Determination and Quantification of Petroleum Mixtures*

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Abstract

Petroleum accumulations are often derived from multiple source rocks. Basin analyses and petroleum system models that fail to include all the active sources indicated by such mixtures miss potential exploration targets, while models that assume unrealized sources may lead to dry holes. Yet such crude oil mixtures often escape recognition, and quantification of the source components is elusive.

Crude oil mixtures can be unraveled by using new geochemical technologies with high source and maturation specificity. The following analyses can reveal most mixtures:

1. Quantitative diamondoid analysis reveals deep gas and light oil sources that can be masked in mixtures with black oil.
2. Diamondoids of the deep source predominate in such mixtures, and compound specific isotope analysis of the diamondoids (CSIA-D) can be used to identify the deep source.
3. A plethora of age-related biomarker parameters can be used to constrain the shallow source.
4. Biomarkers can differ enormously in their isotope ratios. For example, C29 hopanes in marine and lacustrine oil sources of the South Atlantic margins typically differ by > 14 ‰! Oil mixed from pre-salt and post-salt sources can thus be unraveled.
5. Marine-derived C30 steranes can now be analyzed with two to three orders of magnitude better sensitivity. This analysis detects marine oil contribution to lacustrine oil accumulations down to levels < 1 %!

Once oil mixtures are determined, quantification of the contributors can be made. The better the data bases of the key parameters analyzed in unmixed end-member oil samples, the more precise such quantitative determinations can be achieved. Protocols to tighten-up quantitative determinations are discussed.

In the South Atlantic margin of Brazil the presence or absence of contribution from either the lacustrine or marine source in a given area has important consequences for exploration. Basin models derived from various co-sourcing scenarios is discussed.

References

Dahl, J.E., J.M. Moldowan, K.E. Peters, G.E. Claypool, M.A. Rooney, G.E. Michael, M.R. Mello, and M. L. Kohnen, 1999, Diamondoid hydrocarbons as indicators of natural oil cracking: Nature, v. 399, p. 54-57.

Barbanti, S., M. Moldowan, P. Brooks, and D. Watt, 2009, New triaromatic steroids with taxon and age-specificity (oral presentation): 24th International Meeting on Organic Geochemistry, Bremen, Germany, September 6-11, 2009, Web accessed June 22, 2010, www.imog2009.org.

Determination and Quantification of Petroleum Mixtures

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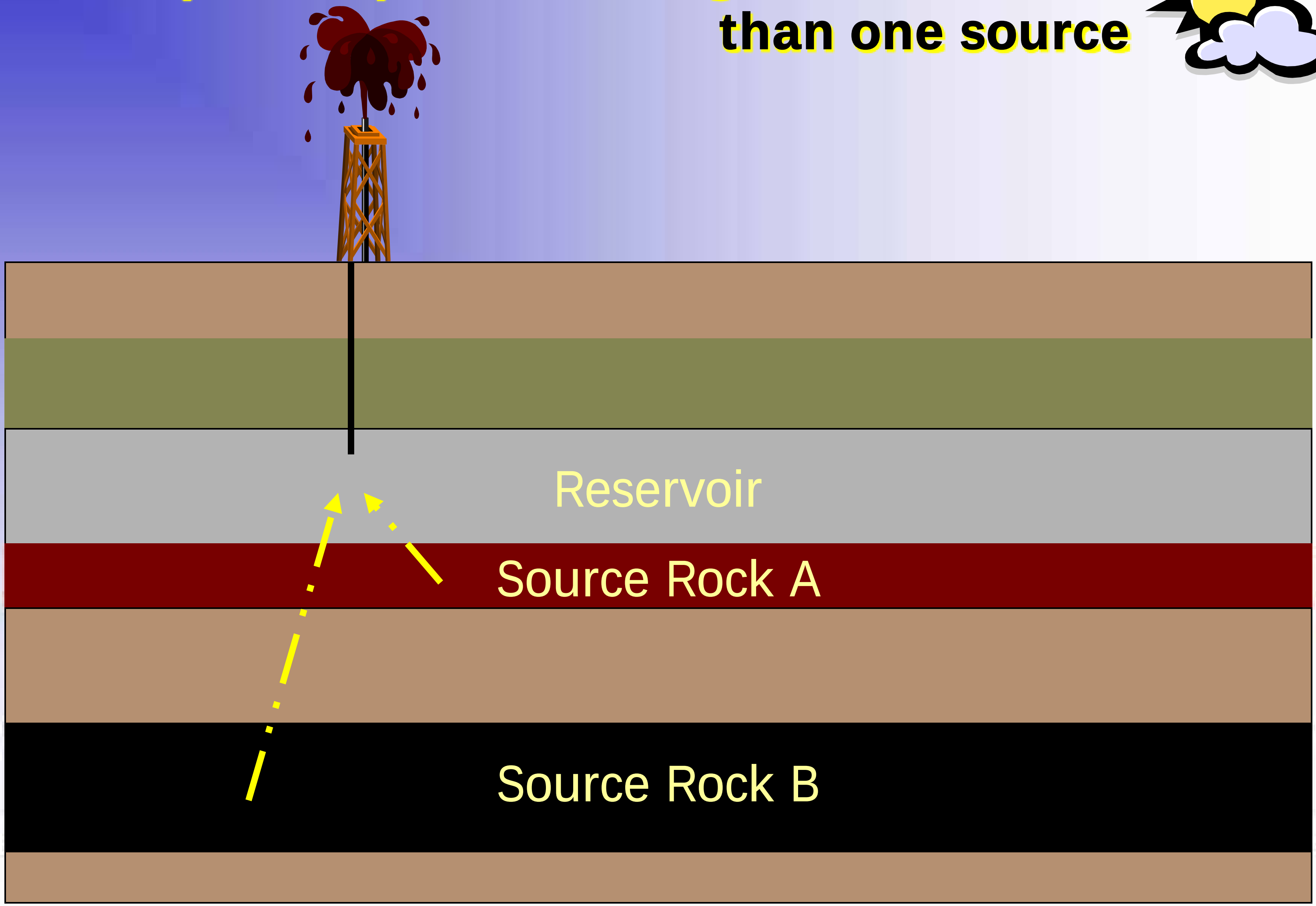
Most prolific petroleum regions have more than one source



Examples include:

- Gulf of Mexico
- Middle East
- Venezuela
- West Africa
- Brazilian Margin
- North Sea
- Alaska North Slope

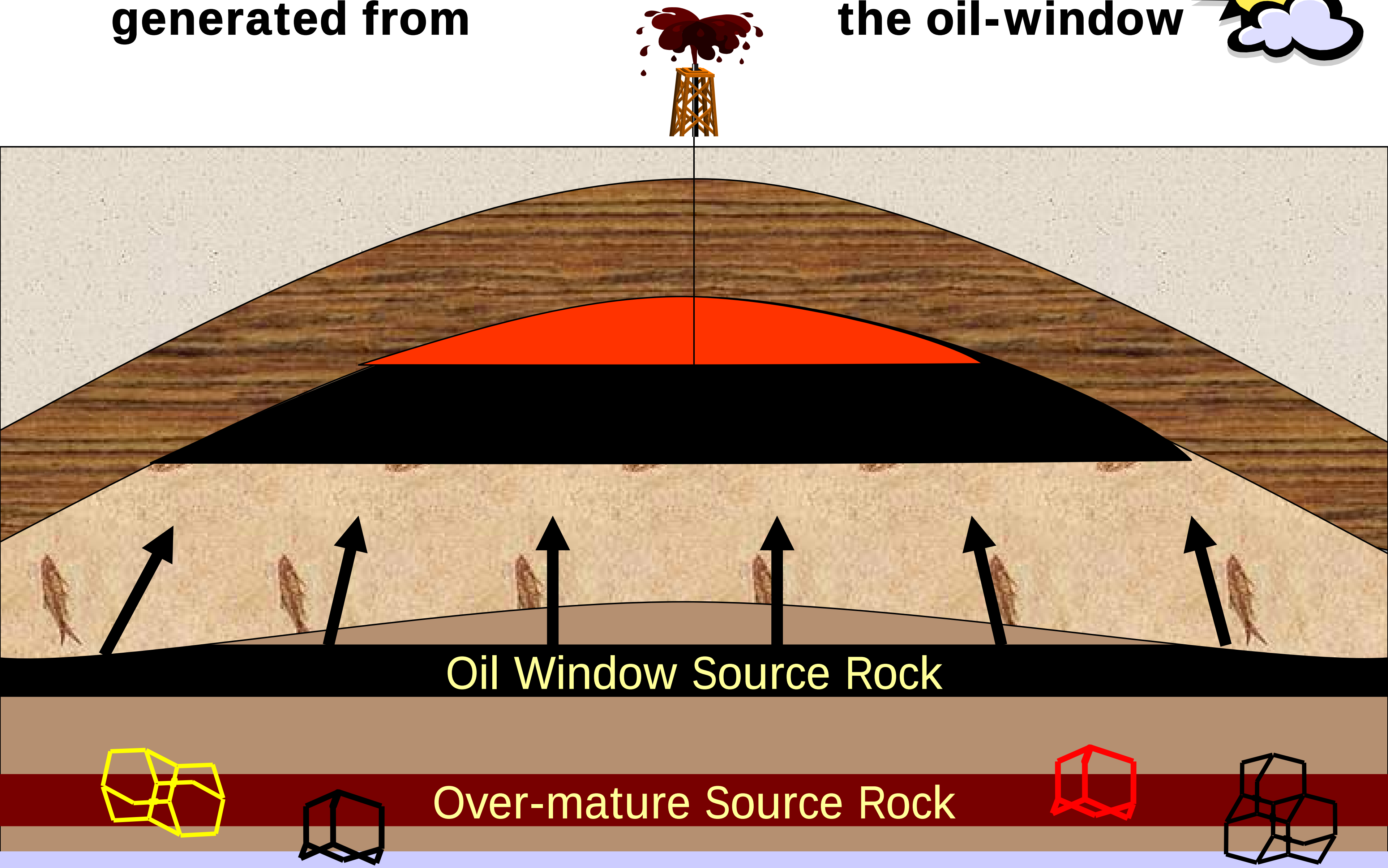
Mixed petroleum may not be self-evident
Case I: Mixed black oil with cracked oil

- PROBLEM: The biomarker-rich source often masks the biomarker-poor source in common GCMS analysis

- RESULT: The biomarker-poor source, which is usually the more mature and deeper source, can be missed

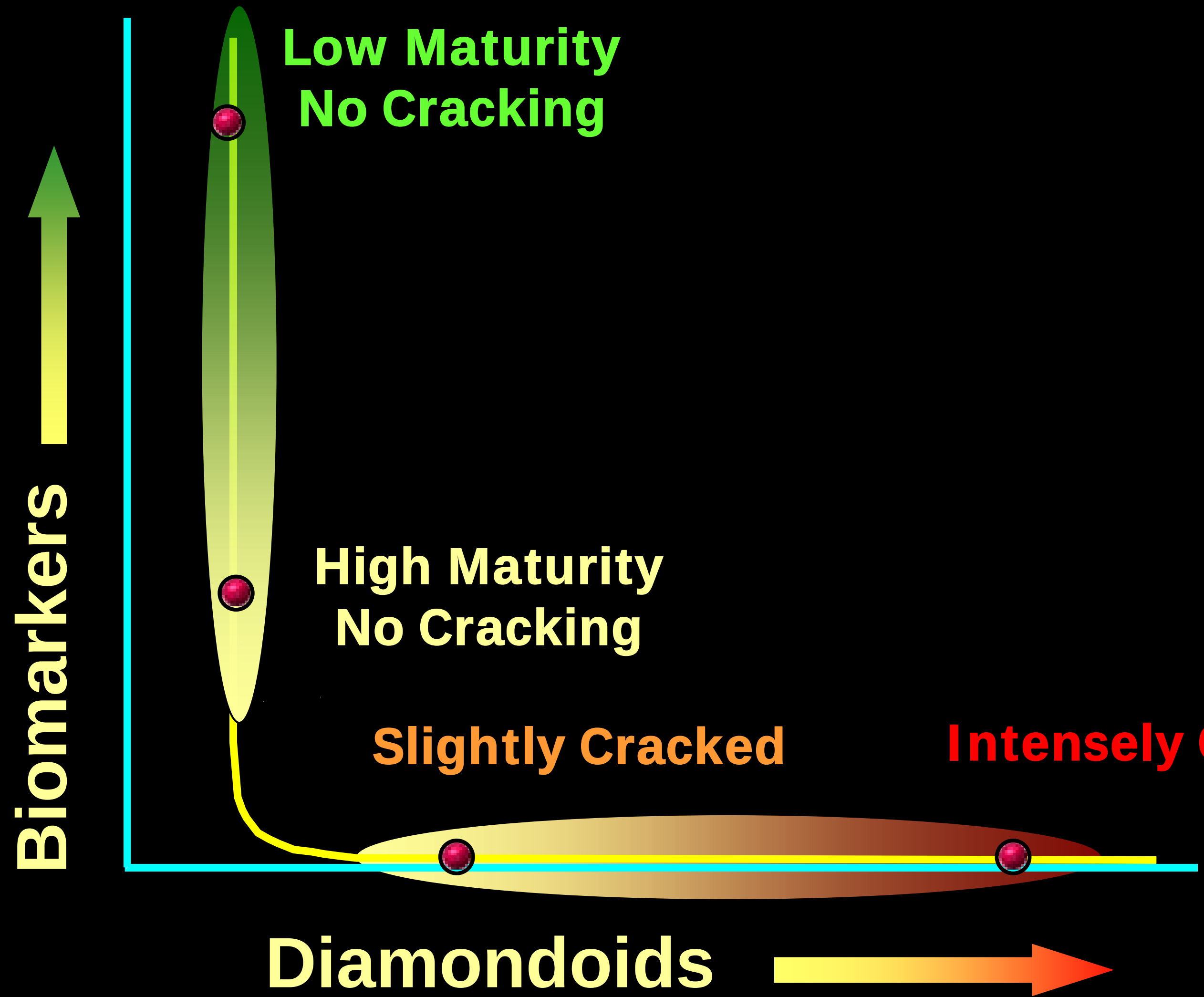
- Solution: The use of diamondoids offers a possible solution

Biomarkers only reveal the charge component generated from the oil-window



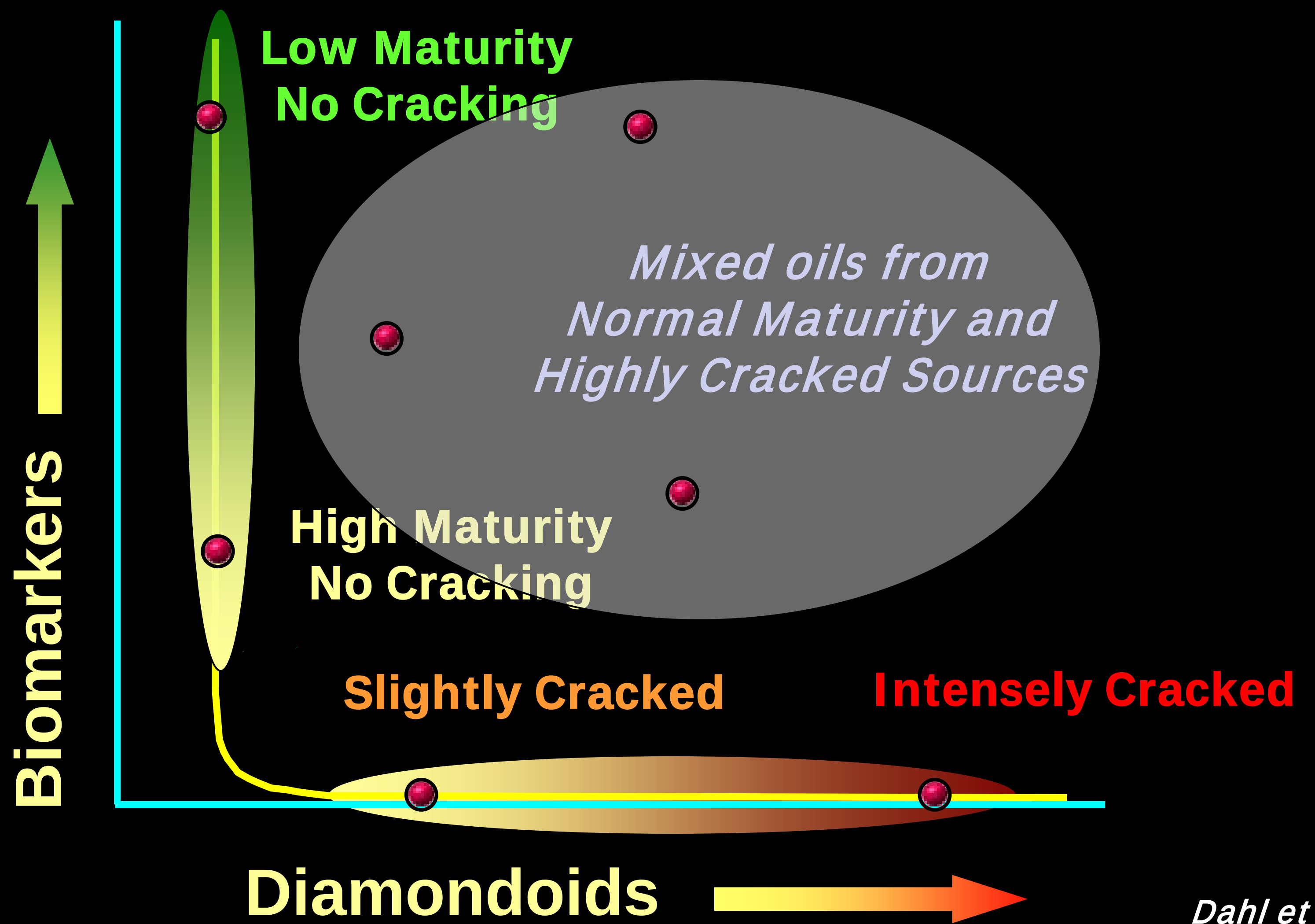
The deep source is revealed by using diamondoids

Diamondoids provide a means to recognize thermally cracked oil



Dahl et al., 1999

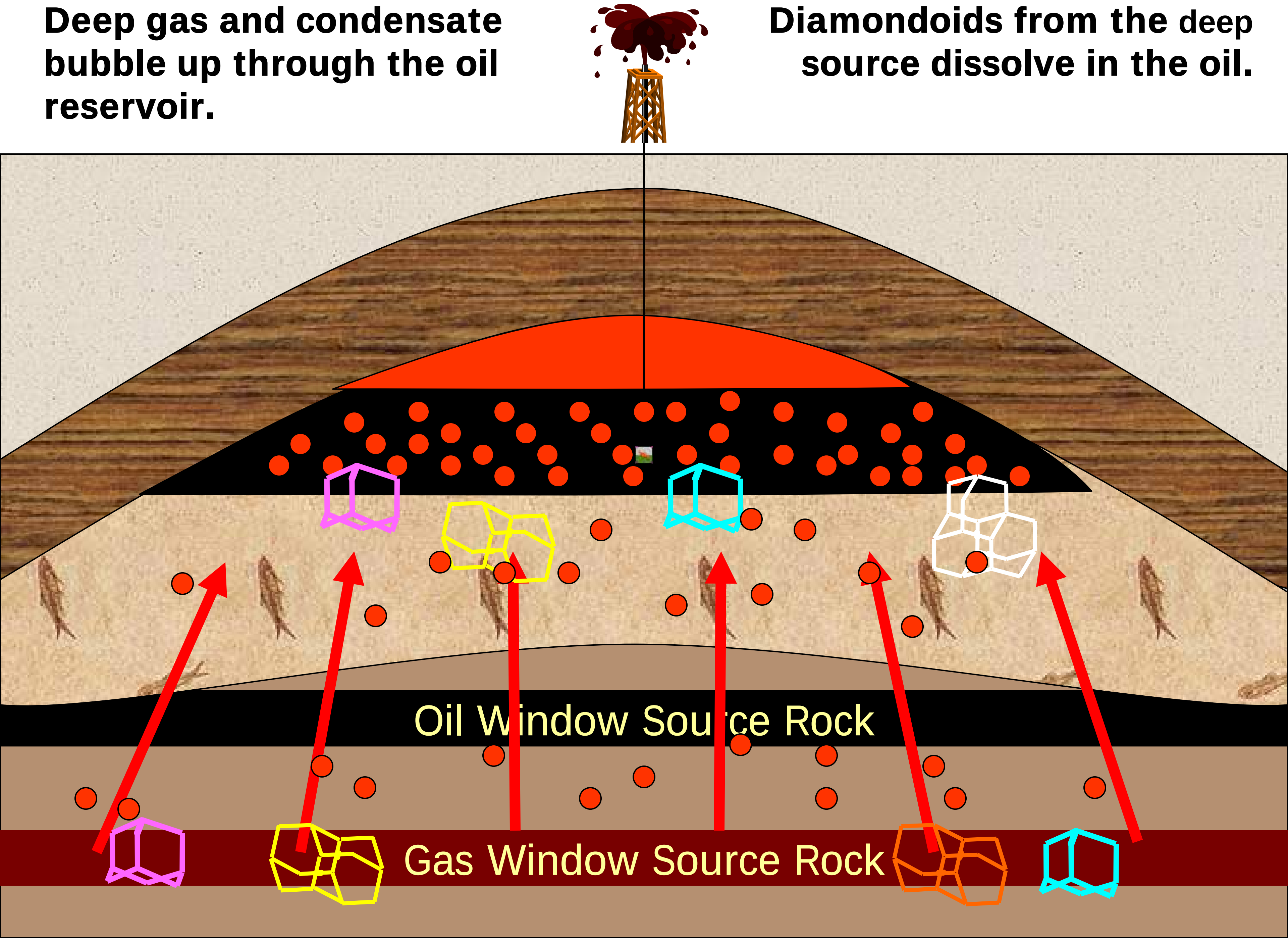
Diamondoids provide a means to recognize cracked oil – black oil mixtures



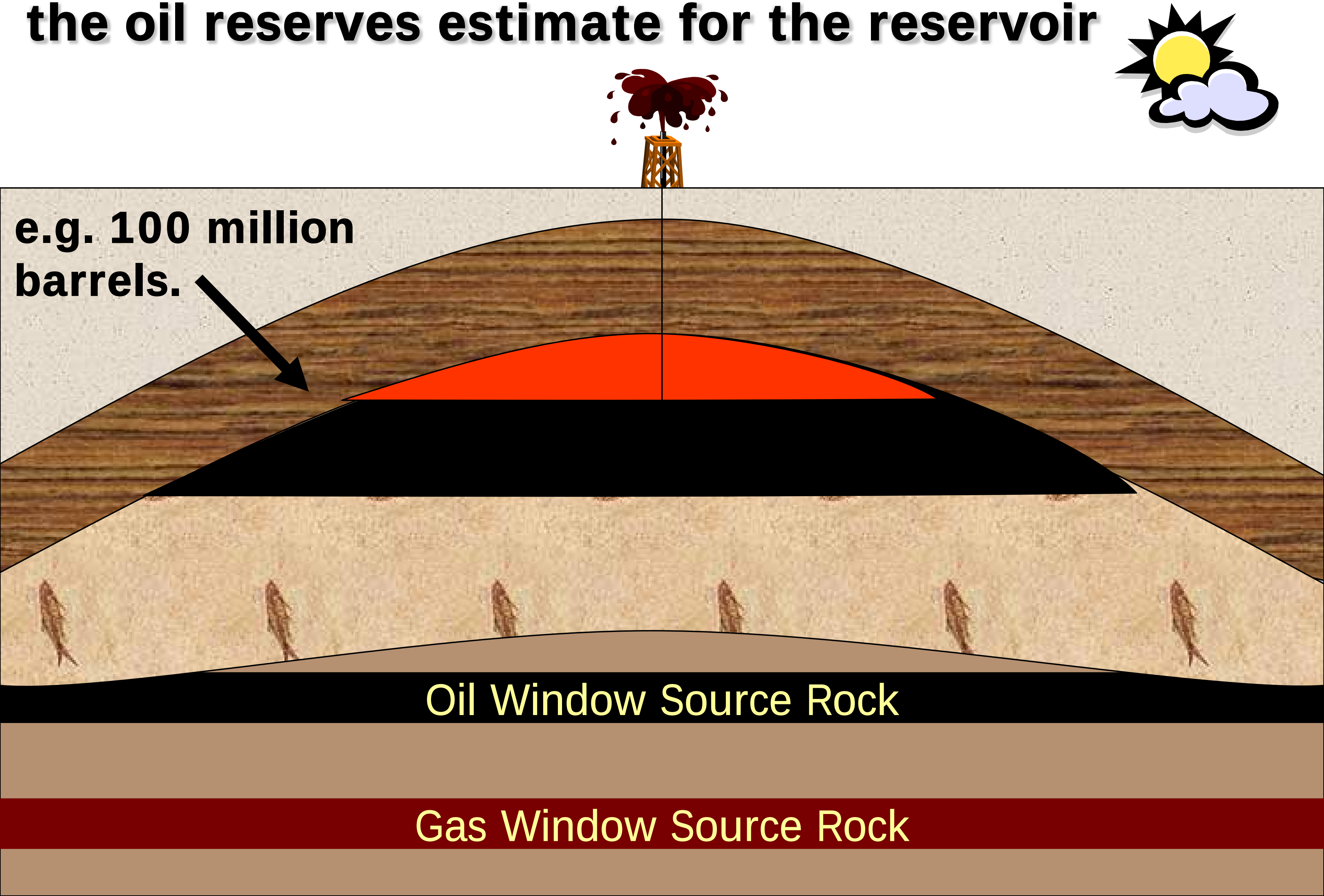
Dahl et al., 1999

Deep gas and condensate bubble up through the oil reservoir.

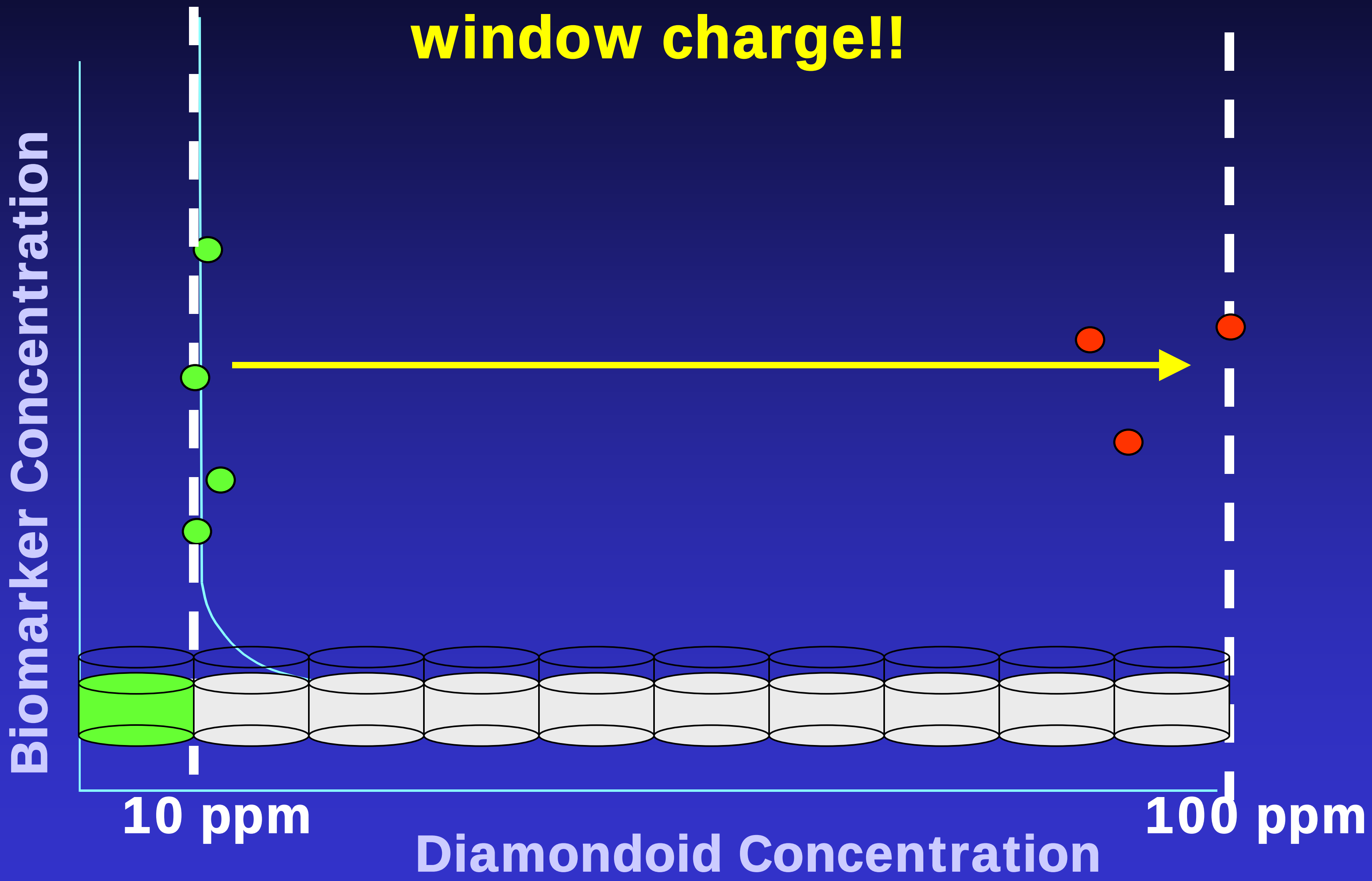
Diamondoids from the deep source dissolve in the oil.



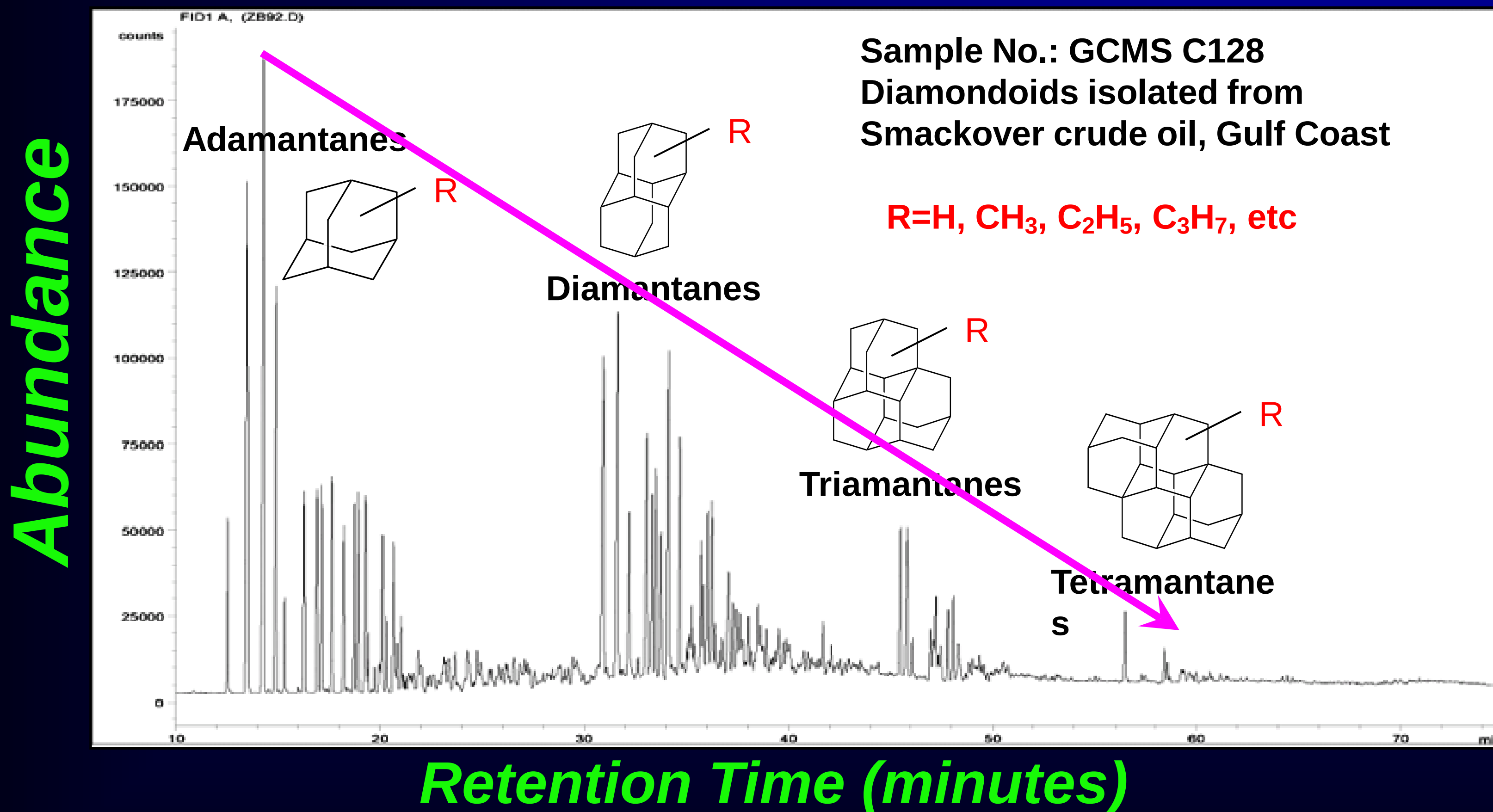
In order to calculate deep source charge, we use the oil reserves estimate for the reservoir



In this example the deep gas charge equivalent is 9 times greater than the oil-window charge!!



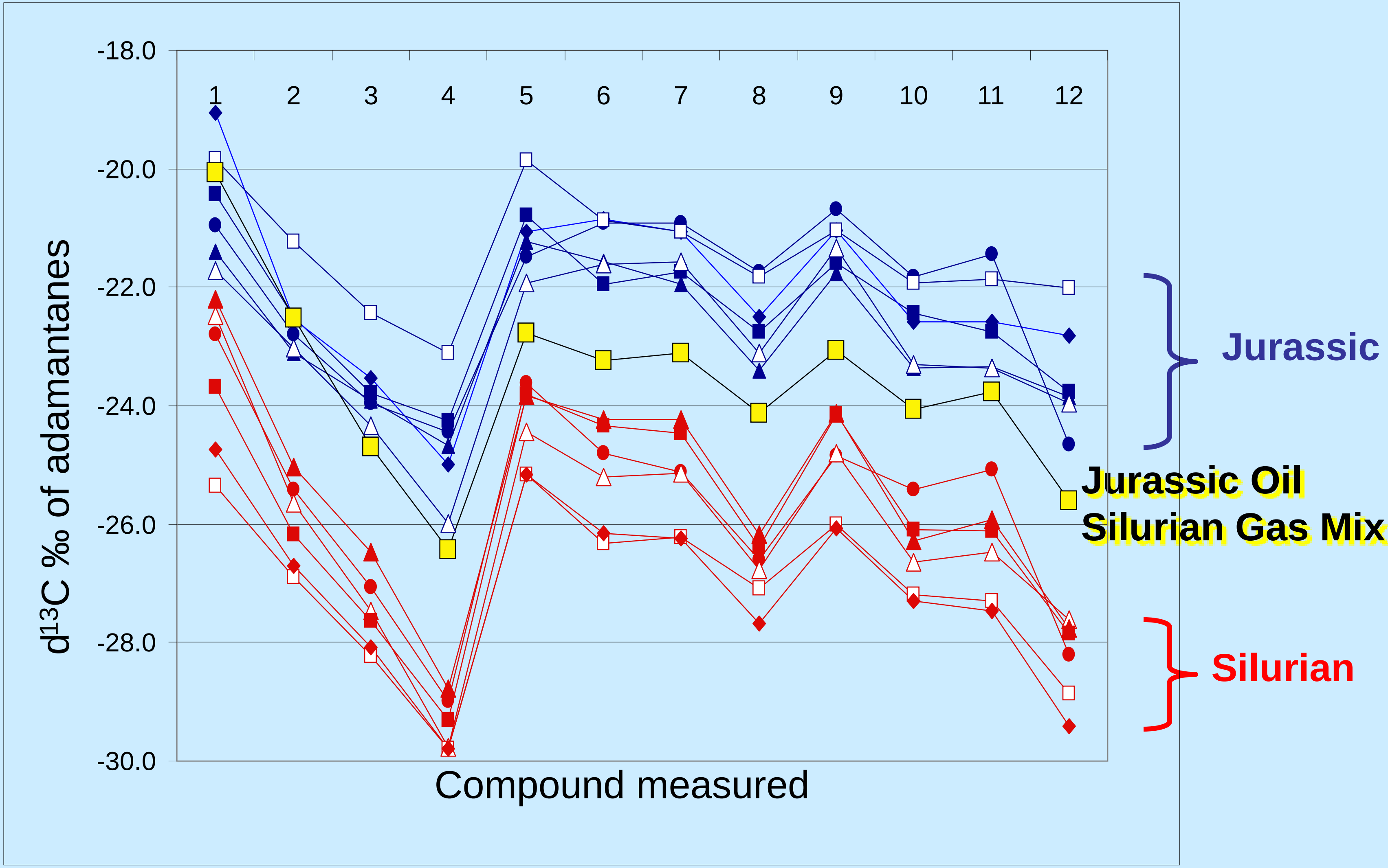
Diamondoids isolated from Petroleum



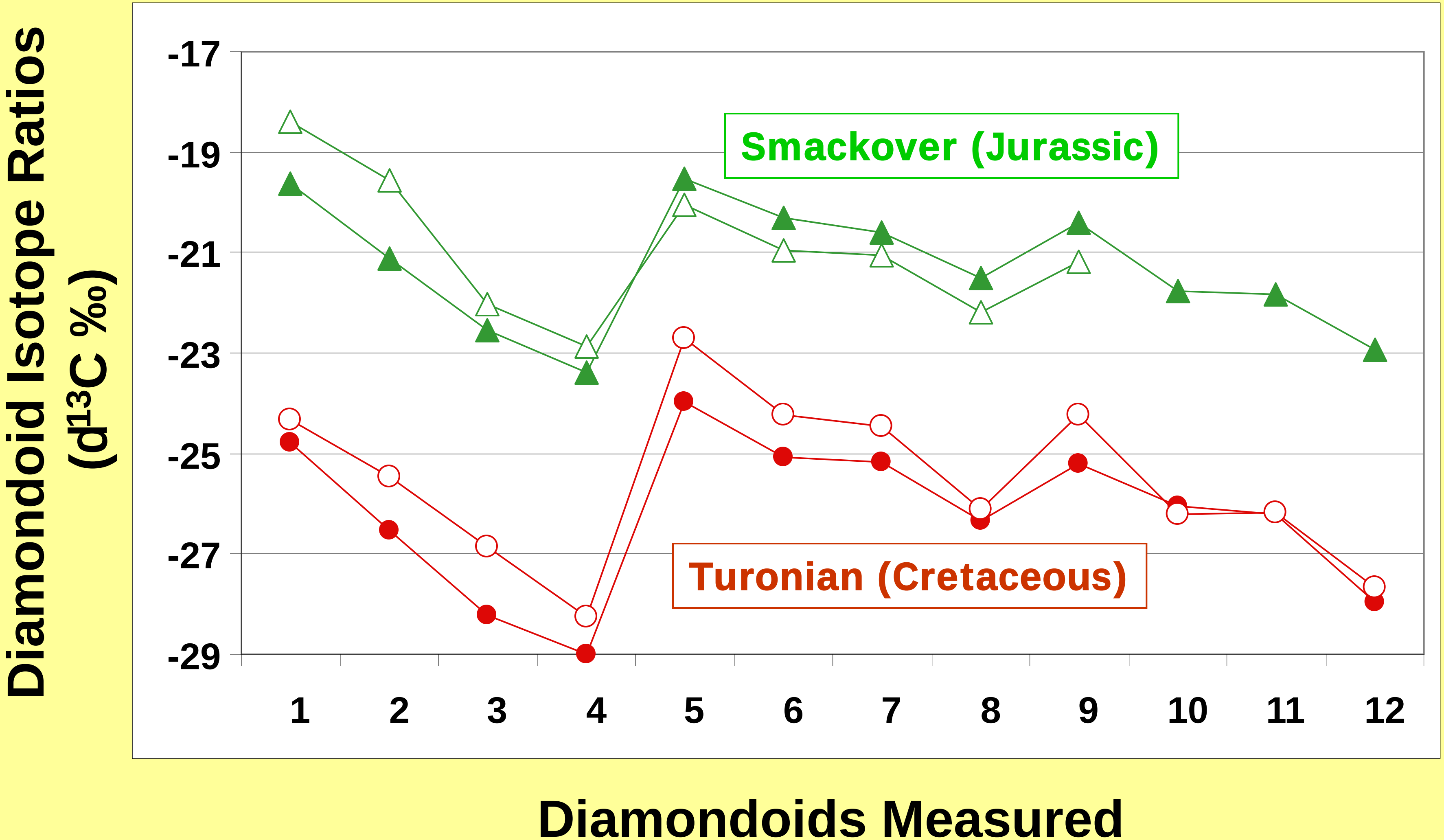
Key to Diamondoids Measured (X-axis) CSIAD

Compound Name	
Adamantane	1
1-Methyladamantane	2
1,3-Dimethyladamantane	3
1,3,5-Trimethyladamantane	4
2-Methyladamantane	5
1,4-Dimethyladamantane(*cis*)	6
1,4-Dimethyladamantane(*trans*)	7
1,3,6-Trimethyladamantane	8
1,2-Dimethyladamantane	9
1,3,4-Trimethyladamantane(cis)	10
1,3,4-Trimethyladamantane(trans)	11
1,2,5,7-Tetramethyladamantane	12

Jurassic and Silurian Sourced Oils Are Distinguished using CSIA-D Middle East



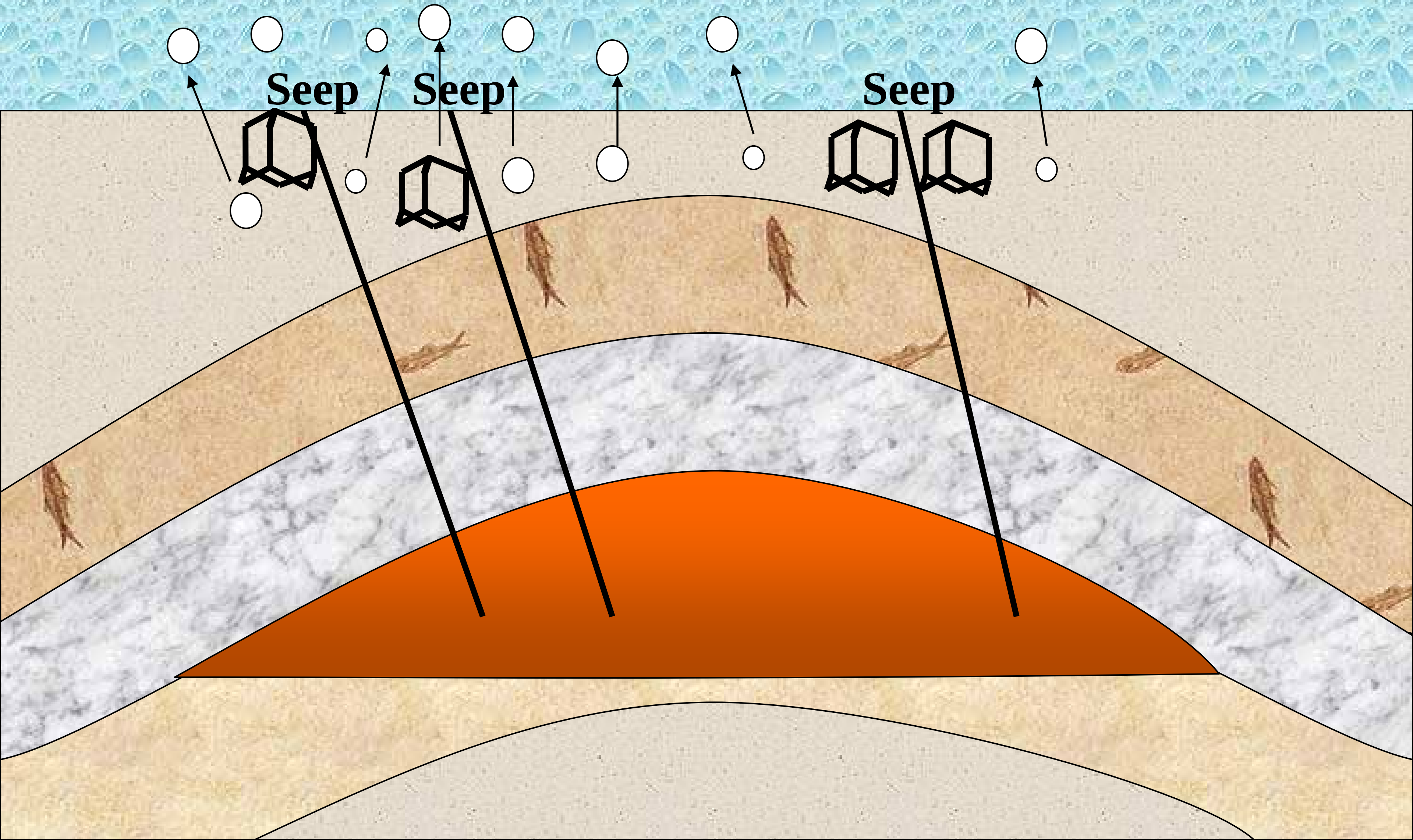
Diamondoid isotopes distinguish certain oil families in the Gulf of Mexico



Gas and Oil Seep Detection in Piston Cores:

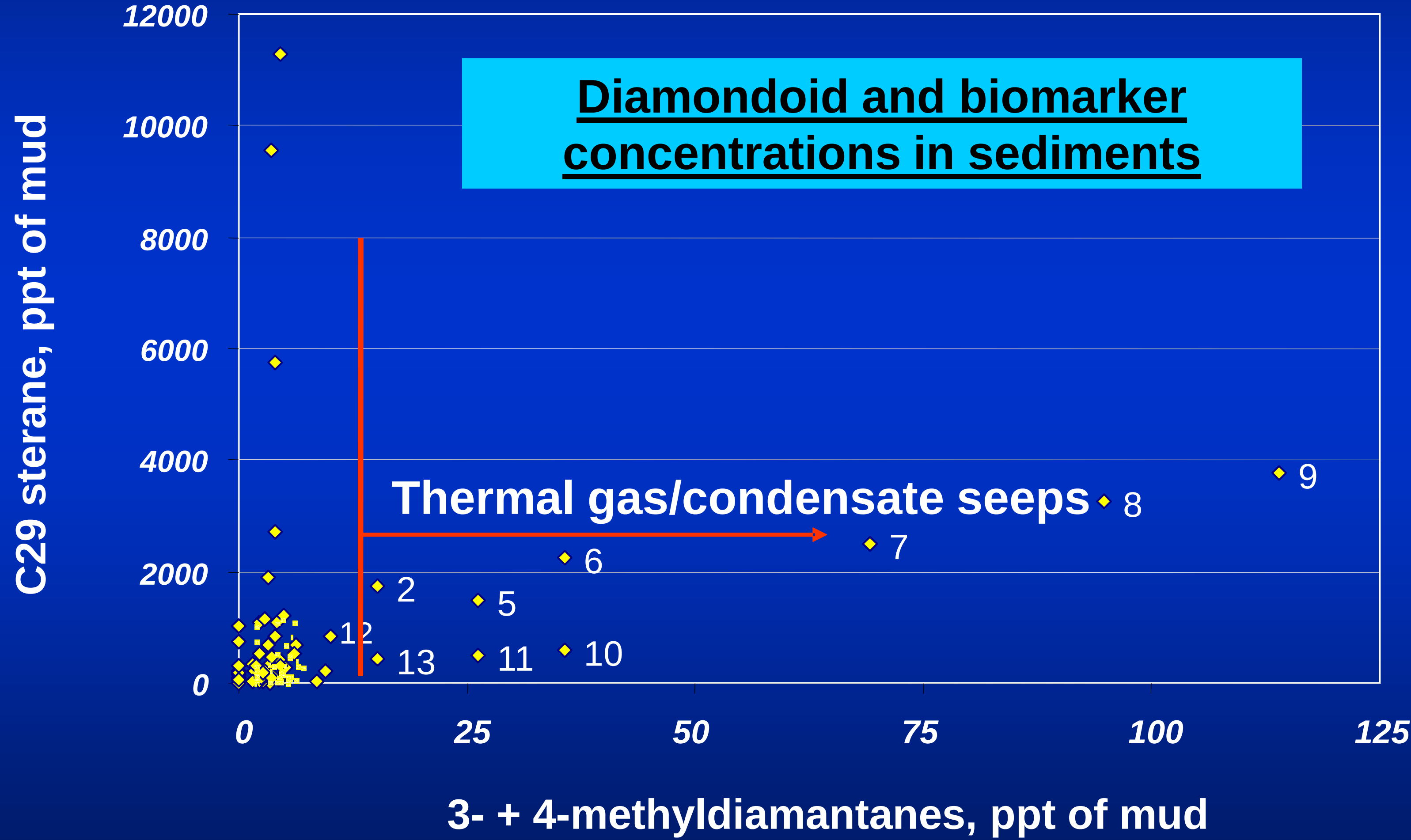
Diamondoids resist biodegradation, less volatile than gas.

Light oil and condensate diamondoid-rich, biomarker-poor.



DIAMONDOIDS IN PISTON CORES

Gas Seeps Are Identified in Atlantic Margin Sediments



ppt = parts per trillion

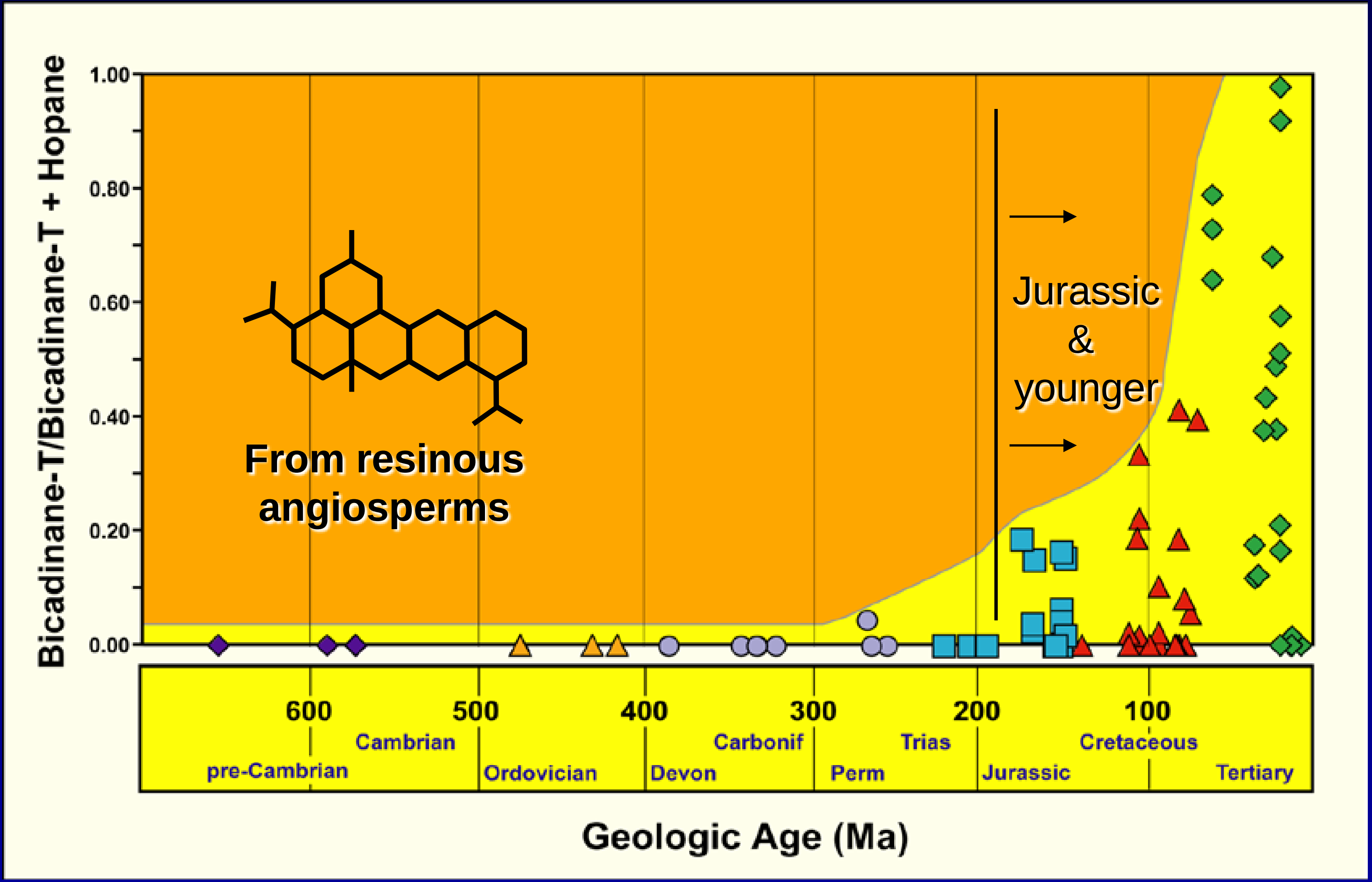
Mixed petroleum may not be self-evident
Case II: Mixed black oil with biomarkers

- PROBLEM: Age-related biomarkers come into the record and usually don’t go away at a later stage

- RESULT: The biomarker signature of an older source can be masked by that of a younger source

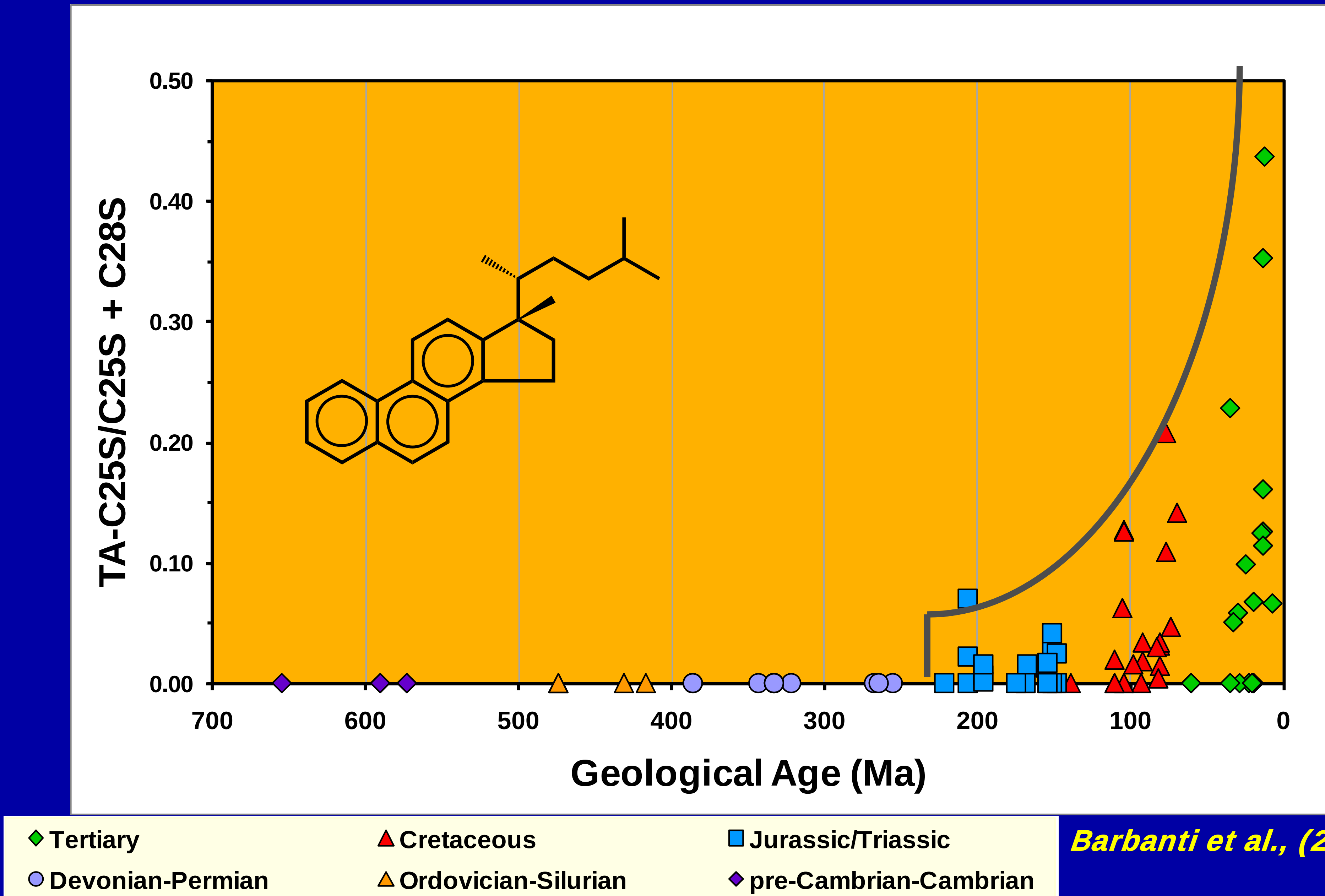
- SOLUTION: Find a unique compositional characteristic that differentiates the older source

Bicadinane index shows age-related curve which begins in the Jurassic



Barbanti and Moldowan, unpubl.

Occurrence of triaromatic 24-norcholesteroid is Jurassic and younger

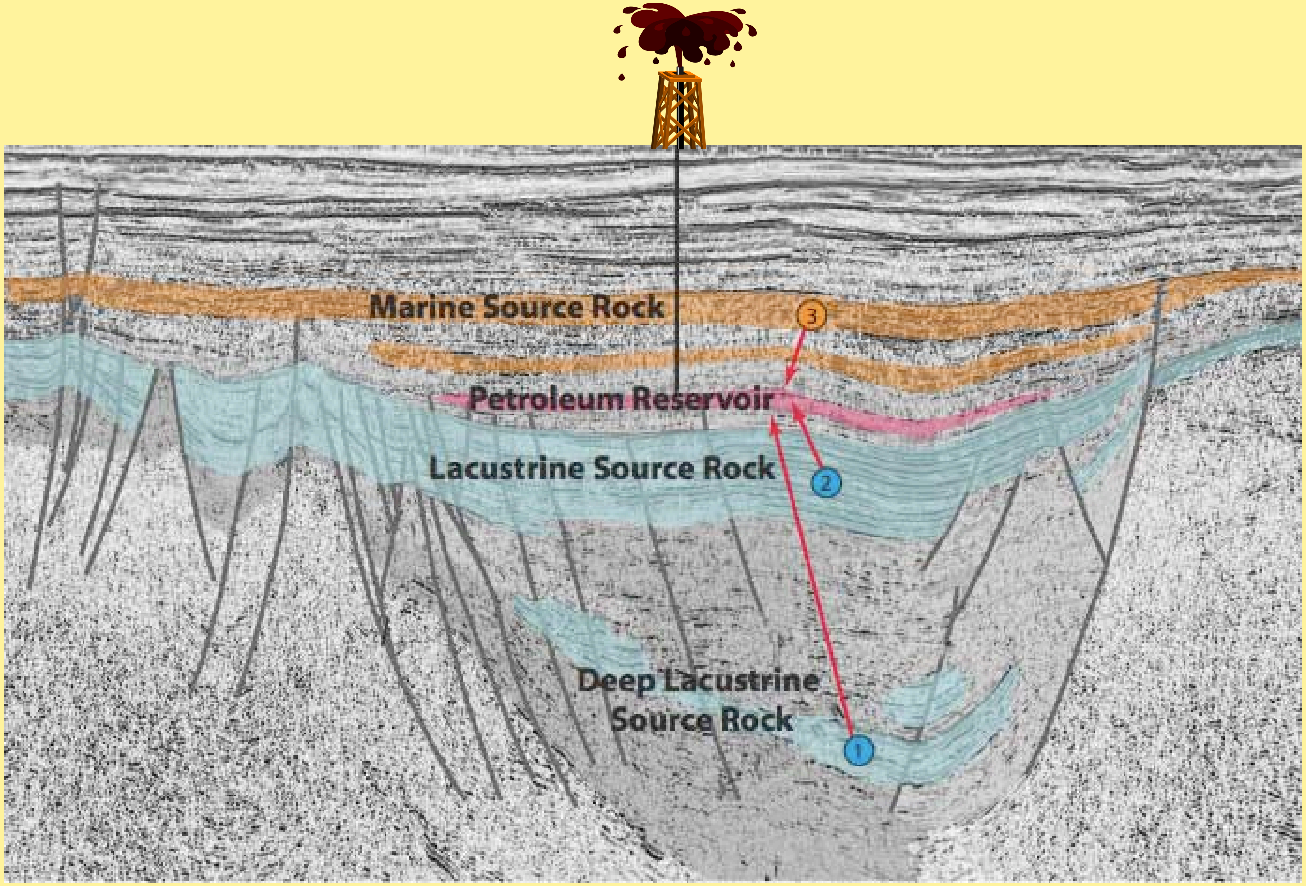


Barbanti et al., (2009)

Mixed petroleum may not be self-evident Case III: Mixed black oil from major and minor contributing sources (Corollary to Case II)

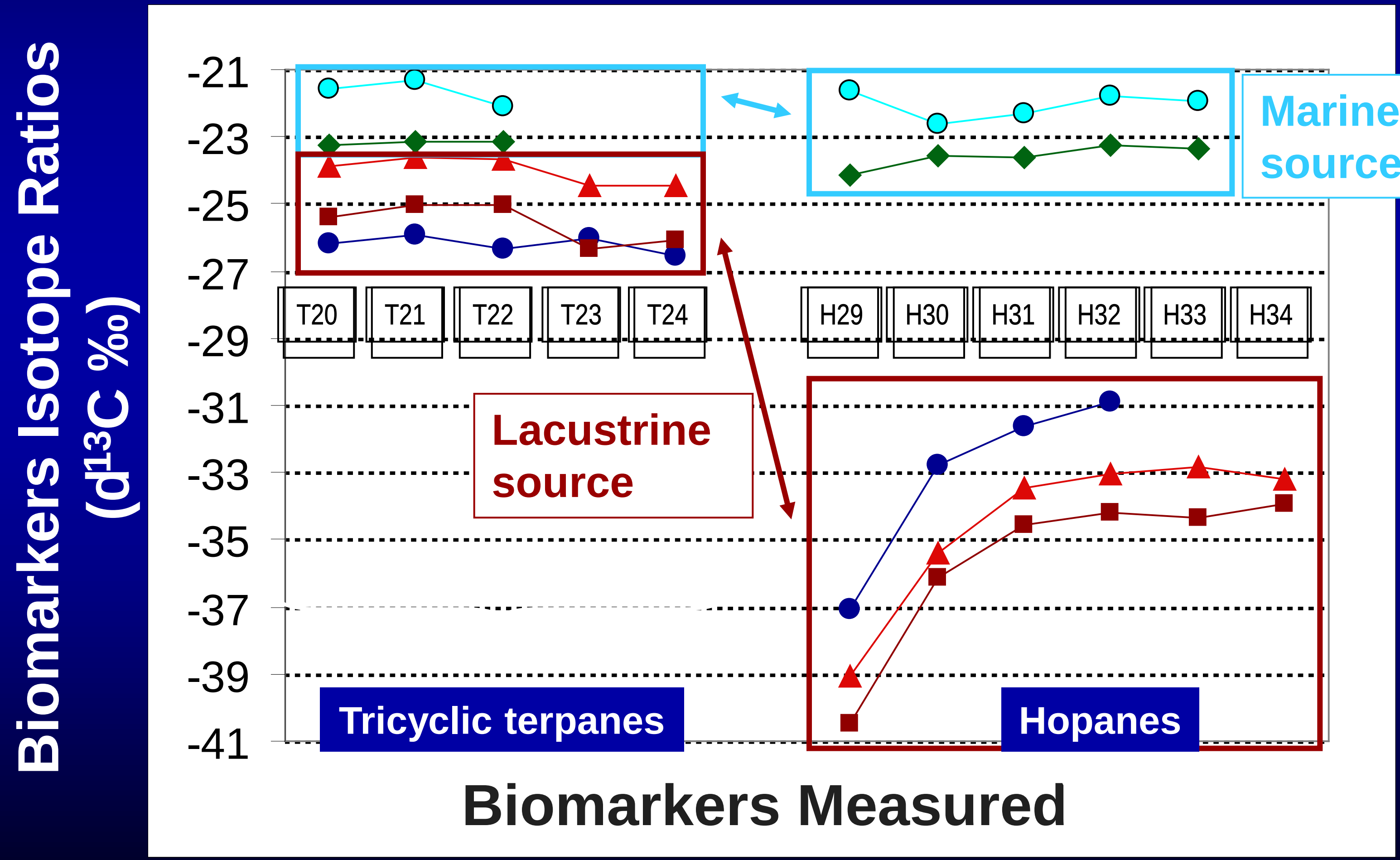
- PROBLEM: Minor sources, important for exploration, economics and basin modeling, can be overwhelmed by the major source fingerprint
- RESULT: The minor source can be missed
- SOLUTION: Utilize wide differences in oil composition between the two sources

Determining marine-lacustrine sourced mixes in the South Atlantic

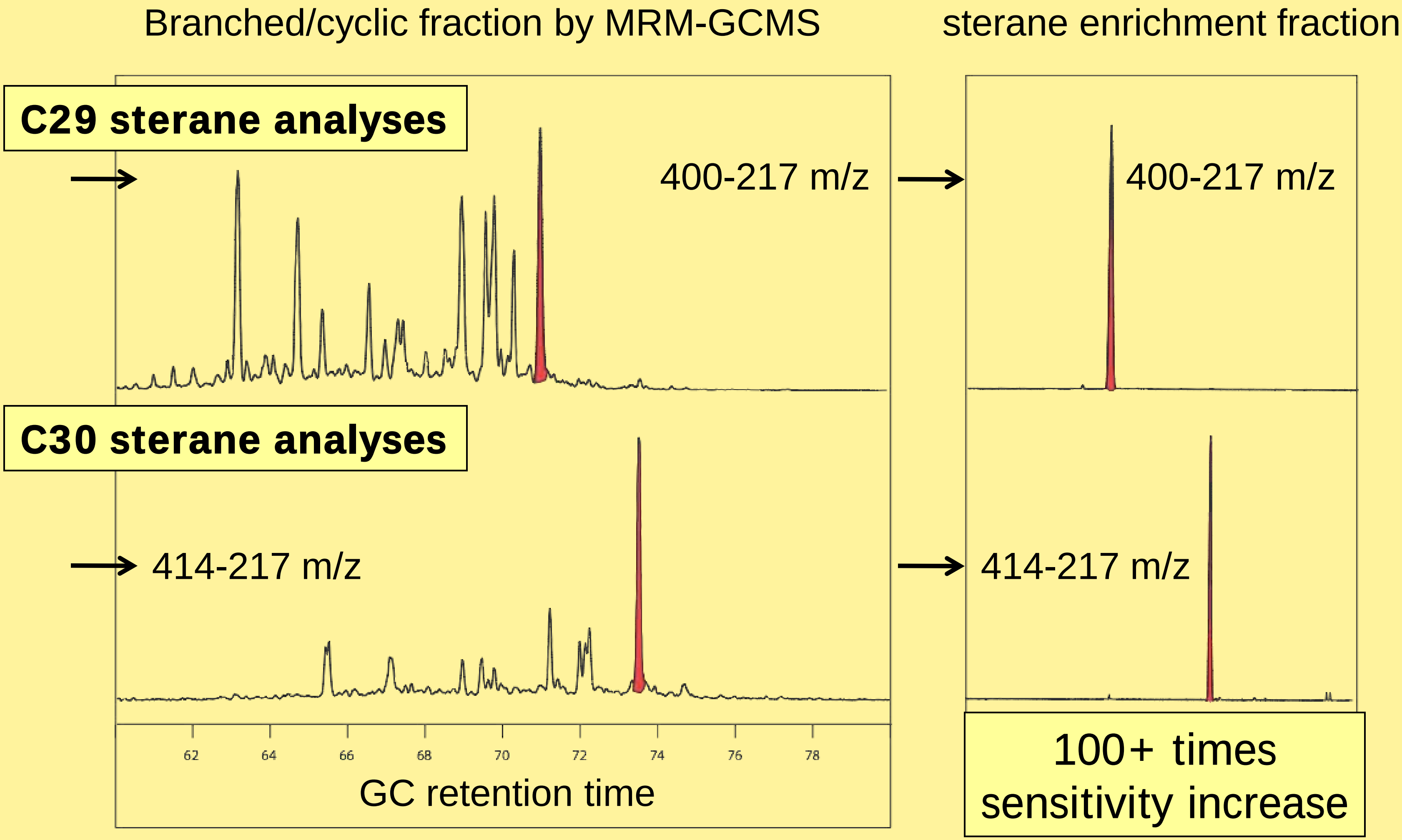


CSIAB distinguishes lacustrine from marine-sourced oil
For example: Brazil or Angola

The large difference between C29 hopane isotope composition can be used to quantify mixed-oil sources

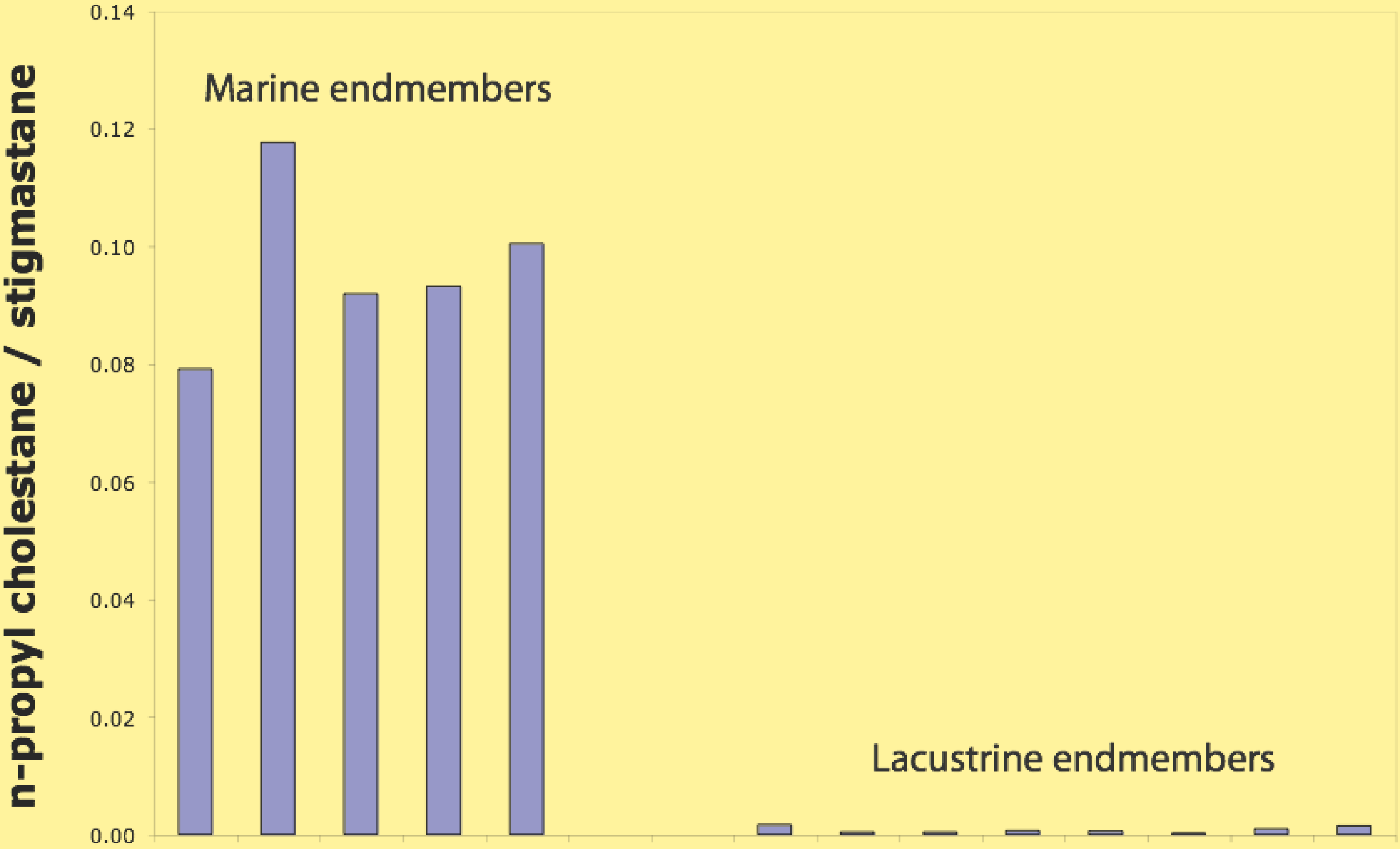


Isolation from chemical noise for improved detection limits

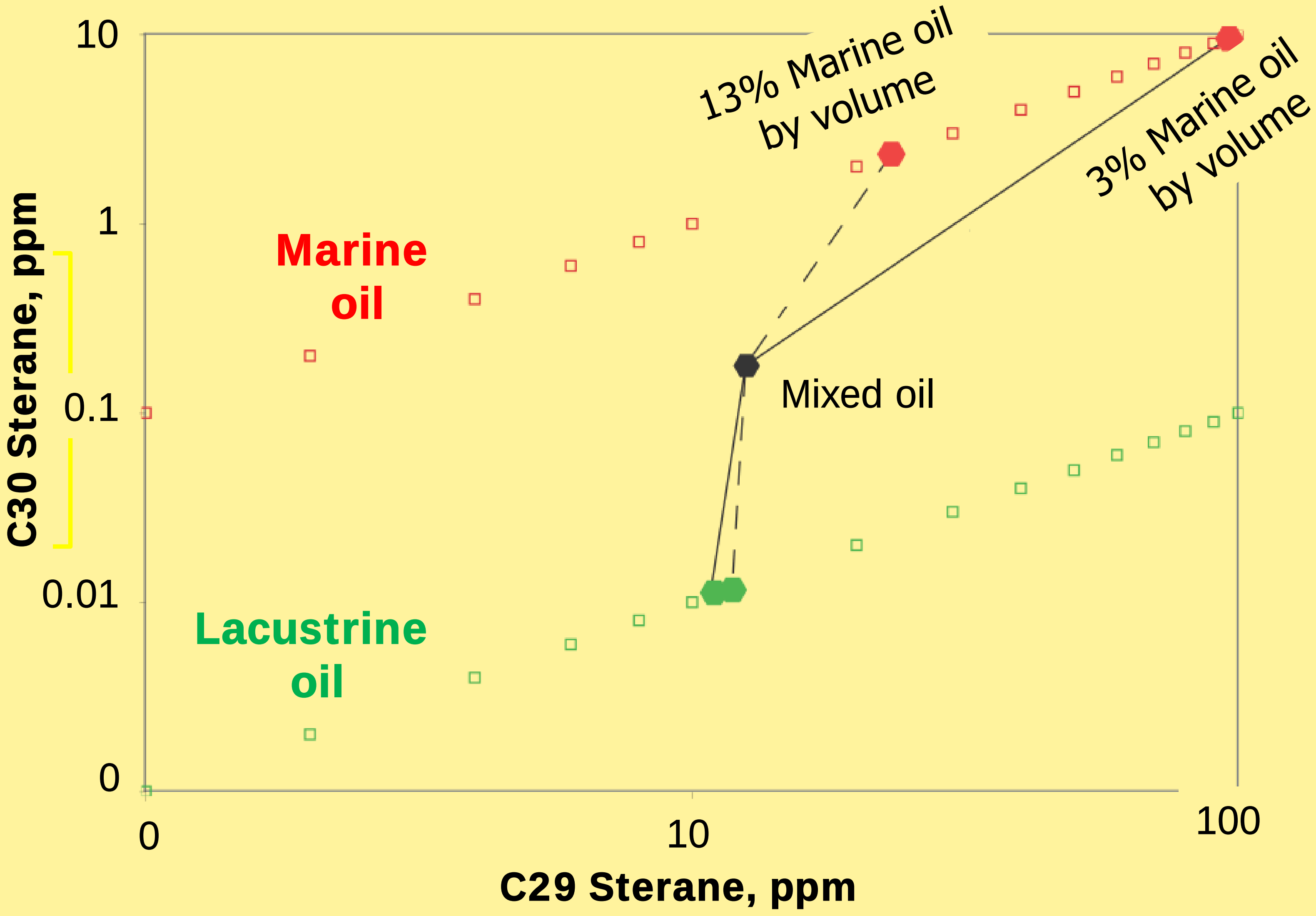


100+ times sensitivity increase

Distinguishing marine and lacustrine petroleum samples around the world



Interpreting mixed lacustrine-marine petroleum



SUMMARY Case I

Deep-sourced condensate with black oil

- Black oil component: Use characteristic biomarker parameters
- Deep source component: Use diagnostic diamondoids, diamondoid isotopes and other light hydrocarbon components abundant in over-mature oil

SUMMARY Cases II & III
Black oil mixed with black oil

In the example ...

- Marine oil component: Marine oil is rich in C30 steranes. Use enhanced C30 sterane analysis to quantify as little as 1% marine oil in lacustrine black oil.

- Lacustrine oil component: Lacustrine oil is richer in hopanes. Quantify as little as 10% lacustrine oil in marine black oil by using isotopic differences in hopanes.

We thank the organizers of this symposium for the invitation to present this paper...

and *thank you* to those in attendance here today!!!

J