

# **Molecular and Isotopic Geochemistry: Technology Development and Applications to Exploration from the Present-Day to Mid-Century\***

**Ye Wang<sup>1</sup> and J. Mike Moldowan<sup>2</sup>**

Search and Discovery Article #42503 (2020)\*\*

Posted February 24, 2020

\*Adapted from oral presentation given at 2019 AAPG Hedberg Conference, The Evolution of Petroleum Systems Analysis: Changing of the Guard from Late Mature Experts to Peak Generating Staff, Houston, Texas, United States, March 4-6, 2019

\*\*Datapages © 2020. Serial rights given by author. For all other rights contact author directly. DOI:10.1306/42503Wang2020

<sup>1</sup>ConocoPhillips, Houston, TX, United States ([wangye0616@gmail.com](mailto:wangye0616@gmail.com))

<sup>2</sup>Biomarker Technologies Inc., Rohnert Park, CA, United States

## **Abstract**

As essential and cost-effective tools, molecular and isotopic geochemistry have largely been applied to petroleum exploration since the late 1970s. Consequently, molecular and isotopic technology development boomed between the 1980s and 2000s. Many novel age-, depositional environment-, lithology-, source facies-, and maturity-related biomarkers had been identified in that period by our pioneering petroleum geochemists. Diamondoids were identified and utilized to estimate maturity and extent of oil-to-gas cracking. C7 parameters were developed for understanding source origin, maturity, correlation, and alteration. Stable isotopic compositions of key elements (C, H, N, O, S) in kerogen, especially carbon and hydrogen, were also used to evaluate source origin, maturity, correlation, and alteration. When source rocks were not penetrated, molecular and isotope geochemistry together could help infer the source rock and its characteristics (e.g., age, lithology, kerogen type, maturity). These inferences, in turn, assist petroleum system analysis and provide the opportunity for more accurate migration modeling and fluid property prediction. As peak generation geochemists, we are very lucky to have been supervised by our world-class petroleum geochemists. Now, it is our responsibility to pass the torch to the next generation. This presentation will review current state-of-the-art biomarker/diamondoids/light hydrocarbon and stable isotope technology developments and their applications to exploration, including new biomarker identification (e.g., Carotenoid biomarkers), new diamondoids applications (e.g., Quantitative Extended Diamondoids Analysis), CSIA (Compound Specific Isotope Analysis) of biomarkers/diamondoids, CSIA of sulfur isotopes of sulfur compounds, and new analytical techniques (e.g., Triple Quadrupole (QQQ) GCMSMS, GCGC-

TOFMS, GC/MS-FID). It will also help envision what petroleum geochemistry will look like in the next 20 to 30 years. The first thing to consider is whether in the next 20 to 30 years petroleum exploration will still occur, since renewable energy sources are taking over to provide part of the energy supply. Assuming there is still a significant need for exploration, we will largely focus on light fluids and gas from unconventional plays. As we know, saturated biomarkers in light fluids are below the detection limits by current analytical techniques. Therefore, we should work with analytical chemists and engineers to develop instruments capable of much greater selectivity and sensitivity. For age-related biomarkers, we should engage in research to develop higher age resolution parameters, e.g., to separate Upper vs. Lower Cretaceous, Upper vs. Lower Jurassic, and Permian vs. Devonian ages. This endeavor will require collaboration between geochemists, paleontologists, and analytical chemists. Geochemical analysis often produces large datasets. Can we identify new biomarkers and new applications by big data analysis of geochemical data and integration with other disciplinary data? The final topic for this presentation will be how we should work together to pass the torch to the younger generation and how we can carry forward our technologies to provide a greater business impact. As well-trained geochemists, we should continue to improve our knowledge, to develop new techniques and to create new business values by collaborating with our seasoned geochemists. At the same time, we should motivate younger generation's interest through mentorship, and advocate business values of geochemistry at exploration and production.

# Molecular and Isotopic Geochemistry: Technology Development and Applications to Exploration from the Present-Day to Mid-Century

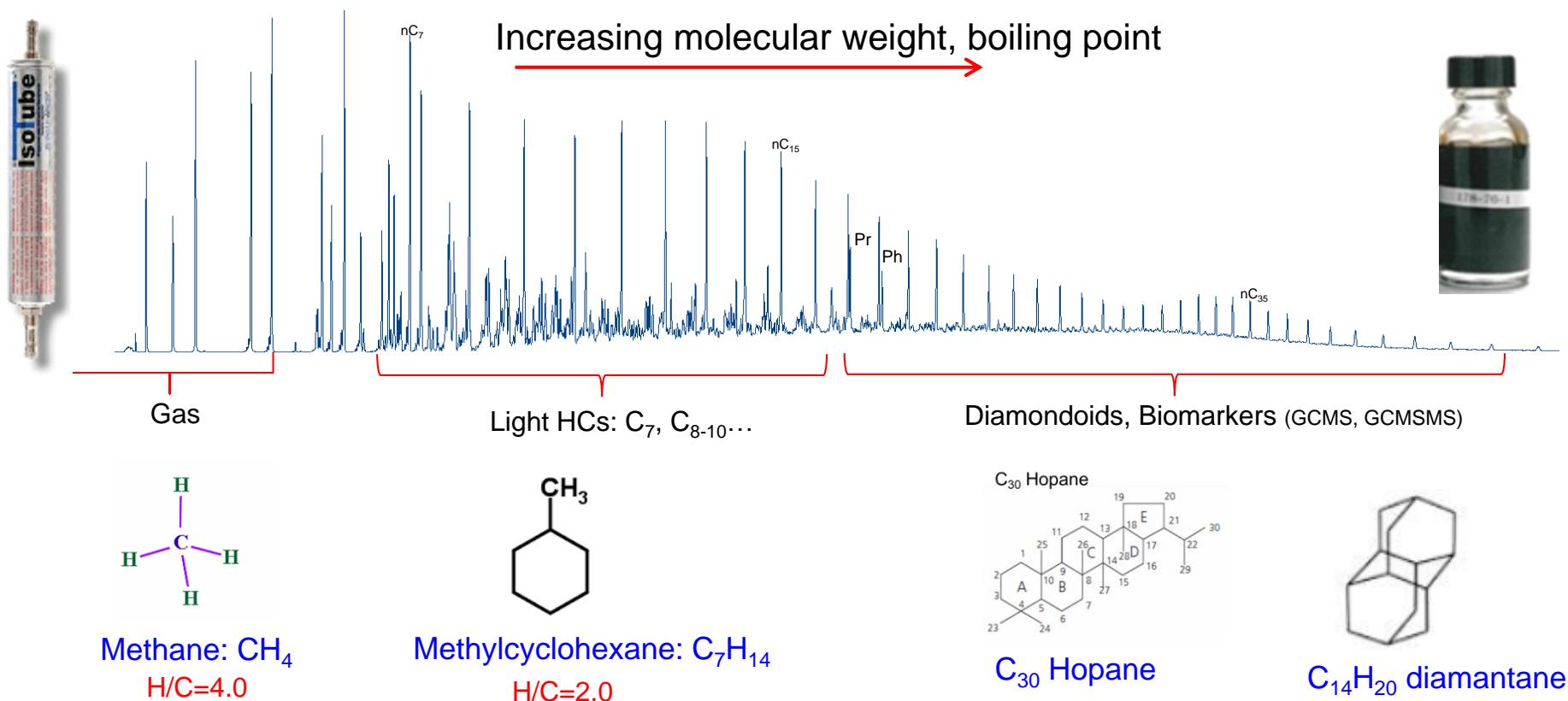
Ye Wang (ConocoPhillips)

J. Mike Moldowan (CEO, Biomarker Technology Inc.)

- Molecular Geochemistry
  - Biomarkers
  - Diamondoids
  - Light Hydrocarbons: e.g., C<sub>7</sub>
  - *GAS (not covered in this presentation)*
- Technology Development
  - Commonly used analytical techniques: GC, GC/MS
  - Advanced techniques:
    - GCMSMS, GCGC-FID, GCGC-ToF MS
    - Compound-Specific-Isotope-Analysis (CSIA) of n-alkanes, biomarkers, and diamondoids
    - CSIA of sulfur-compounds
  - New Biomarker development
- Applications of Molecular Geochemistry to Exploration
- Projection of Geochemistry in Exploration from Present day to Mid-Century

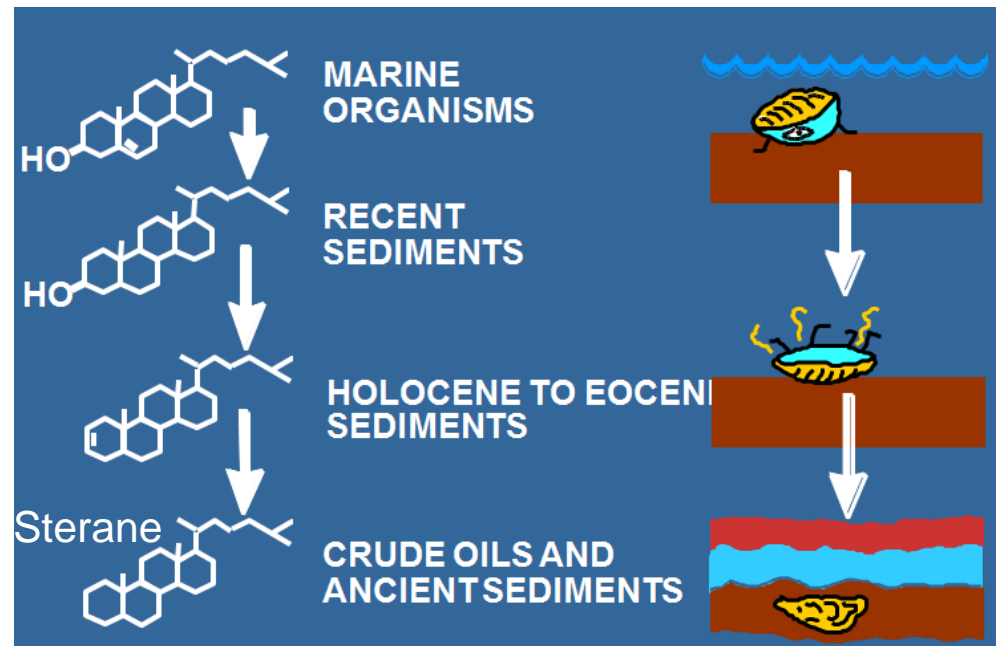
# Molecular Geochemistry

Integrate geochemistry of all the oil fractions: gas, light hydrocarbons ( e.g.,  $C_7$  and Alkyl benzenes), and biomarkers/diamondoids...



# Biomarkers

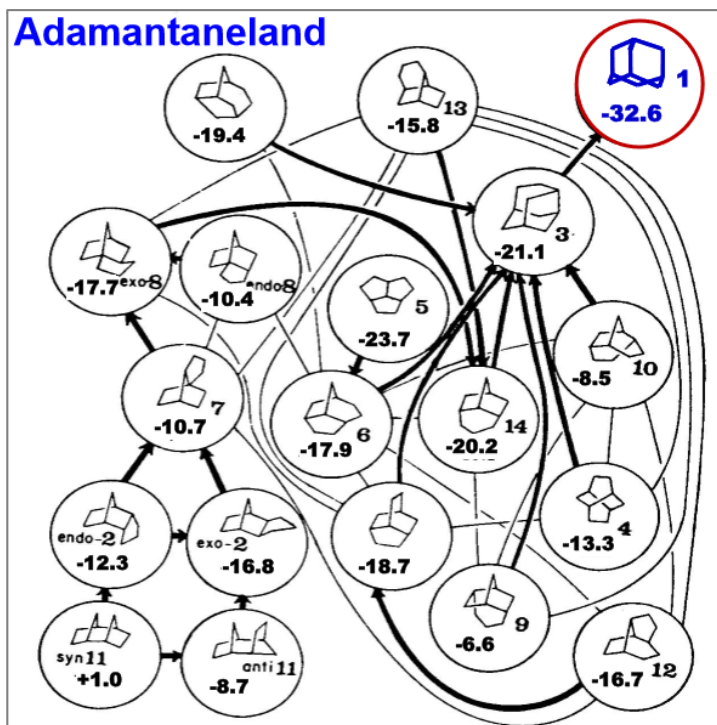
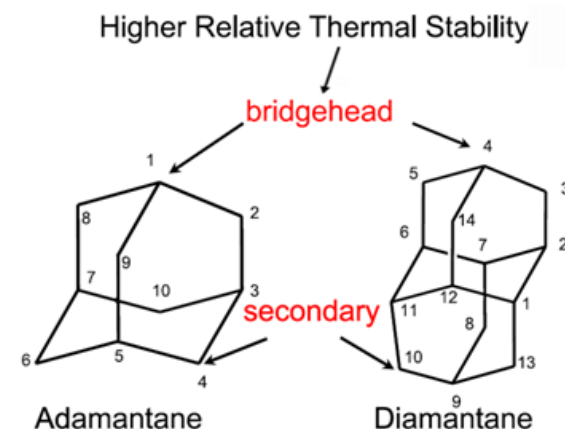
- Complex molecular fossils derived from biochemicals, particularly lipids, in once-living organisms (e.g., freshwater algae, marine algae, and land plants);
- Retain stable molecular structure of original biogenic sources. Therefore, biomarkers provide information on the organic matter inputs, age, lithology, depositional environment, maturity of source rock or oil;
- Resistant to biodegradation, and other processes.



(Picture from Albert Holba)

# Diamondoids

- With increasing maturity and oil cracking, diamondoids can be highly concentrated in the remaining oil/condensate (Dahl et al., 1999)
- Bridgehead substituted diamondoids are more thermally stable than secondary substituted diamondoids (Clark *et al.*, 1979). e.g., 1MA (1-methyladamantane) is more thermally stable than 2MA.



## Speculated formation pathways for adamantane.

Once Adamantane is formed, it should be extremely stable to thermal alteration:

- The calculated  $\Delta H_f^\circ$  of adamantane is -32.6 Kcal/mole, far lower than any other saturated hydrocarbons of comparable formula.
- However, the entropy of formation is extremely high.

# light hydrocarbons (C<sub>6</sub>-C<sub>10</sub>)

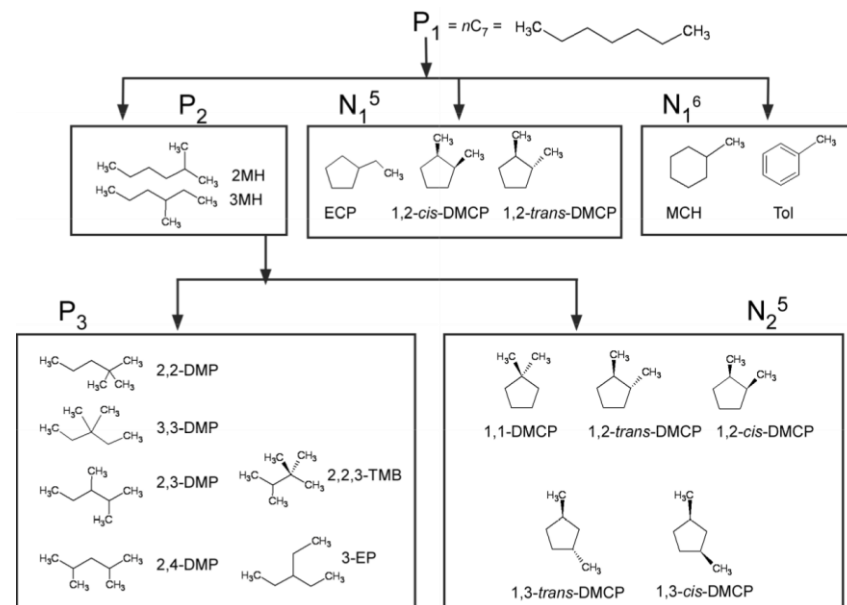
C<sub>7</sub> geochemistry in Exploration: C<sub>7</sub> is the highest carbon number where all 17 hydrocarbon isomers can be fully resolved by HRGC

- Source: shale vs. Carbonate
- Maturity: Ctemp
- Secondary transformations (biodegradation, evaporation, water washing, gas stripping...)

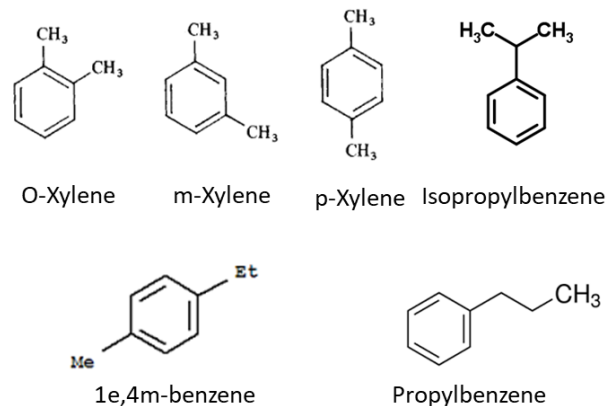
Reservoir Geochemistry (C<sub>6</sub>-C<sub>10</sub>): Shell method MDGC fingerprinting (public information):

- MDGC performs separation using two columns that have different characteristics.
- Advantage: long-term reproducibility, oils do not need to be re-analyzed

## C7 Hydrocarbons by Mango kinetic reaction model



## Alkyl Benzenes

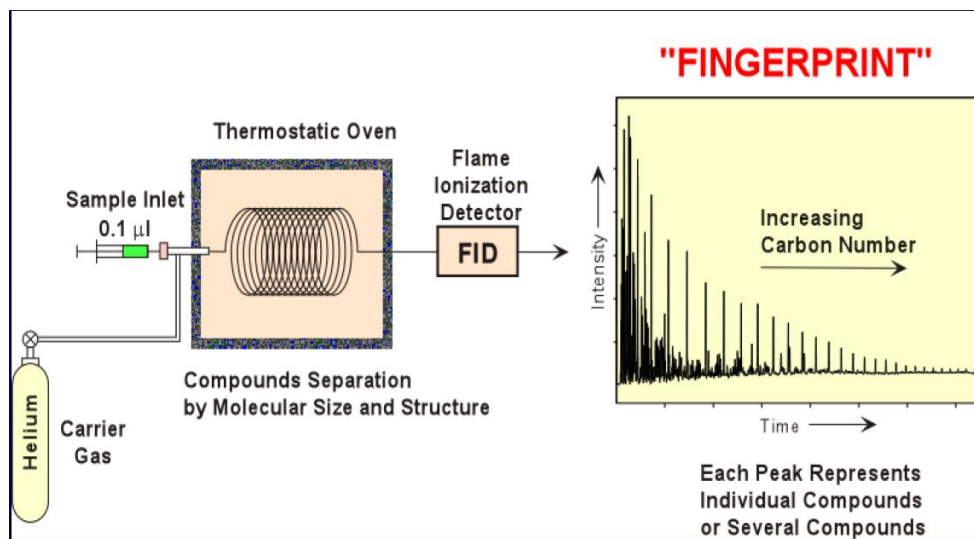




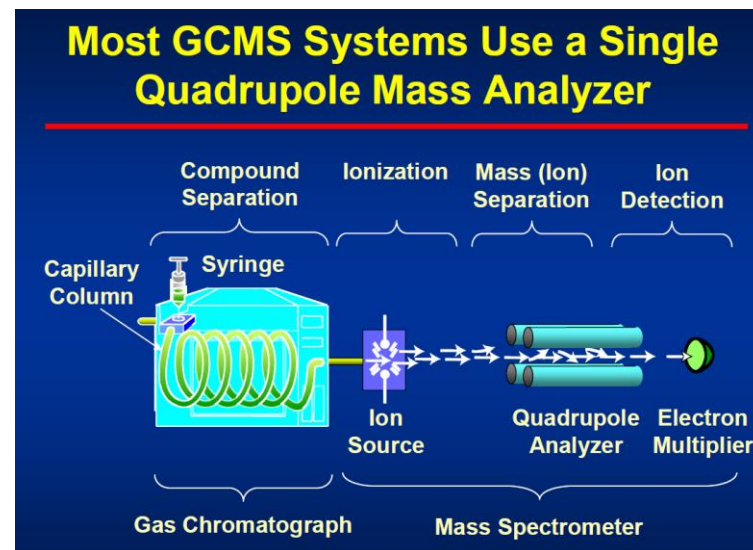
# Commonly Used Analytical instruments

- GC-FID (see left) = Gas Chromatography- Flame Ionization Detector

- Separation is controlled mostly by molecular weight, specifically by boiling point.

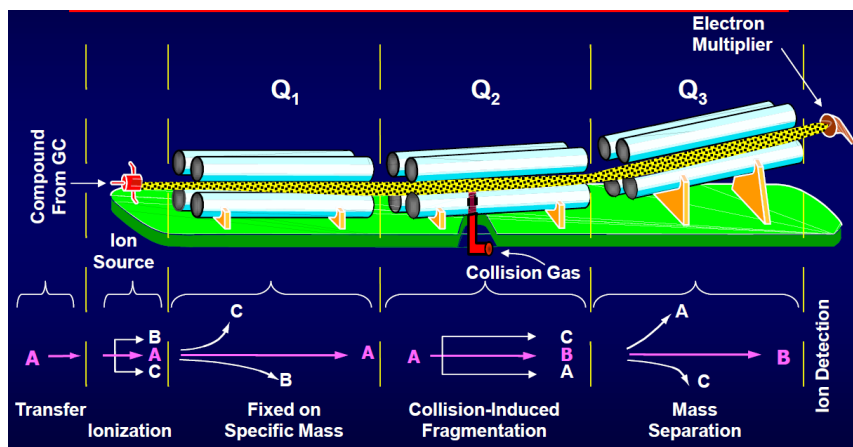
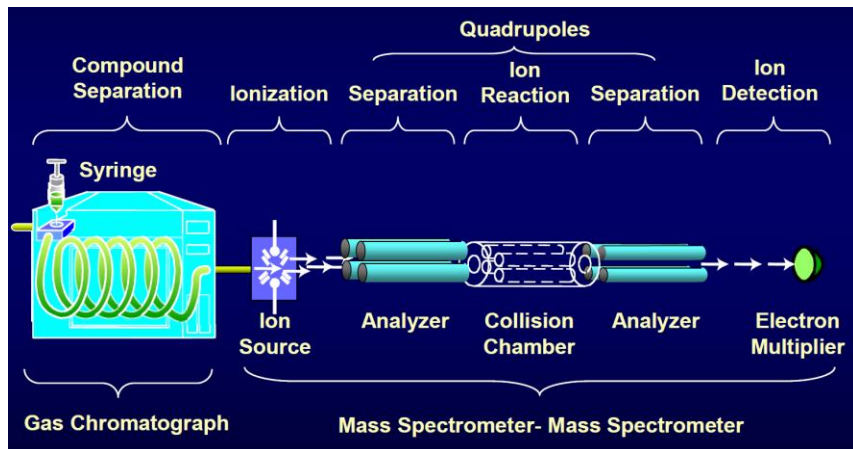


- GC/MS = Gas Chromatography/Mass Spectrometry: Analyze biomarkers and diamondoids

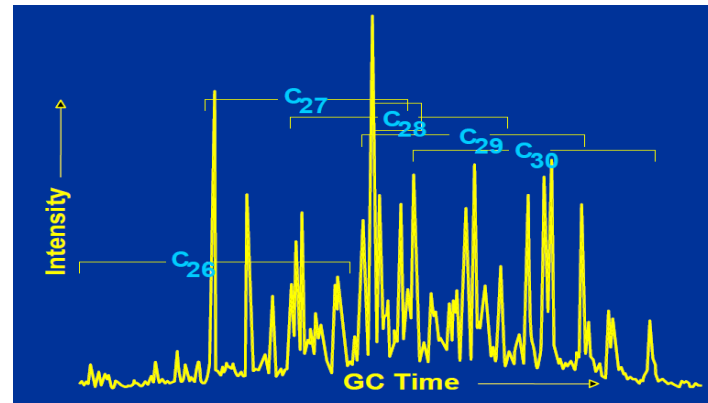


# Advanced Geochemical Analysis: GCMSMS

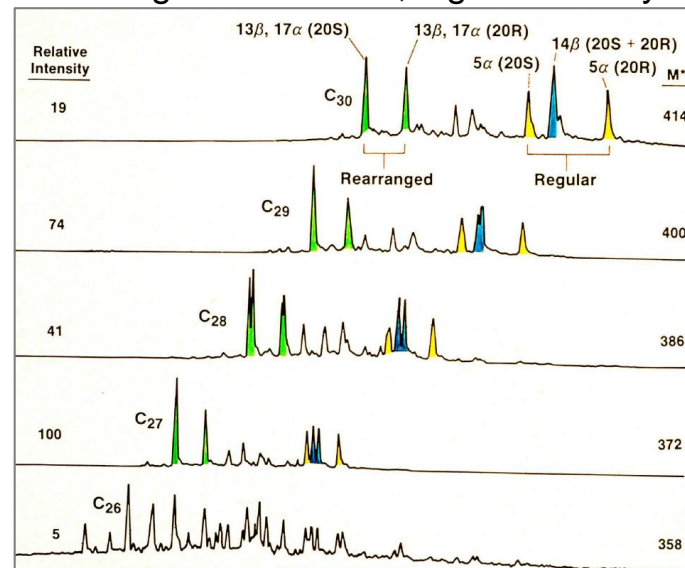
Bench Top QQQ GCMSMS System Allows  
Parent-Daughter Monitoring That  
Reduces Interference



SIM-GCMS  $m/z$  217:  
Overlap or interfere.



GCMSMS: Better separation,  
higher resolution, high sensitivity.

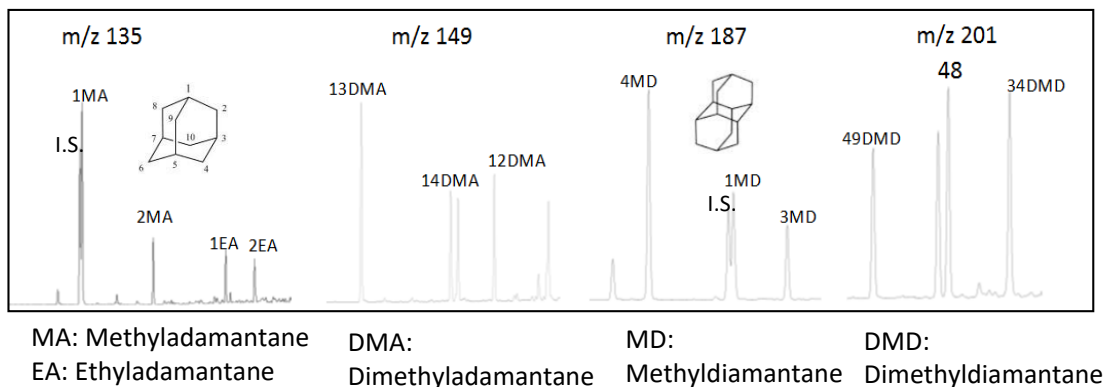


# Diamondoids Analysis by Biomarker Technology Inc. (BTI)

## Well established method by BTI. Commonly Analyzed by GCMS or GCMSMS

- The saturated fraction was separated by column chromatography using silica gel. Zeolites are used to increase diamondoid concentrations before GC-MS analysis.
- **“Cocktail”** Standards: Before separation, oil samples were spiked using a deuterated diamondoid internal standard: A mixture of D<sub>16</sub>-adamantane, D<sub>3</sub>-1-methyladamantane, D<sub>4</sub>-diamantane, D<sub>3</sub>-methyldiamantane, D<sub>5</sub>-ethyldiamantane, cholane, and D<sub>4</sub>-triamantane.

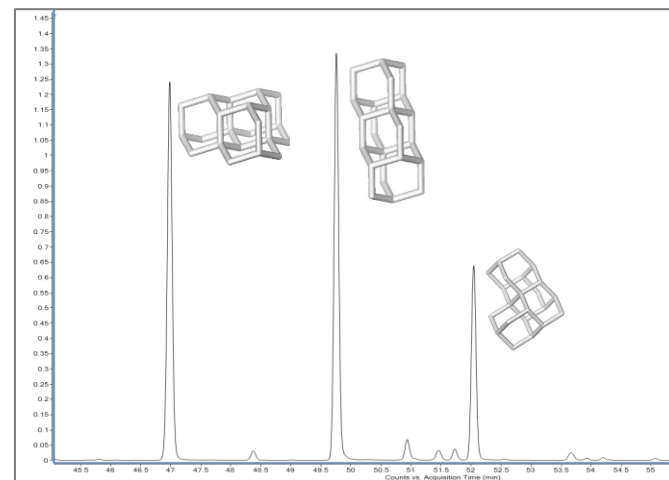
## Accuracy of Diamondoid Quantification Depends on Internal Standards



## Quantitative Extended Diamondoids Analysis (QEDA) was developed recently at BTI.

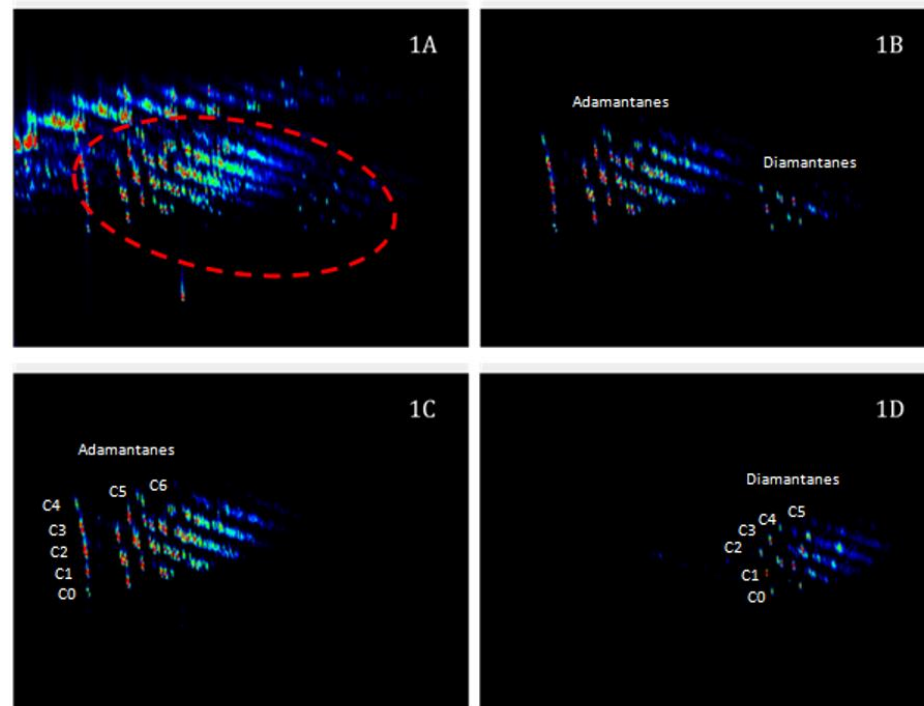
- This method is used to correlate oils of any maturity and to correlate the high-maturity portion of a mixed-source oil.
- QEDA also uses a **“cocktail”** of deuterated tetramantanes, pentamantanes and cyclohexamantane with which the oil is spiked prior to workup and analysis.

## High Cage Diamondoids Tetramantanes, m/z 292, three isomers



# Diamondoids Analysis by Other Labs: GCGC-ToF MS

- GCGC-ToF MS ( *Comprehensive Two-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry*): Applied, but have not been commercialized
- Advantage: Circumvent response factors of diamondoids. Better separation and quantification of diamondoids, and thus more accurate thermal maturity calibration



1A: TIC of a GCGC-ToF MS analysis of a condensate highly enriched in diamondoids

1B: Combined diamondoids filter

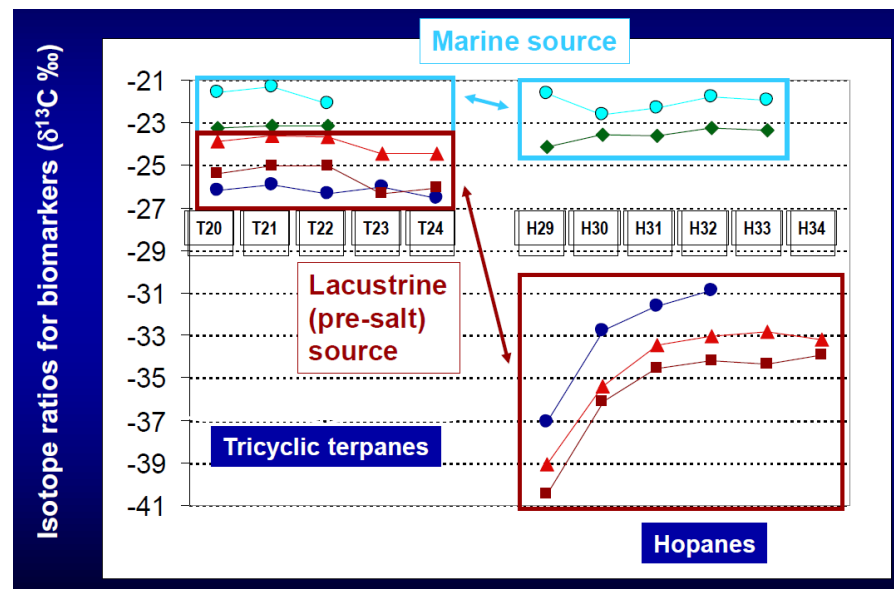
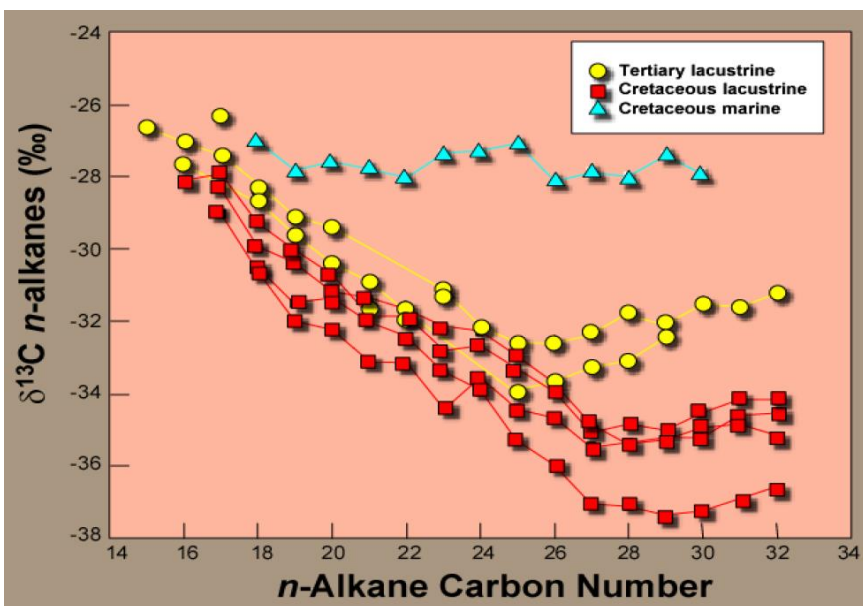
1C: Adamantane filter

1D: Diamantane filter

(Erik Tegelaar, 2013, Shell)

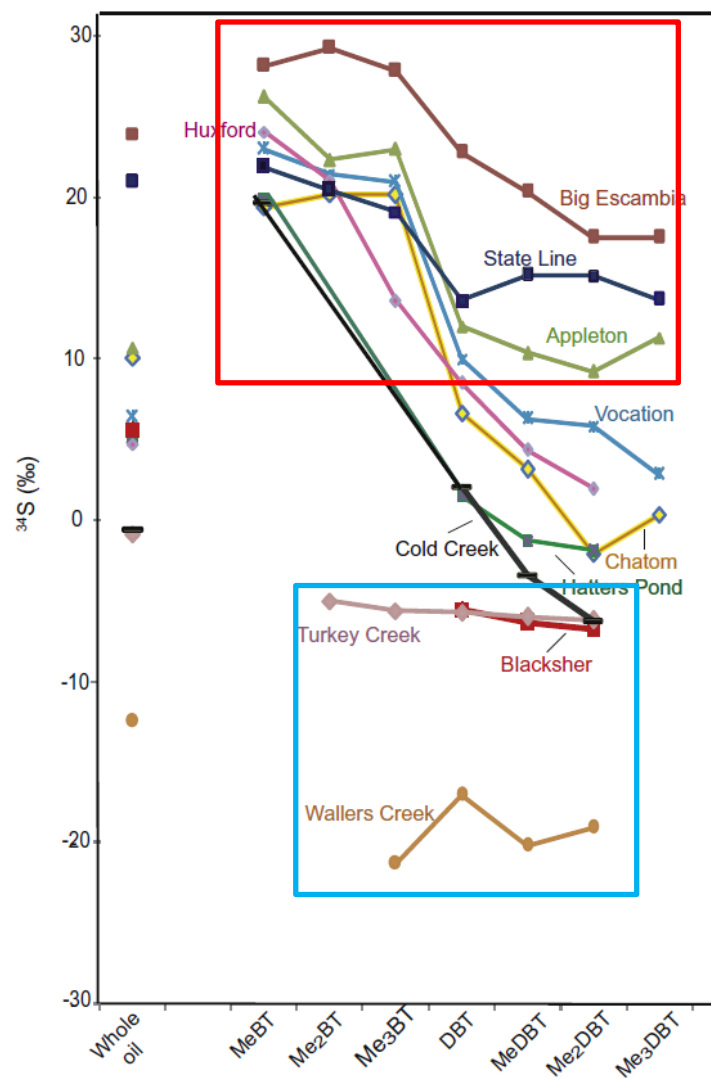
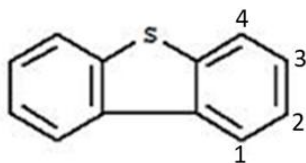
# CSIA of n-alkanes, biomarkers, diamondoids

**Compound specific isotope analysis (CSIA) adds indispensable data for source correlation, mixed sources**



# CSIA of sulfur-compounds: GC-MC-ICP-MS

- GC-ICP-MS: An Agilent 6890 GC equipped with a split/splitless injector that is coupled to a Thermo Scientific Neptune multicollector ICP-MS via a heated transfer line (Amrani et al., 2009)
- GC-ICP-MS analyses revealed a wide distribution of  $\delta^{34}\text{S}$  values for individual OSC (organosulfur) compounds in the oils
- CSIA of sulfur compounds are used to understand origins of high  $\text{H}_2\text{S}$ : TSR, BSR, or else?



(Amrani et al., 2012)



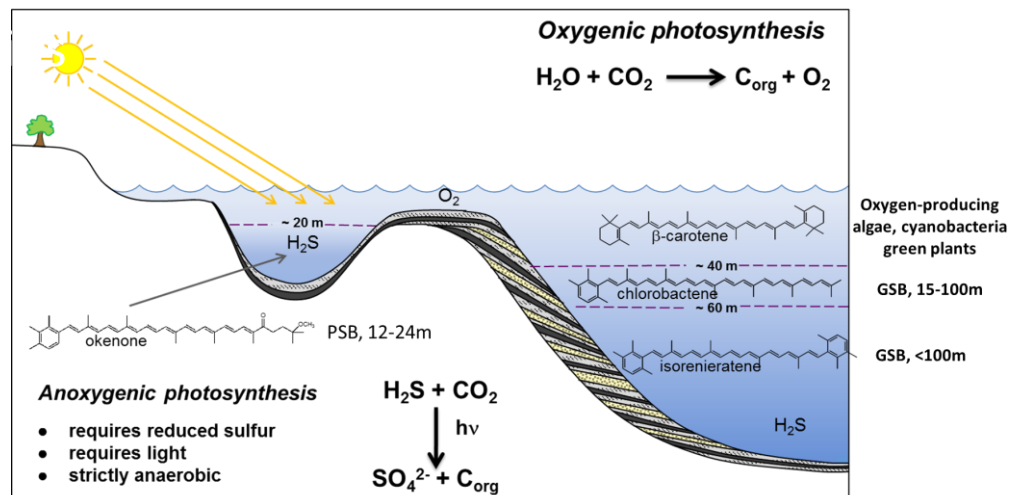
# Biomarker Development: C<sub>40</sub> Carotenoids

## JIP effort with Geomark and MIT

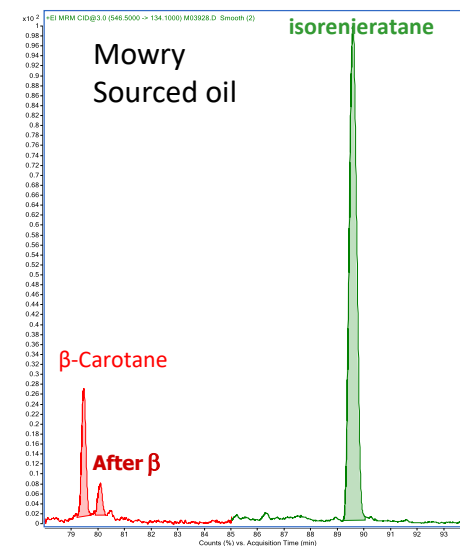
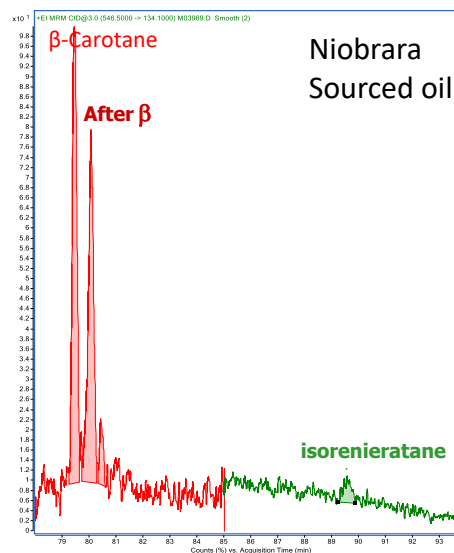
**Business Driver:** Complex oil-source rock correlation and Paleo-depositional model construction for E&P projects

**Background:** Diagnostic biomarkers derived from the pigments of algae and photosynthetic bacteria. Carotenoid hydrocarbons convey information about the redox structure of sedimentary environments and, thus, provide information that complements that of the more commonly used sterane, hopane and tricyclic terpane biomarkers.

**Analytical method:** QQQ-GCMSMS enhances sensitivity and selectivity



## Example: Powder River Basin



# Applications to Exploration: Biomarkers

## Petroleum exploration (our focus today)

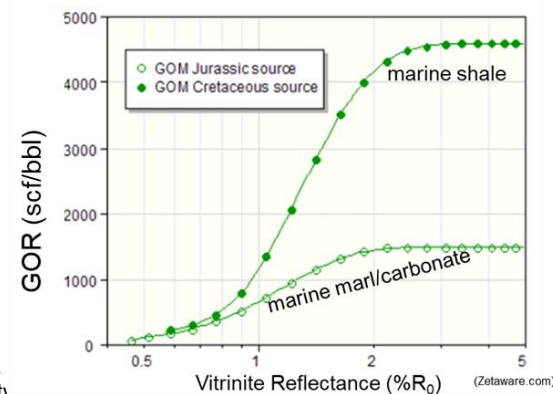
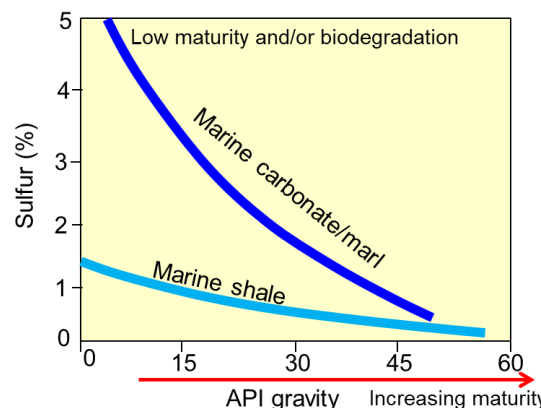
➤ Biomarkers can be used to infer characteristics of the source rock that generated the oil **WITHOUT** examining the source rock itself:

- Age
- Organic matter input: one controlling factor on source rock kerogen type
- Lithology
- Depositional environment: another controlling factor on source rock kerogen type
- Maturity



## Fluid properties in the reservoirs are controlled by:

- Source rock kerogen type (Organic matter type)
  - Oil-prone (Type I, II or IIS) vs. gas-prone (Type III)
- Source rock thermal maturity
  - Immature – Oil window – Wet gas – Dry gas – Post mature
- Phase behaviour (PVT): reservoir conditions
- Secondary transformations: evaporation, biodegradation, water washing, gas stripping...



*Don't forget multi-disciplinary integration!*

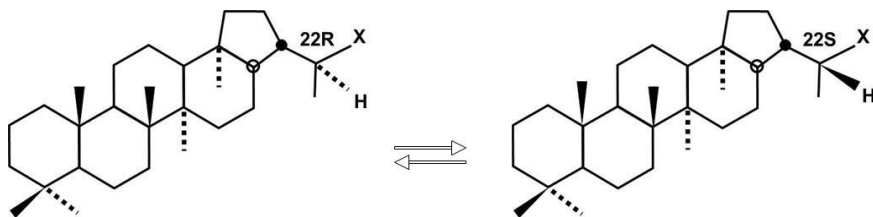


# Maturity Calibration: Saturated Biomarkers

## Equilibration between 22R (biological epimer) and 22S (geological epimer) for C<sub>31</sub>-C<sub>35</sub> homohopanes.

22R: biological epimer

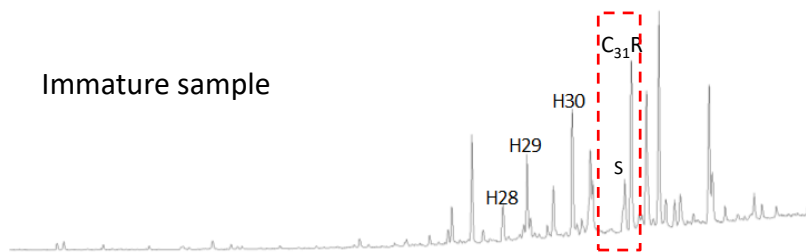
22S: geological epimer



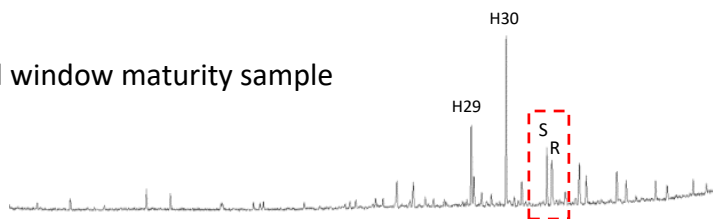
X = n-C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>, n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>6</sub>H<sub>13</sub>

## Biomarker analysis: GCMS m/z 191

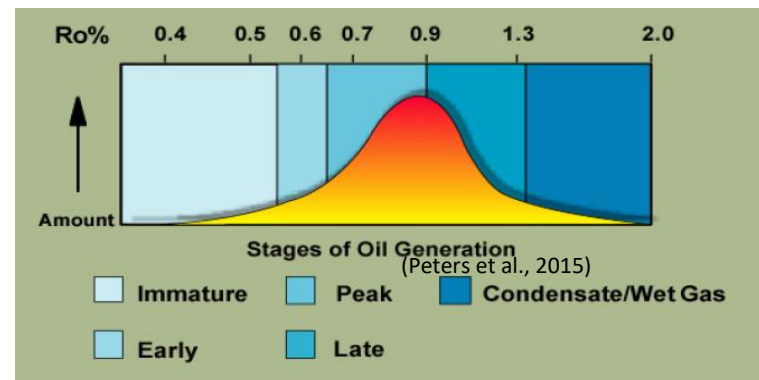
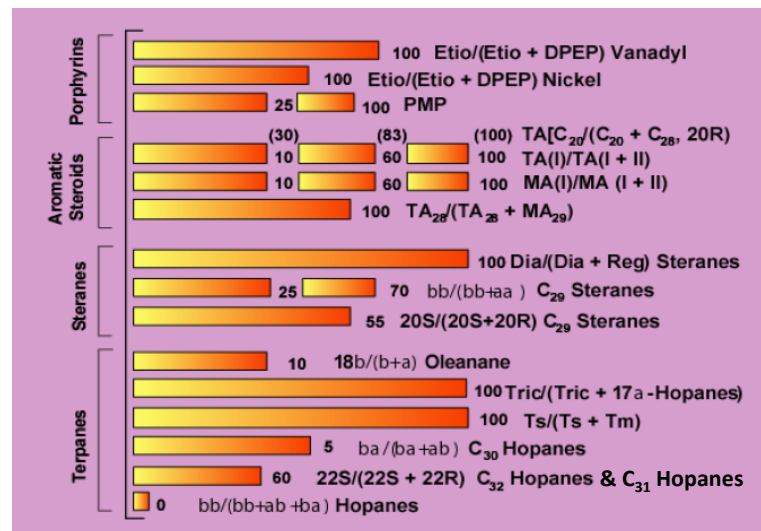
Immature sample



Oil window maturity sample



22S/(22S+22R) isomerization: High specificity for immature to early oil generation (Peters et al., 2015)



## Example maturity parameters

H<sub>32</sub> 22S/22R & H<sub>31</sub> 22S/22R

S29BBS\_AAR

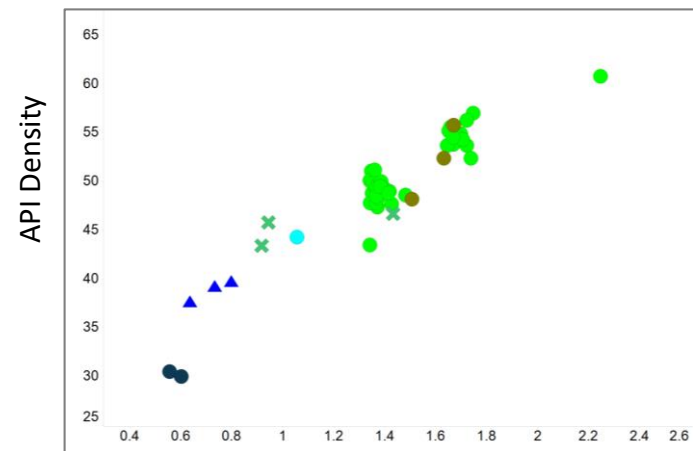
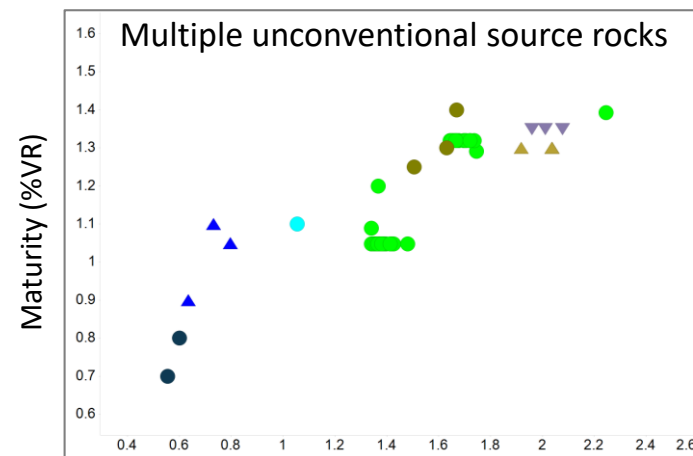
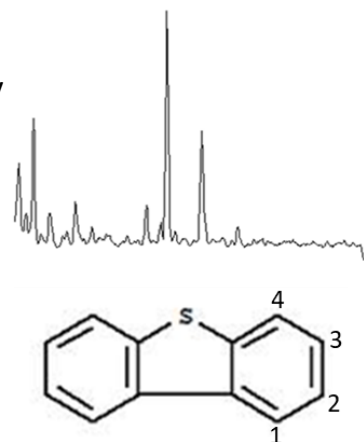
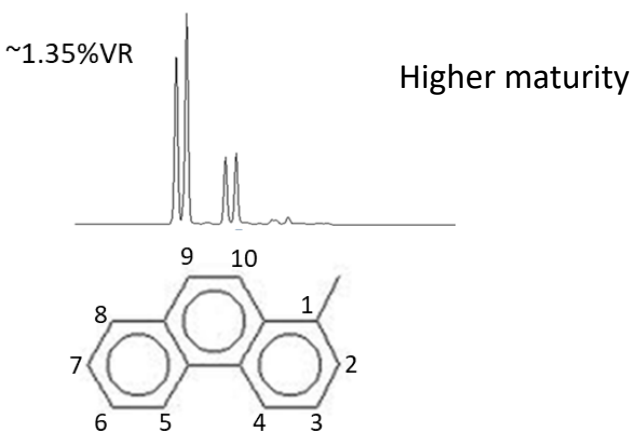
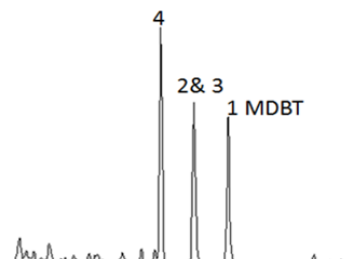
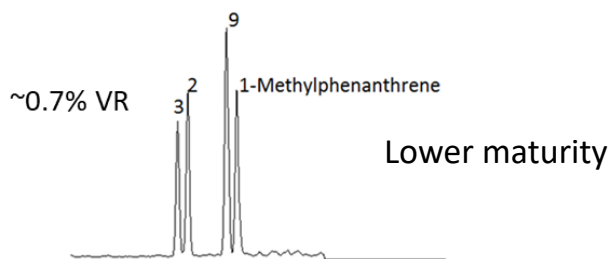
M30\_H30, M30

# Maturity Calibration: Aromatic Biomarkers

Examples:

**Methylphenanthrene (m/z 192)**

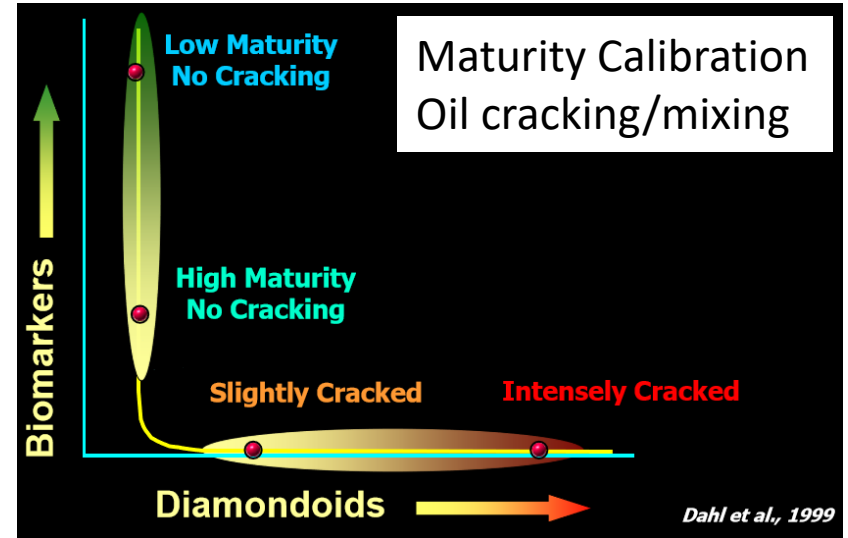
**Methyl Dibenzothiophene (m/z 198)**



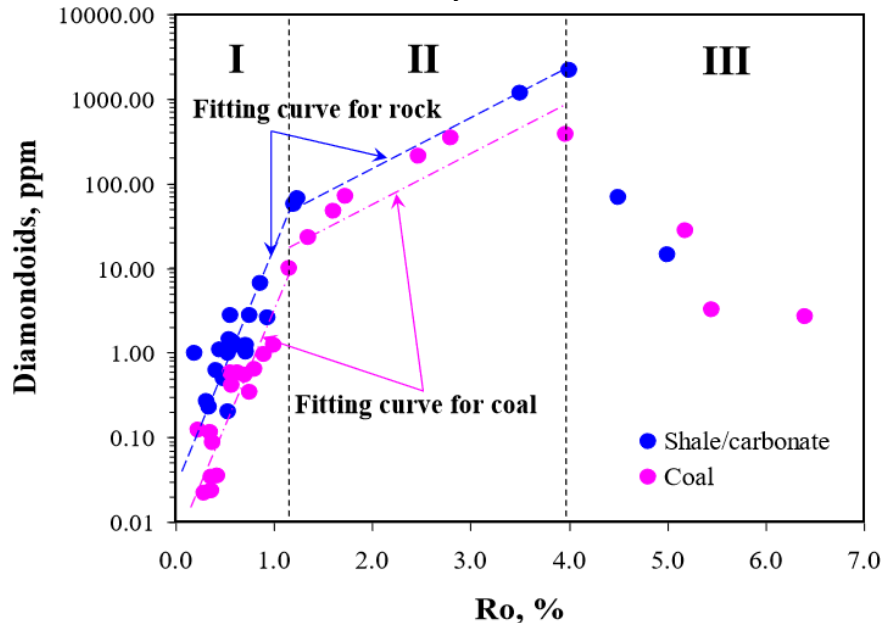
Aromatic biomarker ratio

# Applications to Exploration: Diamondoids

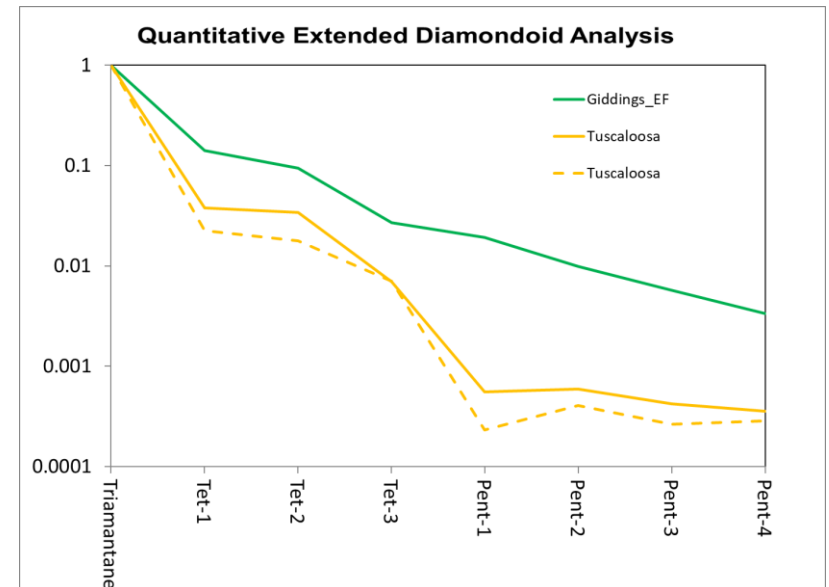
- **Diamondoids are used to improve fluid property prediction by**
  - More accurately calibrating thermal maturity
  - Recognizing cracked oil which was overlooked due to absence of biomarkers;
  - Determining the source of highly mature oil
    - CSIA of diamondoids
    - QEDA



**Maturity Calibration**

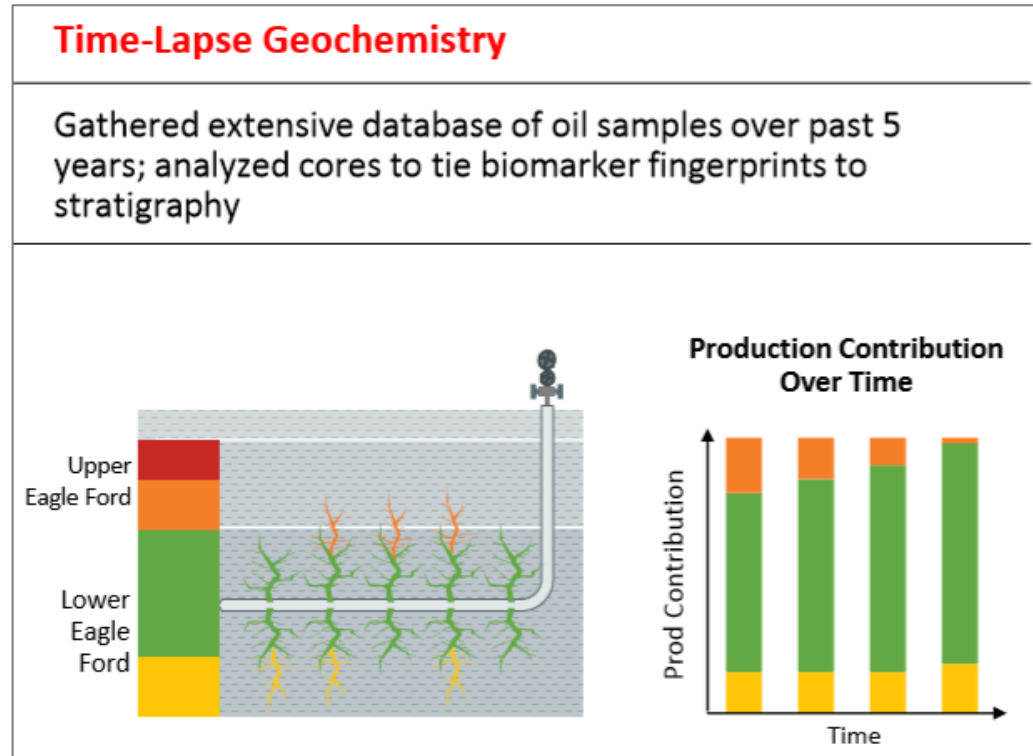


**Source Correlation**



# Geochemistry As Cost-Effective Tool at Field Development

- **Well Stacking/Spacing:** Estimate frac height by allocating produced fluids to different potential producing zone/intervals, by comparing geochemical fingerprints between produced oil/gas/water versus zone-specific end-members (Core/Brine cutting extracts).
- COP proprietary data analytic toolkit was developed in 2016.
- Integrate with reservoir engineer, completion, geology...
  - Reservoir engineer: "Great thanks for the info – allocations like this help build confidence in the Mangrove modelling..."
  - Geologist: "Finally, some data/results that actually makes sense Liquids predominantly coming from Formation A is looking quite plausible."



(2016 ConocoPhillips Analyst Meeting)

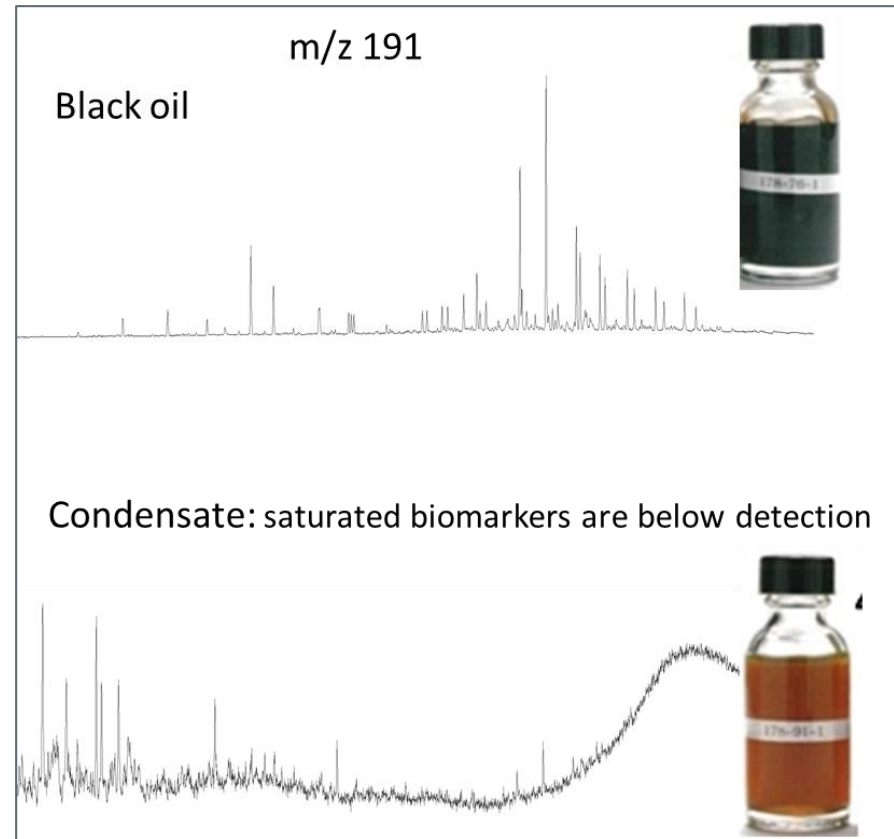
# Projection of Geochemistry in Exploration

Geochemistry will play significant role in exploration in the next 20-30 years, especially for unconventional exploration.

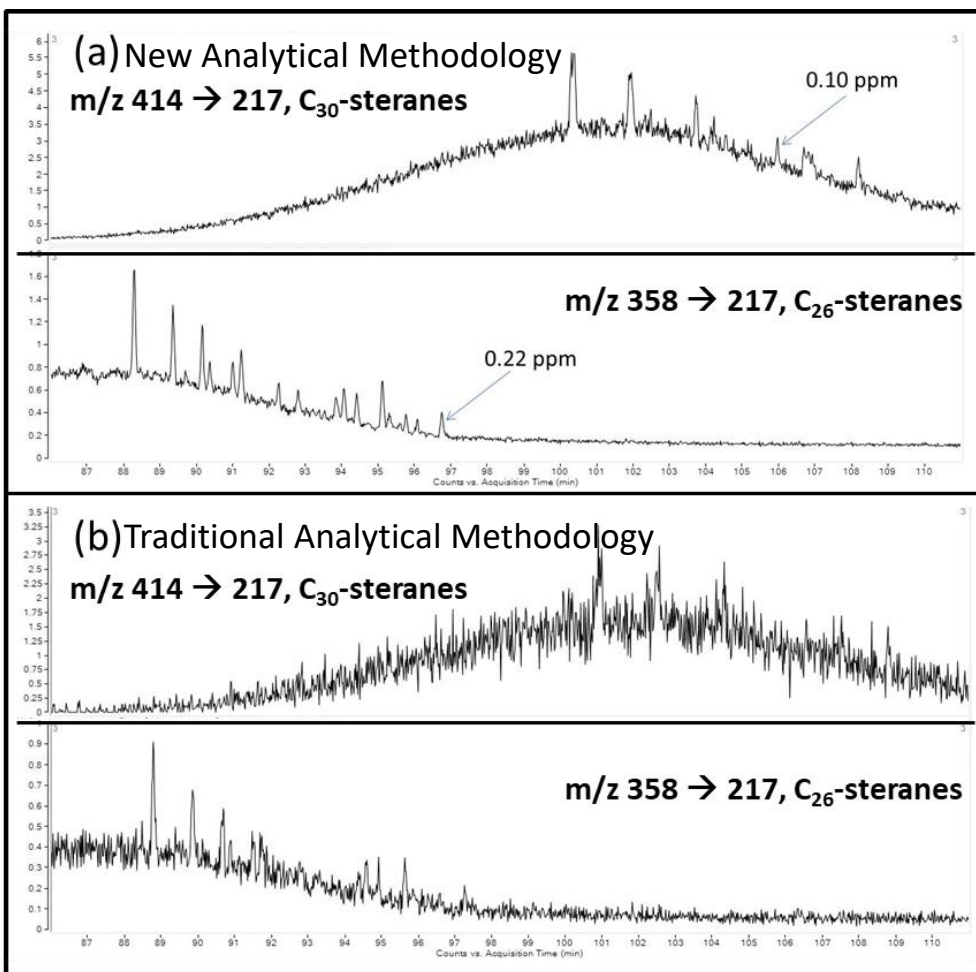
To fit for exploration purposes, potential development for geochemical technologies?

# Analytical Technology Development

- Successful unconventional exploration acquires high fluid quality/mobility with maturity > ~0.9% VRE.
- At such maturity, many source-related biomarkers are already cracked to low concentrations and can not be detected by current analytical instruments
- Shall we collaborate with analytical chemists and engineers to develop instruments capable of much greater selectivity and sensitivity?
- Can we use distributions of large diamondoids to allocate unconventional oils?



# Analytical Technology Development



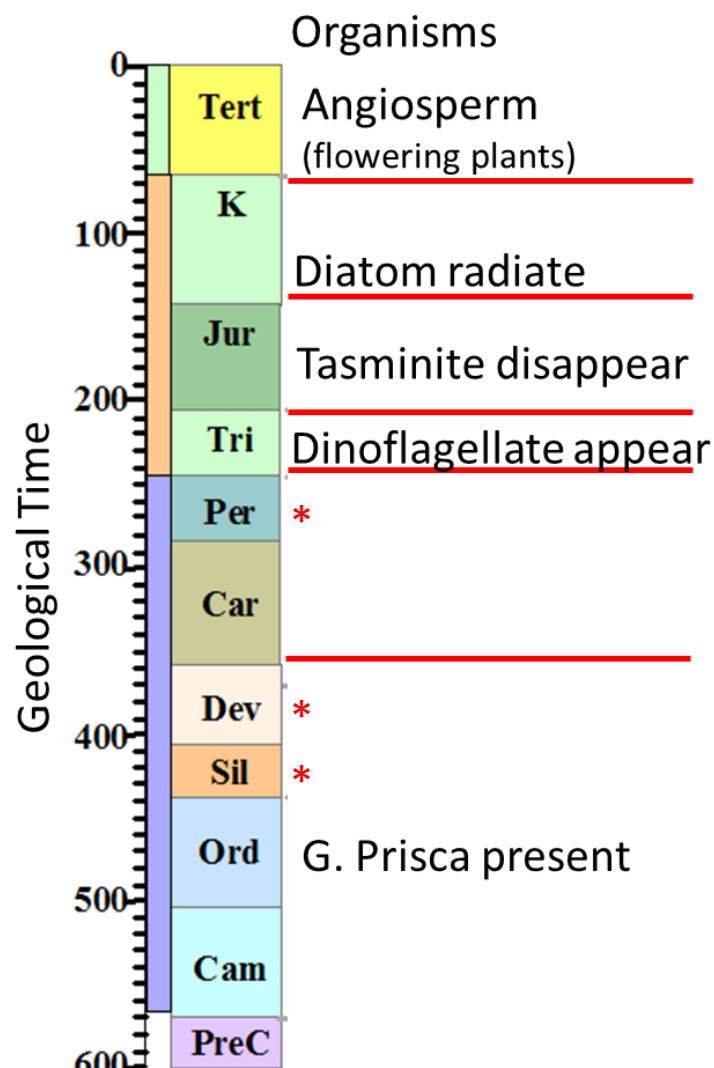
(Biomarker Technology Inc.)

Current Effort from BTI:

Comparison of GC-MS-MS analyses by QQQ-GCMSMS of biomarkers in a highly mature light oil from the North Slope of Alaska.

Recently developed analytical enhancement (a) helps increase signal/noise factor by about one order of magnitude compared with traditional methodology (b)

# Age-Related Biomarker Gaps?



## Age-Related Biomarkers (examples)

Oleanane

C<sub>26</sub> 24-norcholestanes and 24-nordiacholestane

Tricyclic terpanes

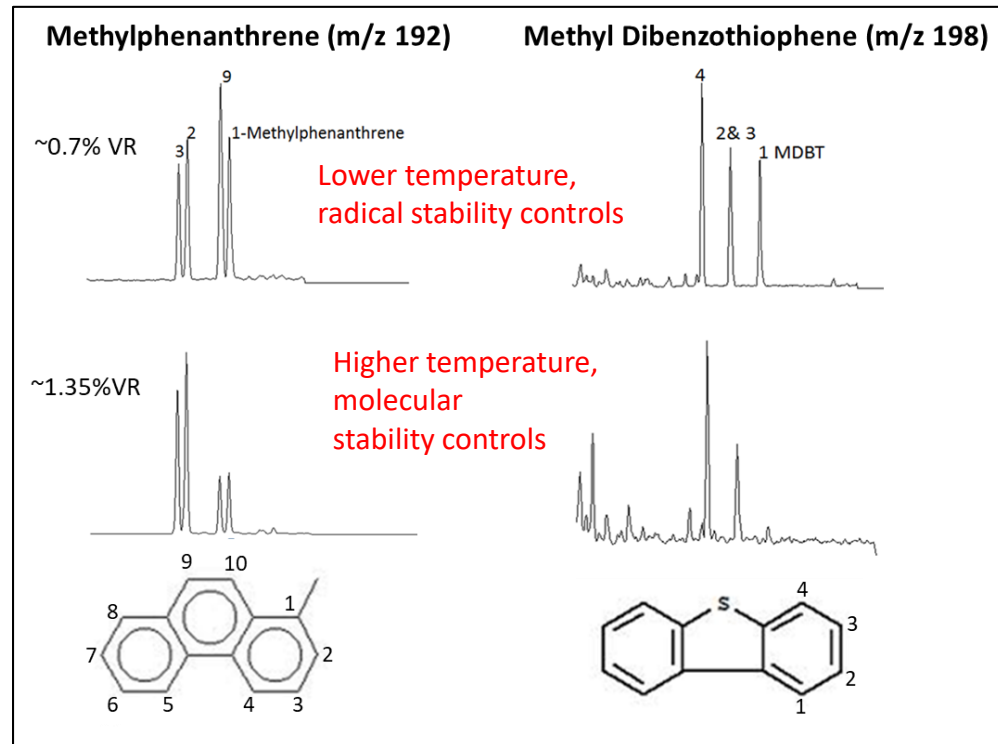
Triaromatic dinosteroids

- Controlling factors on biological organism evolution:
  - Radiation of new species after a global mass extinction.
  - Disappearance of species after a global mass extinction.
  - Big changes in biota with a change in climate or oceanographic conditions.
- Gaps for key source rocks? Which are key exploration target for source rock plays?
  - Paleozoic age: Permian, Silurian
  - Upper vs. Low Cretaceous ages?



# Improve Thermal Maturity Calibration?

- Improve thermal maturity calibration by identifying most maturity-sensitive markers/ratios
- Fundamental understanding of isomer stability for hydrocarbon compounds:
  - At 333K (60 °C), reaction time (1/k)  $\sim 4 \cdot 10^{20}$  seconds =  $1.3 \cdot 10^{13}$  years. the ratio of the isomers should be determined by the relative stabilities of the radicals (intermediates).
  - At 423K (150 °C), reaction time (1/k)  $\sim 5 \cdot 10^{13}$  seconds = 1.6 million years. the ratio of the isomers should be determined by the relative stabilities of the final products.
  - The reaction must be aided by some substances, e.g. some transition metals (ions or compounds) or acids.

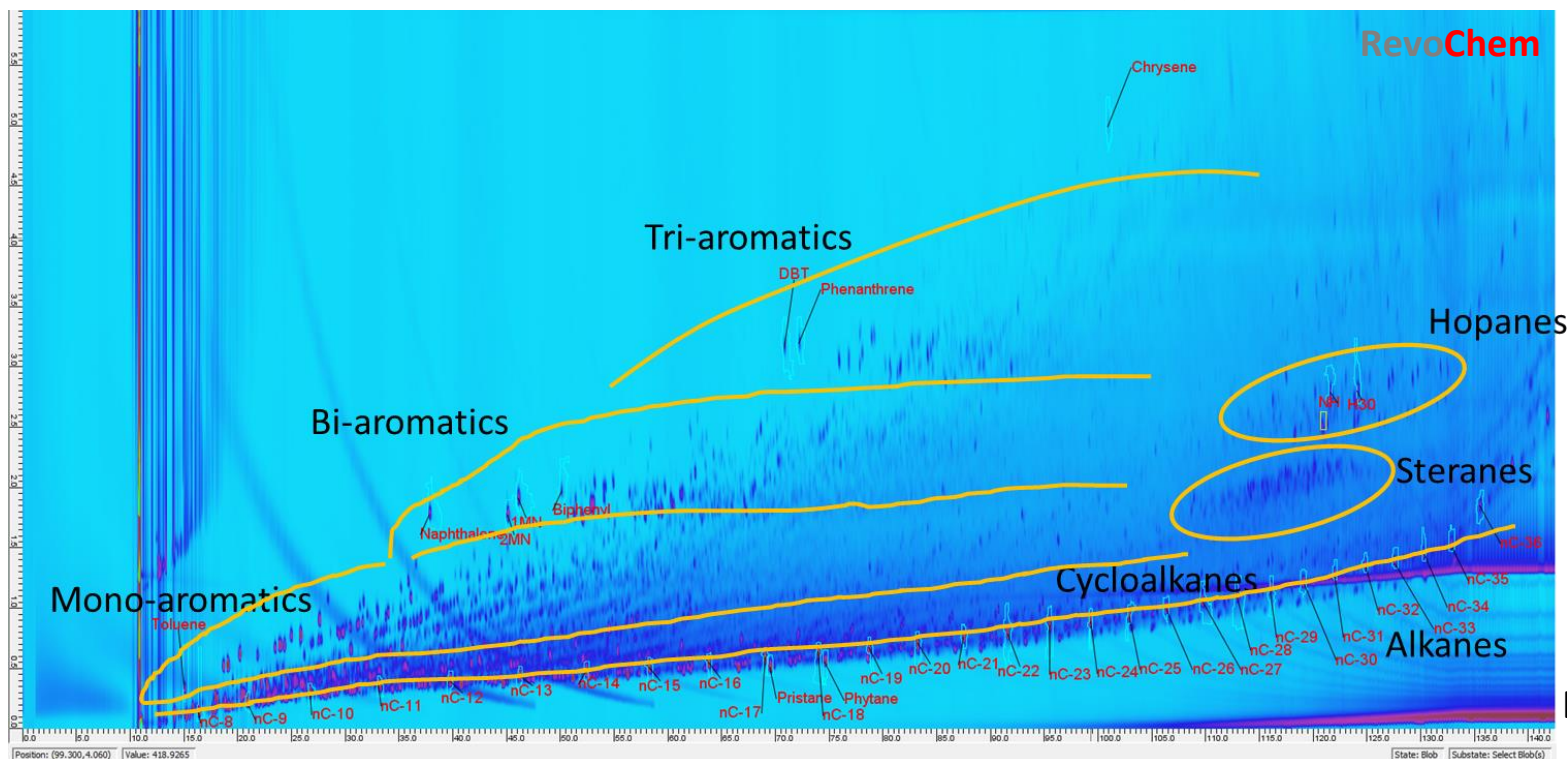


| m/z | Compounds | Molecular stability |                   |                              | Radical stability |                   |                              |
|-----|-----------|---------------------|-------------------|------------------------------|-------------------|-------------------|------------------------------|
|     |           | Energy (a.u)        | Energy (kcal/mol) | Normalized Energy (kcal/mol) | Energy (a.u)      | Energy (kcal/mol) | Normalized Energy (kcal/mol) |
| 192 | 1-MP      | -578.8916168        | -363260.05152526  | 1.3598                       | -538.8838297      | -338154.78076790  | 0.0359                       |
|     | 2-MP      | -578.8937837        | -363261.41130093  | 0.0000                       | -538.883419       | -338154.52305598  | 0.2936                       |
|     | 3-MP      | -578.8930551        | -363260.95410371  | 0.4572                       | -538.883824       | -338154.77719109  | 0.0395                       |
|     | 9-MP      | -578.8923345        | -363260.50190146  | 0.9094                       | -538.883869       | -338154.81664262  | 0.0000                       |
| 198 | 1-MDBT    | -899.6540824        | -564541.9332      | 2.5073                       | -859.6478142      | -539437.5999      | 0                            |
|     | 2-MDBT    | -899.6565937        | -564543.5091      | 0.9315                       | -859.6465364      | -539436.798       | 0.8019                       |
|     | 3-MDBT    | -899.6566341        | -564543.5345      | 0.9061                       | -859.6468477      | -539436.9934      | 0.6065                       |
|     | 4-MDBT    | -899.6580781        | -564544.4406      | 0.0000                       | -859.6466132      | -539436.8463      | 0.7536                       |

# Geochemistry + Big Data

- Geochemical analysis often produces “Big Data”. Through data analytic approach on quality data, what information we can extract?
  - Better fluid property prediction?
  - New biomarker development?
  - Reservoir quality estimation?
  - More accurate production allocation?

GCXGC technology resolves ~2,000 to 3,000 compounds



Dr. Faye Liu

# Lots of Other E&P Questions

- Mobile vs. in-situ fluid?
- Production CGR vs. in-situ CGR?
- And more...

# Be A Strong Advocate of Geochemistry in Your Company!

- Always advertise importance of geochemistry as a cost-effective and fundamental tool for exploration & production
- As geochemists:
  - Deliver solid technical work:
    - Don't overinterpret data
    - Integrate with other disciplines
  - Keep learning
  - Mentor new geochemists
  - Collaborate/Support R&D development
  - Advocate for the use of advanced technologies to improve interpretive capabilities



# Acknowledgement

- ConocoPhillips Management: Kristie McLin, Stephanie Erickson
- ConocoPhillips Colleagues: Eric Michael, Brad Huizinga, Albert Holba...
- Shell Colleagues: Andy Bishop, Alan Konachi, and many others...
- Ph.D. Supervisor and Committees: J. Mike Moldowan, Ken Peters, Jeremy Dahl...