SOCIETY OF PETROPHYSICISTS AND WELL LOG ANALYSTS
SAUDI ARABIA CHAPTER

SPWLA SAUDI ARABIA CHAPTER (SAC)
9th Topical Workshop

CORING AND CORE ANALYSIS: CHALLENGES AND BEST PRACTICES

Virtual Workshop Series (Feb, Mar & Apr 2021)

Reservoir fluid Geochemistry Analysis and Data Interpretation

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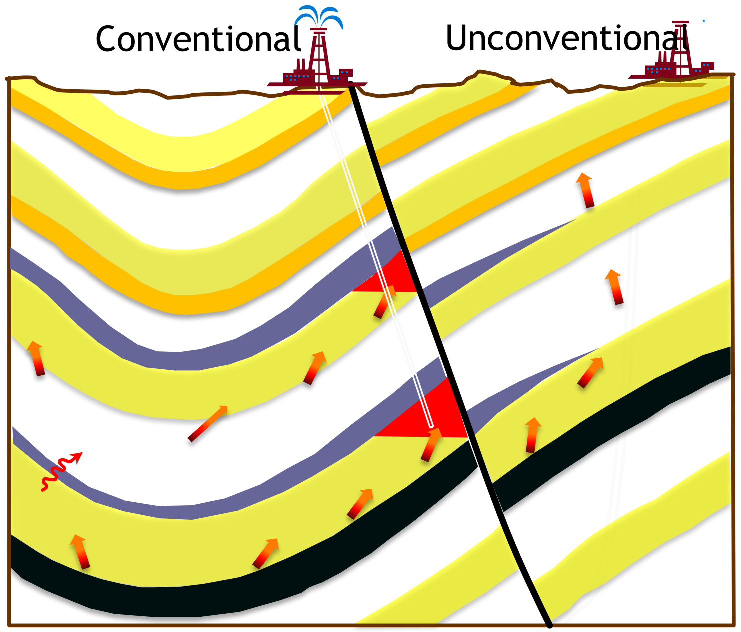
March 10, 2021

Schlumberger

Why Do Operators Need Petroleum Geochemistry?

- Origin of hydrocarbons
- Generation and migration
- In-reservoir processes
  - Biodegradation
  - Gas and water washing
  - Evaporative loss
  - Thermochemical sulfate reduction (TSR)
  - Oil-to-gas cracking (OTGC)
- Present-day hydrocarbons distribution in the field
  - Gradients and compartments
  - To understand controls on fluids properties distribution in reservoirs



Exploration

Core | Cuttings | Isotubes
Wellhead | STO | Oil shows

- Source Rock Characterization /Petroleum System
- Oil-Source Rock & Oil-Oil Correlation
- Petroleum Migration / Charge History
- Oil Biodegradation Risk Assessment
- Seal Integrity Assessment / Contacts

Appraisal

BHS | Separator | Wellhead
Core | STO

- Reservoir Continuity/Gradients
- Control on physical properties
- Characterization of tar mats
- In-reservoir Alteration:
  Oil Biodegrading
  TSR
  Thermal alteration

Production

BHS | Separator | Wellhead
Core | STO

- Reservoir Conectivity
- Production Allocation
- Time-lapse Studies (monitoring)
- Forensic Studies (e.g. leaks)

Sampling and Analytical Methods

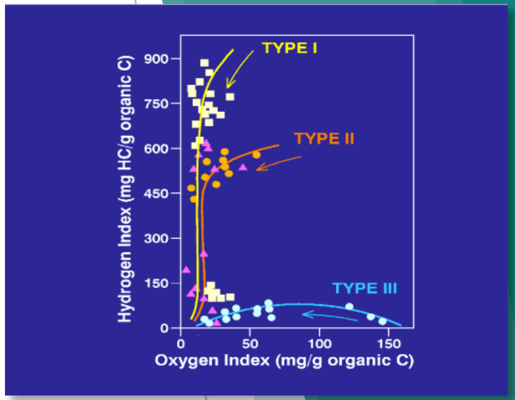
- **Samples:** surface and downhole samples, produced gases, oils and waters, core/cuttings (extracts) – small samples (a few grams)





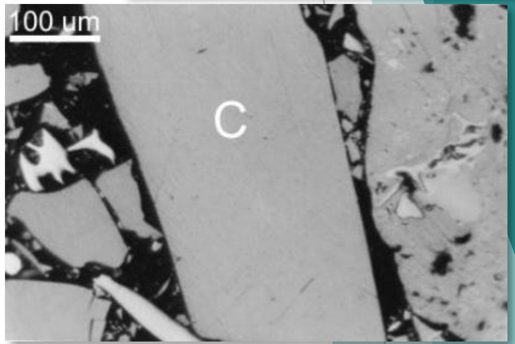
- **Analytical Techniques:** Rock pyrolysis, Fingerprinting by gas chromatography, gas chromatography coupled to other tools, Isotopic composition, bulk properties


Exploration (& Unconventionals)- Source Rock Geochemistry



- **Rock Eval Pyrolysis, TOC –** screening techniques of large number of samples; preliminary est. of maturity, generating potential of source rocks

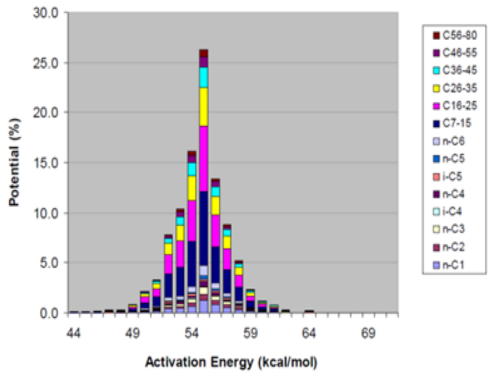
- **Organic petrography, pyrolysis-GC (GC/MS), micro-FTIR –** kerogen typing and its chemistry, maturity



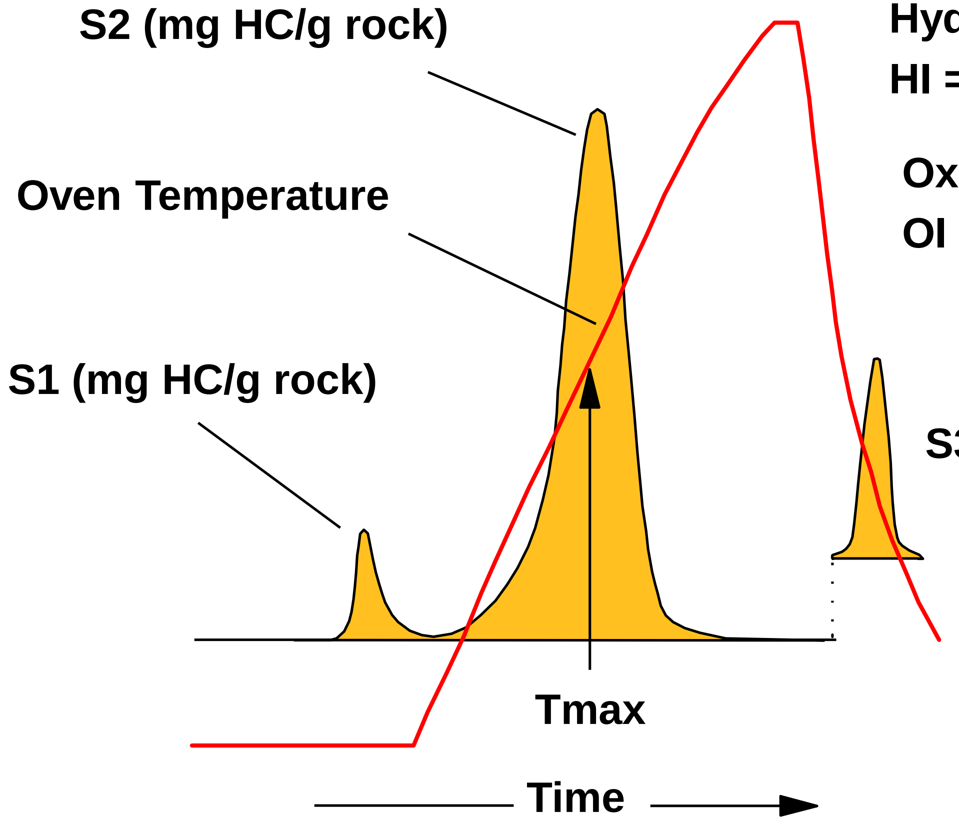
- **Biomarkers on solvent extracts from source rocks** (e.g., GC/MS) – in depth information about origin, sedimentary facies, maturity

- **Kerogen separation** in combination with above – density and detailed description of individual macerals

- **Kerogen kinetics** – fundamental for basin modeling



Rock-Eval Basics and Important Parameters



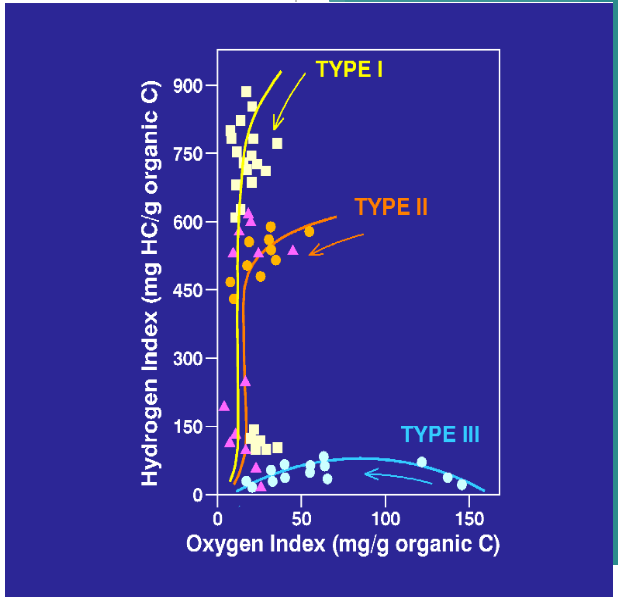
Hydrogen Index

HI = $(S_2 /TOC) \times 100$

Oxygen Index

OI = $(S_3 /TOC) \times 100$

Biomarker Guide, p. 77



Vinci Technologies

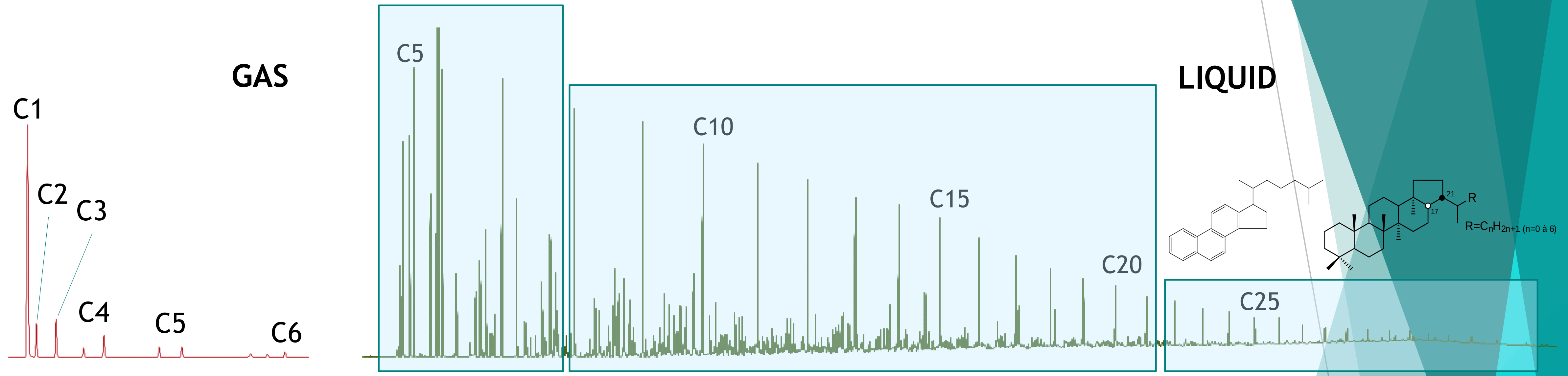
Source Rock Evaluation Criteria

Quality	TOC (%)	Rock Eval S2 (mg HC/g rock)	EOM Wt %	HC (ppm)
None	< 0.5	< 2	< 0.05	< 200
Poor	0.5 -1	2 - 3	0.05 - 0.1	200-500
Fair	1-2	3 - 5	0.1-0.2	500-800
Good	2-5	5 - 10	> 0.2	> 1200
Very Good	> 5	> 10	-	-

Product Type	Hydrogen Index
Gas	50- 200
Gas & Oil	200 - 300
Oil	> 300

Stage	Tmax
Onset Oil	
Type I #	445 °C
Type II	~ 435 °C
Type III	~ 440 °C
Onset Gas	~ 460 °C

Rock Extracts and Fluid Samples: Fluids History from Charge to Present (Exploration-Production-Appraisal)



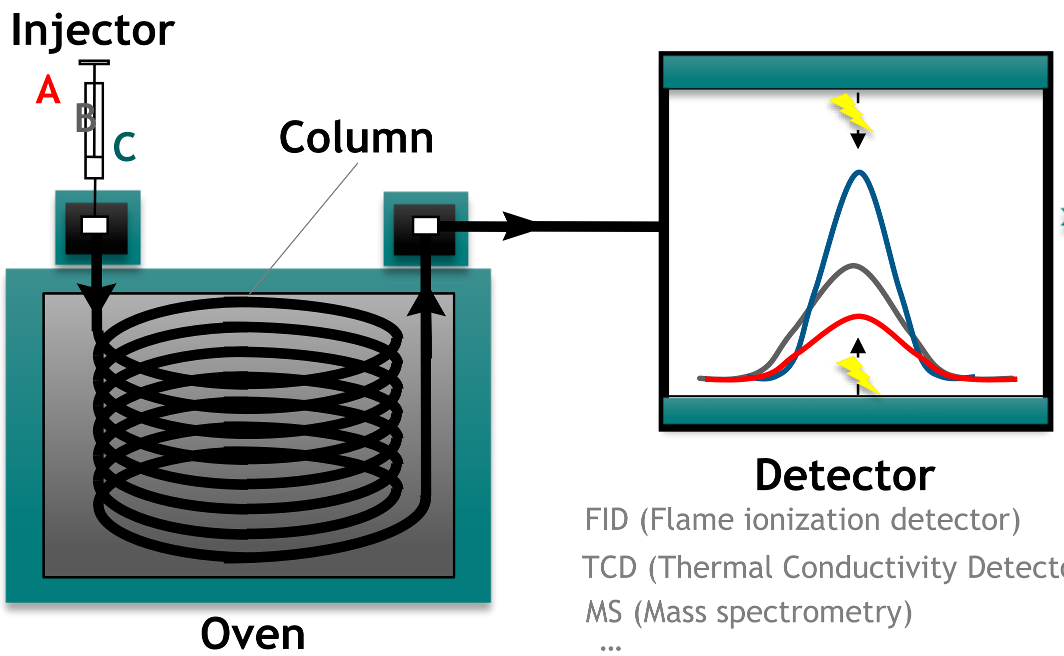
- Gas and light liquid (C7) fractions
- C1-5 C and H isotopes ($\delta^{13}C$ & δD)
- $\delta^{13}C$, $\delta^{18}O$ for CO_2, $\delta^{34}S$ H_2S, $\delta^{15}N$ N_2
- Compositions and CSIA
- Diagnostic of source and in-reservoir transformations

- Mid range fraction (geochemical fingerprinting)
  - C8-20 HRGC reservoir continuity
  - Pr/Ph, Pr/n-C17, aromatics, diamandoids
  - CSIA
- Captures minute compositional differences between fluids

- C_{20+} fraction
  - Biomarkers (age, origin, maturity, redox, lithology, correlations)
- Limited application in mature fluids

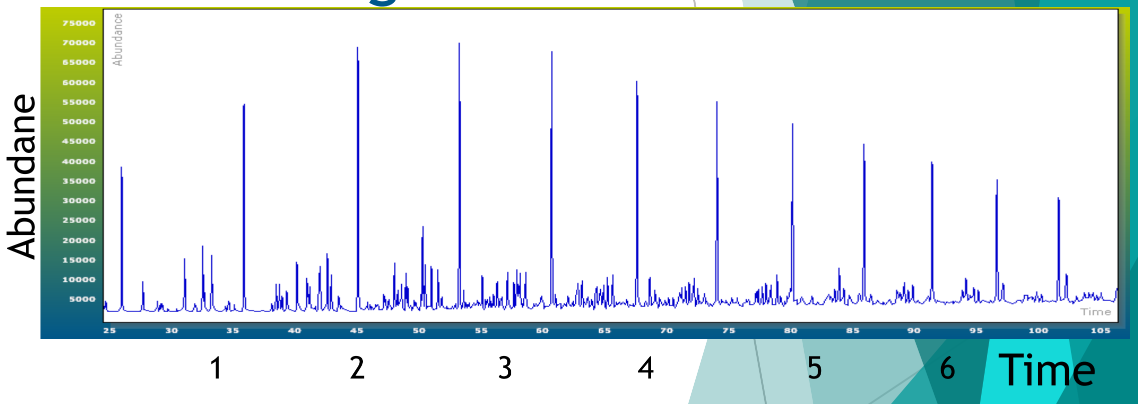
Principle of Gas Chromatography

Gas chromatography



FID (Flame ionization detector)
TCD (Thermal Conductivity Detector)
MS (Mass spectrometry)
...

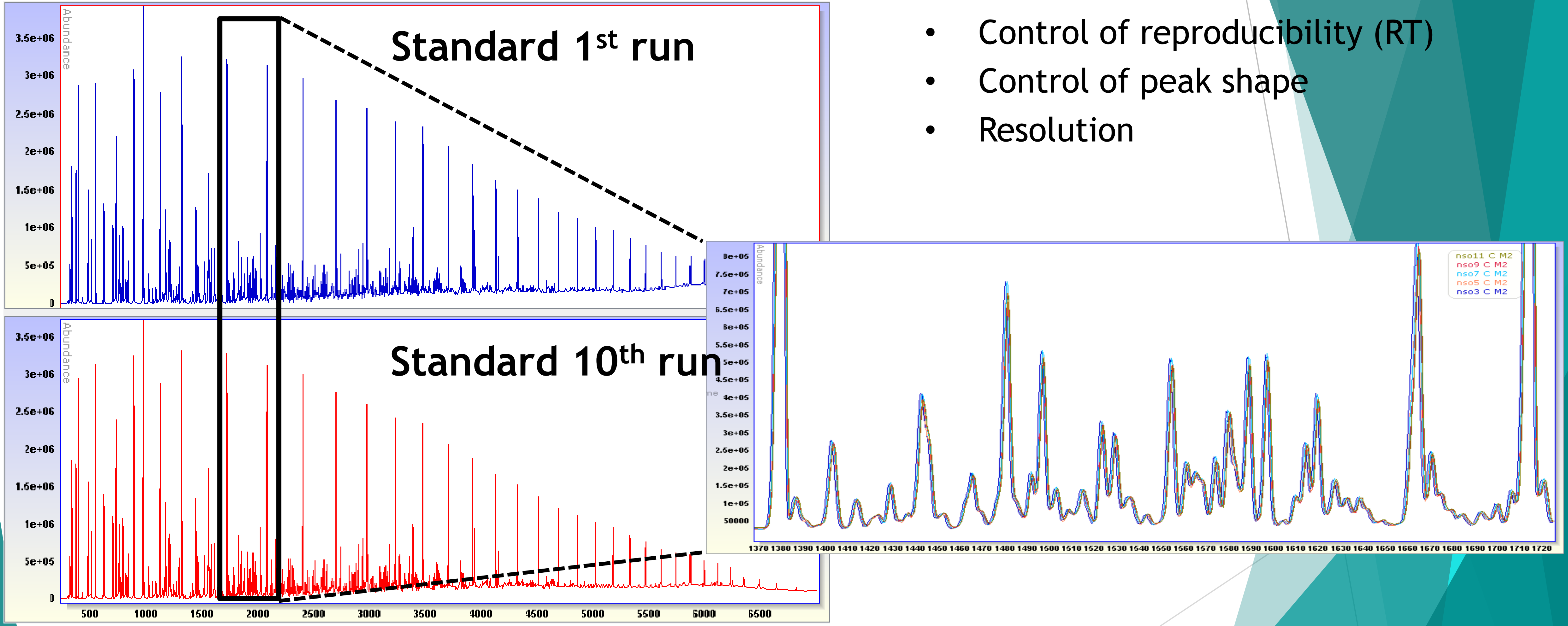
Chromatogram:



Separation based on:

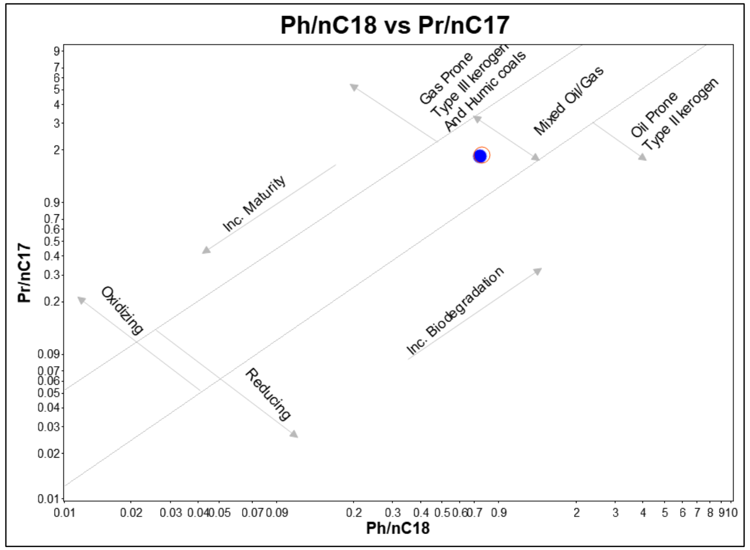
- Molecular weight
- Polarity

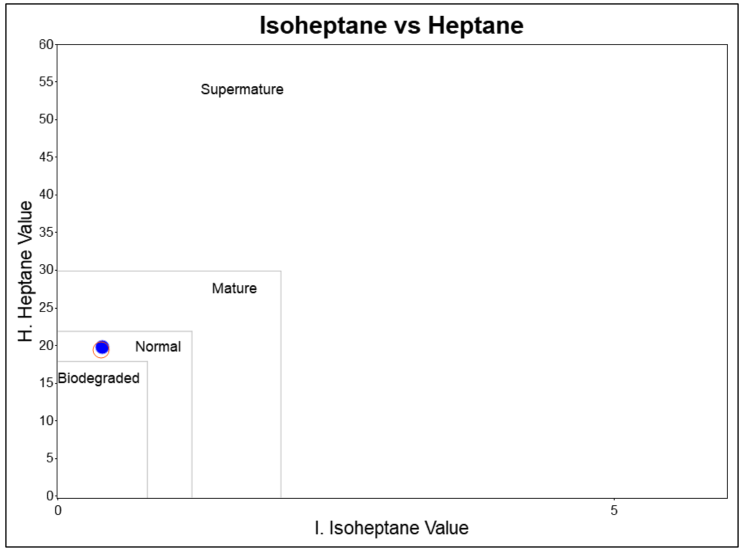
High Resolution GC – Geochemical Fingerprinting

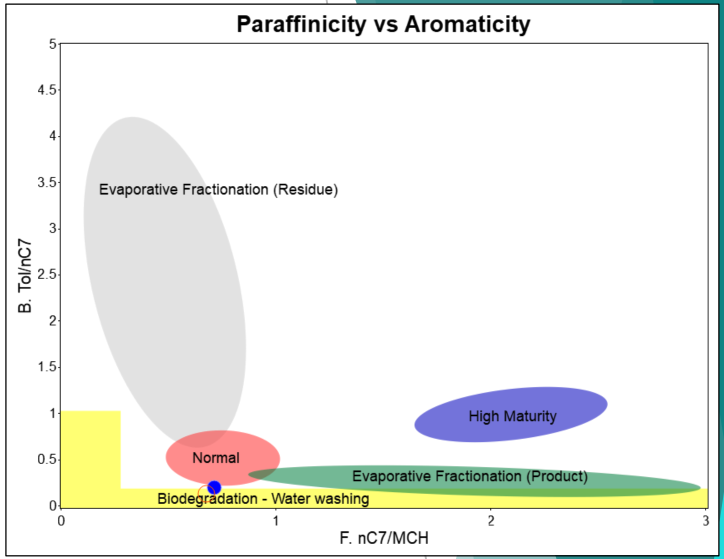


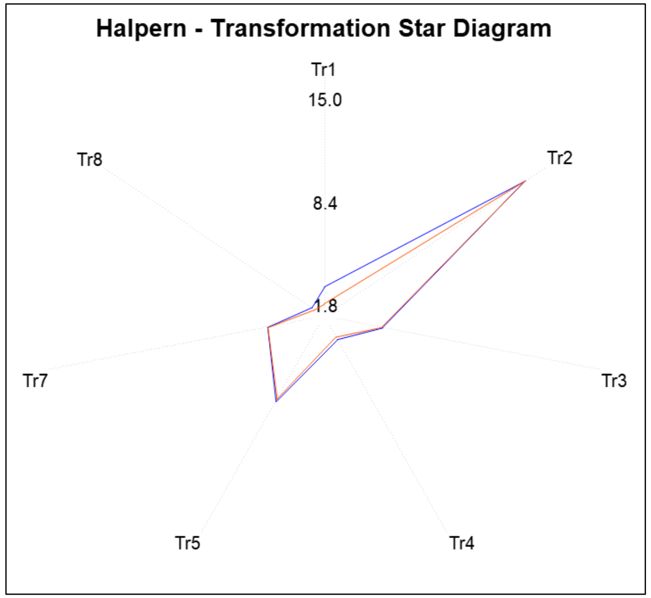
- Control of reproducibility (RT)
- Control of peak shape
- Resolution

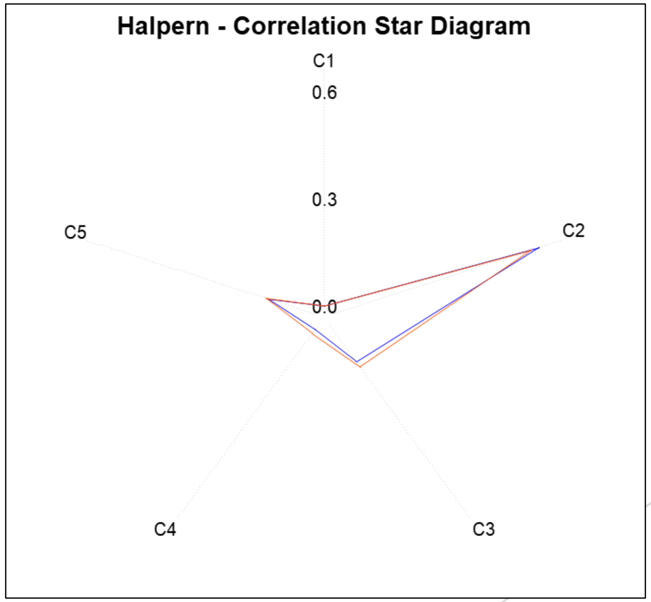
Gas Chromatography Fingerprints – Geochemical Screening



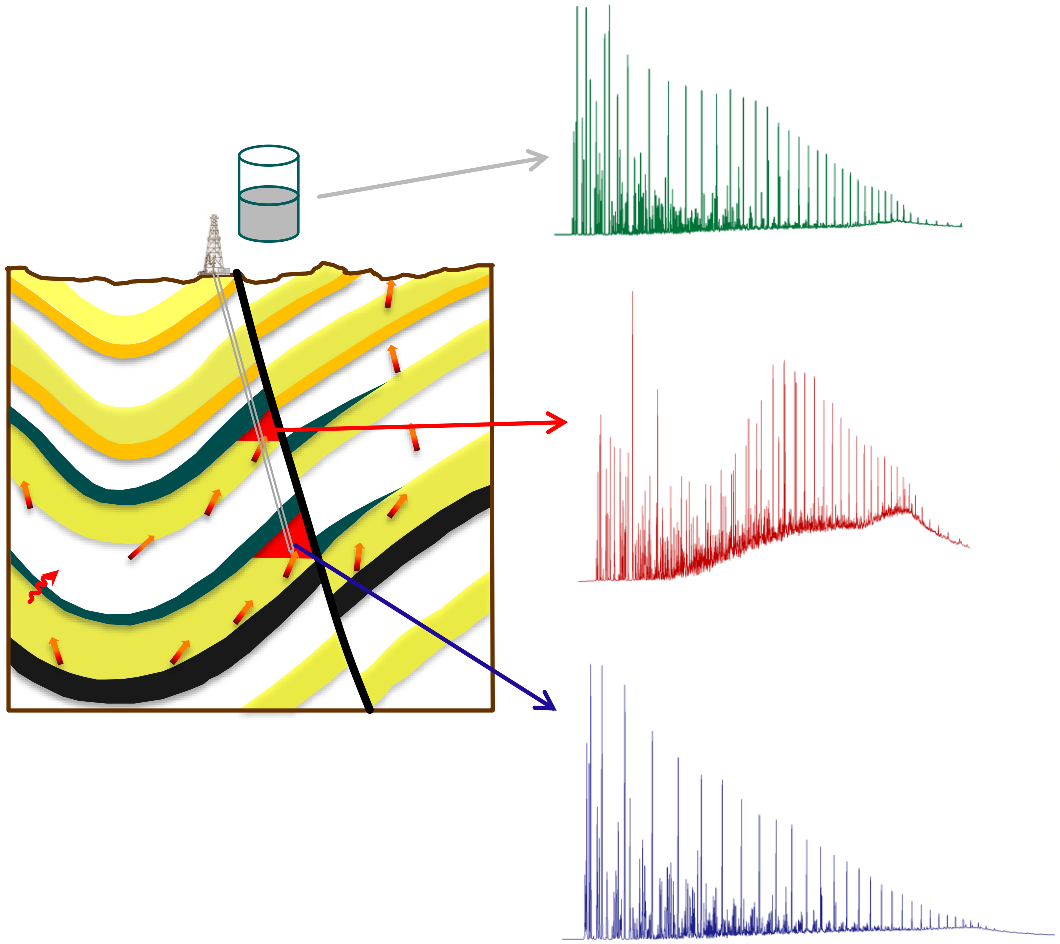


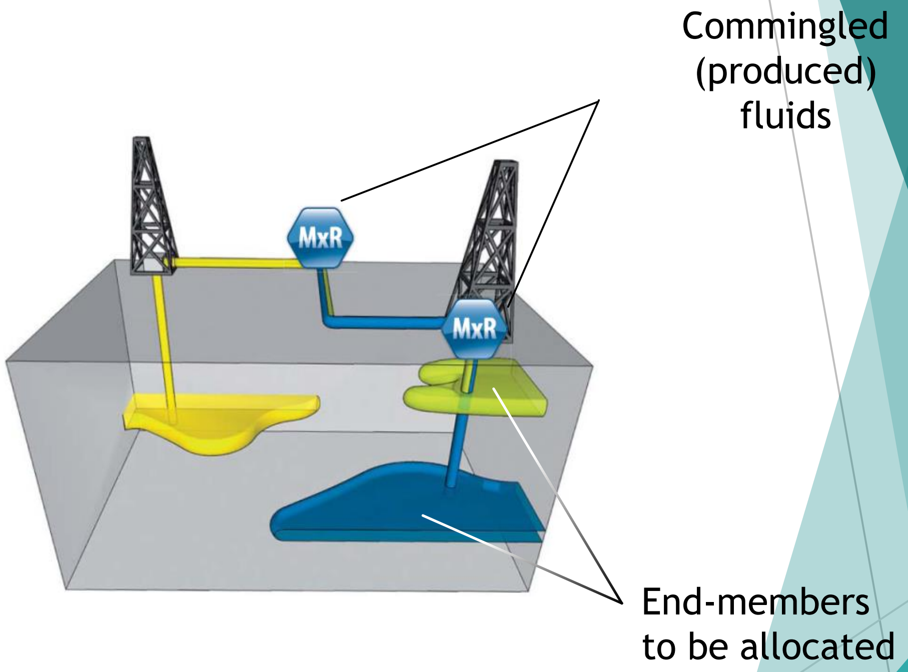






Reservoir continuity and Production Allocation using geochemical fingerprinting

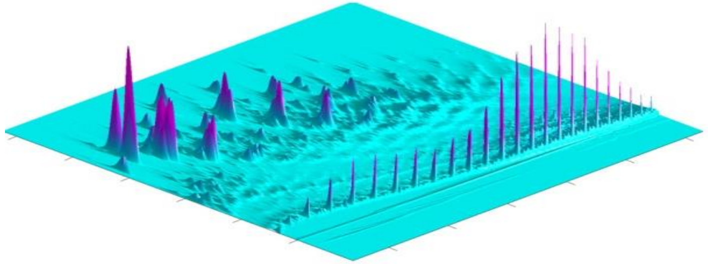




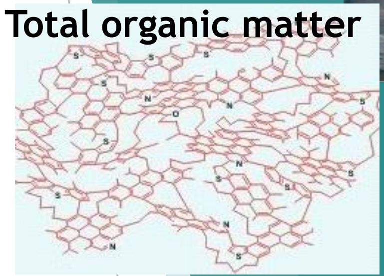
Gas Chromatography – Coupled to Other Tools

More in-depth investigation

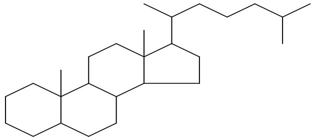
- GC with a Mass Spectrometer gives detailed molecular composition (GC/MS and GC/MSMS) - identification of major biomarker families and of specific compounds
- GC combined with a second gas chromatograph and valve system (e.g., GCxGC)
- GC with an Isotope Ratio Mass Spectrometer (GC-IRMS) gives the 13C/12C ratio for each individual compound – Isotopes Analysis



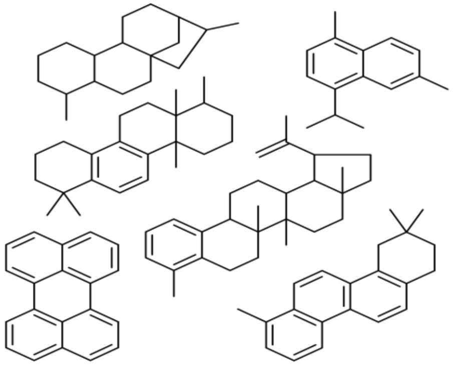
Molecular Composition - Biomarkers

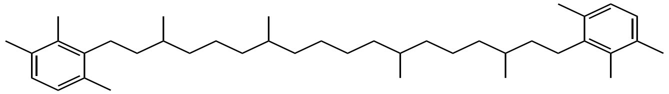


- Biomarkers: molecular fossils, markers for organic matter burial, migration, and subsequent in-reservoir processes



  - Source rock characterization
  - Correlation studies
  - Organic matter thermal history
  - Biodegradation





The quest for securing reliable data :- Separation of Hydrocarbons Fractions Rapid and Reproducible Quantification of Hydrocarbon Compounds

SPE - pre-treatment (THC)

C18 non end - capped SPE

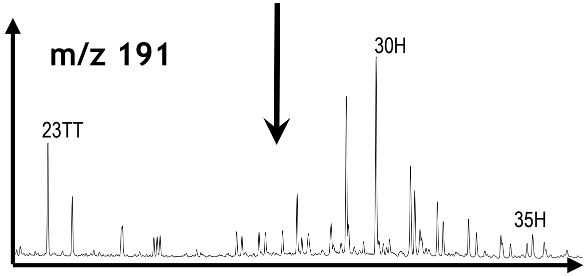
Hydrocarbons (HCs)

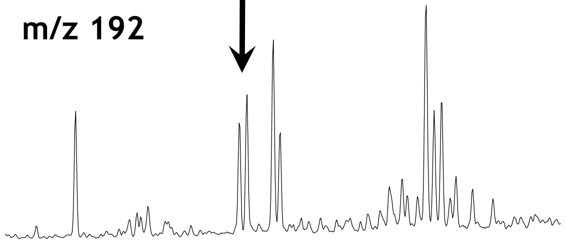
Polar Non-hydrocarbons

Micro pipette separation

Saturated Hydrocarbons

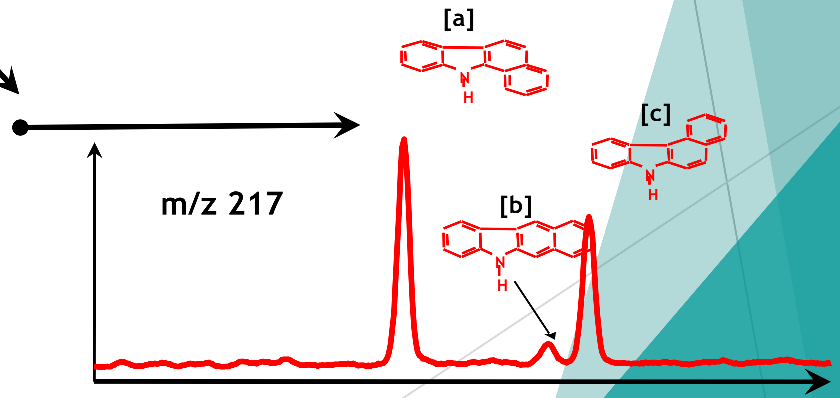
S + Aromatic Hydrocarbons



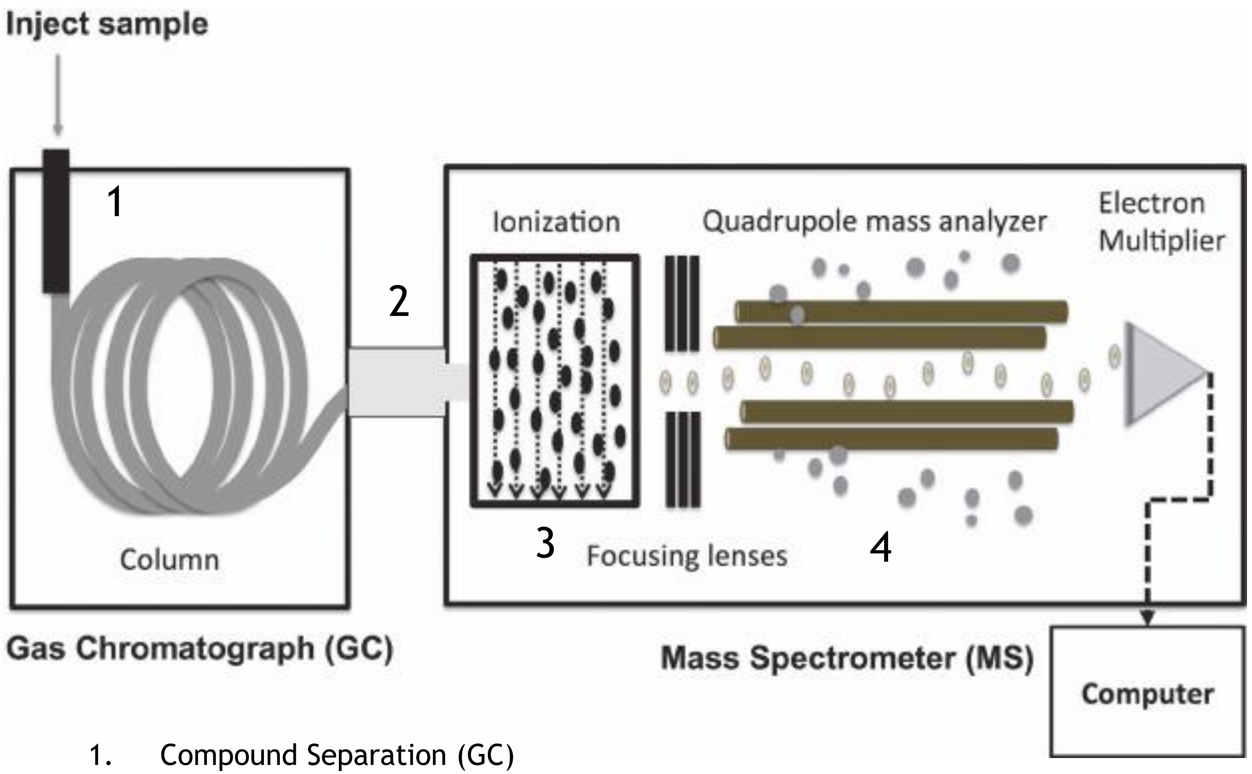


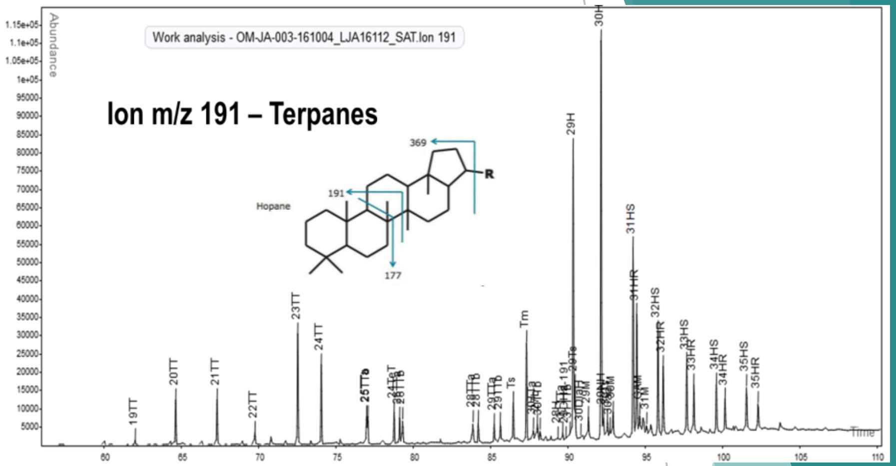
- ✓ Preservation of light ends is Key!
- ✓ Low sample volume
- ✓ Low solvent volume – Reduced environmental impact
- ✓ Rapid processing
- ✓ High Reproducibility

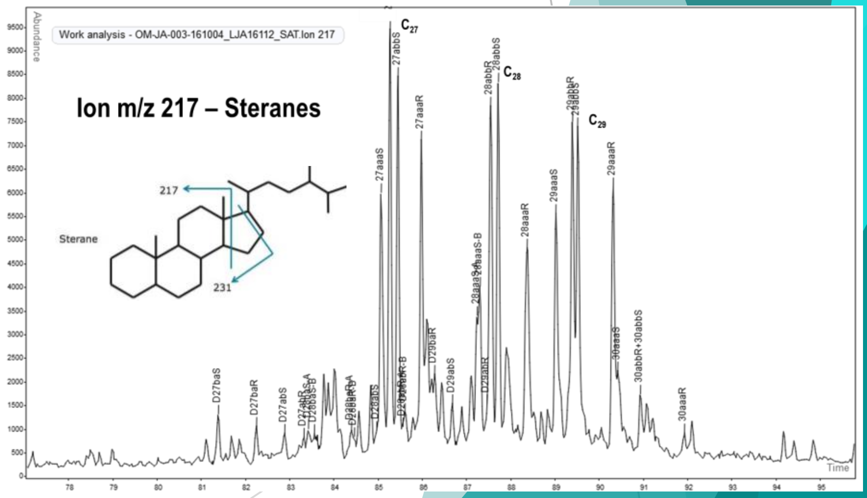
e.g. Benzocarbazoles



Gas Chromatography – Mass Spectrometry







1. Compound Separation (GC)
2. Transfer of separated compounds to ionization chamber
3. Ionization and acceleration of compounds
4. Mass analysis of the ions (m/z)
5. Detection of focus ions by electron multiplier
6. Acquisition, processing

Molecular concentration data

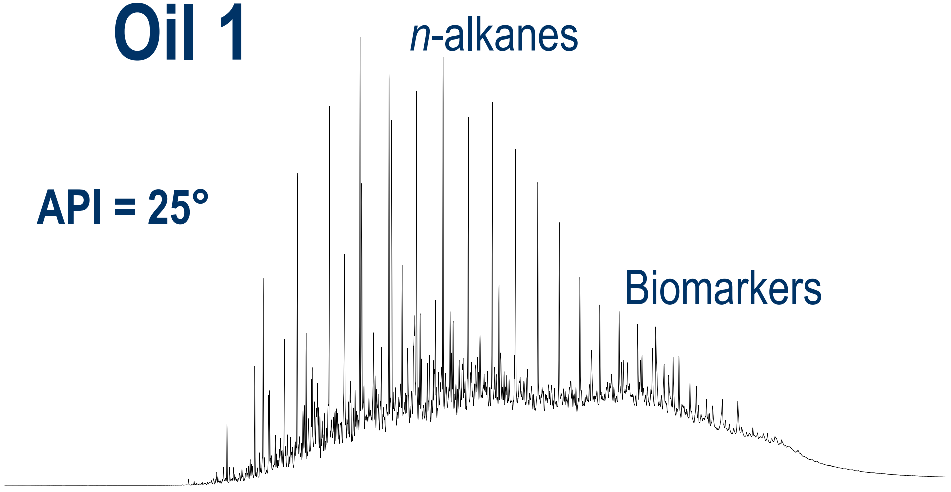
Sample	N	2MN	26,27DMN	DBT	4MDBT	1MDBT	P	3MP	2MP	9MP	1MP
4660-1	19.95	136.7	223.73	52.79	88.20	51.13	83.71	54.77	61.16	95.89	57.65
4660-2	20.16	137.78	225.14	53.86	90.47	52.62	85.14	55.52	62.10	97.48	58.39
4660-3	19.84	137.10	223.66	53.06	88.61	51.43	83.61	55.00	59.70	94.94	57.97
4660-4	19.92	136.10	222.38	52.96	88.56	50.66	82.73	54.84	61.50	94.76	57.93
4660-5	20.36	139.84	229.49	54.49	91.35	53.15	84.38	56.66	63.33	99.25	59.35
4660-6	19.94	136.93	222.51	53.01	88.87	51.89	83.52	55.12	61.14	95.54	57.77
Max	20.36	139.84	229.49	54.49	91.35	53.15	85.14	56.66	63.33	99.25	59.35
Min	19.84	136.10	222.38	52.79	88.20	50.66	82.73	54.77	59.70	94.76	57.65
STD Dev	0.19	1.30	2.65	0.67	1.26	0.94	0.82	0.71	1.20	1.74	0.63
Average	20.03	137.42	224.49	53.36	89.34	51.81	83.85	55.32	61.49	96.31	58.18
% std dev	**0.97**	**0.95**	**1.18**	**1.25**	**1.41**	**1.81**	**0.98**	**1.28**	**1.95**	**1.80**	**1.08**

- ✓ Geochemical data validated reduced % error using standards and
- ✓ Absolute concentrations of a robust number of oil components is a must

Sample Quality and Preservation!

Oil 1

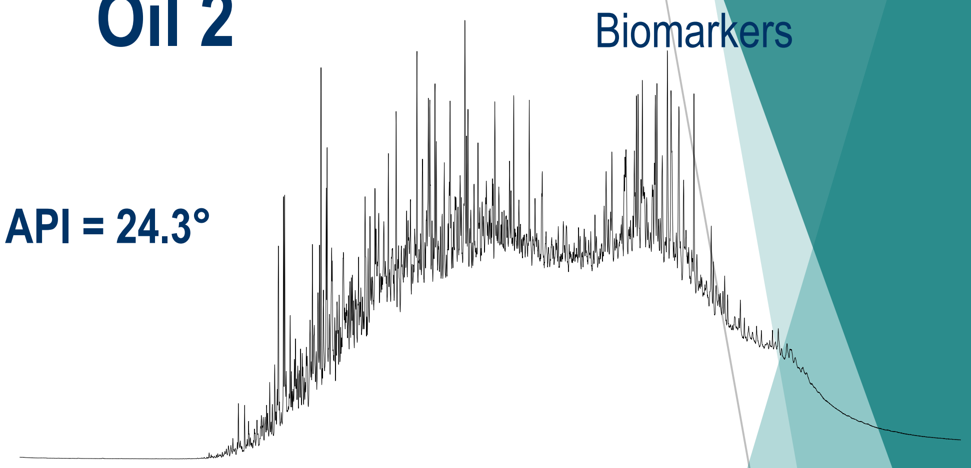
API = 25°



Light biodegradation: *n*-alkanes present

Oil 2

API = 24.3°



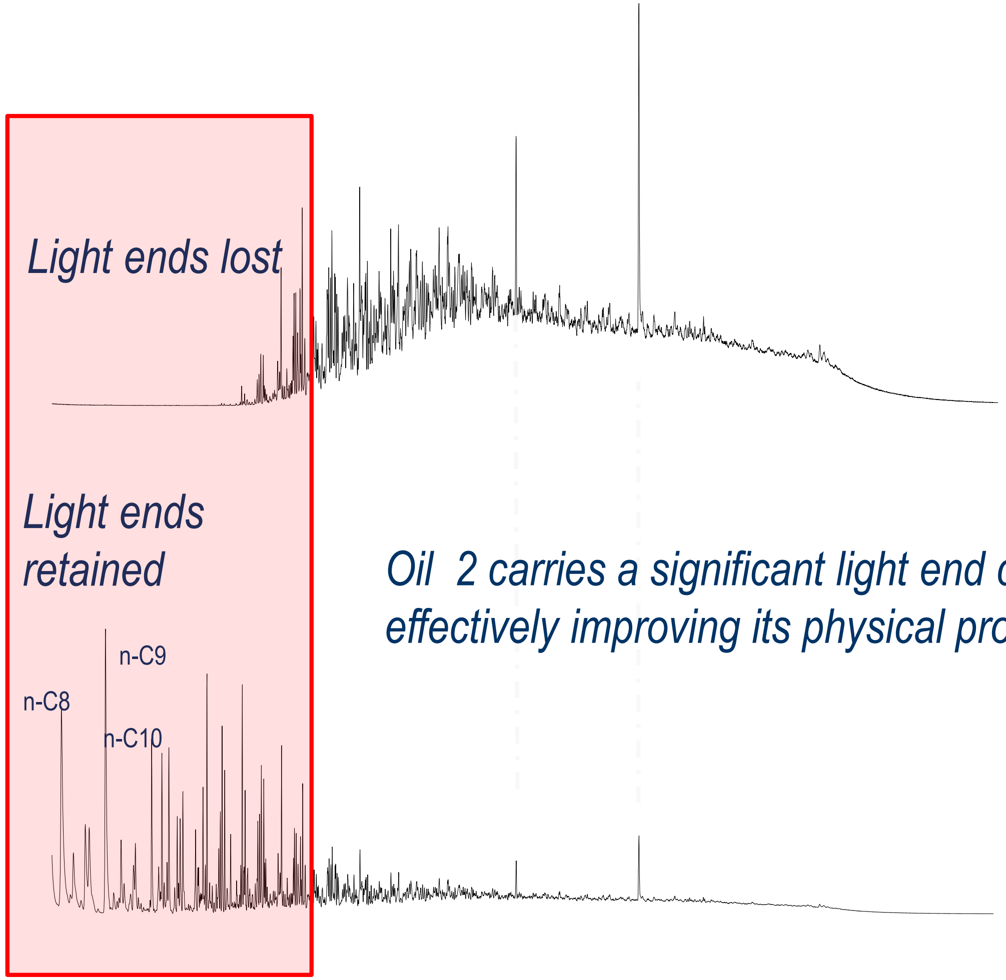
Moderate to heavy biodegradation -*n*-alkanes removed

Sample 2 is evidently more biodegraded than 1. Using GCMS TIC fingerprints, it is difficult to explain why the 2 oils have similar API gravities

Traditional methods (i.e. topping) used for separating hydrocarbon fractions from heavy oil in preparation for GC analysis resulted in the loss of light ends

Better quality sample and preservation reveals the presence of light ends

Oil 2 – *n*-alkane fingerprints (m/z 85)



Oil 2 carries a significant light end contribution effectively improving its physical property

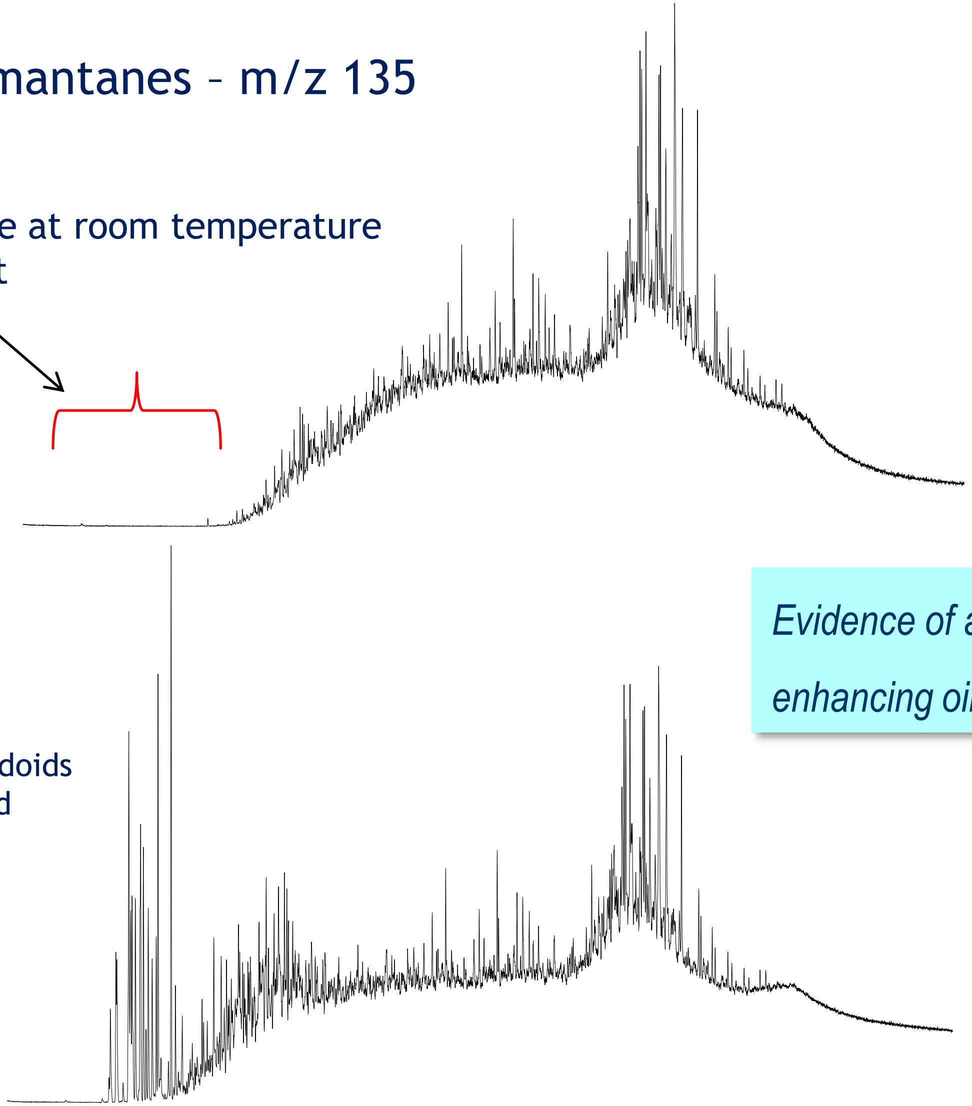
Preservation of volatile front ends (light ends) is critical

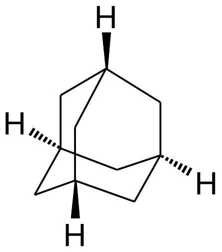
- ✓ Note that traditional methodologies, e.g. topping or Buchi evaporation or Nitrogen blowdown, promotes evaporation of light ends
- ✓ Sampling conditions may also cause volatiles lost
- ✓ Improper long-term storage can also impact composition of light fraction

Diamondoids

Methyladamantanes – m/z 135

Diamondoids sublime at room temperature
– they are easily lost



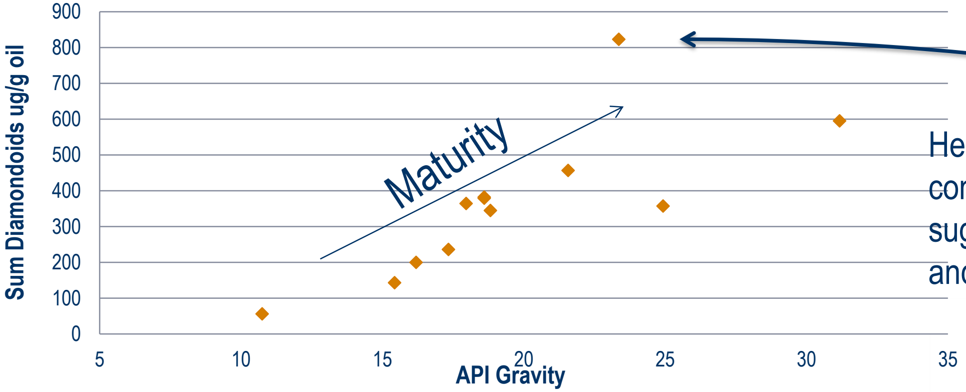


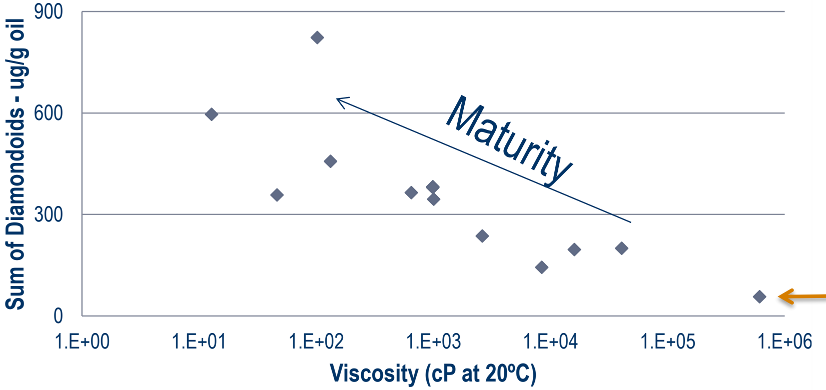
Diamondoids
retained

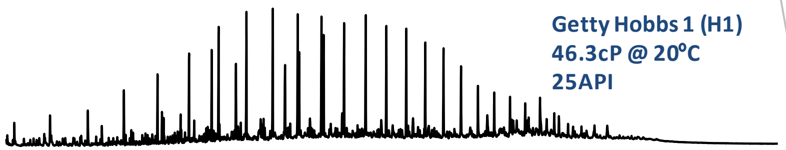
Evidence of a high-maturity late charge (stored in light ends) enhancing oil quality

Impact of oil mixing – Fresh oil charge

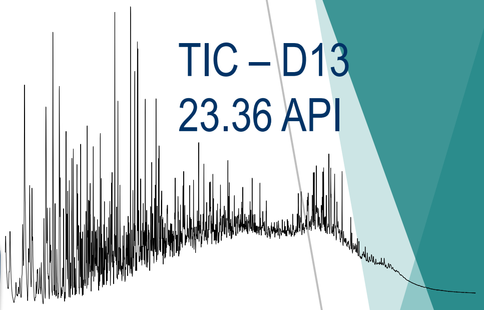
Orcutt: Diamondoids





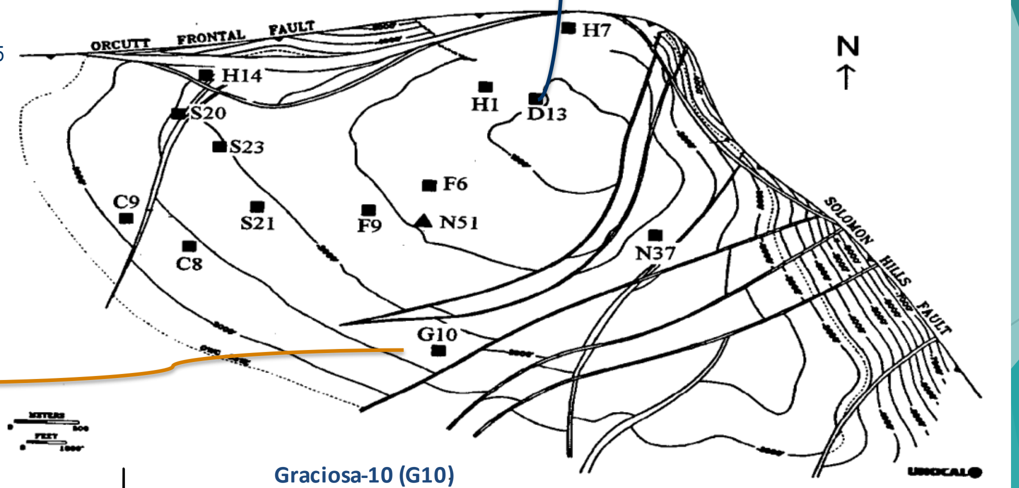


Getty Hobbs 1 (H1)
46.3cP @ 20°C
25API



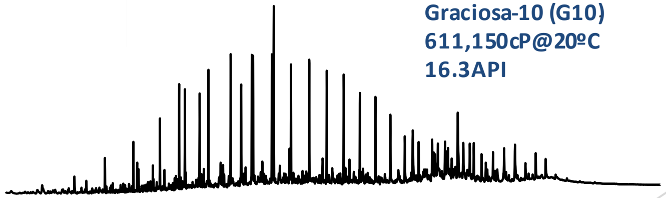
TIC – D13
23.36 API

Heavily biodegraded D13 appears to contain a light charge component suggested by diamondoids, n-alkanes and AMCH



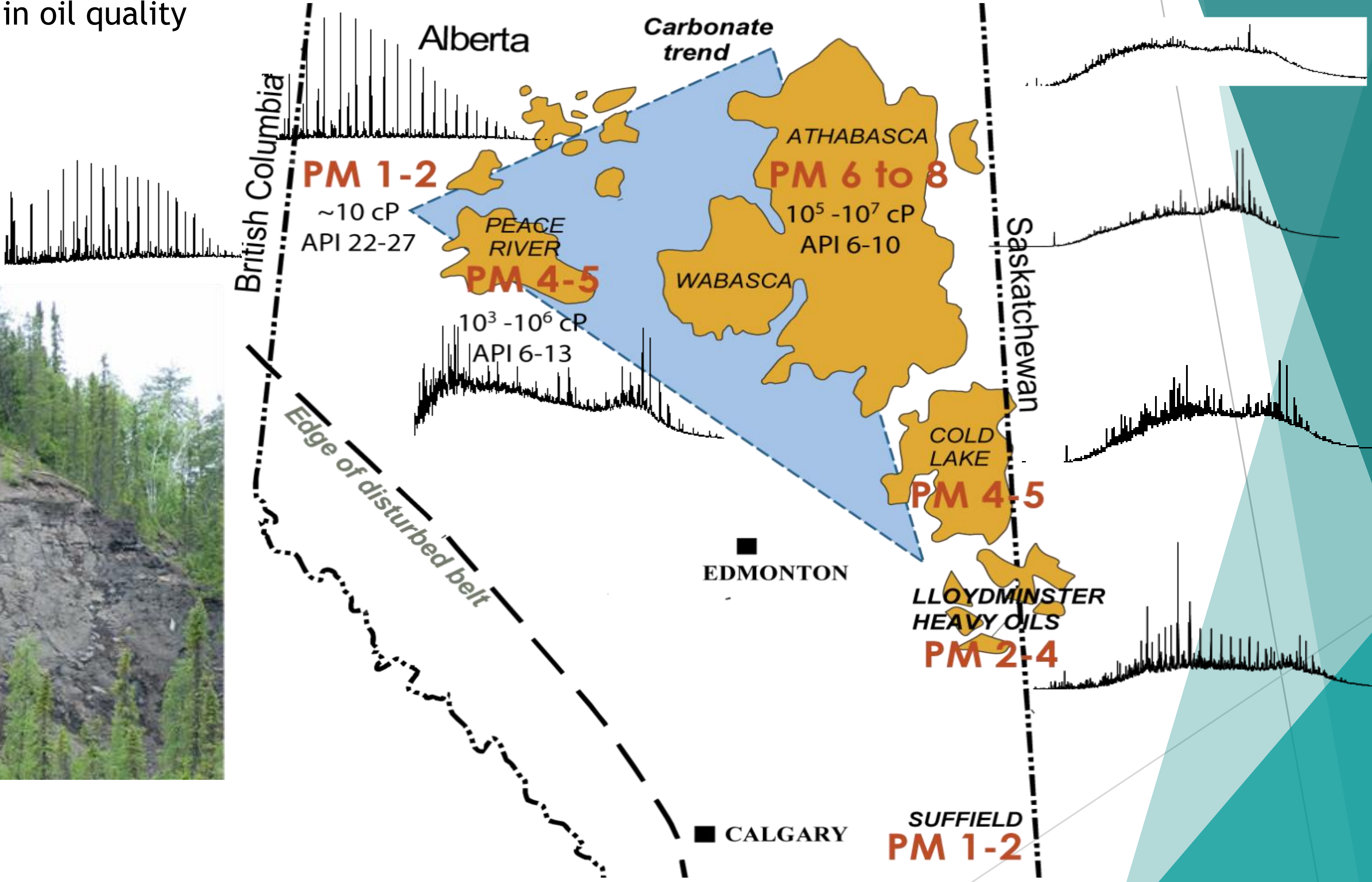
California division of Oil and Gas, 1974

Graciosa-10 (G10)
611,150cP@20ºC
16.3API



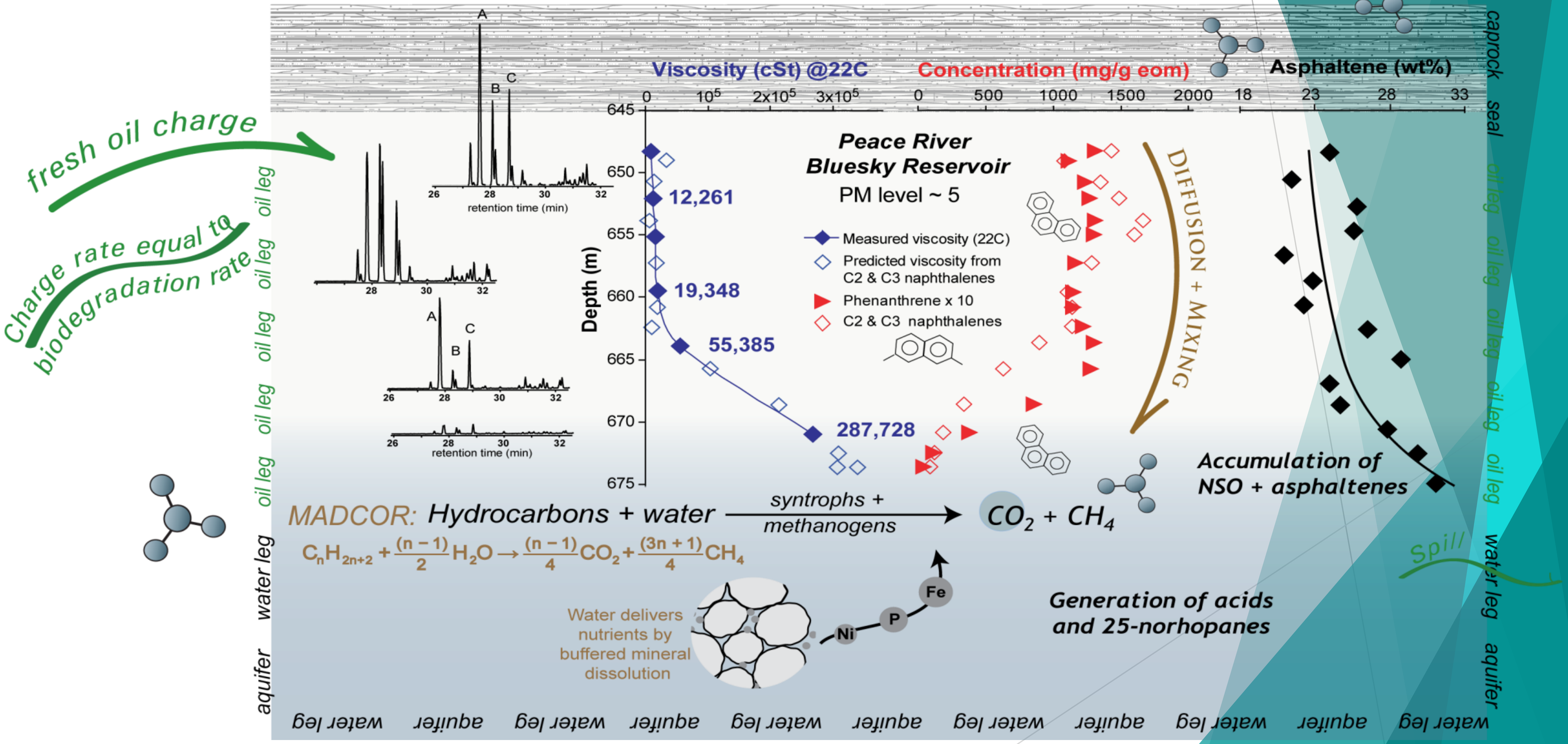
Identification of Regional Variations

Biodegraded system typically show regional variation in oil quality



dams, 2008; Marcano, 2011

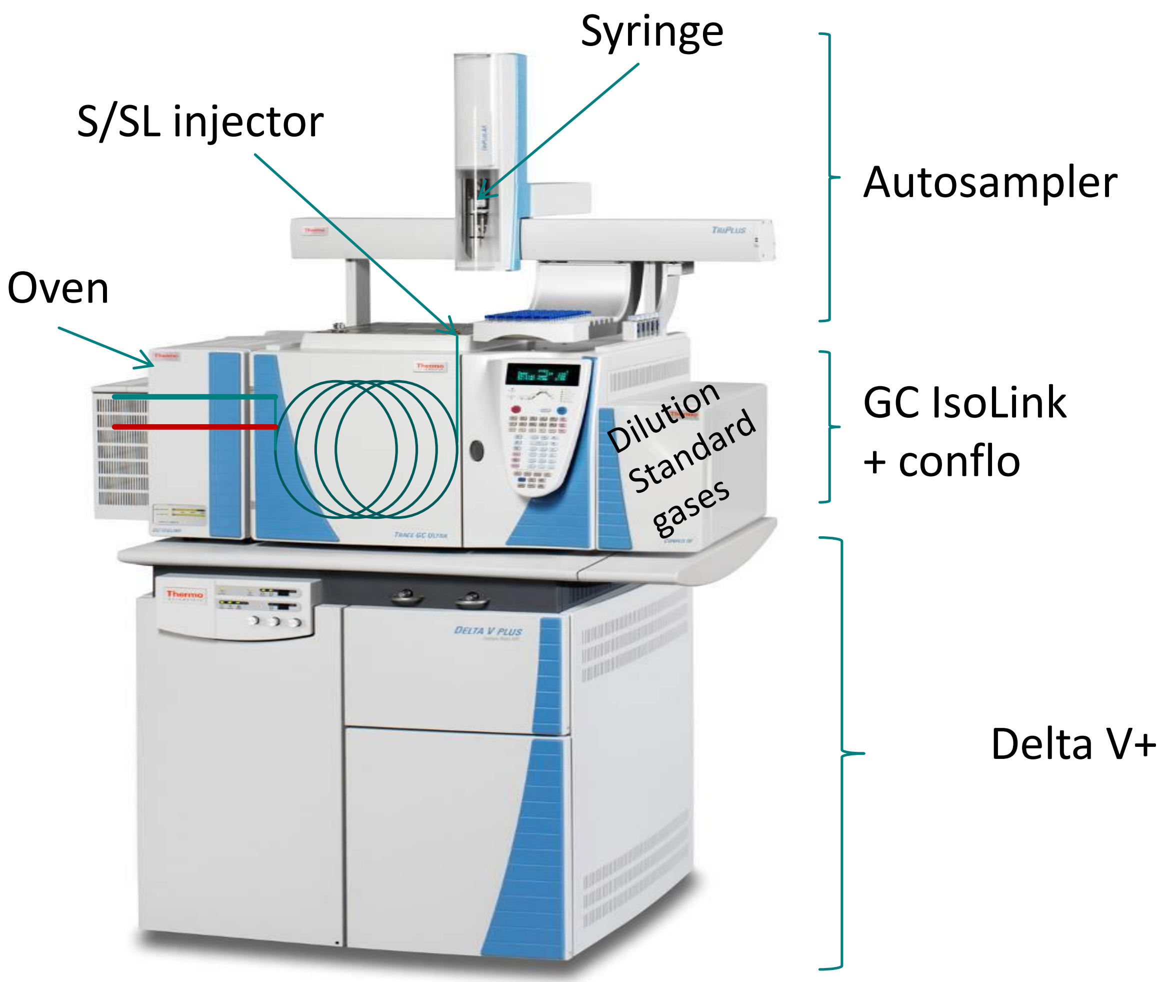
Variations within oil columns



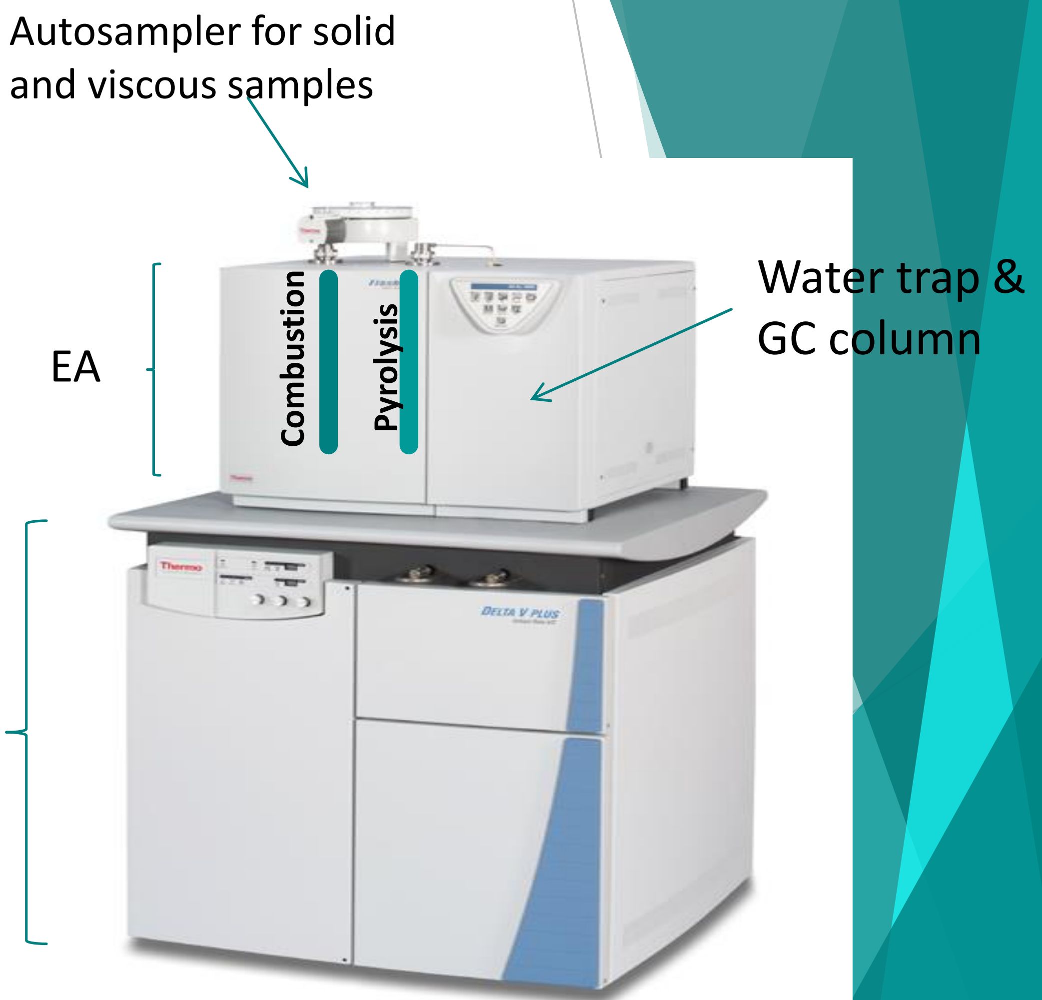
Stable Isotopes

- Gas Isotope Analysis
  - Carbon and hydrogen isotopes for C_1 to C_5 gases (including iC_4 and iC_5)
  - Isotopes on CO_2, H_2S ($\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$)
- Compound Specific Isotope Analysis (CSIA)
  - n-alkanes $\delta^{13}C$ & δD
  - Biomarkers
- Bulk Isotope Analysis
  - Whole oil and SARA fractions bulk isotopes ($\delta^{15}N$, $\delta^{18}O$, $\delta^{34}S$, $\delta^{13}C$ and δD) by elemental analyzer
- Mud gas from drilling: real time carbon isotopes

GC-IRMS

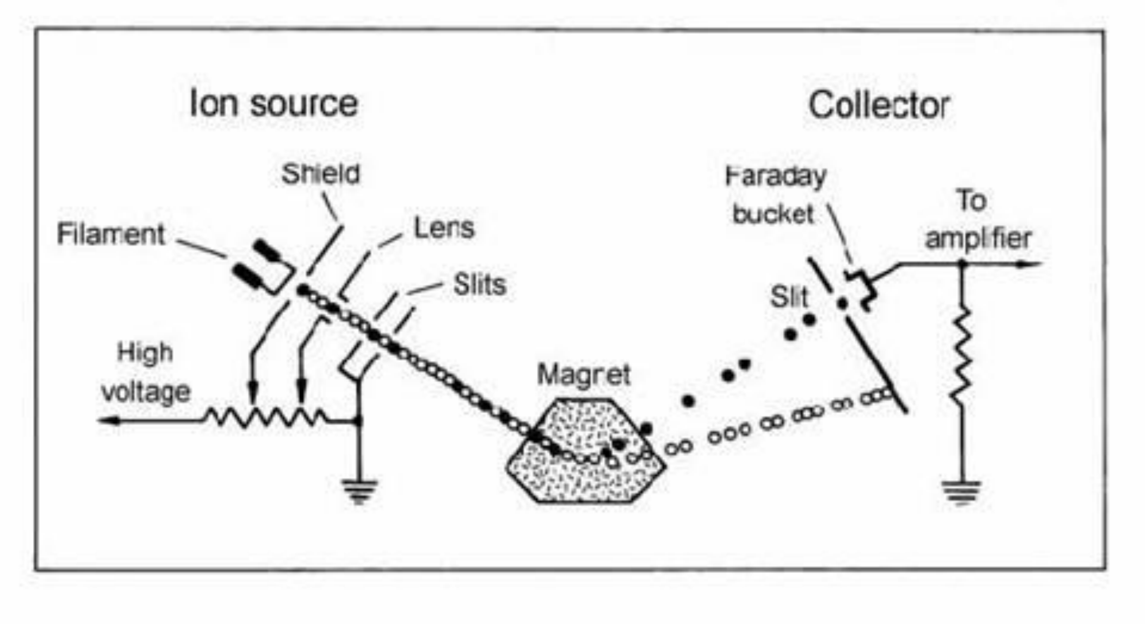


EA-IRMS

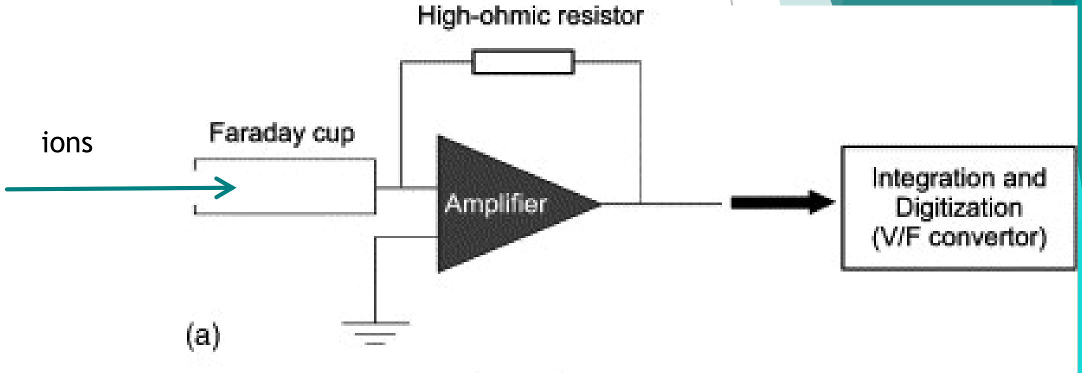


Analytical Advancement of Stable Isotope Mass Spectrometry

The basic design for laboratory isotope ratio mass spectrometers.



Ions impact a surface, and a current neutralizes the positive ions; The current is a measure of the ion flux.



Detection by "Faraday cups"

Isotope International Standards

Isotope ratio	Primary Standard	Accepted value[1]
$^{2}H/^{1}H$ $^{18}O/^{16}O$	SMOW (Standard Mean Ocean Water)	0.00015576 0.00200520
$^{13}C/^{12}C$ $^{18}O/^{16}O$	PDB (Pee Dee Belemnite)	0.011180 0.0020672
$^{15}N/^{14}N$	AIR (Air)	0.0036765
$^{34}S/^{32}S$	CDT (Canyon Diablo Troilite)	0.0450045

- International Atomic Energy Agency (IAEA, Vienna, Austria)
- National Institute of Standards and Technology (NIST, USA)

[1] Practice and Principles of Isotopic Measurements in Organic Geochemistry, John M. Hayes

Isotope International Standards

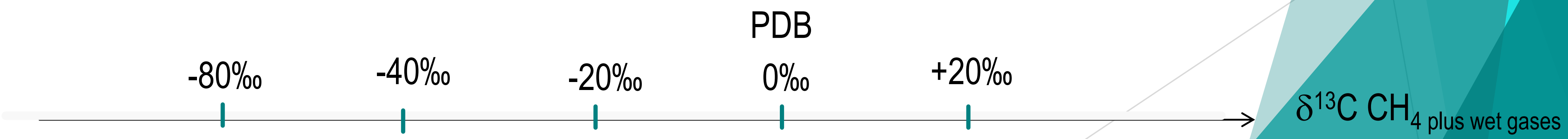
- The stable isotopic compositions of low-mass (light) elements:
    - reported as "delta" (δ) in parts per thousand (noted as ‰)
    - enrichments or depletions relative to a standard

$$\delta(\text{in ‰}) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

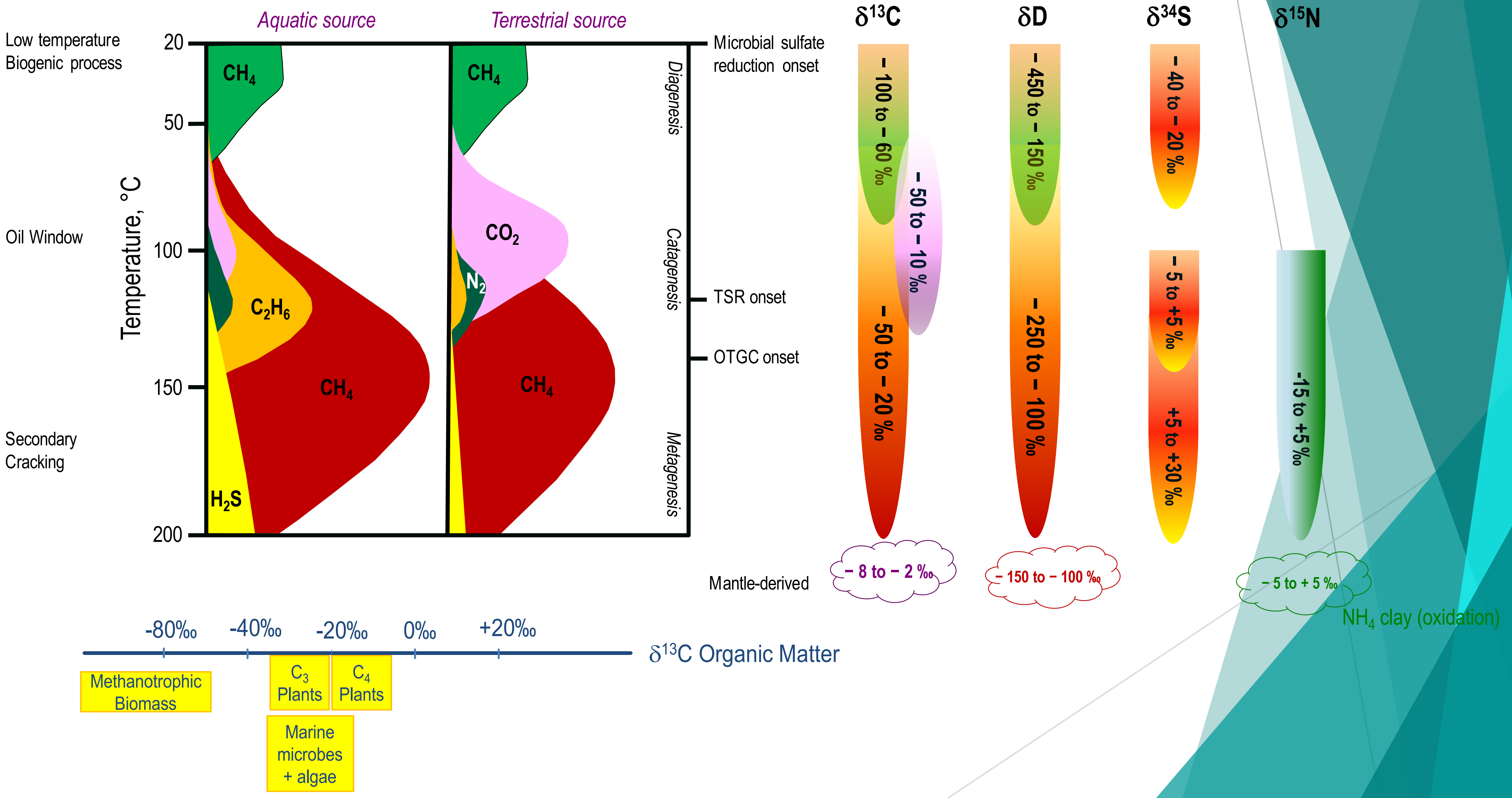
R: ratio of the heavy to the light isotope

Example:

$$\delta^{13}C(\text{‰}) = \left(\frac{\left({}^{13}C/{}^{12}C\right)_{sample} - \left({}^{13}C/{}^{12}C\right)_{standard}}{\left({}^{13}C/{}^{12}C\right)_{standard}} \right) \times 1000$$

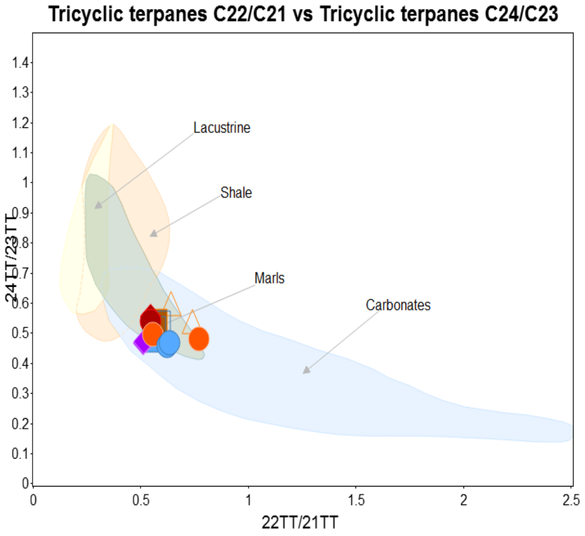


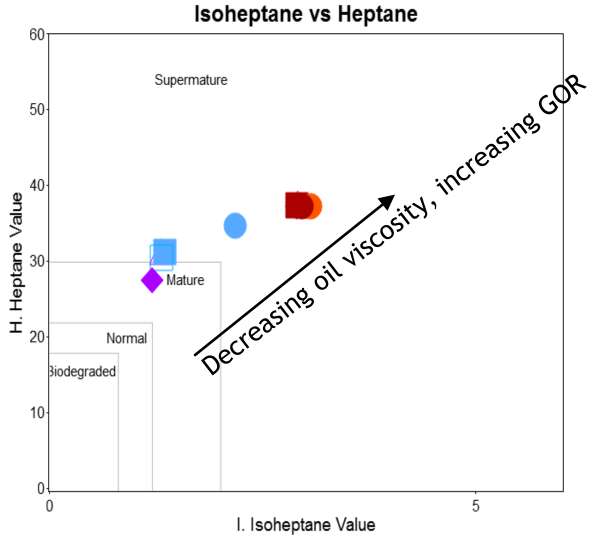
Organic Matter Transformations and Isotopes



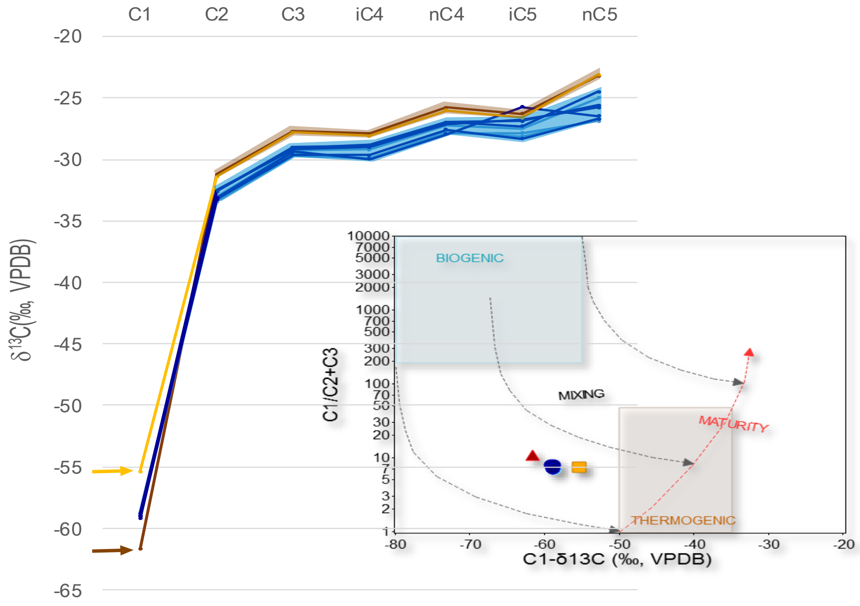
Source Facies, Maturity, Compositional Variations

Similar Source, different maturities controlling fluid physical properties

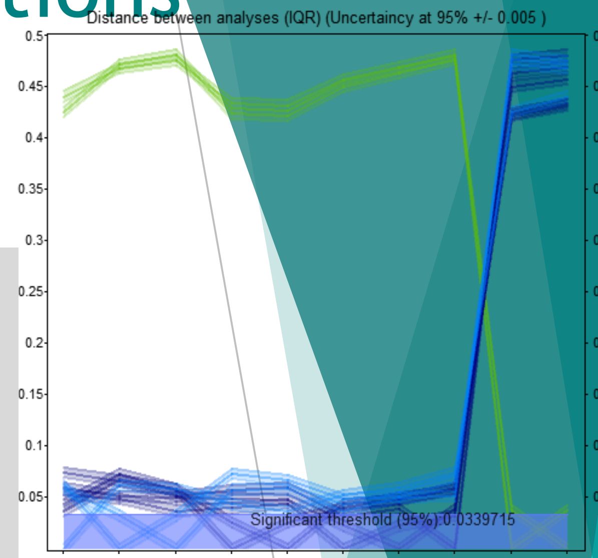




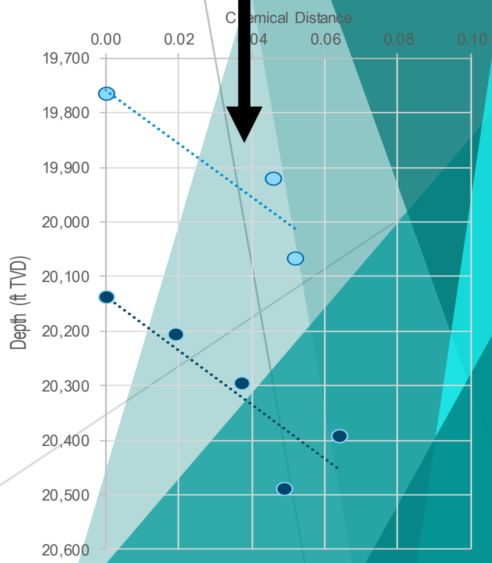
Changes in GOR related to biogenic methane contribution



Concentration gradients identified using HRGC fingerprinting



Chemical distance vs Depth in B6 Sand



Summary

- Petroleum Geochemistry tools can be utilized along the entire subsurface value chain from exploration to production

- Reservoir geochemistry may be applied to a range of practical engineering problems including reservoir compartmentalization, production allocation, understanding mixing scenarios, and the prediction of fluid property during appraisal

- The development of compositional baselines, early in the reservoir history, is essential for taking advantages of reservoir geochemistry tools. The sampling strategy is key

- **Samples:** surface and downhole samples, produced gases, oils and waters, core/cuttings (extracts) – small samples (a few grams)

- **Analytical Techniques:** Rock Pyrolysis (-GC), Fingerprinting by gas chromatography, gas chromatography-mass spectrometry, Isotopic composition

- Integrated studies, combining all available data are more likely to be successful

- Generated data can be used to refeed and enhance models

Thank You

SOCIETY OF PETROPHYSICISTS AND WELL LOG ANALYSTS

SAUDI ARABIA CHAPTER

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