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

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CHESAPEAKE ENERGY

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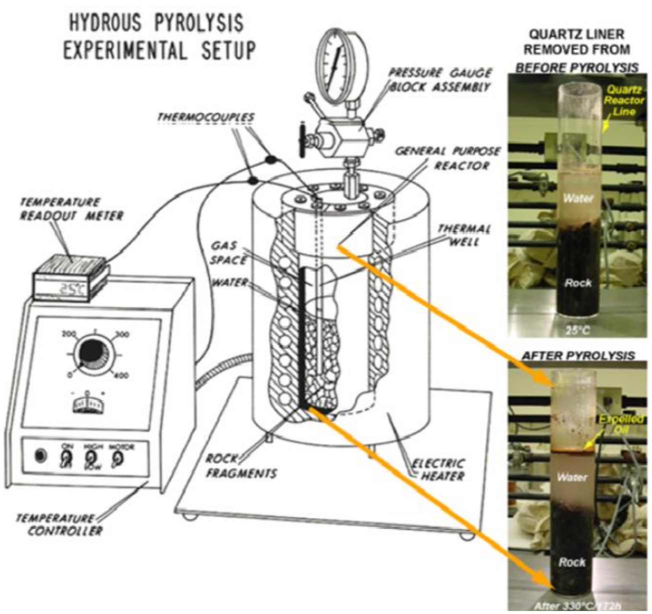
- Lesley Evans for good suggestions on expanding LTHP into non-source-rock intervals.

PURPOSE

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



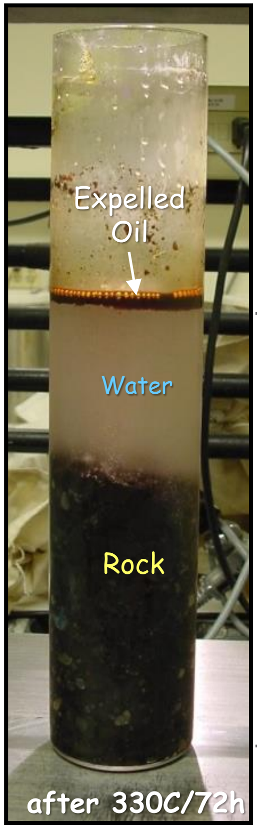
It has previously been shown that LTHP at 300°C for 24 h released retained oil in mature Niobrara cores that was similar in composition and API-gravity to produced oil.
(Lewan and Sonnenfeld, 2017)

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

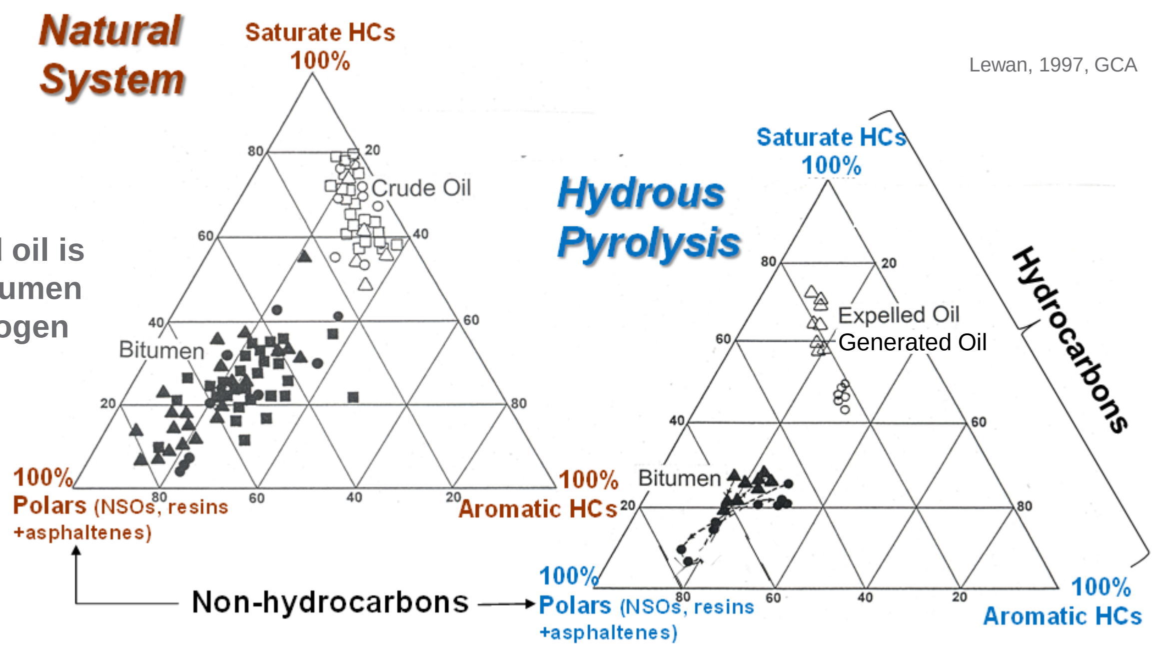
RATIONALE OF LTHP



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

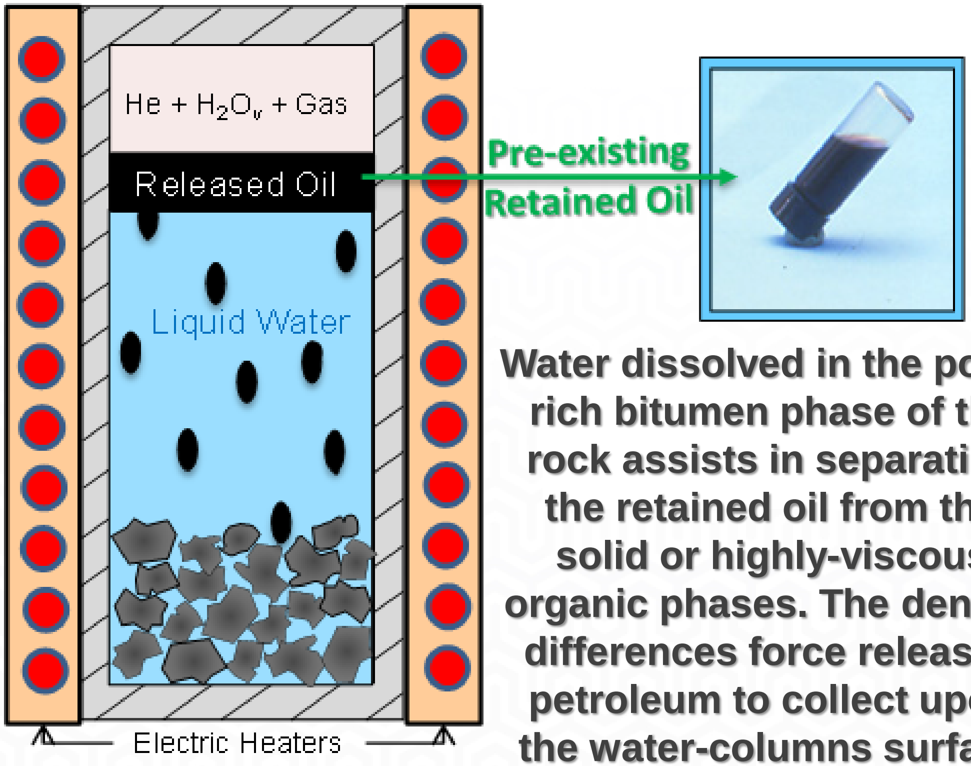
Rationale of LTHP at 300°C/24 or 72h was to use this immiscibility to differentiate retained oil from the polar-rich bitumen within a mature source rock, which Lewan & Sonnenfeld (2017) showed was possible with mature Niobrara cores.

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



CHESAPEAKE LTHP-METHODOLOGY

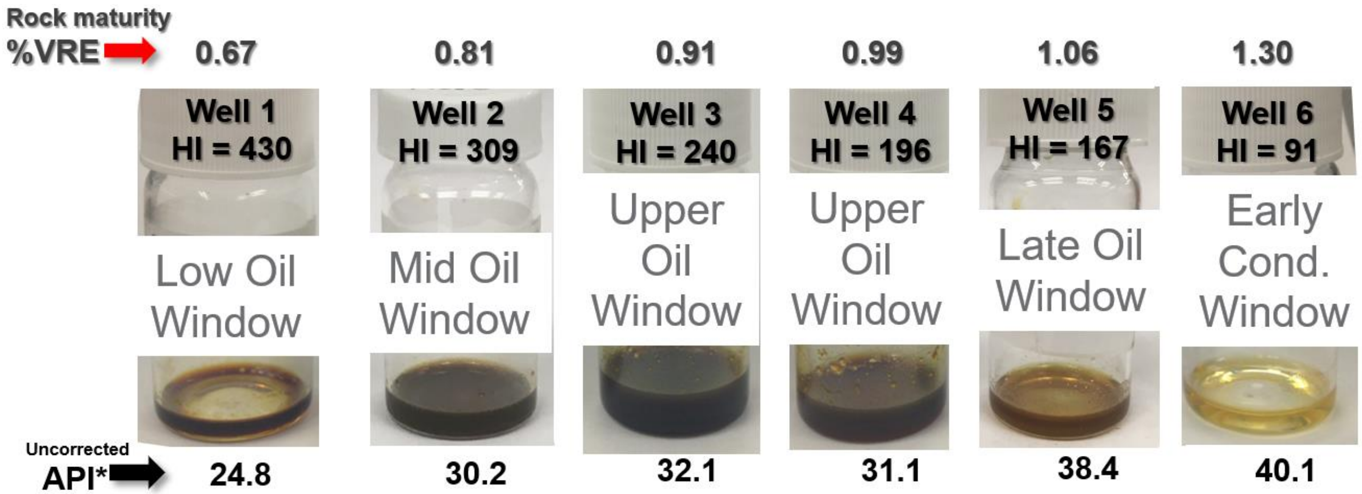
500g of rushed core (0.5 to 2.0 cm) placed in 1-liter stainless-steel (316) reactor with sufficient water to maintain a submerged rock before, during, and after heating isothermally at 300°C for 72 hours.



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

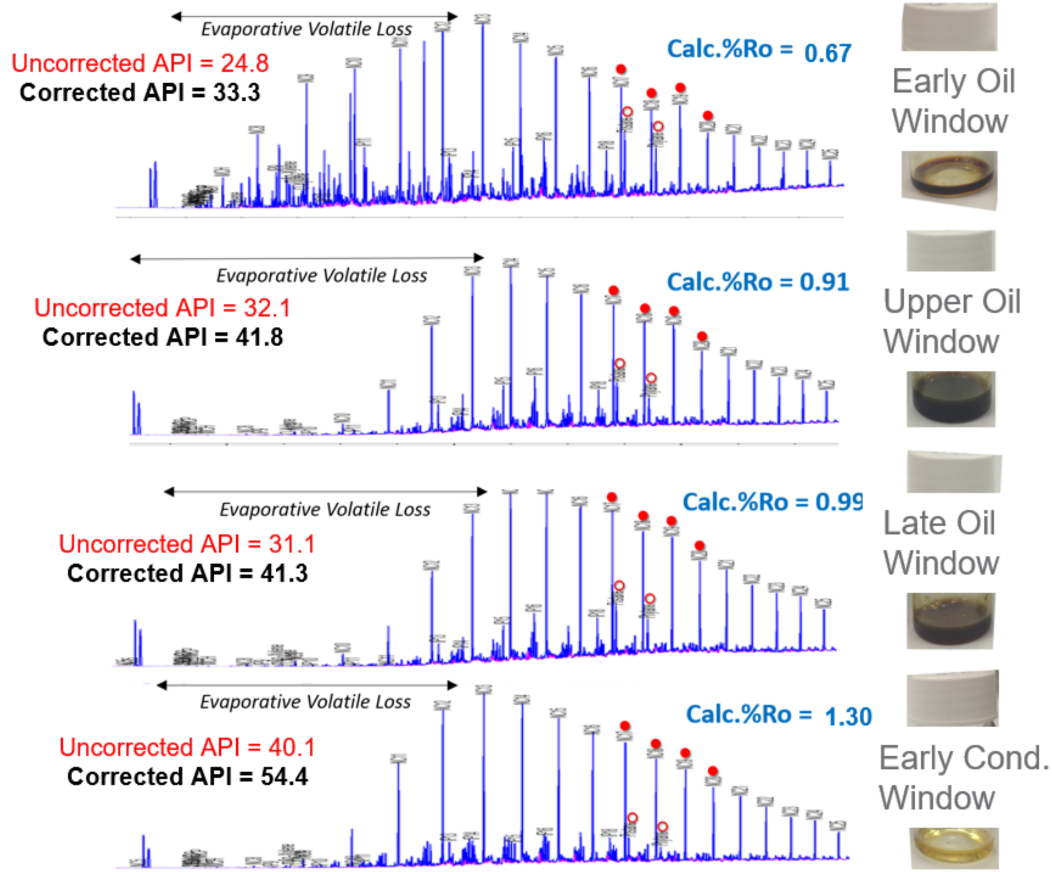
RELEASED OILS FROM SOURCE ROCK SHOW QUANTITY AND QUALITY CHANGES WITH THERMAL MATURITY

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)



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*

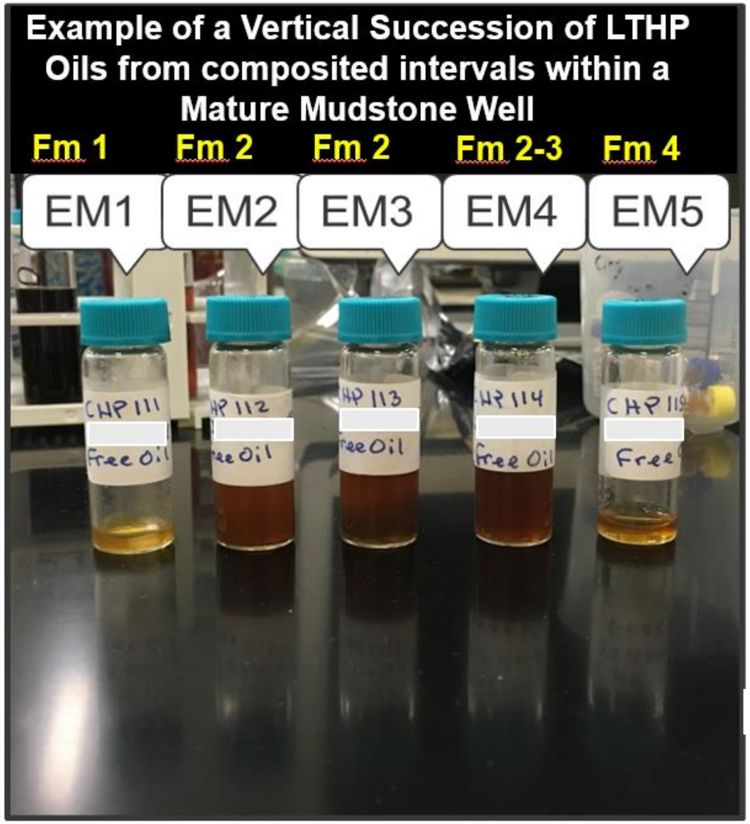
*** This is even a greater problem with other methods like TRA, Dean Stark, and solvent extractions.**

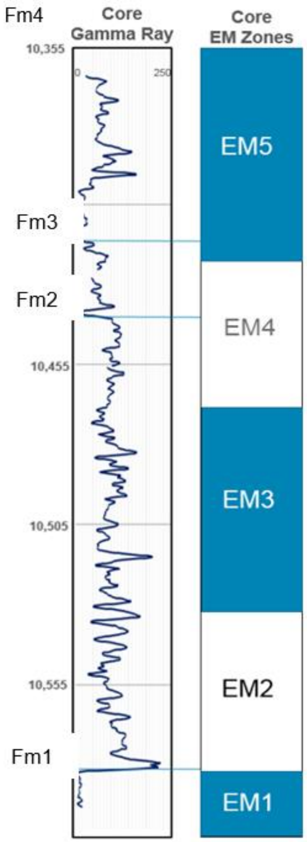
RELEASED OIL CAN BE USED TO ESTABLISH END MEMBERS IN STACKED PAY INTERVALS

- 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.

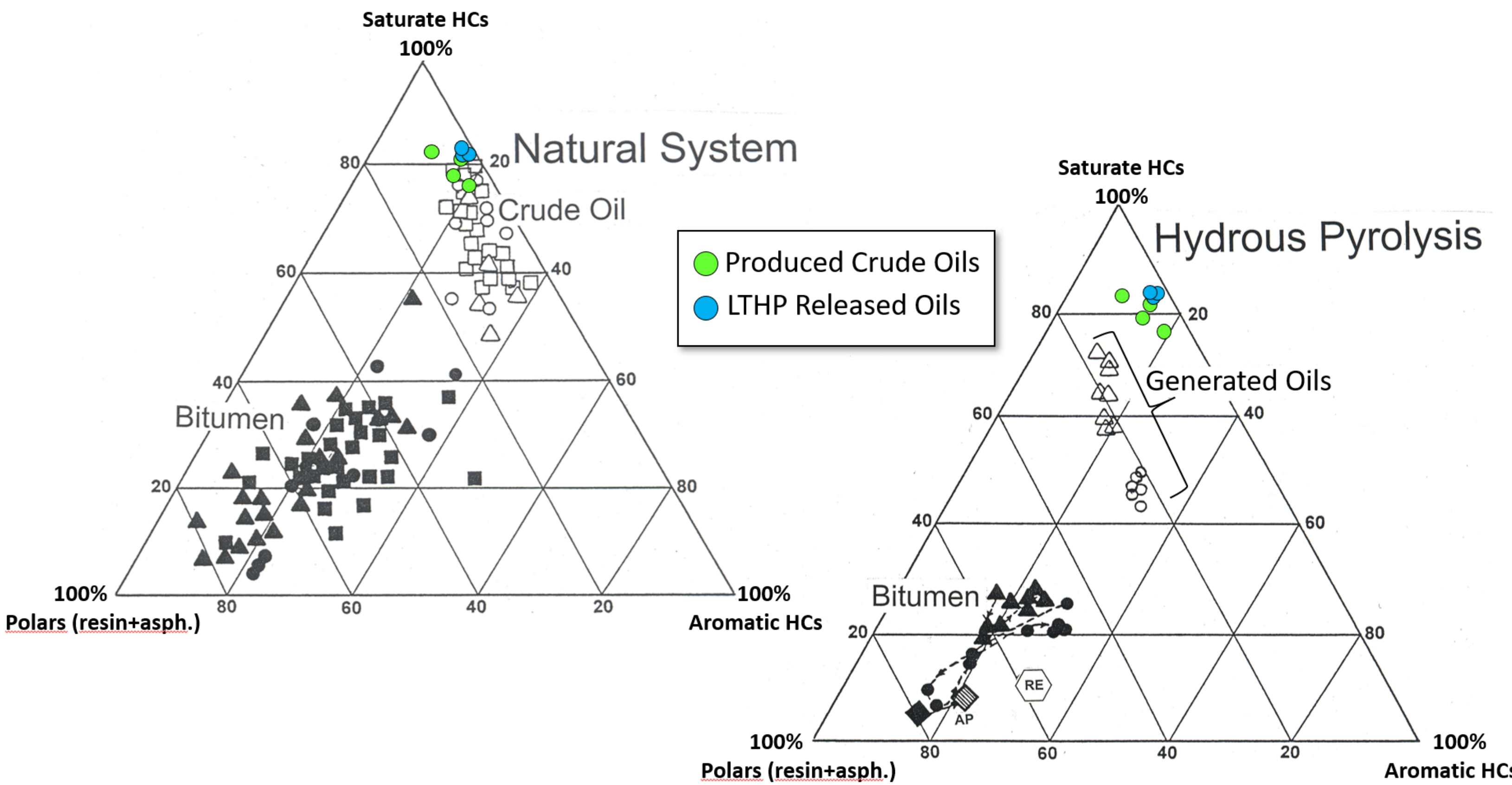
- With, neatly separated and relatively unaltered petroleum phases, we can also estimate in a reasonably accurate way, the contribution of any oil-based-mud to oil-saturations.

- 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.

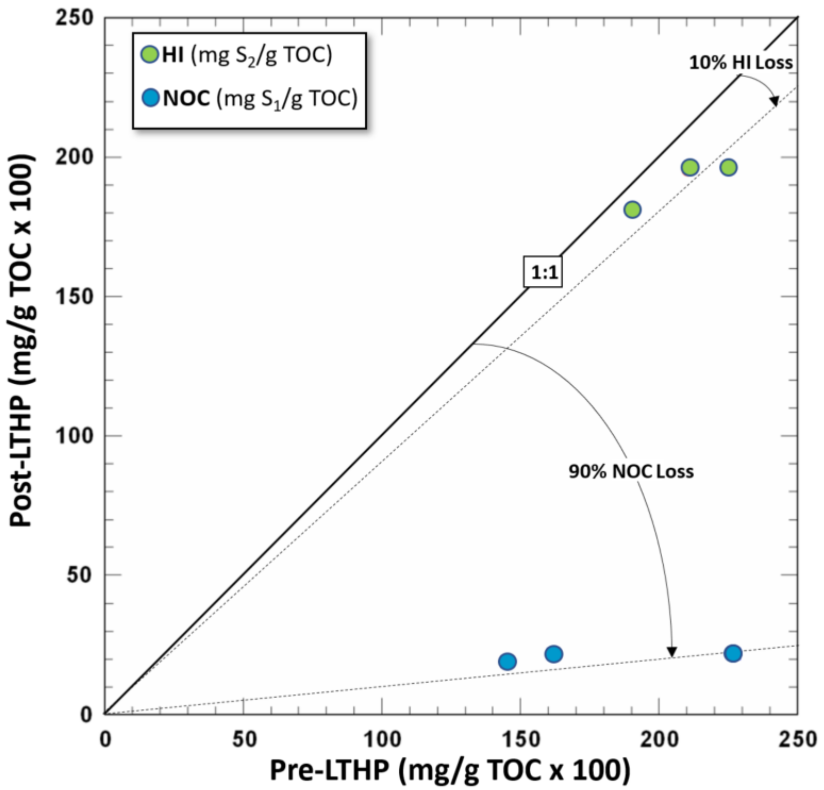




RELEASED OILS HAVE SIMILAR SARA COMPOSITIONS TO PRODUCED OILS



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

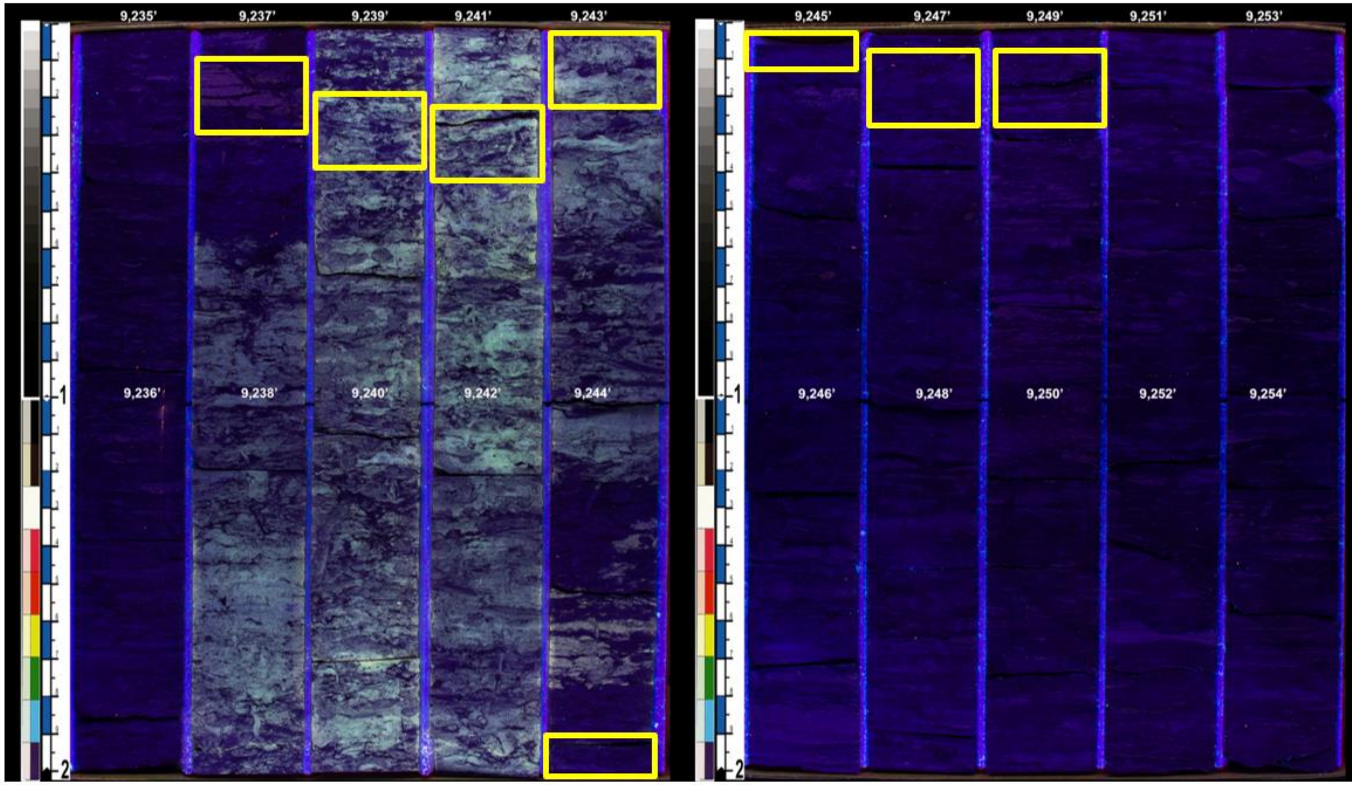


LTHP at 300°C for 72 h releases retained oils and does not generate oil.

Kerogen Atomic H/C Ratio	
Pre-LTHP	Post-LTHP
0.66	0.65
0.64	0.64
0.64	0.64

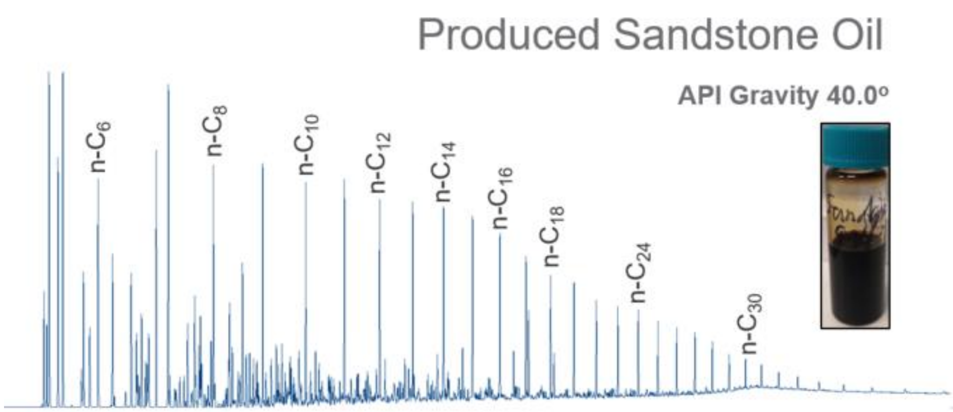
EXAMPLE SAMPLE COMPOSITE FROM A TIGHT OIL SANDSTONE—NON SOURCE ROCK

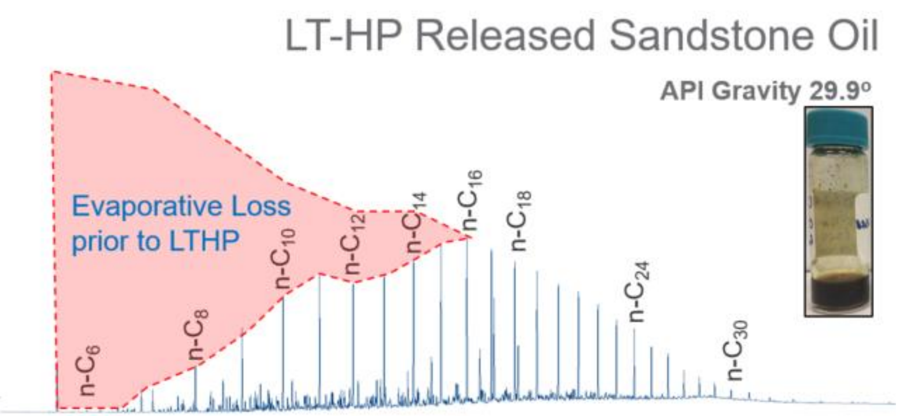
- At time of sample selection the whole interval fluoresced.
- By the time the core was slabbed and the photos taken certain portions of that interval had apparently lost their fluorescence.
- Highlights the importance in mD-scale-rock to take samples intended for saturation measurements as quickly as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



GAS CHROMATOGRAPHY COMPARISON—SANDSTONE LTHP OIL

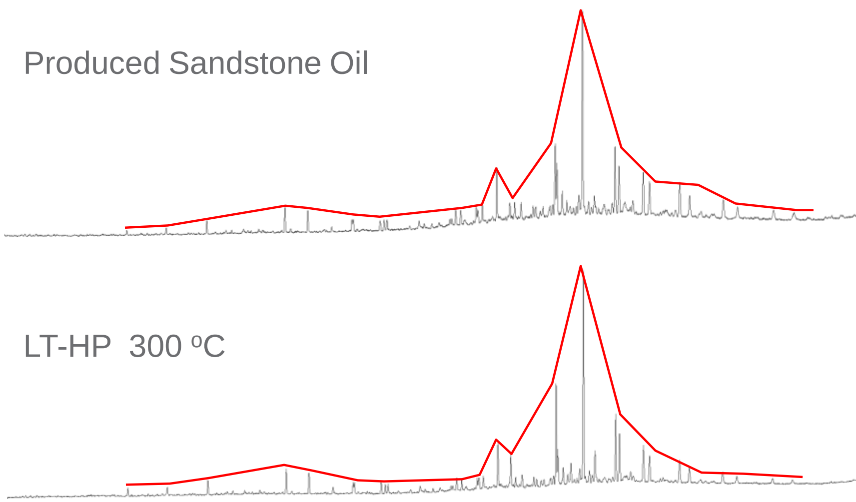
The LTHP oil indicates loss of the light ends as a result of evaporation from the core prior to LTHP, and demonstrates the importance of subjecting relatively high permeability samples to LTHP as soon as possible.

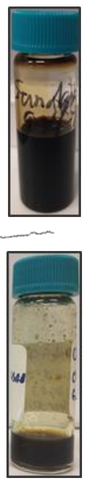




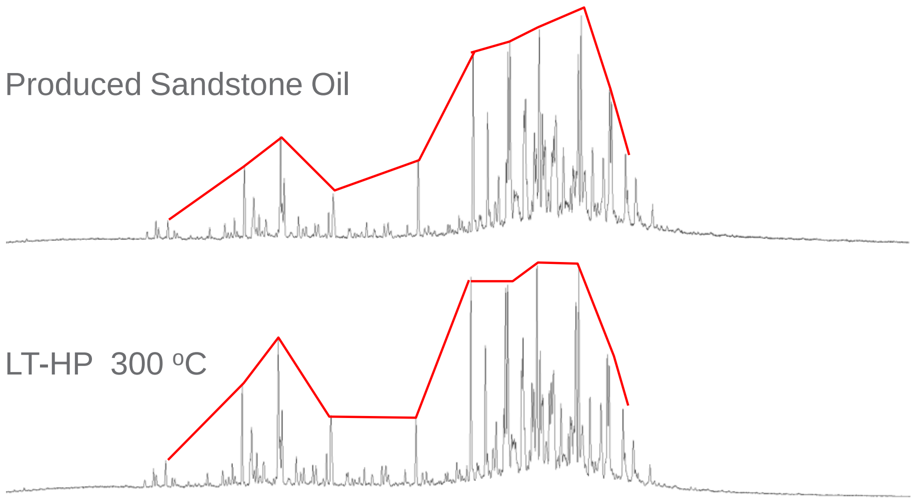
COMPARISON OF STANDARD GCMS TRACES

Terpanes (m/z 191)





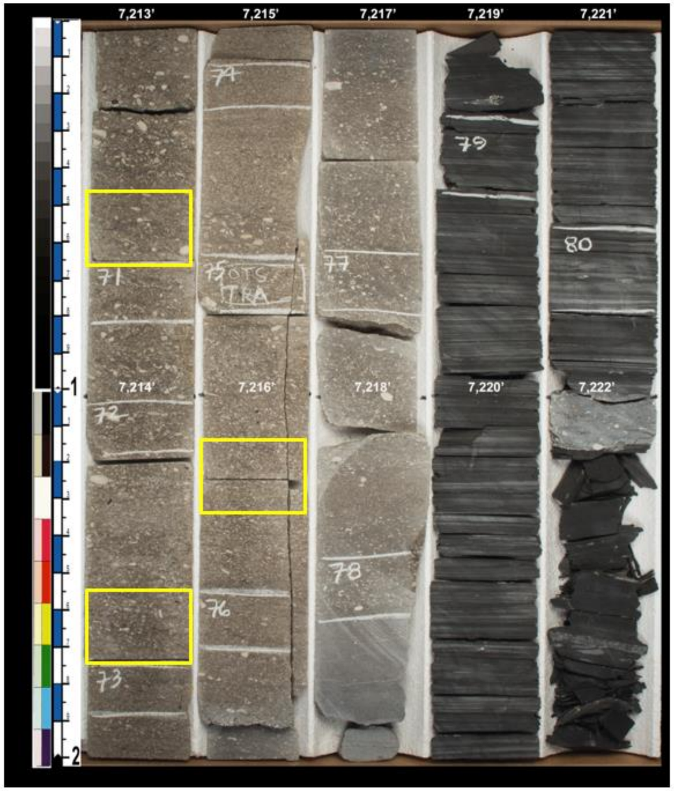
Steranes (m/z 217)



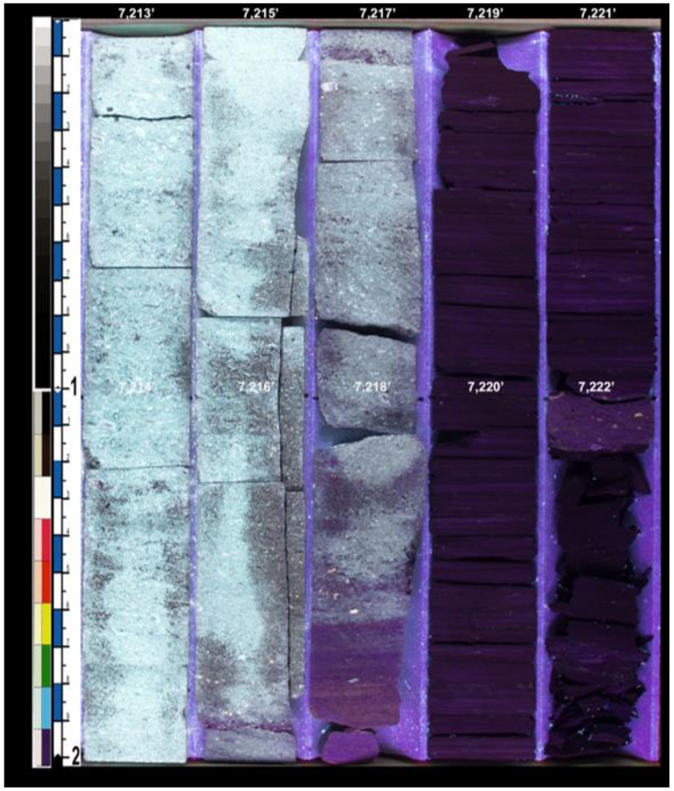
The GCMS data from the LT-HP fluid are very similar to the produced oil

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

White-Light 1/3 Section Photograph



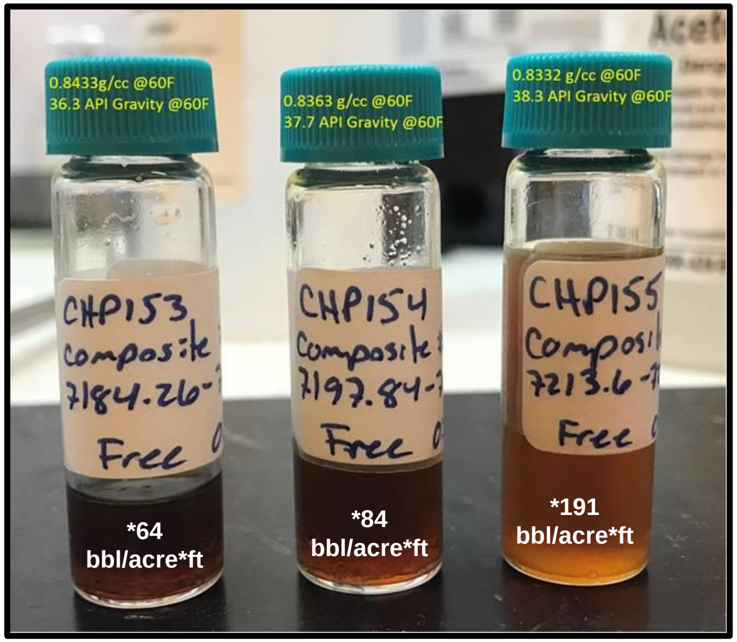
UV-Light 1/3 Section Photograph



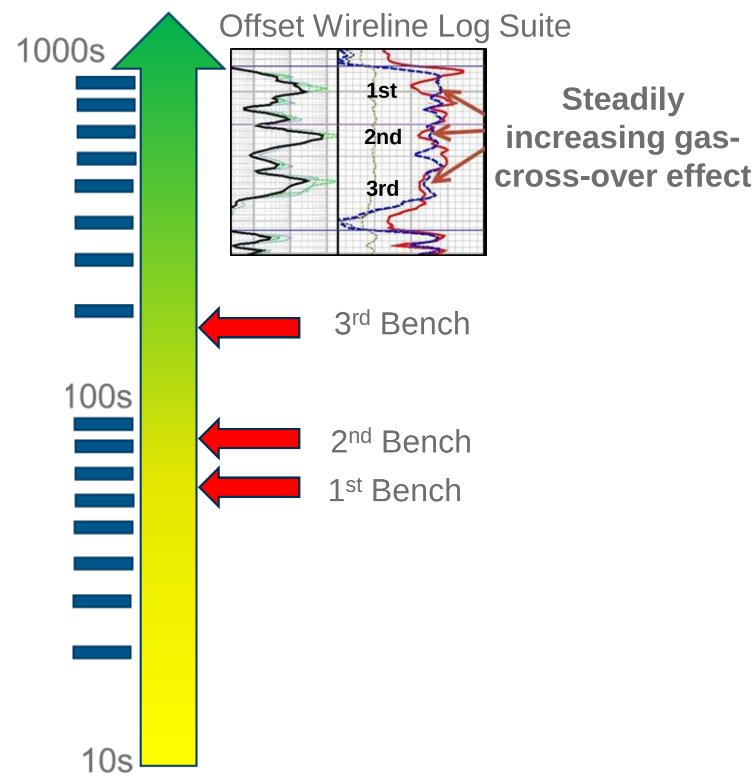
SIGNIFICANT DIFFERENCES IN QUALITY AND QUANTITIES OF LTHP RETAINED OIL RELEASED FROM DIFFERENT BENCHES

Stock-Tank-Oil Resource Density Scale

1st Bench | 2nd Bench | 3rd Bench

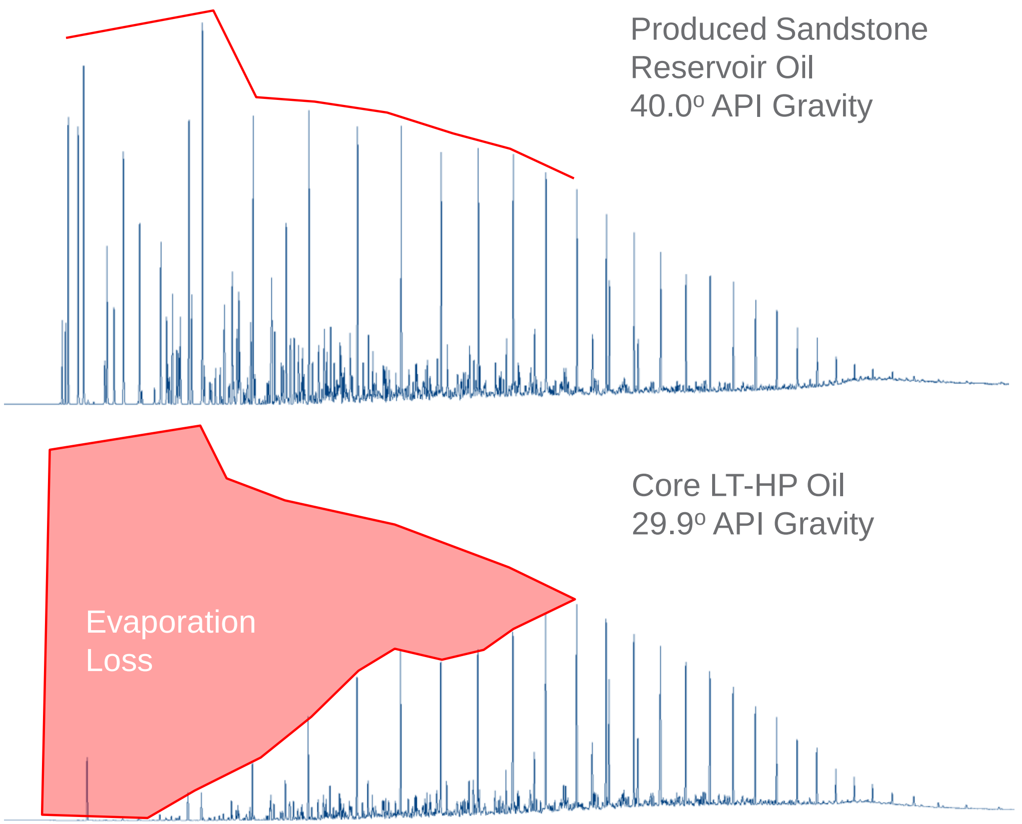


*Totally uncorrected yields—as received free oil resource densities final yields and expected producing API will increase a certain amount with corrections.



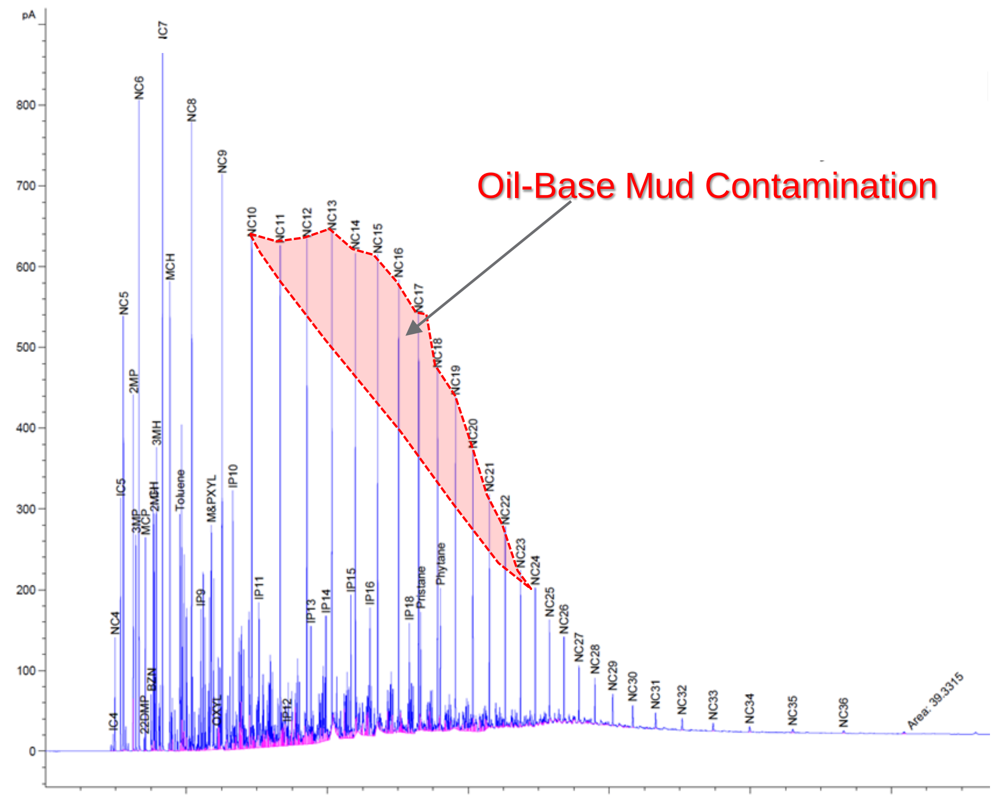
THE IMPORTANCE OF TIME AND PERMEABILITY: 1000'S OF NANO-D ROCK

- 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 1000's of nD's 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 straight-forward means of estimating the amount of contamination of retained oils by the non-native product.
- Since, diesel has a relatively range of compounds compared with natural oils, significant contamination is manifest by a secondary mode of peaks in the n-C_{10} to n-C_{24} range.
- 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-base mud contamination and provides a means to evaluate its impact on the quality and quantity of retained oil.
- LTHP may provide insights on which targeted intervals are major contributors to production and geochemical signatures (e.g., biomarkers) that are diagnostic to these intervals, particularly in stacked plays.
- LTHP can provide information on changes in quantity and quality of retained oils with changes in thermal maturity.

APPENDIX

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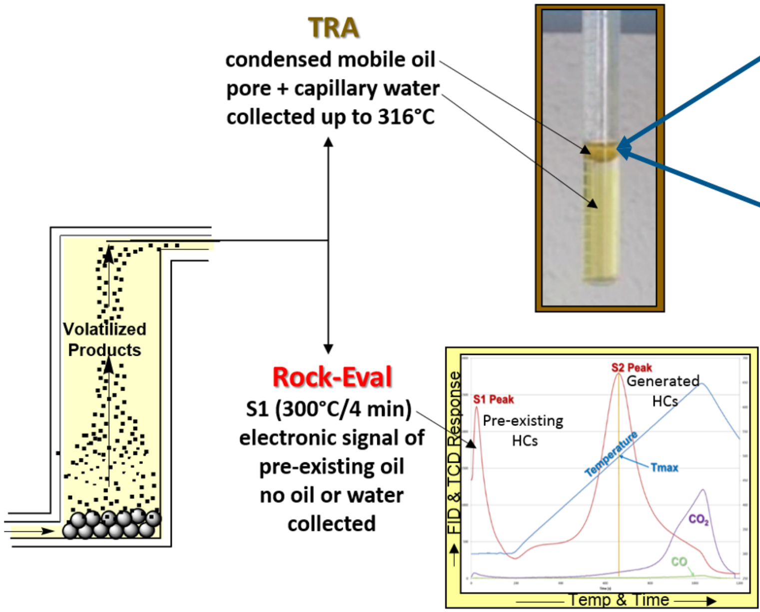
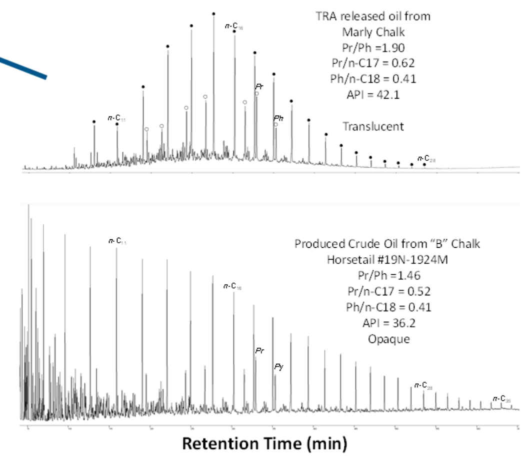
PRE-EXISTING TECHNIQUES PROVIDE LIMITED COMPOSITIONAL INFORMATION

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.

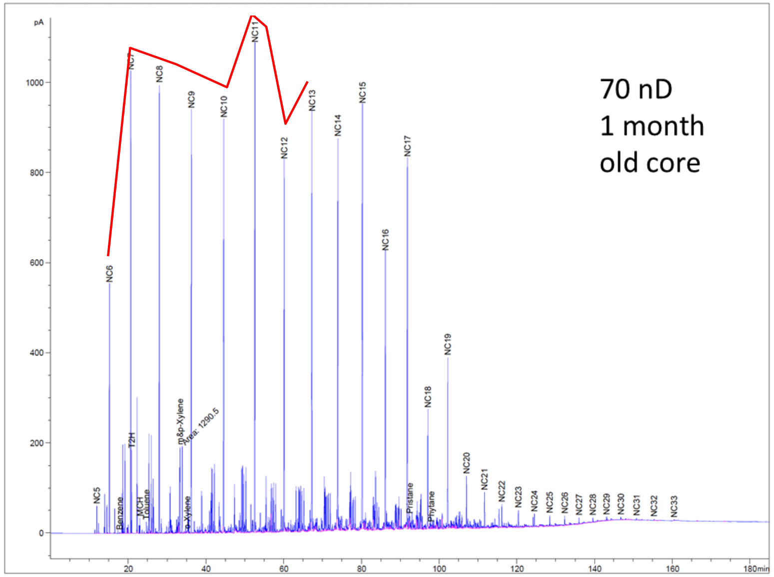


Lewan and Sonnenfeld, URTeC (2017) Niobrara, Denver Basin

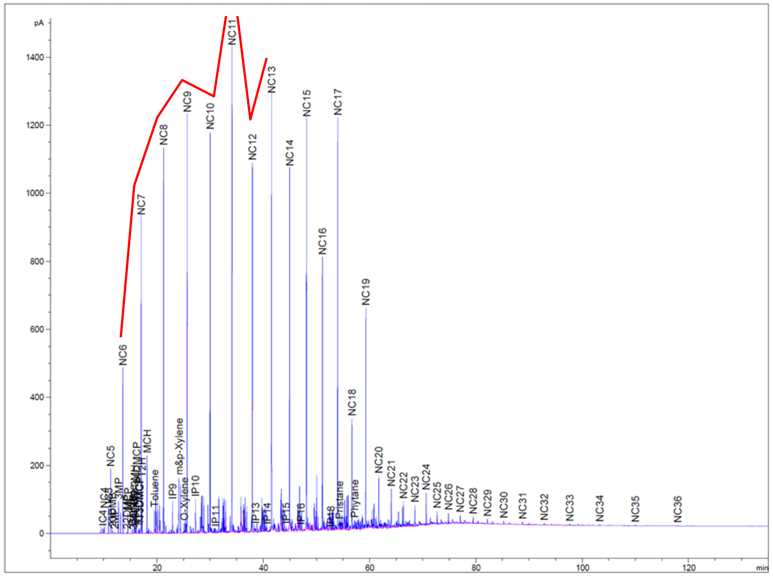
- TRA produces a physically collectable fluid, but appears more like a refined product rather than natural fluid.
- Rock Eval and those of its ilk may give general quantification of light petroleum components but compositional insight is very generalized.
- ***Useful to have a technique that produces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

THE IMPORTANCE OF TIME AND PERMEABILITY: 10'S 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.