Reservoir Geochemistry: The Changing Landscape from the 1950's to the Present*

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Abstract

In the late 1950's, R. Milhone (Chevron, production dept.) was using constant temperature GC to separate gases. Observing this work, L. W. Slentz and J. Andersen (Chevron) conceived of trying to expand this work to oils, and perhaps identify a "fingerprint" of one oil for comparison with others. Slentz and Andersen (late 1950's) applied heat tape to a GC column and periodically increased the temperature (first use of temperature programming in oil industry), and resolved C6-C9 compounds. In February 1960, they conducted the first technical service application of this technology, differentiating Summerland, California beach tar from oil produced from a nearby well. During the 1960's-70's, P. Elmer and H. Packard developed temp-programmable gas chromatographs, and Slentz/Andersen developed packed columns to generate reproducible C6-C18 chromatograms. They went on to install ~10 of these instruments in Chevron US laboratories and overseas operating companies. In the 1970's, the term "reservoir geochemistry" was coined by petroleum geochemists at Chevron to distinguish new, reservoir-management applications from the more established, exploration-related applications of petroleum geochemistry. Then Chevron published a suite of studies to showcase different applications of reservoir geochemistry in the oil/gas industry: Slentz (1981) proposed that the composition of an oil or water could be used as a 'fingerprint' characteristic of a reservoir; Kaufman et al. (1990) showed that tubing string leaks can be identified and quantified using this fingerprint method; Hwang and Baskin (1995) showed that oil fingerprints (and other bulk properties) did not change in a large-scale reservoir during 20-plus years; and McCaffrey et al. (1996) showed that matrix algebra applied to GC and GCMS peak heights can be used for production

allocation from discrete reservoirs, and GCMS data can be used to predict fluid viscosity variations with depth in heavy oil reservoirs.

In the early-mid 90's, geochemists at BP, Shell, Total, Statoil and University of Newcastle, improved geochemical assessments of reservoir continuity by integrating geochemical data with geological and engineering data, and by modeling the rates of different fluid mixing mechanisms in the reservoir (e.g. England, 2007). Shell geochemists developed two independent methods of measuring the similarity of oil samples to evaluate reservoir connectivity: (i) Multi-dimensional gas chromatography (MDGC) measures the abundance of 12 gasoline-range alkyl-benzene compounds and (ii) the second technique determines the similarity of two oil samples by performing a pair-wise comparison of a large number of HRGC peaks. Fuex et al. (2003) described a centrifuge experiment on a live oil sample demonstrating gravity segregation can explain the origin of a large compositional gradient. In the 2000's, workers at the University of Calgary and elsewhere dramatically improved our understanding of in-reservoir oil biodegradation, allowing petroleum geochemistry to be used to understand and predict viscosity variations in biodegraded oil accumulations. The advent of mud gas isotope logging in the early 2000's provided new high-resolution natural tracers for characterizing gases in reservoirs. Integrated time lapse studies, such as Chouparova et al. (2010), illustrated dynamic changes in communication between conventional reservoirs. Recently, with the advent of unconventional reservoirs, time-lapse petroleum geochemistry has become key to assessing changes in drained rock volume over time, and to optimizing development strategies for stacked pay in plays such as the Permian Basin, Eagle Ford, and Bakken (e.g. Laughland and Baskin, 2015; Kornacki, 2017; Jweda et al., 2017).

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Reservoir Geochemistry:
The changing landscape from the 1970's to the Present

by

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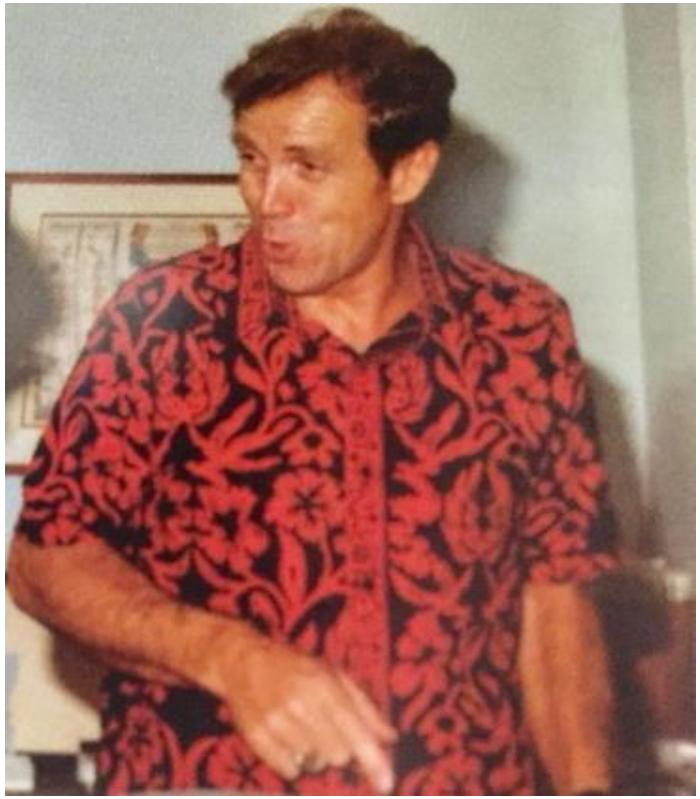

Tribute to Loren (Slatz) Slentz

Hedberg Conference

The Evolution of Petroleum Systems Analysis: Changing of the Guard from Late Mature Experts to Peak Generating Staff

March 4-6 2019
Houston, Texas, United States

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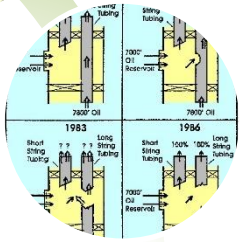
Outline: Growing Applications of Reservoir Geochemistry Over Time

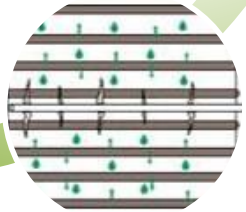
Late 1950-1960's development of GC-based "oil fingerprinting

'70's –Present
Assessment of Reservoir Continuity



'80's- Present
Diagnosing of Completion Problems, 2-zone Allocation

'90's-Present
2-7 zone Production Allocation,
Fluid Property Prediction



2000's- Present
Biodegradation Gradients/ Time Lapse Geochem/ Characterization of UR frac height/DRV

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1950's-80's Early Gas Chromatography Development in Chevron

- **Late 1950s:**
  - **Ralph Milhone (Chevron Production Dept., La Habra, CA) used constant temperature GC with packed columns to separate methane to ~n-pentane.**
  - **Loren Slentz and Jim Anderson expanded the GC range to include HC's beyond n-C_5, by applying heat tape to a packed column and periodically increasing the temperature (first use known to us of GC temperature programming in oil industry) allowing some HC to be separated out to ~ n-C_9.**

- **February 1960: the first internal technical service application using these chromatograms (C_6-C_9's) showed that local beach tar was not from nearby wells in the Summerland Field, CA.**

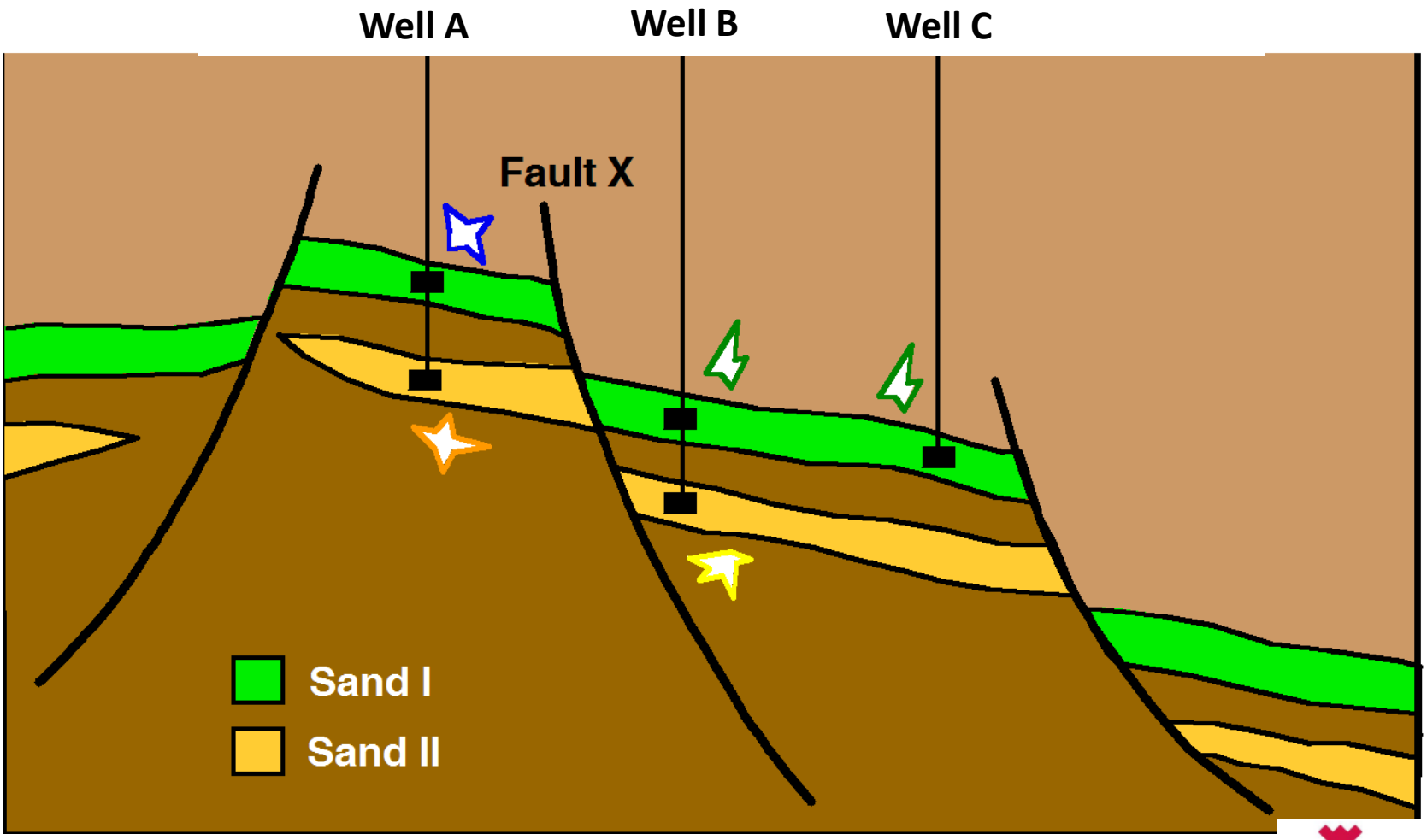
- **1960-70's:**
  - **Perkin Elmer and Hewlet Packard develop temp-programmable GC's.**
  - **Slentz and Anderson develop copper-tube columns packed with silica gel warmed in Apiazon grease that were very reproducible and extended resolvable hydrocarbons through n-C_{18}. Within Chevron, these were called PTC chromatograms (Programmed Temperature Chromatography).**

- **Late 1970s- early 1980s: Chevron installed chromatographs capable of generating PTC chromatograms in 11 US and overseas operating company labs.**

- **1981: Slentz published first paper using oil fingerprinting as a reservoir management tool. *"Geochemistry of Reservoir Fluids as a Unique Approach to Optimum Reservoir Management,"* 1981 SPE 9582, presented at Middle East Oil Technical Conference, Bahrain.**

- **This paper Introduced the concept of "oil and water" fingerprint as "characteristic of a specific reservoir" and can be used to evaluate vertical and lateral reservoir fluid continuity. Also introduced the cluster diagram and star diagram as easy ways to display multivariate peak ratio data.**

Chevron validated the utility of this technology in hundreds of internal reports



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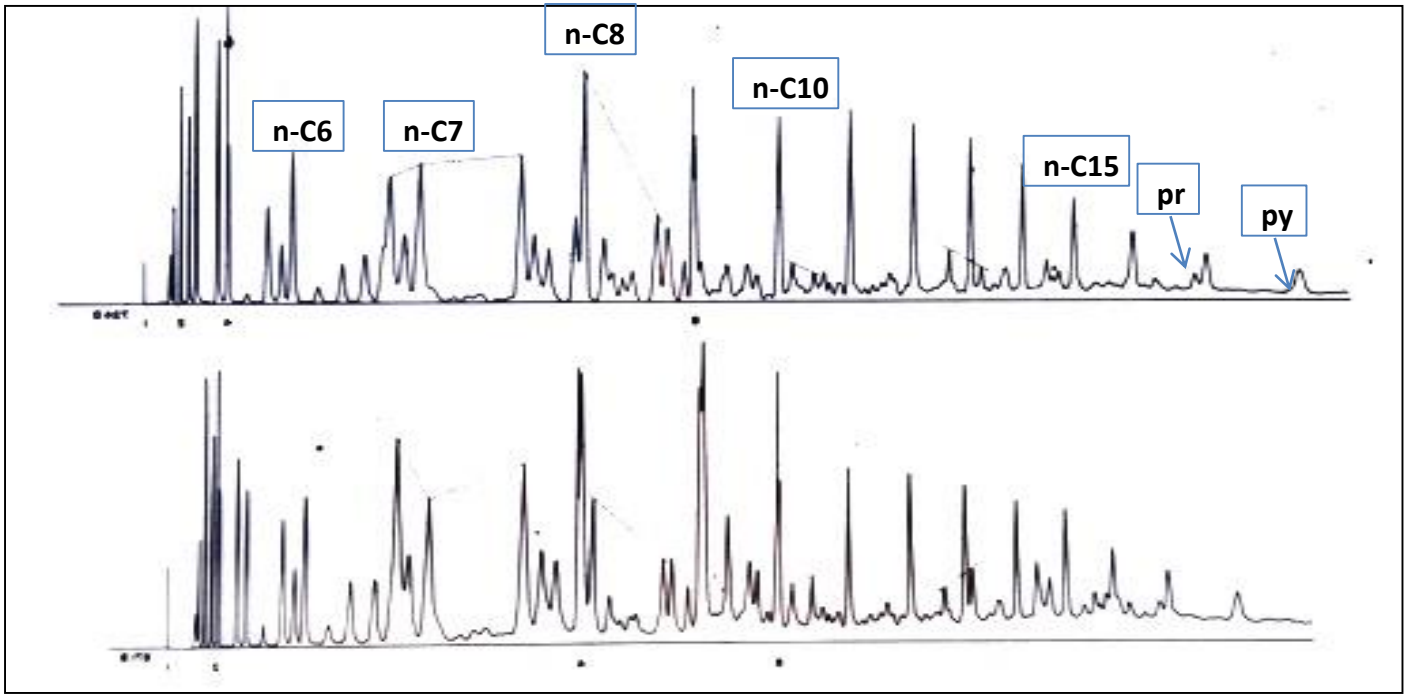
Typical PTC Chromatograms showing Hydrocarbon range from n-C1 through n-C18

(*first GC's right to left, later switched to left-right*)

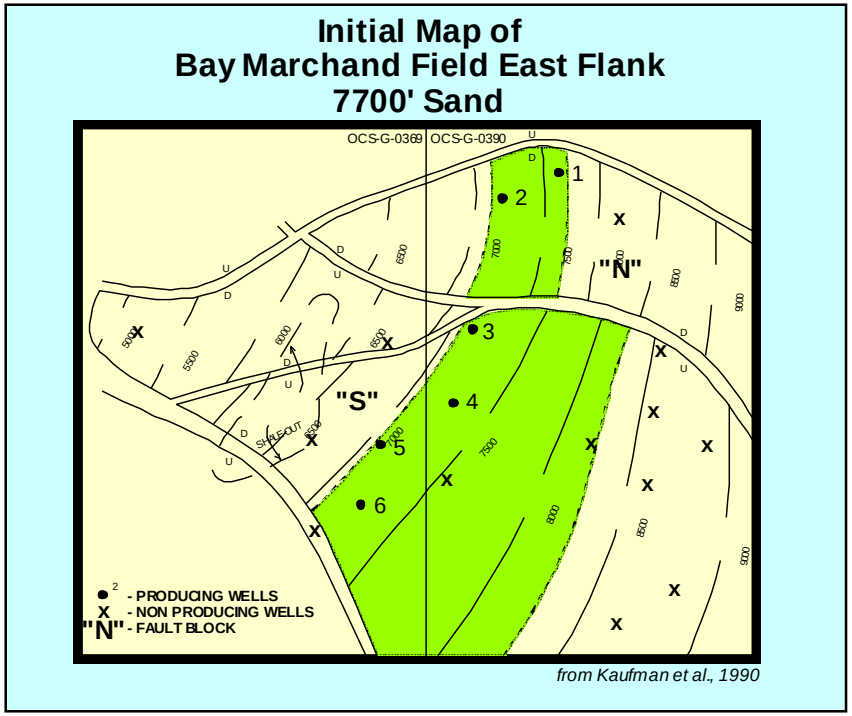


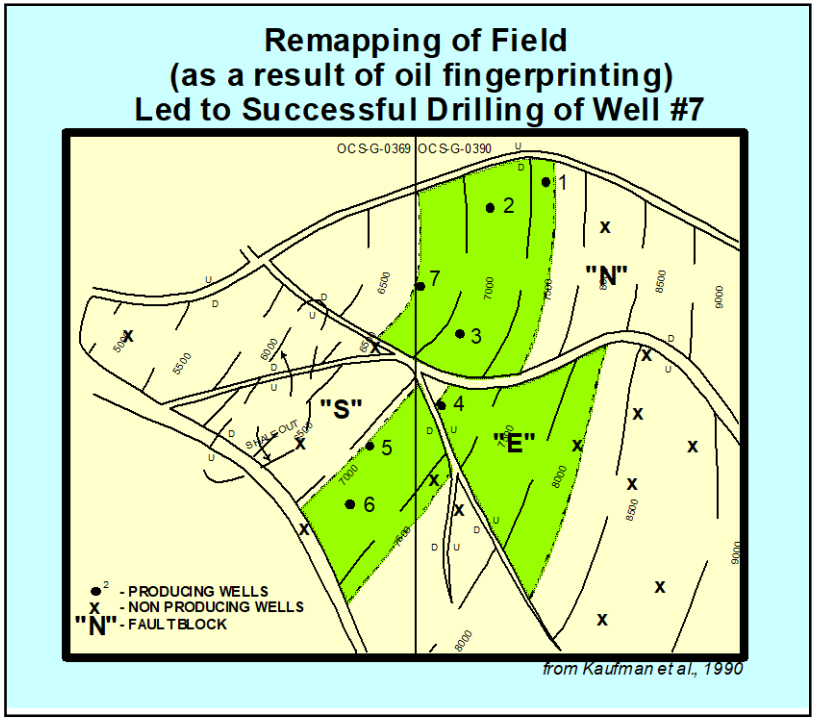
- In late 1980s, Chevron was involved in an 'Equity Dispute' and wanted to use gas chromatography results as part of their legal argument.
- However, the other litigant clamed that this technology was an in-house Chevron technique, not scrutinized or validated by the scientific community.
- To be able to use this technology in equity disputes, Chevron's decided to publish the method and its applications to reservoir management.
- This led to landmark paper by Kaufman et al., 1990, and a series of other Chevon papers in the early 1990's

Gas Chromatography as a Development and Production Tool for Fingerprinting Oils from Individual Reservoirs in the Gulf of Mexico, 1990, R. L. Kaufman, A.S. Ahmed, and R. J. Elsinger.

This paper contained :

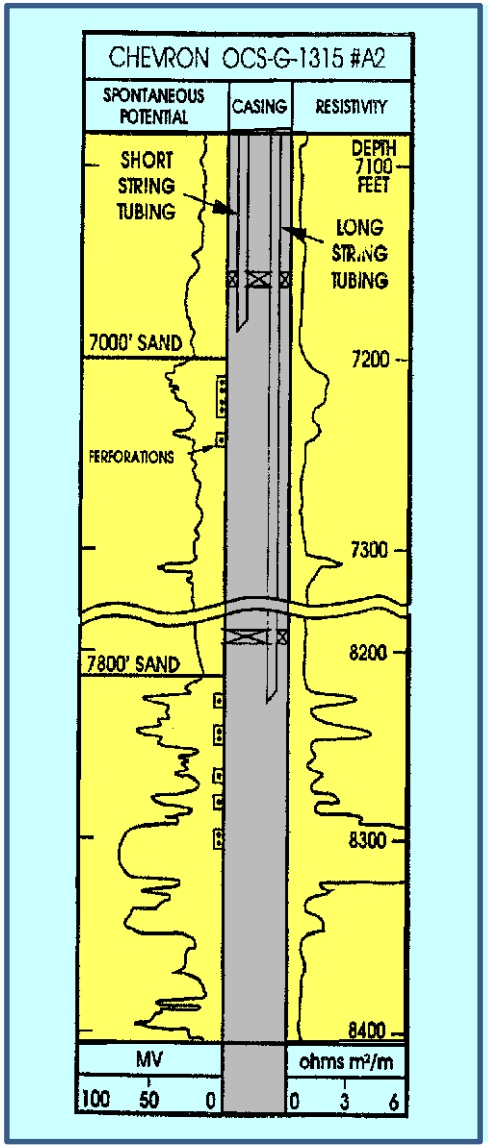
- detailed the methodology using F-SCOT gas chromatography
- reservoir continuity case study in the Bay Marchand Field, GOM
- tubing string communication case study in Main Pass 299 Field, GOM
- 2-zone production allocation case study in Main Pass 299 Field, GOM

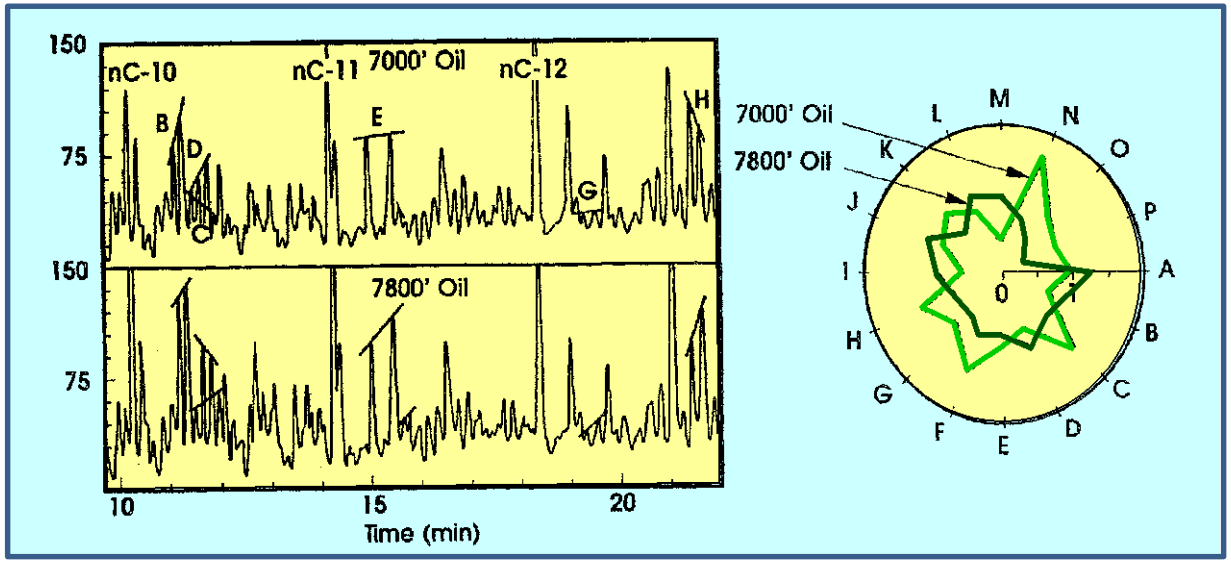




Modified from Kaufman et al. (1990)

Tubing String Communication Case Study in Chevron OCS-G-1315 #A2 Well

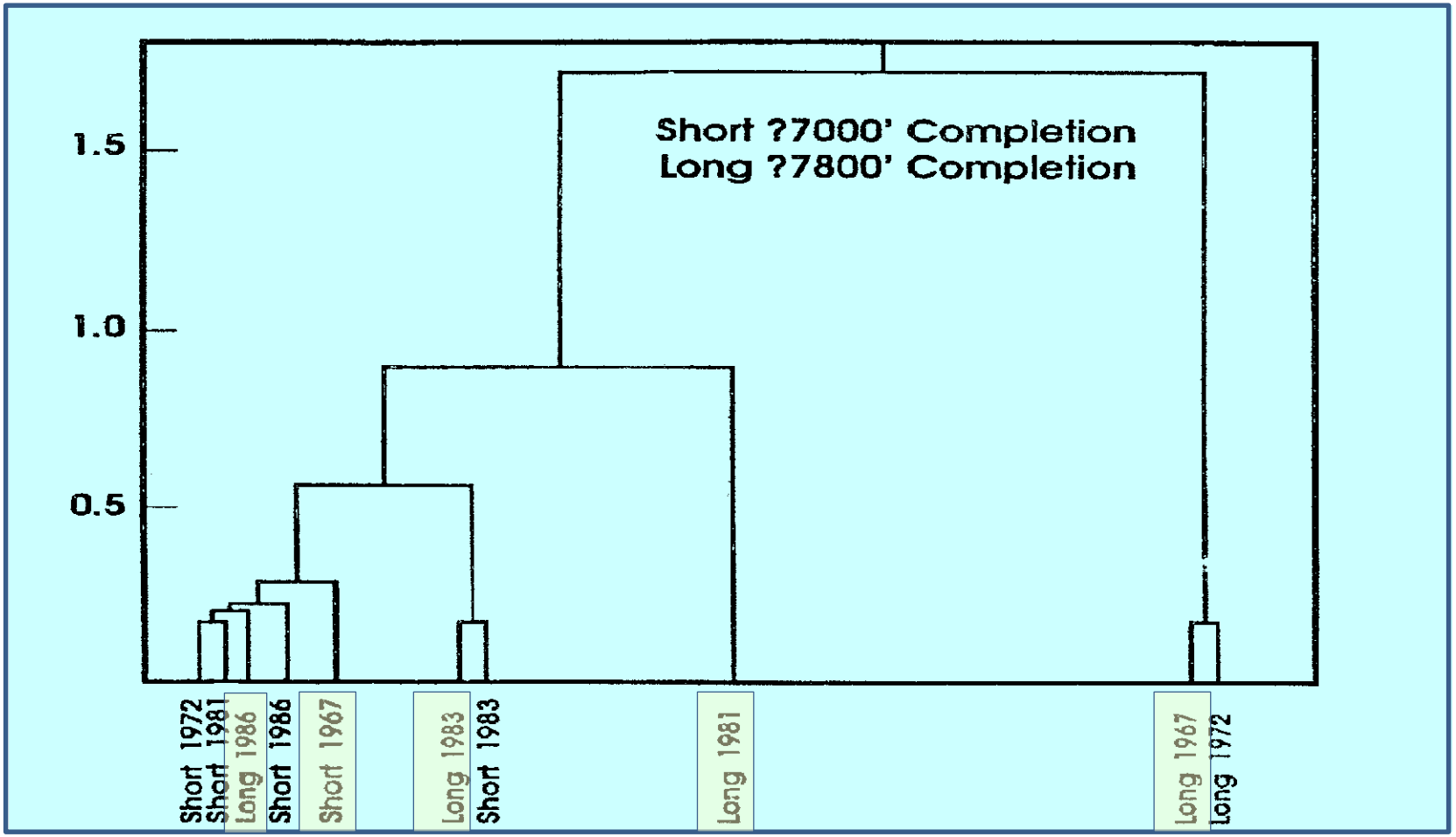




- Main Pass 299 well has two pay zones and is produced with a dual completion
- Oils from the 7000' and 7800' sands can be distinguished by gas chromatography

Modified from Kaufman et al. (1990)

Production in the Chevron OCS-G-1315 #A2 Well Over Time



- In 1967 long and short string production were compositionally distinct.
- Oil geochemistry cluster analysis suggests a leak in the long string began after 1972, but prior to or during 1981.
- By 1986 both long string and short string produced virtually identically oil.

Modified from Kaufman et al. (1990)

Reservoir Connectivity and Oil Homogeneity in a Large Scale Reservoir, 1994, Rong J. Hwang and David K. Baskin, *Middle East Petroleum Geoscience Geo 94* **2**, 529-541.

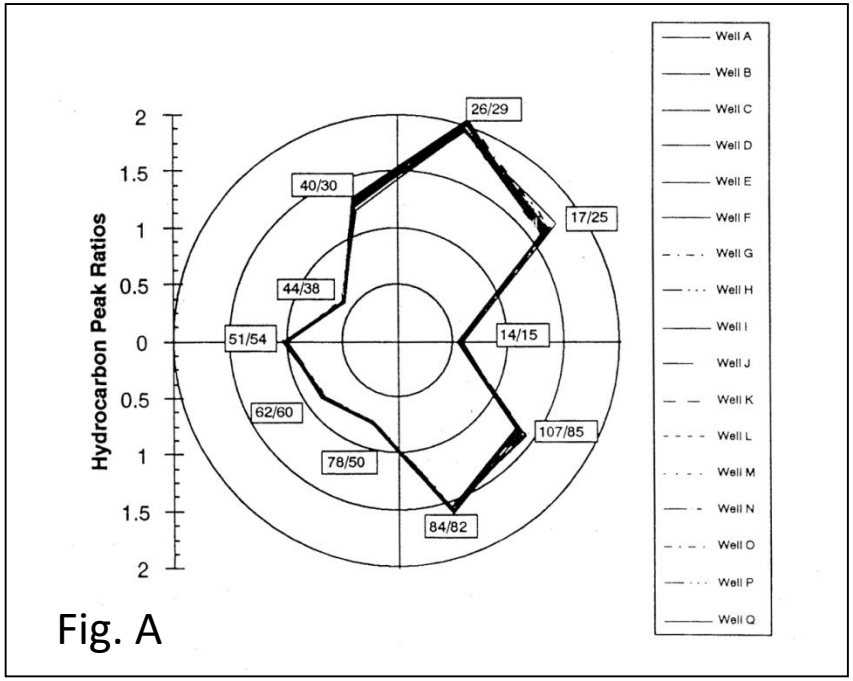


Fig. A

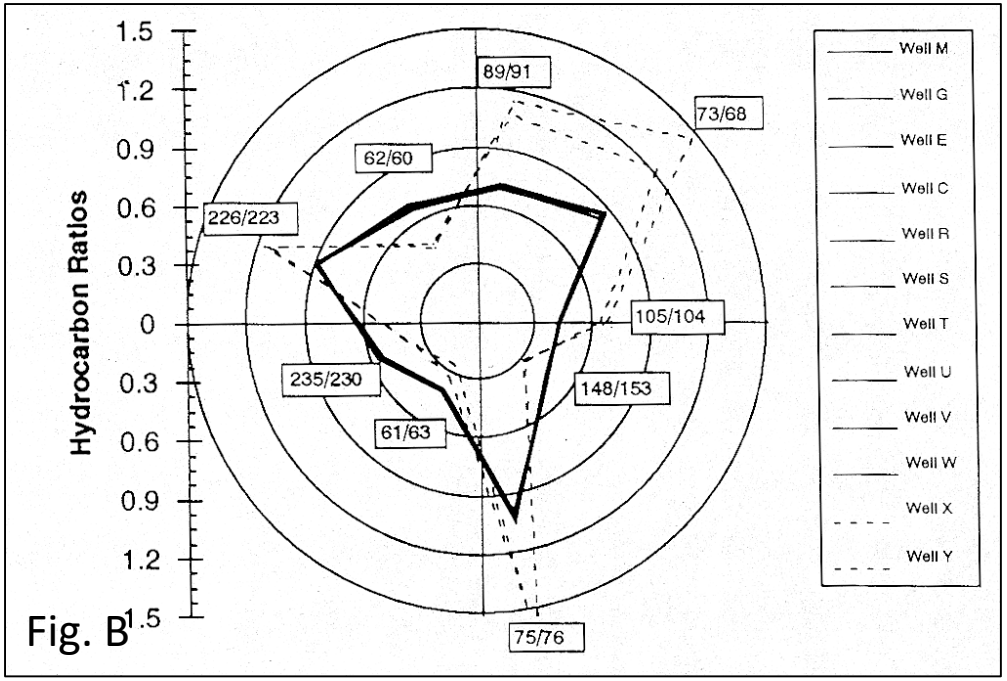


Fig. B

- Large scale reservoir in Middle East (~30 km by 7 km) with 1 oil-water contact
- Figure A shows very small compositional differences among 17 oils widely distributed from Main Reservoir
- Figure B shows that 10 oils from the main and underlying reservoirs are compositionally distinct.
- Figure B also shows composition in Main Reservoir has not changed during more than 20 years and millions of barrels of production
- Paper also showed that biomarker maturity and source concentrations had not changed across the Main reservoir in over 20 years of production.

Modified from Hwang and Baskin (1994)

1990's: Production Allocation

- McCaffrey et al (1996) AAPG Bulletin **80(6)**, 898-913 introduced a different method for geochemical allocation of commingled production, a method that was not limited to two zones, but could be expanded to as many as 6 or 7 zones.

- That method was based on using as natural tracers the abundance of a large number compounds in end member and commingled oils and using a matrix algebra approach to express a commingled oil as a combination of the end members oils.

- That method led to inexpensive, multiyear production monitoring of fields. For example, production monitoring of one North Slope field began in 1997, and continues to this day, with production allocation having been applied in that field more than six thousand times thus far, including 81 times last month.

- That production allocation methodology was later described by McCaffrey and coworkers in more detail in various conference presentations, culminating in SPE paper #144618 in 2011

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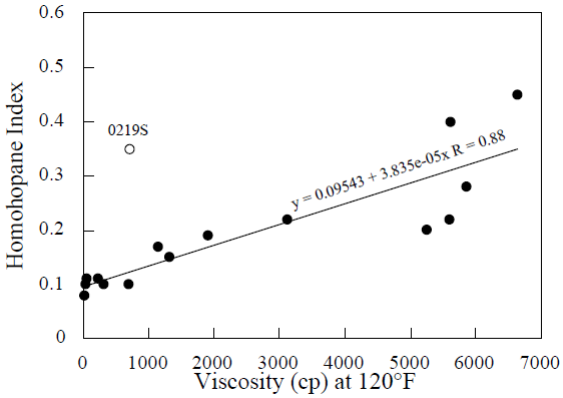
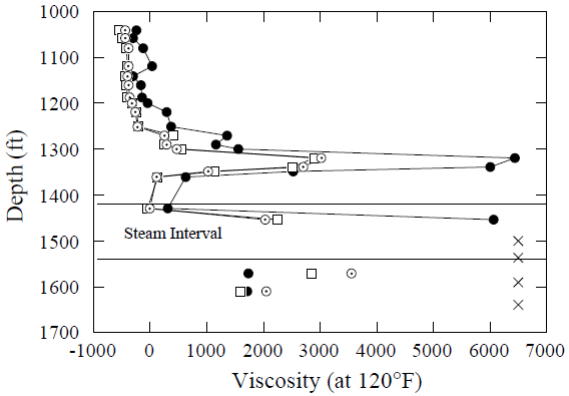
1990's: Fluid Property Prediction

- Tools for using geochemistry to identify sweet spots within heavy oil columns were proposed by:
  - Smalley et al. (1996) SPE 36652 and
  - McCaffrey et al. (1996) AAPG Bulletin 80(6), 898-913

- In short, the technique that they proposed worked as follows:
  - Using a set of "calibration oils" from the field, construct transforms relating oil viscosity to one or more geochemical parameters
  - Measure the geochemical parameter(s) in the sidewall cores or core samples or cuttings from the zone of interest
  - Use the transform(s) to convert the core or cuttings data into viscosity data.
  - Design field development strategies to high-grade most productive intervals





Modified from McCaffrey et al. (1995)

2000's: Biodegradation/ Compositional Gradients

Our understanding of in-reservoir oil degradation was completely changed by:

- Wilhelms et al. (2001) Nature v 411, pp1034-1037 and
- Larter et al. (2003) Organic Geochemistry v 34, 601-613
- Adams et al. (2006) Journal of Geochemical Exploration, v. 89, p. 1-4

They showed that for degradation in the reservoir :

- The electron acceptor is NOT oxygen (not aerobic) – electron acceptors inorganic
- Degradation is much slower than at the surface (~0.1-1 g/m^2 of OWC/yr.)
- Compositional gradients exist within a biodegrading oil accumulation
- Overall rate of degradation of a subsurface oil accumulation related to the ratio of the oil volume to the area of the OWC.
- Temperature must be <80°C (rate near 0 at 80°C, increasing with decreasing T, maximum rate @ < 40°C).
- "Nutrient supply from the aquifer and adjacent shales, mostly buffered by mineral dissolution, probably provides the ultimate control on the range of degradation flux value."
- If reservoir was ***ever*** deeper than the 80°C Isotherm, no degradation
- Bacteria are "descendants" of bacteria syn-depositional with reservoir.

2000's: Compositional Gradients Unrelated to Biodegradation

Our understanding of gravity-segregation-induced compositional gradients within thick oil accumulations was enhanced by:

Ratulowski et al. (2000) Theoretical and experimental investigation of isothermal compositional grading. SPE #63084.

- They described a sophisticated centrifuge experiment that simulated the effects of ~1,000 feet of gravitational head, and was able to mimic a compositional gradient present in the Bullwinkle field, GOM.
- They showed that the gradient represents the equilibrium state between the effects of gravity (which creates a compositional gradient) and the chemical potential of each component in the fluid, and was particularly sensitive to the saturate/aromatic ratio of the fluids.

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2000's: Time-Lapse Geochemistry of Conventional Reservoirs

Extensive integration of geochemistry with geological, geophysical and engineering data to elucidate reservoir compartmentalization was advanced by various authors, including:

- Milkov et al. (2007) Compartmentalization and time-lapse geochemical surveillance of the Horn Mountain oil field, deep-water Gulf of Mexico. AAPG Bulletin, v. 91, pp. 841-876.
- Chouparova et al. (2010) Integration of time-lapse geochemistry with well logging and seismic data to monitor dynamic reservoir fluid communication: Auger field case-study, deep water Gulf of Mexico,. In *Reservoir Compartmentalization*, Geological Society, London, Special Publication 347, pp. 55-70

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2010's: Time-Lapse Geochemistry of Shale Reservoirs

- Assessment as to whether or not induced fractures have propagated out of the formation containing the lateral and into either an overlying or underlying zone, causing the commingling of production from multiple intervals.
- Quantitative allocation of the contribution of individual pay zones to commingled oil or gas production.
- Monitoring the change over time in Drained Rock Volume (DRV)
- Identifying "cross-talk" between the induced fracture networks in wells completed in adjacent formations

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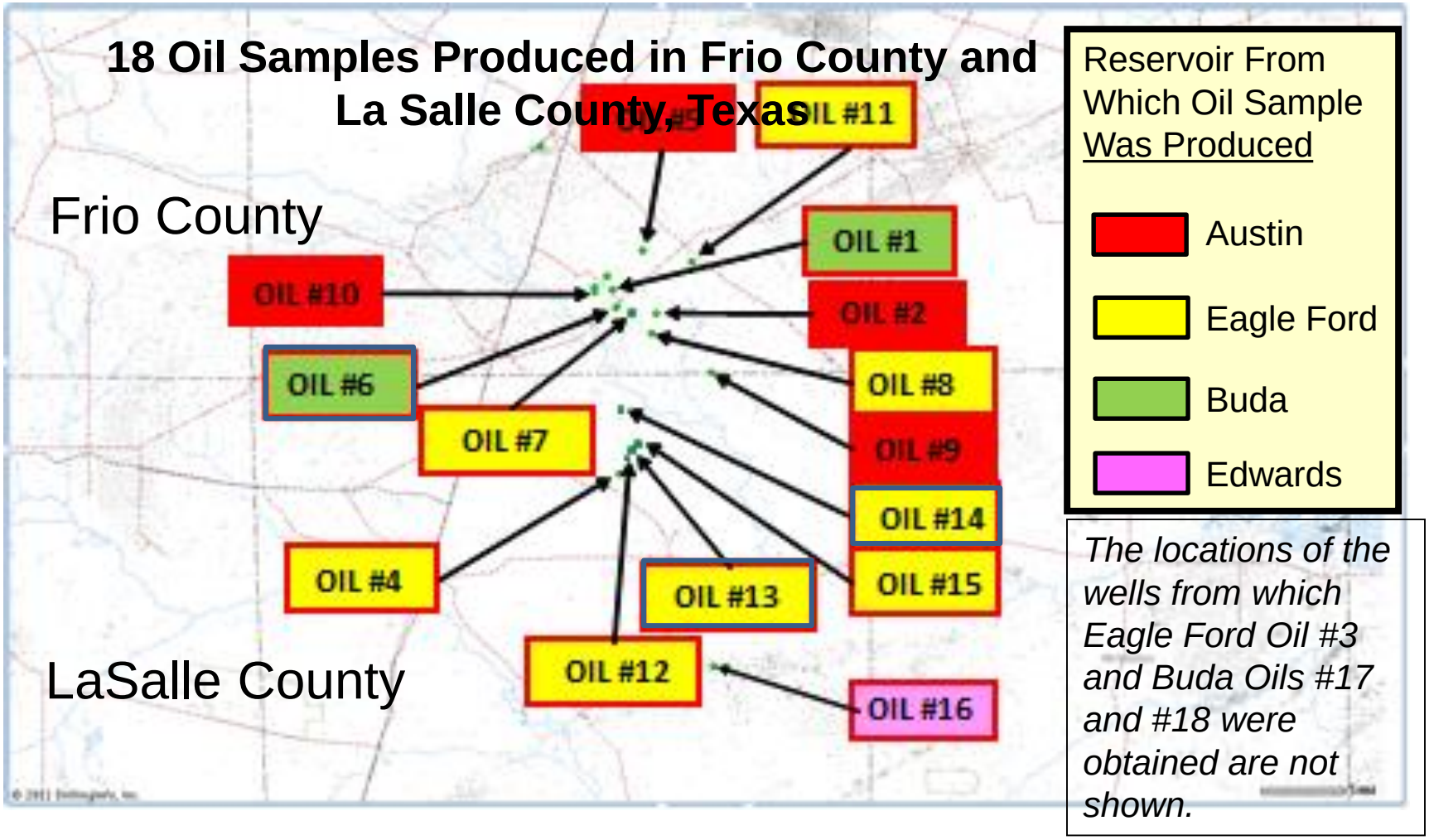
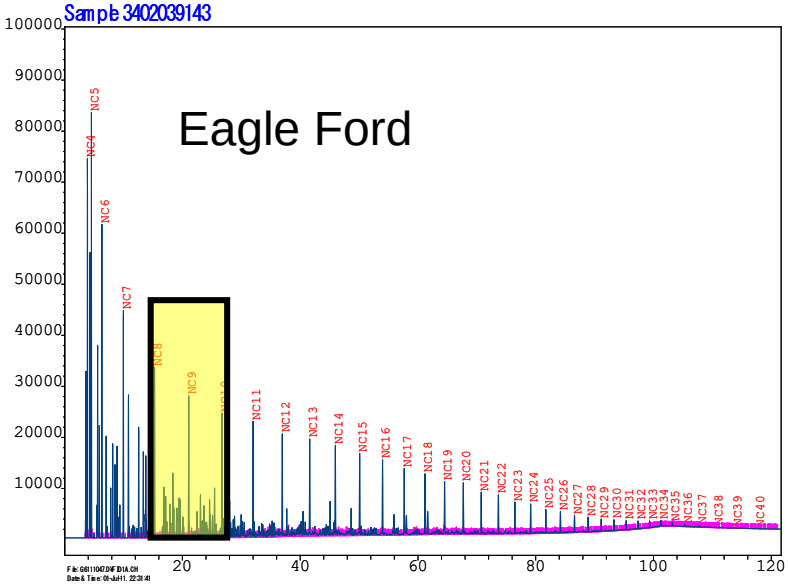
Quantifying Commingled Oil Production from Eagle Ford and Buda Reservoirs

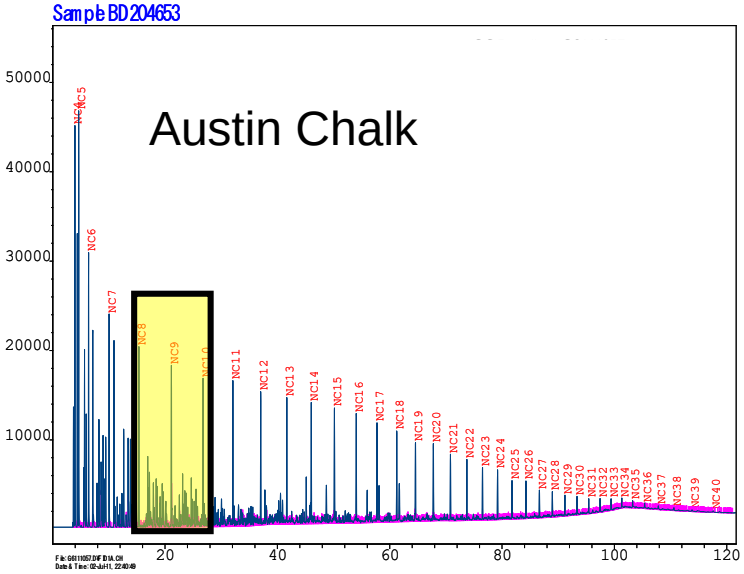


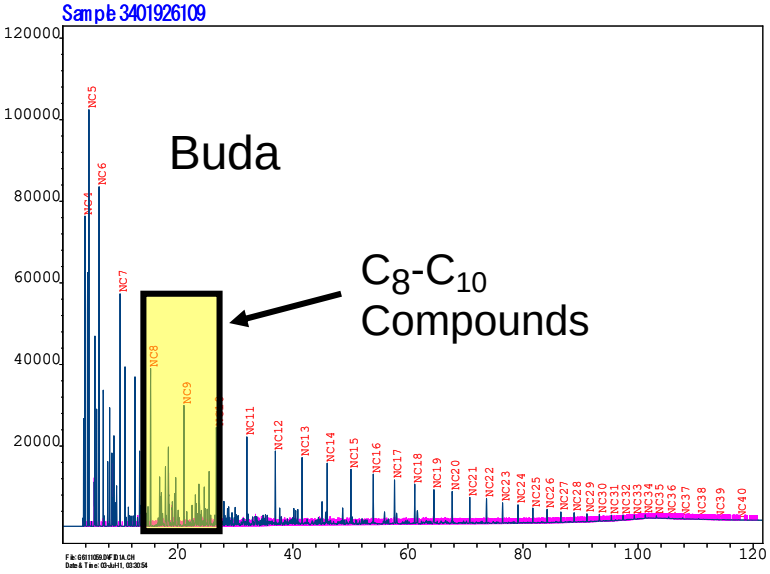
Modified from Baskin et al. (2013)

Quantifying Commingled Oil Production from Eagle Ford and Buda Reservoirs

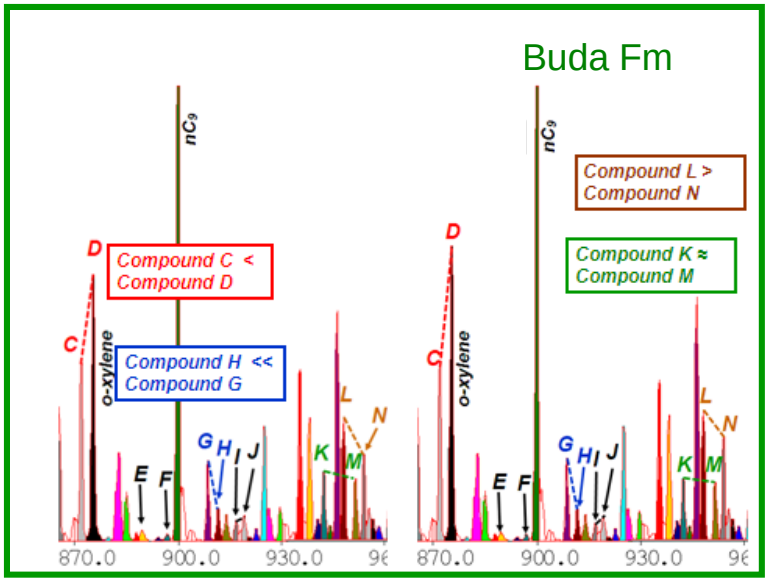
At this level of magnification, whole-oil gas chromatograms do not differentiate oils produced from the Eagle Ford or the Buda Formation. Austin Chalk oils are slightly different.

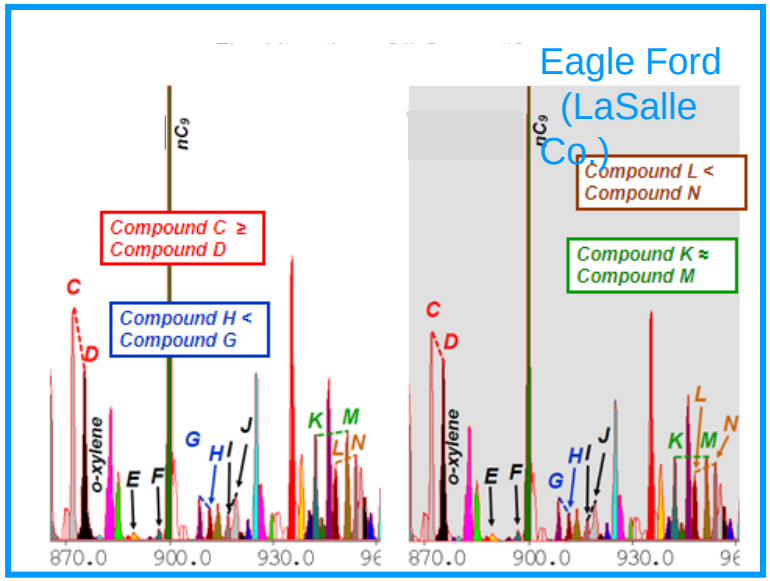


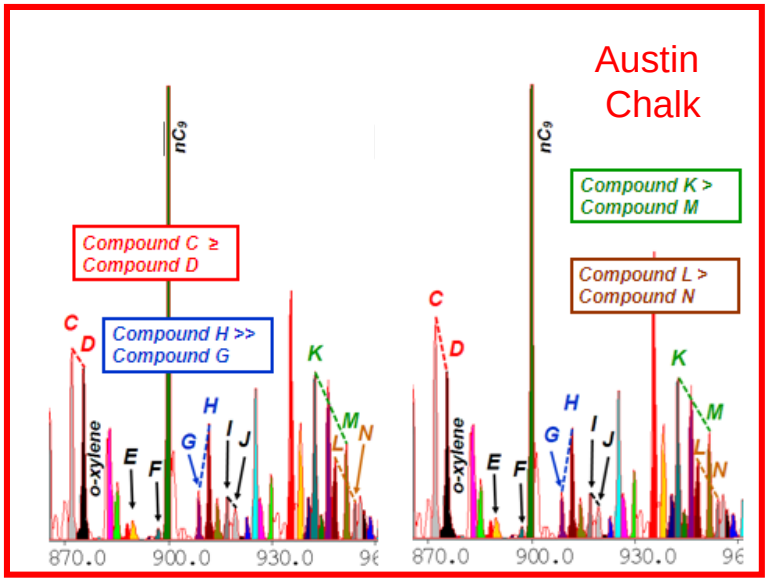


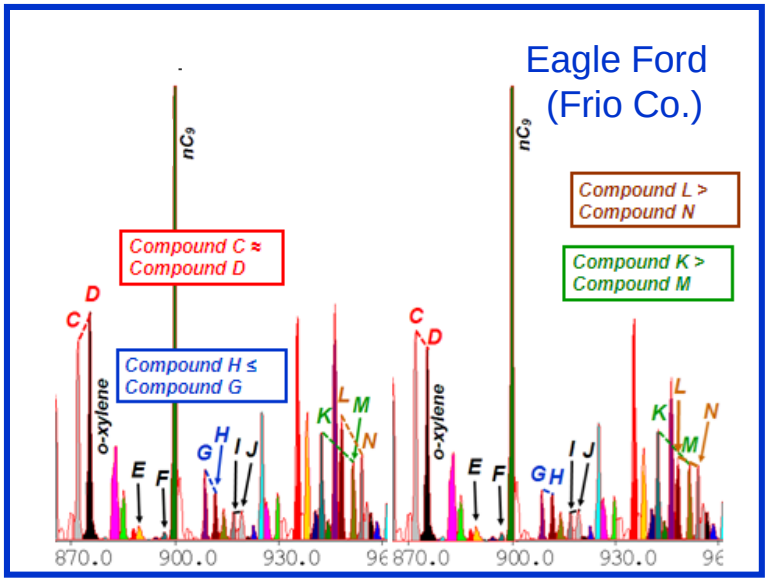


Fingerprinting Oils Produced from the Austin Chalk, Eagle Ford, and Buda Formation





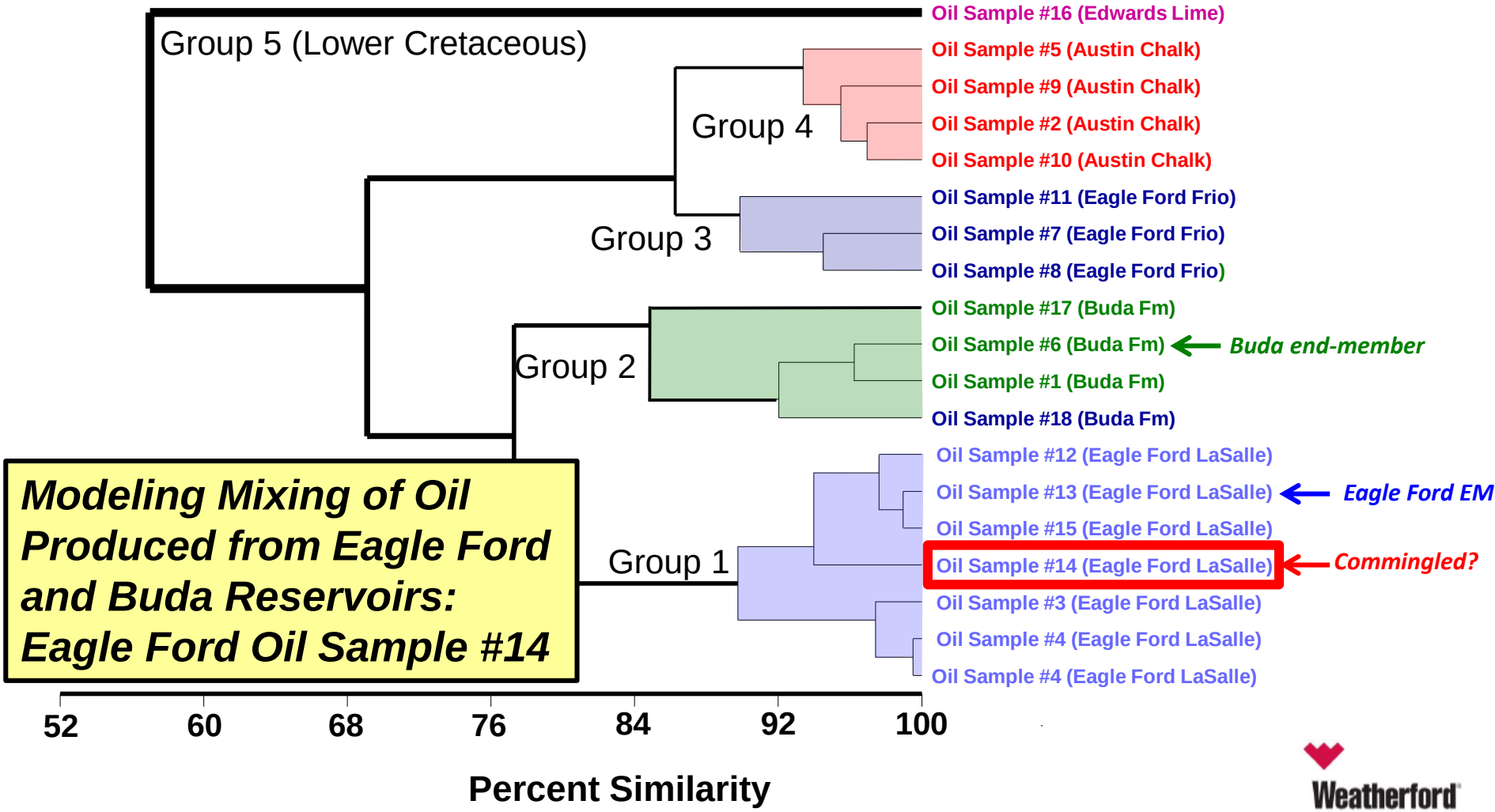




Modified from Baskin et al. (2013)

Quantifying Commingled Oil Production from Eagle Ford and Buda Reservoirs

Five Oil Groups Were Identified Using Hierarchical Clustering Analysis



Modeling Mixing of Oil Produced from Eagle Ford and Buda Reservoirs: Eagle Ford Oil Sample #14

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Quantifying Commingled Oil Production from Eagle Ford and Buda Reservoirs

Assuming Oil Sample #13 is an end-member oil in the Eagle Ford reservoir and Oil Sample #6 is an end-member oil in the Buda reservoir, Oil Sample #14 (produced from a well completed in the Eagle Ford) actually contains ~11.5% Buda oil.

Summary of Allocation Results

Commingled Well:	Oil Sample #14
Date of Collection of Commingled Oil:	5/15/2011
Commingled Oil GC File:	G6111046
Number Of Commingled Zones:	2
Names Of Commingled Zones:	Eagle Ford Buda
Number Of GC Peaks Used For Result:	231
Number Of GC Peaks Rejected:	0
Allowed Impact of Each Peak on Solution:	1.00 %
Number Of End Members:	2
Names Of End Members:	Oil Sample #13 (Eagle Ford) Oil Sample #6 (Buda)

ALLOCATION RESULT:

Values in Weight (wt.%)

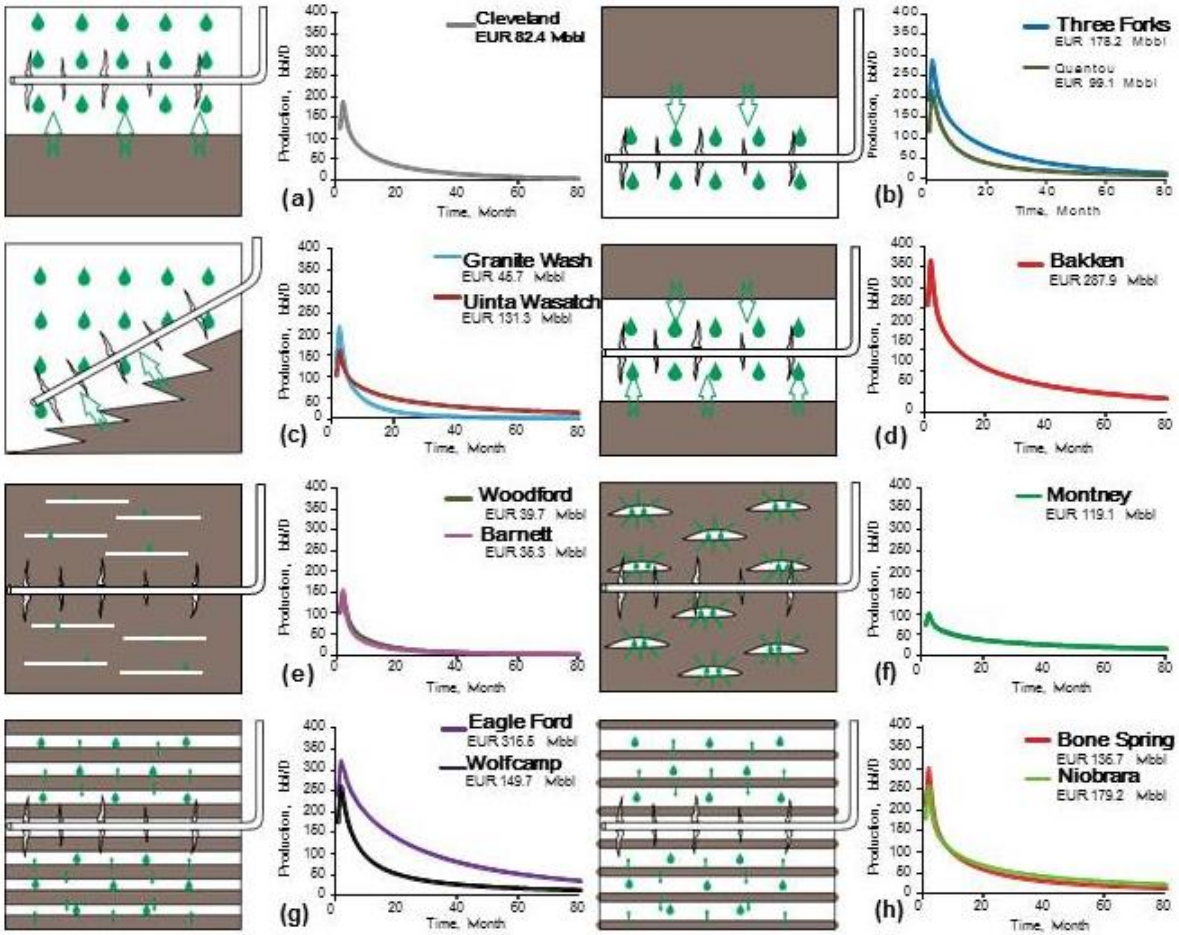
	Raw Result	Normalized	Confidence Level: (Error +/-) 80%	90%	95%	97.5%	99%
%Eagle Ford	0.8403	**88.48%**	**1.75%**	**2.24%**	**2.67%**	**3.17%**	**3.51%**
%Buda	0.1094	**11.52%**	**1.44%**	**1.85%**	**2.20%**	**2.61%**	**2.89%**
Totals	**0.9496**	100.00%					

Modified from Baskin et al. (2013)

Where are the Produced Fluids Coming from?

Zhang et al. 2016

- In depth discussion about where production comes from in tight oils sands world-wide.
- Based on source-reservoir relationships, they classified 8 types of plays.
- Also noted the highest mobility fluid will be produced from the largest pores in a well's Drained Rock Volume.



Can conclude from this publication that in heterogeneous reservoirs, it is difficult to predict where the oil is coming from, but production allocation helps, particularly Time-Lapse Allocation.

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Estimating Drained Rock Volume using Fingerprinting

Constraining Frac Height in Unconventional Plays

- Time series geochemistry (TLG) on produced fluids: Multiple samples from the same well over time can monitor the 'decay' of the fracture network → **PROVIDES pseudo-drained rock volume**
- Can be accomplished using produced oil end members from mature wells OR from core plug extracts

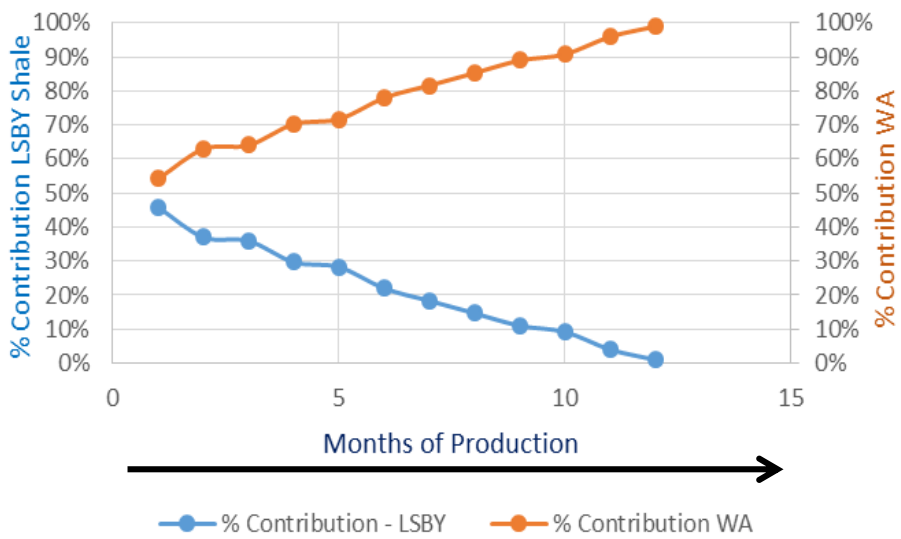
Two recent papers show extensive studies in the Eagle Ford & Bakken

URTeC: 2671245 Austin, TX 2017	**Optimizing field development strategy using time-lapse geochemistry and production allocation in Eagle Ford** Jason Jweda*, Eric Michael, Olufemi Jokanola†, Robert Hofer, and Victoria Parisi
URTeC: 2670186 Austin, TX 2017	**Time-lapse Geochemistry (TLG) Application in Unconventional Reservoir Development** Faye Liu*, Eric Michael, Kyrre Johansen, David Brown, Jeff Allwardt ConocoPhillips, 600 N. Dairy Ashford, Houston, TX

Slide Courtesy J. Adams

Example of Monitoring Fracture Healing Using Time-Lapse Geochemistry

- Need to collect and analyze multiple samples from the same well over time.
- Can monitor the 'decay' of the fracture network by allocating contribution from each zone over time.
- Can provide useful estimates of "drained rock volume" oved time.
- Requires end member oils come from discrete landing zones in mature wells.
- Assumes oil comes from the intended landing zonetime.



- Shortly after fracking in the WFMP A Target, allocation results showed frack heights extended into the overlying Lower Spraberry Shale
- Well initially contributed about equal amounts of Lower Spraberry Shale and WFMP A production.
- Additional allocations over time showed the rate of fracture healing.
- After about 12 months, fractures in overlying Lower Spraberry Shale completely healed and 100% of production from WFMP A.

Slide Courtesy J. Adams

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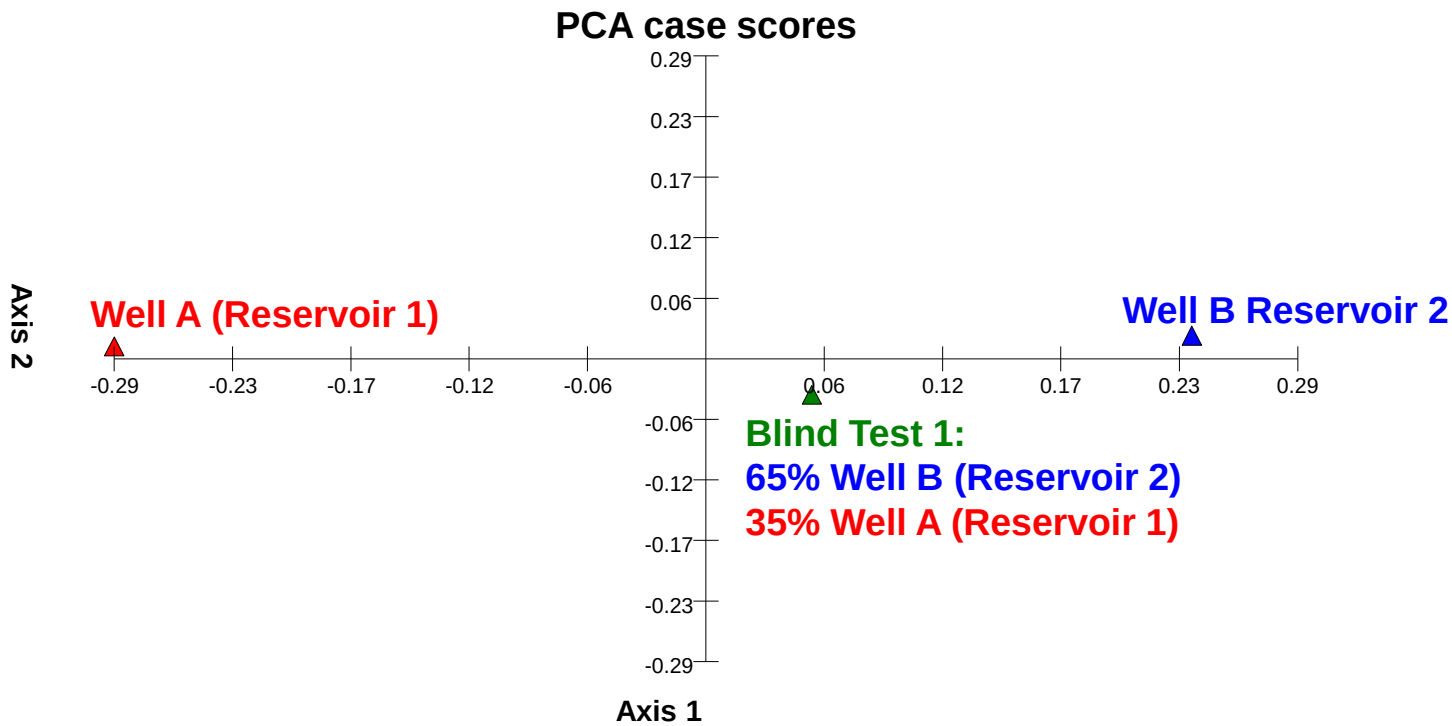
PCA plots can be useful in identifying end member oils for allocation calculations – particularly in large data sets.

(Kornacki et al. AAPG 2018)

PCA Plot of 2-Component **Blind Test** Allocation. **Results show almost all variability distributed quasi-linearly between end members in approximately proportion to calculated mixture.**

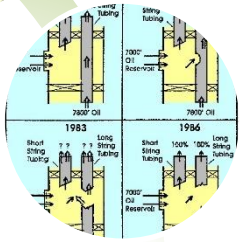


Commingled Production	Well	Reservoir	Allocation	Calculated %Uncertainty	Target Value	Actual % Lab Mix by wt.	% Difference Allocation vs. Lab Mixture
Blind Test 1	Wall B	Reservoir 2	65%	+/- 0.76	65%	64.98%	0.02%
	Well A	Reservoir 1	35%	+/- 0.80	35%	35.02%	-0.02%

Growing Applications of Reservoir Geochemistry Over Time

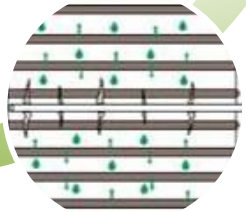
Late 1950-1960's development of GC-based "oil fingerprinting

'70's –Present
Assessment of Reservoir Continuity



'80's- Present
Diagnosing of Completion Problems, 2-zone Allocation

'90's-Present
2-7 zone Production Allocation,
Fluid Property Prediction



2000's- Present
Biodegradation Gradients/ Time Lapse Geochem/ Characterization of UR frac height/DRV