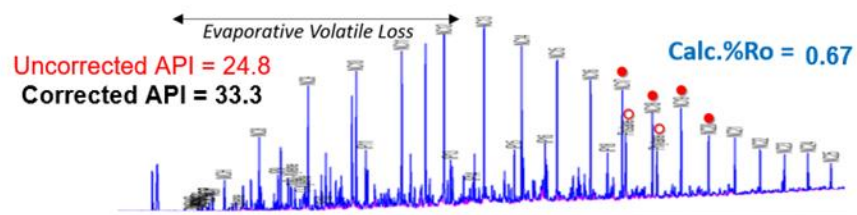
RELEASED OILS FROM SOURCE ROCK SHOW QUANTITY AND QUALITY CHANGES WITH THERMAL MATURITY

Low-temperature hydrous pyrolysis (LTHP) releases retained oil with increasing uncorrected API gravities with increasing thermal maturity of a source rock



* Not corrected for evaporative losses.

CORRECTING API FOR EVAPORATIVE LOSSES AS SHOWN BY GAS CHROMATOGRAMS (GC)



Early Oil Window



Upper Oil Window



Late Oil Window



Early Cond. Window



GCs can show obvious evaporative losses in the light end of retained oils.

These evaporative losses can be in part attributed to large volume collection vials but are primarily do to storage of the core samples prior to LTHP and not during LTHP.

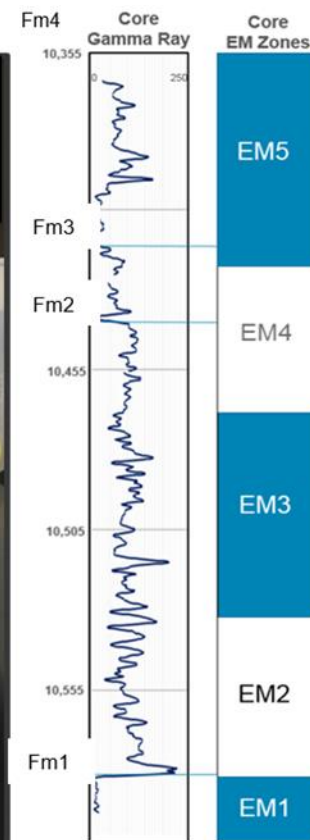
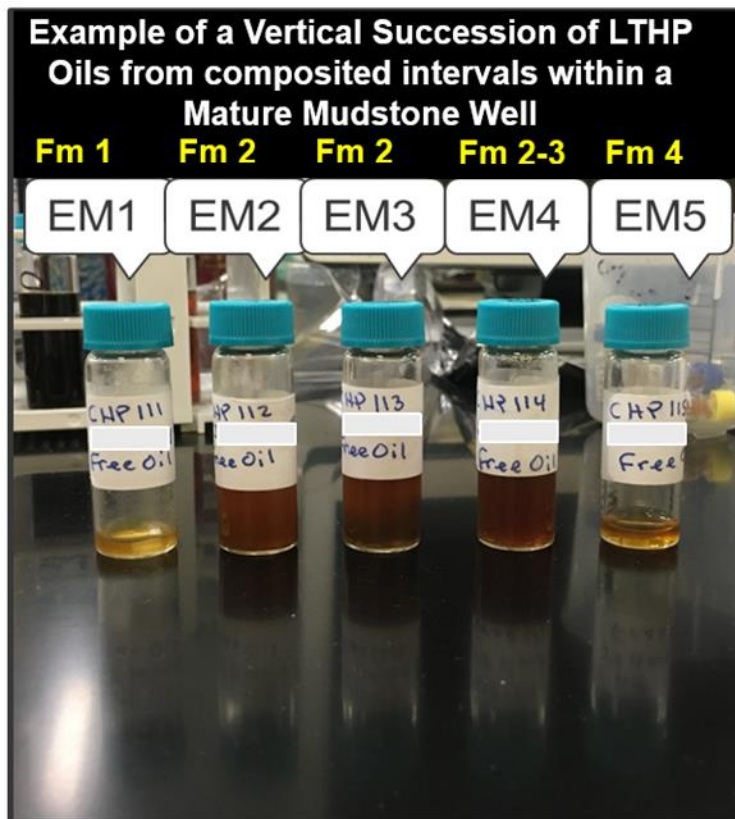
There are various ways to correct for evaporative losses with comparisons of produced oil as done in this case.

These corrections for pre-LTHP evaporative losses must also be taken into account in determining quantities of retained oil*

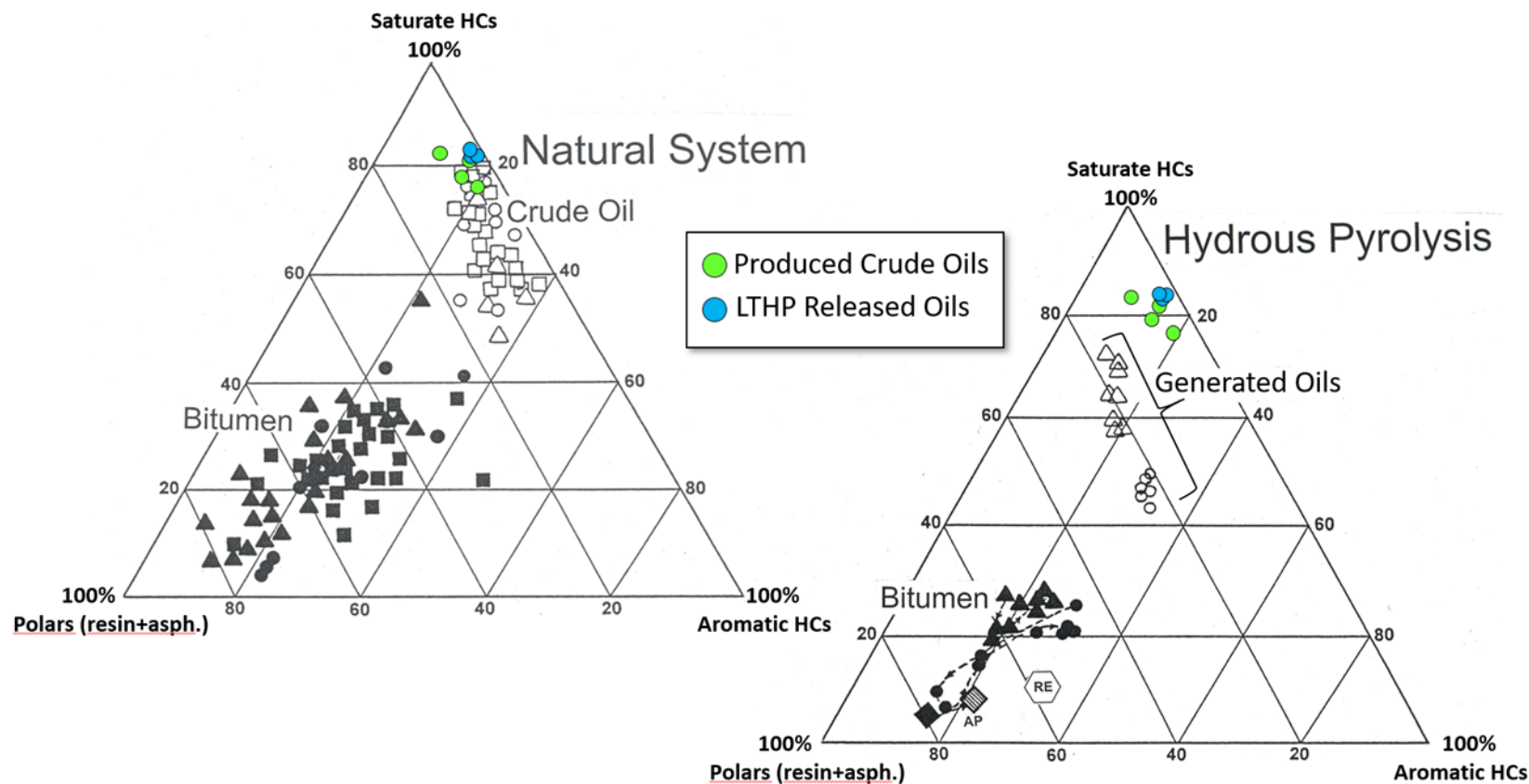
* This is even a greater problem with other methods like TRA, Dean Stark, and solvent extractions.

RELEASED OIL CAN BE USED TO ESTABLISH END MEMBERS IN STACKED PAY INTERVALS

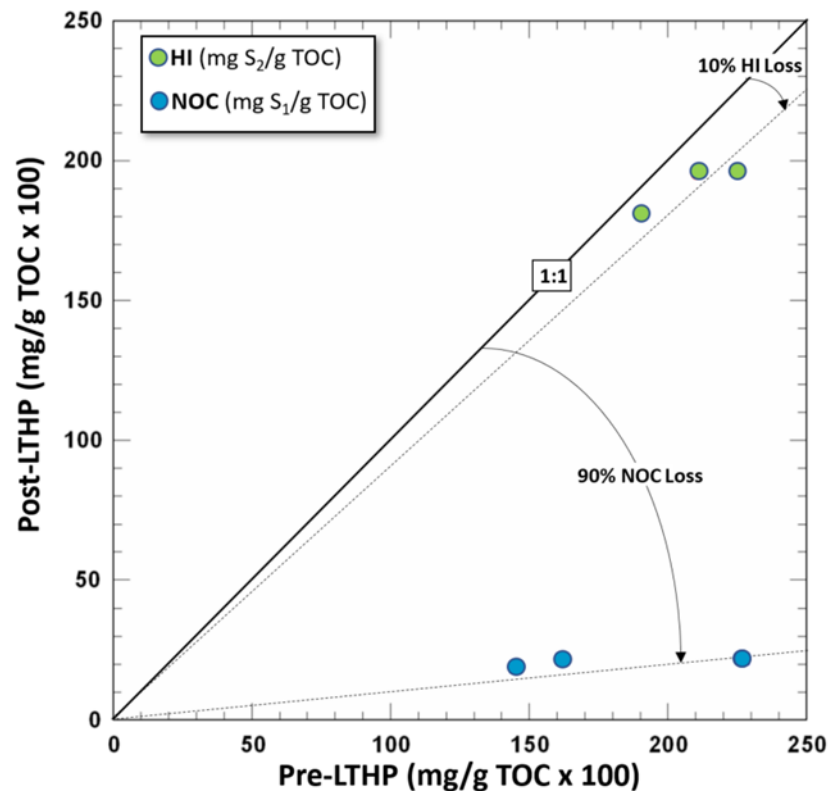
- The changes in color, density, molecular and isotopic character and absolute amount of oil in a succession of reservoir levels may allow us to gauge vertical contributions to production through statistical comparisons.
- With neatly separated and relatively unaltered petroleum phases, we can also estimate in a reasonably accurate way the contribution of any oil-based mud to oil saturations.
- In tight reservoirs it is challenging to acquire fluid samples. LTHP provides a way of at least being able to recover a stock-tank oil phase from core samples that would be otherwise very expensive or impossible to obtain.



RELEASED OILS HAVE SIMILAR SARA COMPOSITIONS TO PRODUCED OILS



ROCK EVAL AND KEROGEN ATOMIC H/C RATIO PRE- AND POST-LTHP



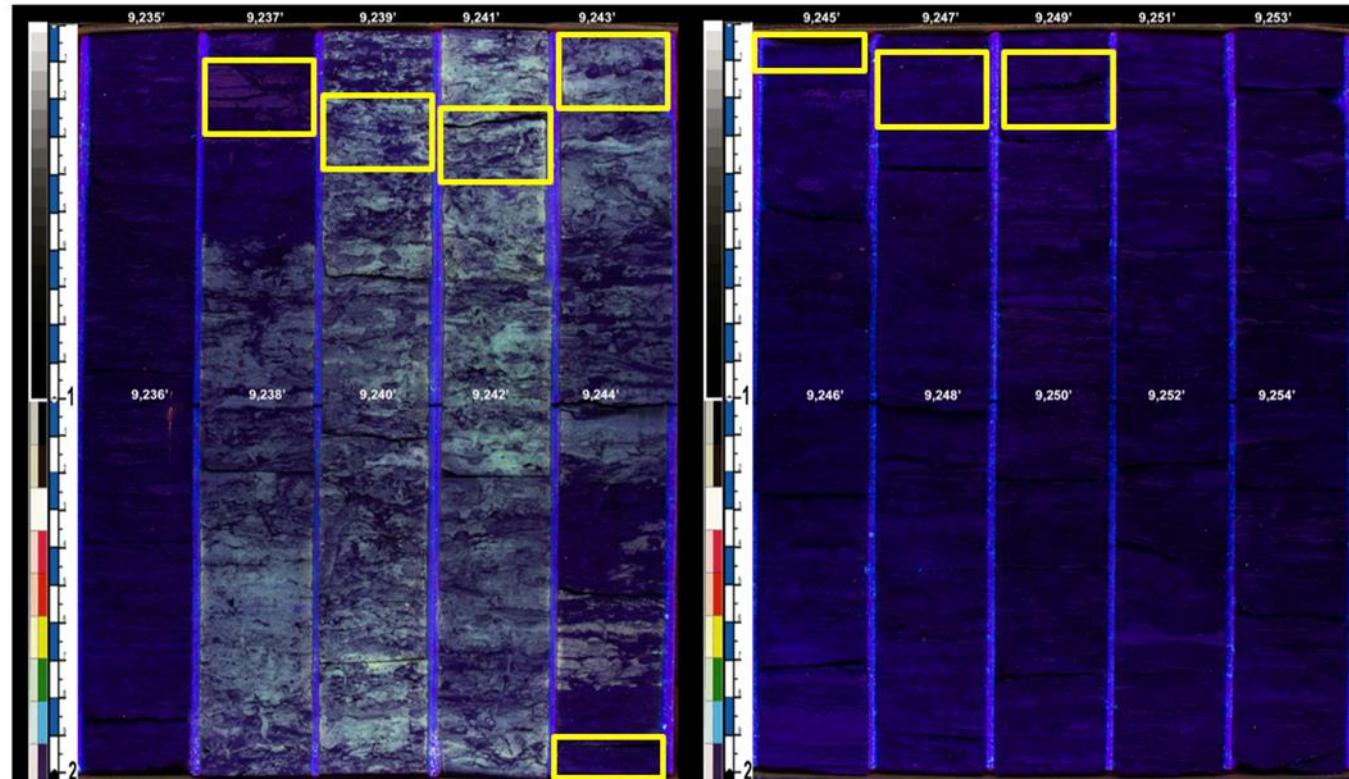
LTHP at 300°C for 72 h releases retained oils and does not generate oil.

Kerogen Atomic H/C Ratio

Pre-LTHP	Post-LTHP
0.66	0.65
0.64	0.64
0.64	0.64

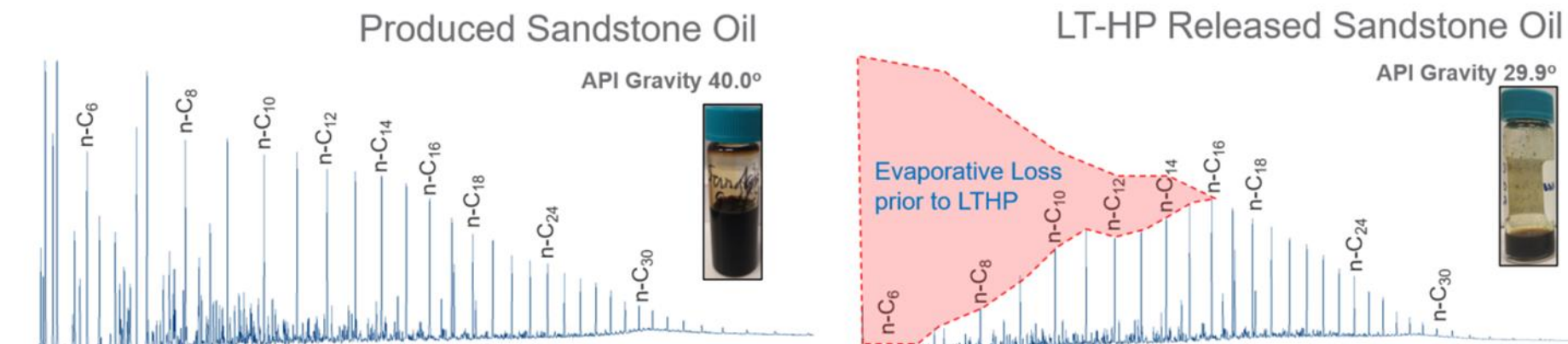
EXAMPLE SAMPLE COMPOSITE FROM A TIGHT OIL SANDSTONE — NON-SOURCE ROCK

- At time of sample selection the whole interval fluoresced.
- By the time the core was slabbed and the photos taken certain portions of that interval had apparently lost their fluorescence.
- Highlights the importance in mD-scale rock to take samples intended for saturation measurements as quickly as possible.



GAS CHROMATOGRAPHY COMPARISON — SANDSTONE LTHP OIL

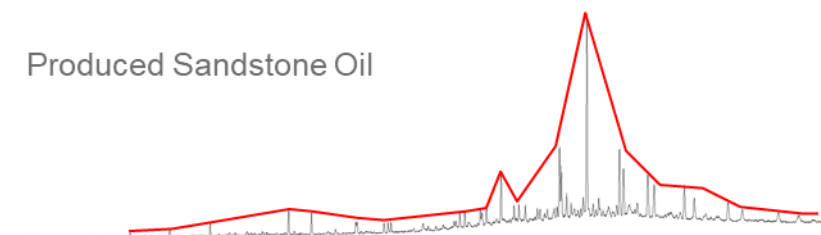
The LTHP oil indicates loss of the light ends as a result of evaporation from the core prior to LTHP, and demonstrates the importance of subjecting relatively high permeability samples to LTHP as soon as possible.



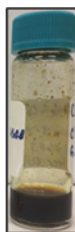
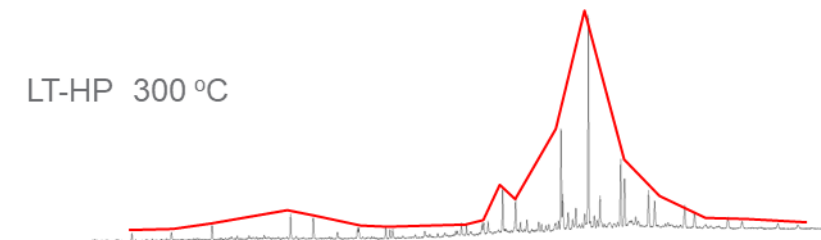
COMPARISON OF STANDARD GCMS TRACES

Terpanes (m/z 191)

Produced Sandstone Oil

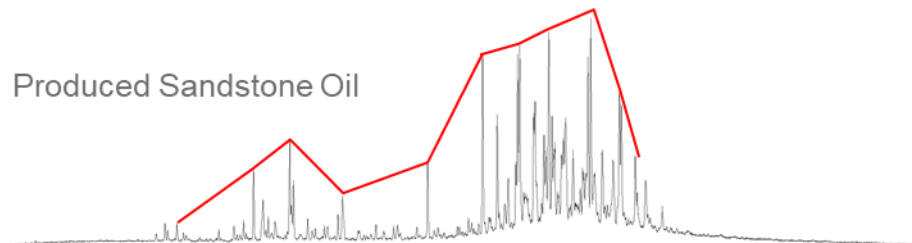


LT-HP 300 °C

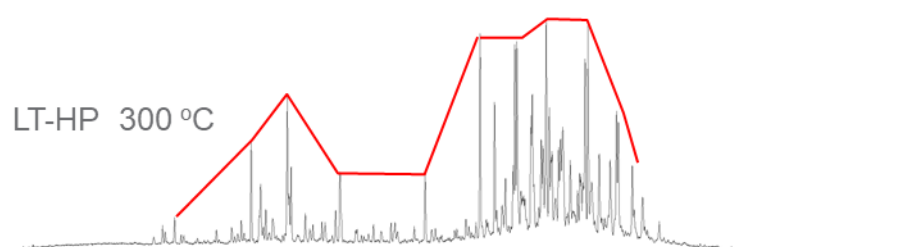


Steranes (m/z 217)

Produced Sandstone Oil



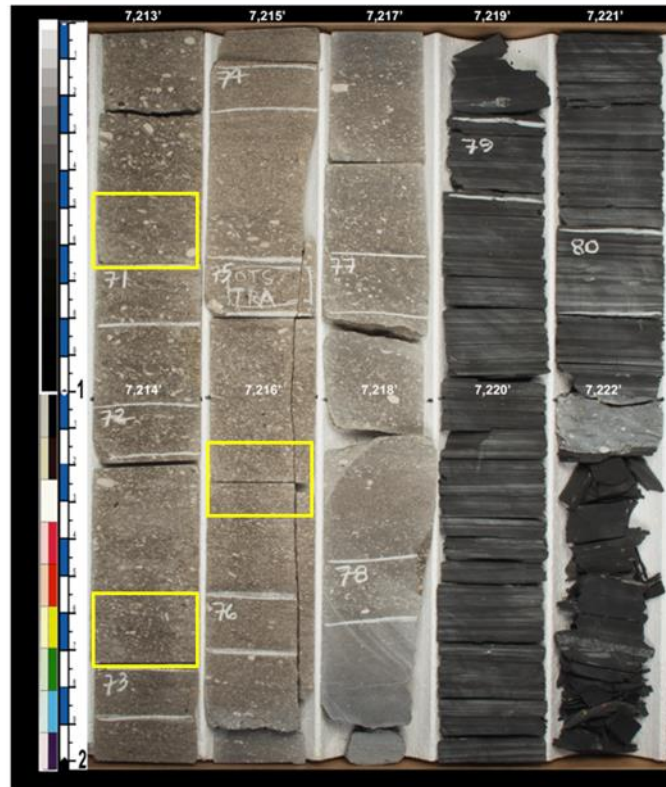
LT-HP 300 °C



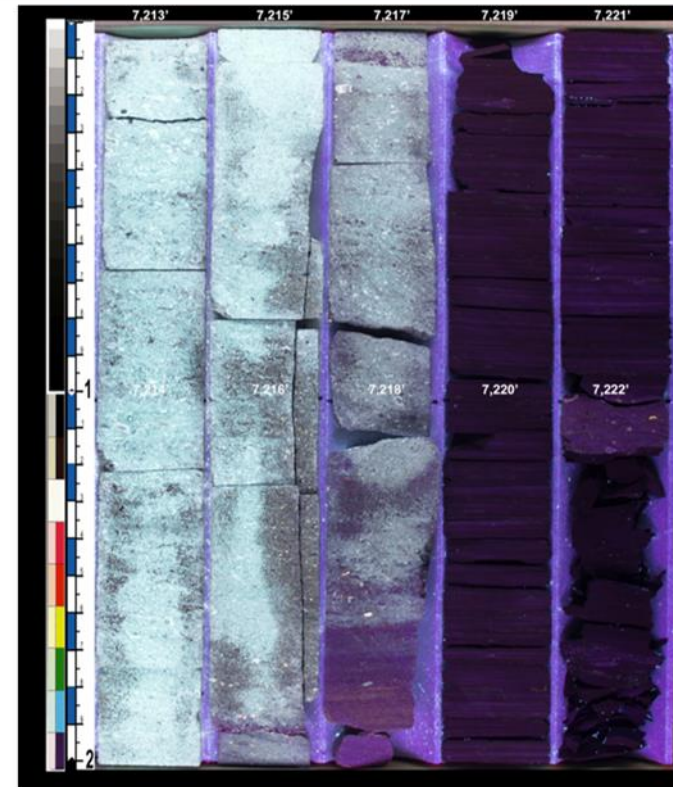
The GCMS data from the LT-HP fluid are very similar to the produced oil

EXAMPLE COMPOSITE FROM A TIGHT-OIL LIMESTONE UNIT — NON-SOURCE ROCK

White-Light 1/3 Section Photograph

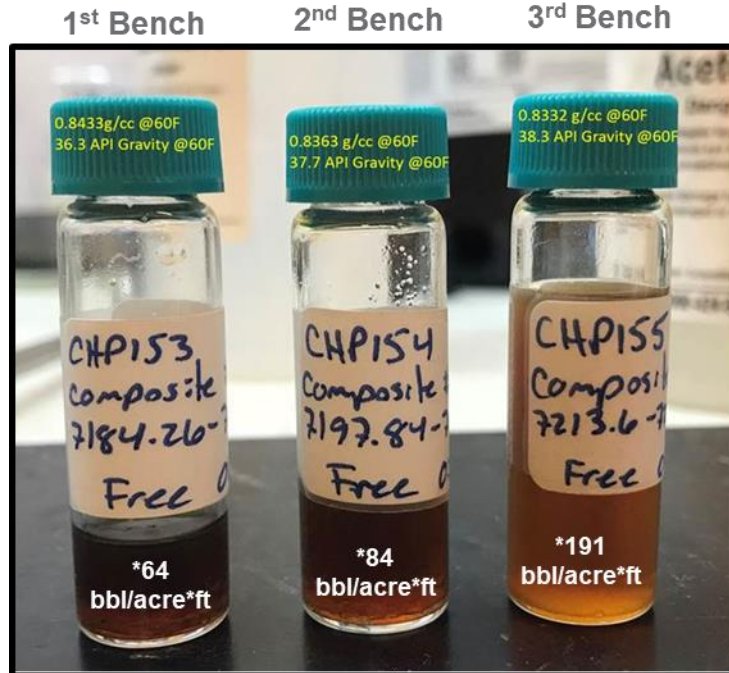


UV-Light 1/3 Section Photograph

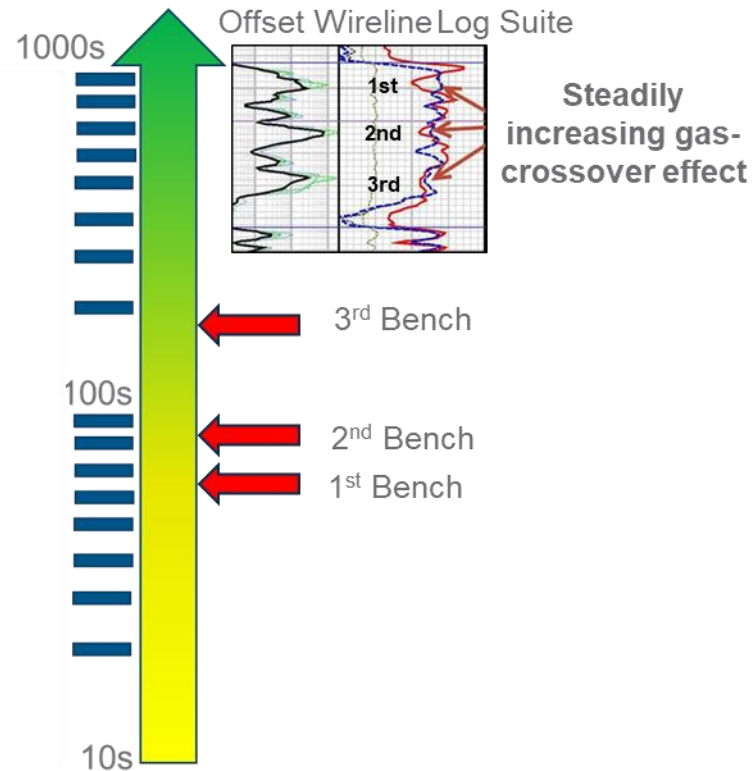


SIGNIFICANT DIFFERENCES IN QUALITY AND QUANTITIES OF LTHP RETAINED OIL RELEASED FROM DIFFERENT BENCHES

Stock-Tank-Oil Resource Density Scale

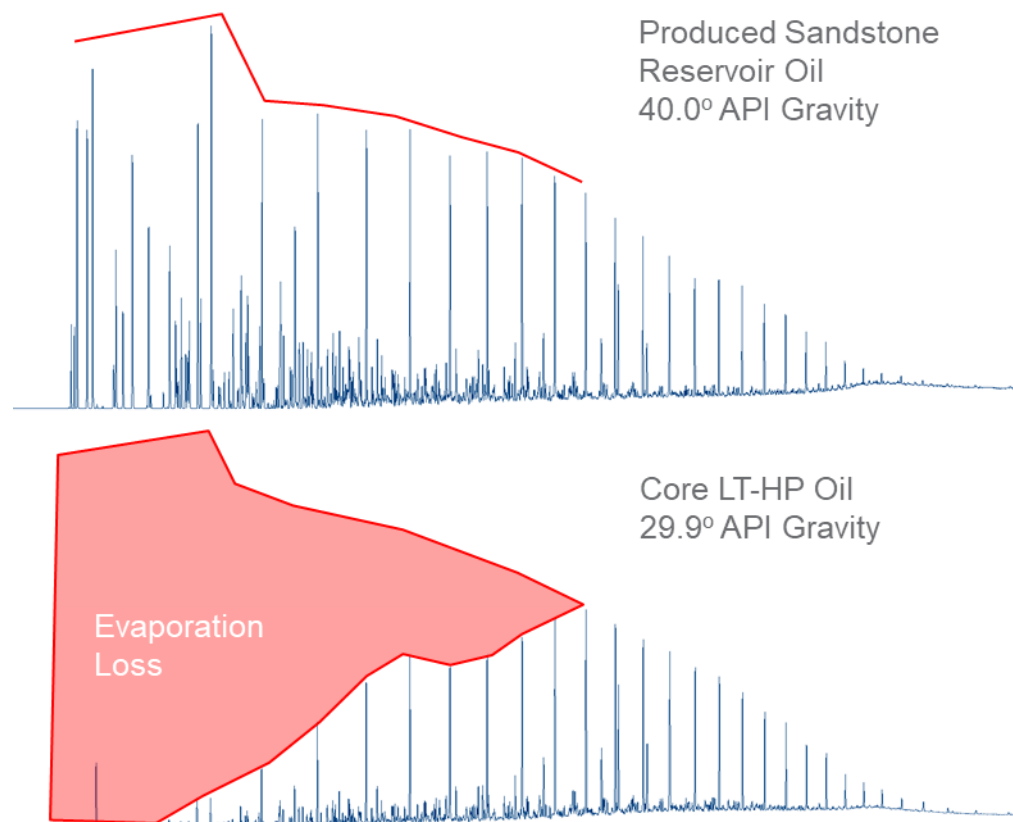


*Totally uncorrected yields—as received free oil resource densities final yields and expected producing API will increase a certain amount with corrections.



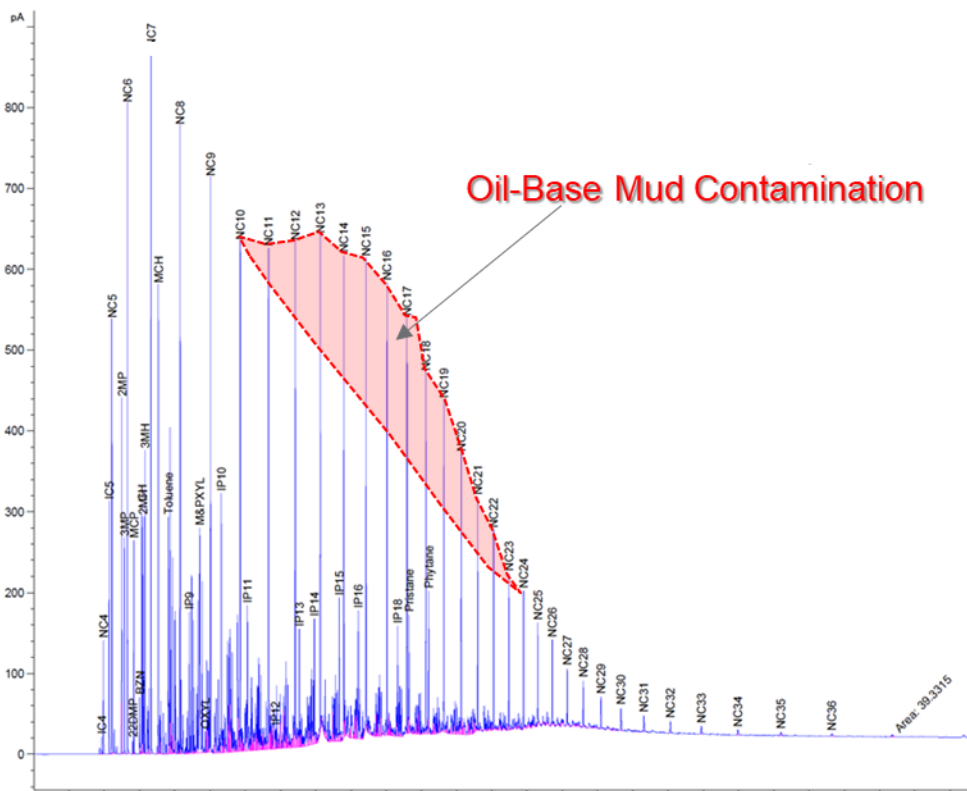
THE IMPORTANCE OF TIME AND PERMEABILITY: 1000S OF NANO-D ROCK

- Major evaporation loss occurred here in a sandstone core sample after only 13 hours had elapsed between arrival at the laboratory and sealing within the HP reactor.
- At 1000s of nDs if we do not have the rock sealed or aggressively refrigerated, chances of recovering a good petroleum phase go down after the first 24 hours of exposure.
- Getting samples in the reactor as soon as possible becomes more critical with increasing permeability of a rock and increasing API gravity of retained oil. A common problem for all analyses.



RETAINED OIL RELEASED BY LTHP MAY ALSO SHOW CONTAMINATION FROM OIL-BASE MUDS

- When oil-based muds (OBM) are largely diesel based, released oils provide a relatively straightforward means of estimating the amount of contamination of retained oils by the non-native product.
- Since diesel has a relatively-narrow-range of compounds compared with natural oils, significant contamination is manifest by a secondary mode of peaks in the n-C₁₀ to n-C₂₄ paraffins.
- By quantitatively comparing LTHP oils with field-produced oils, or other oils considered characteristic of the system, the amount of contamination can be estimated.



CONCLUSIONS

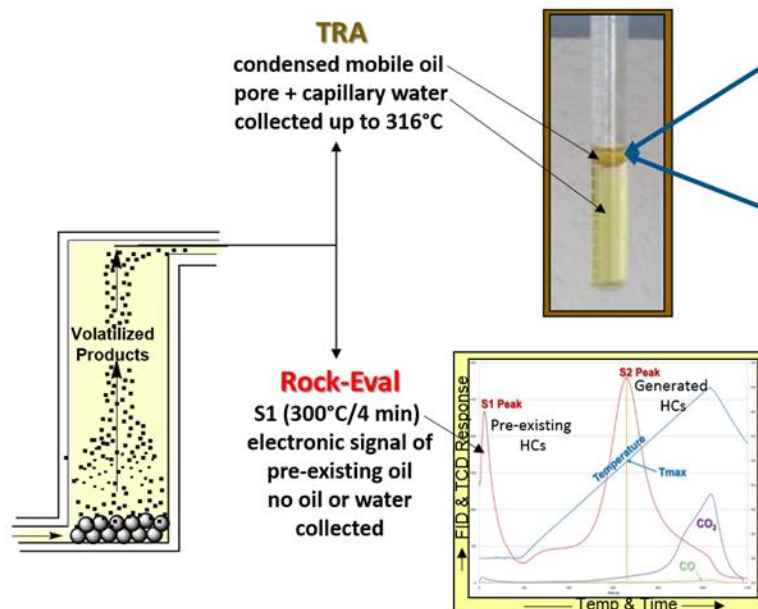
- ▶ LTHP releases retained oil in mature source rocks and tight reservoirs (sandstones and carbonates) that is similar in character to producible oil.
- ▶ The retained oil released by LTHP is more representative of producible oil in quantity and quality than current methods that require volatilization or solvent extraction.
- ▶ LTHP provides a means of differentiating retained oil from polar-rich bitumen, which is not producible within a mature source rock or readably distinguished by other methods.
- ▶ As with other methods, it is critical to minimize the time between sample collection and analyses. This practice becomes increasingly important with increasing permeability of the rock and increasing API gravity of the retained oil.
- ▶ LTHP reveals the presence of oil-based mud contamination and provides a means to evaluate its impact on the quality and quantity of retained oil.
- ▶ LTHP provides insights on geochemical signatures (e.g., biomarkers) that may be diagnostic to different zones within a targeted interval(s), and has the potential to provide information regarding the storage contribution relating to those intervals.
- ▶ The RTC-Lab has developed complete capability to characterize retained oils in core samples by LTHP.

APPENDIX

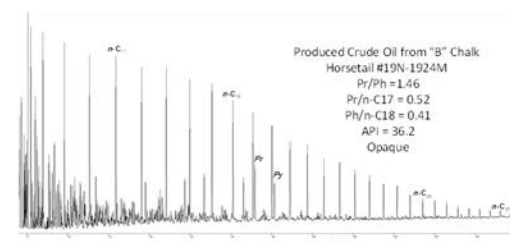
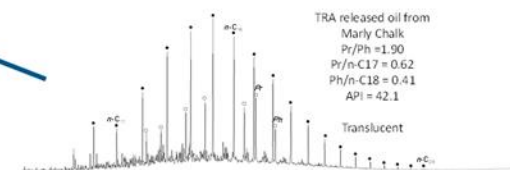
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PRE-EXISTING TECHNIQUES PROVIDE LIMITED COMPOSITIONAL INFORMATION

Open-System Anhydrous Pyrolysis



TRA gives a measurement of water types and oil, and gives the condensed volatilized oil collected. However, the TRA oil does not resemble the produced retained oil.

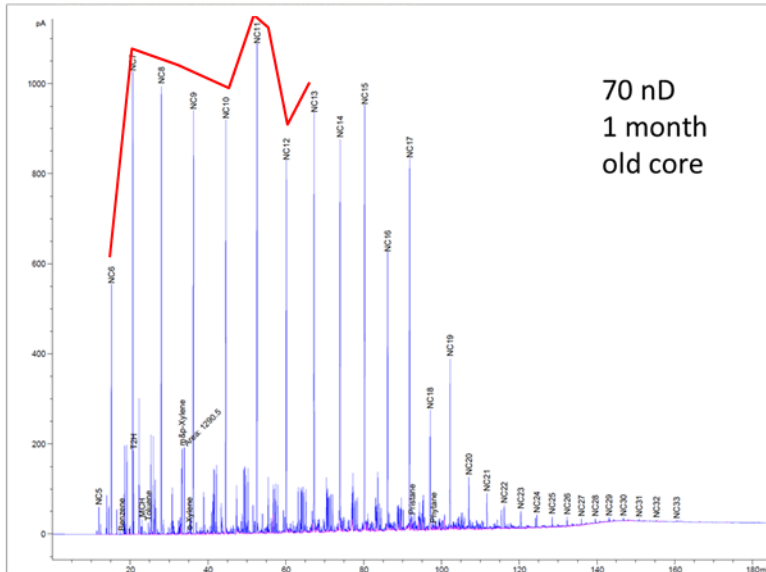


Lewan and Sonnenfeld, URTeC (2017) Niobrara, Denver Basin

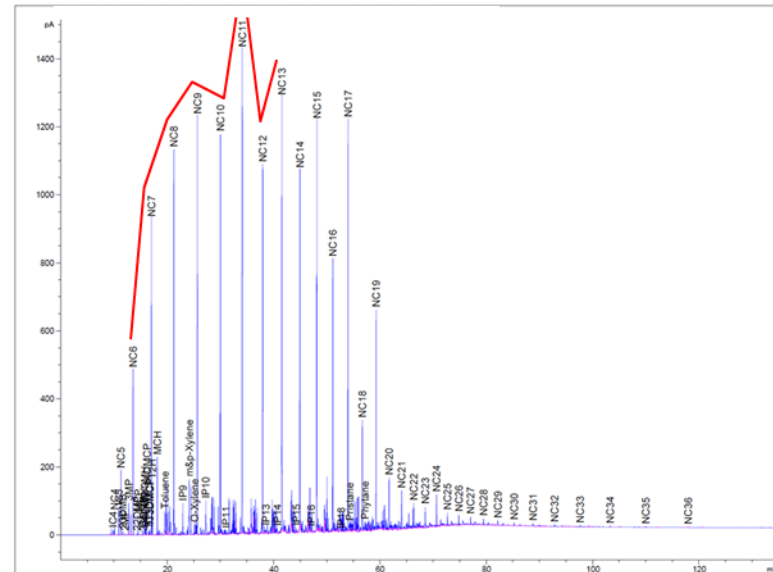
- TRA produces a physically collectable fluid, but appears more like a refined product rather than natural fluid.
- Rock Eval and those of its ilk may give general quantification of light petroleum components but compositional insight is very generalized.
- Useful to have a technique that produces a physically collectable fluid closely resembling natural products.

THE IMPORTANCE OF TIME AND PERMEABILITY: 10S OF NANO-D ROCK

LTHP Oil GC trace from a Lower Paleozoic Source Rock



Stock Tank Oil Retrieved from Well Test



- In very low permeability mudstones we can recover a better preserved oil phase from 1-month-old slabbed core than from the stock tank.
- The permeability of the rock is of course in the 10s of nD, though. Somewhat less permeable than tombstone.