

# **Correlation of Highly-Mature Hydrocarbon Liquids Using Higher Diamondoids\***

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## **Abstract**

Higher diamondoids are composed of four or more face-fused diamond cages. Unlike the lower diamondoids, adamantane, diamantane and triamantane, higher diamondoids have a variety of structural isomers. There are four different tetramantane isomers found in petroleum, two of which are enantiomeric. There are nine pentamantane isomers of molecular weight 344, six of which are enantiomeric pairs. There are 39 hexamantanes, but only one of which has a molecular weight of 342, the highly condensed cyclohexamantane. Here we show it is possible to use the relative concentrations and distributions of higher diamondoids to determine source in much the way biomarker sterane and terpane-concentrations and distributions are used. Unlike biomarkers which are among the most thermally labile compounds in petroleum, diamondoids are for their molecular weight, the most thermally stable. As a result, unlike biomarker distributions, higher diamondoid distributions can be used to correlate hydrocarbon liquids of any thermal maturity. We will show (1) oil to oil, (2) oil to condensate, and (3) oil and condensate to source-rock correlations for a variety of samples, including condensates from liquids collected from highly-mature dry gas wells. Several examples representing various sources in both the US and Mexican Gulf of Mexico will be used to illustrate the application.

## **Selected Reference**

Peters, K.E., and J.M. Dolowan, 1993, The biomarker guide: Englewood Cliffs, New Jersey, Prentice Hall, 363 p.

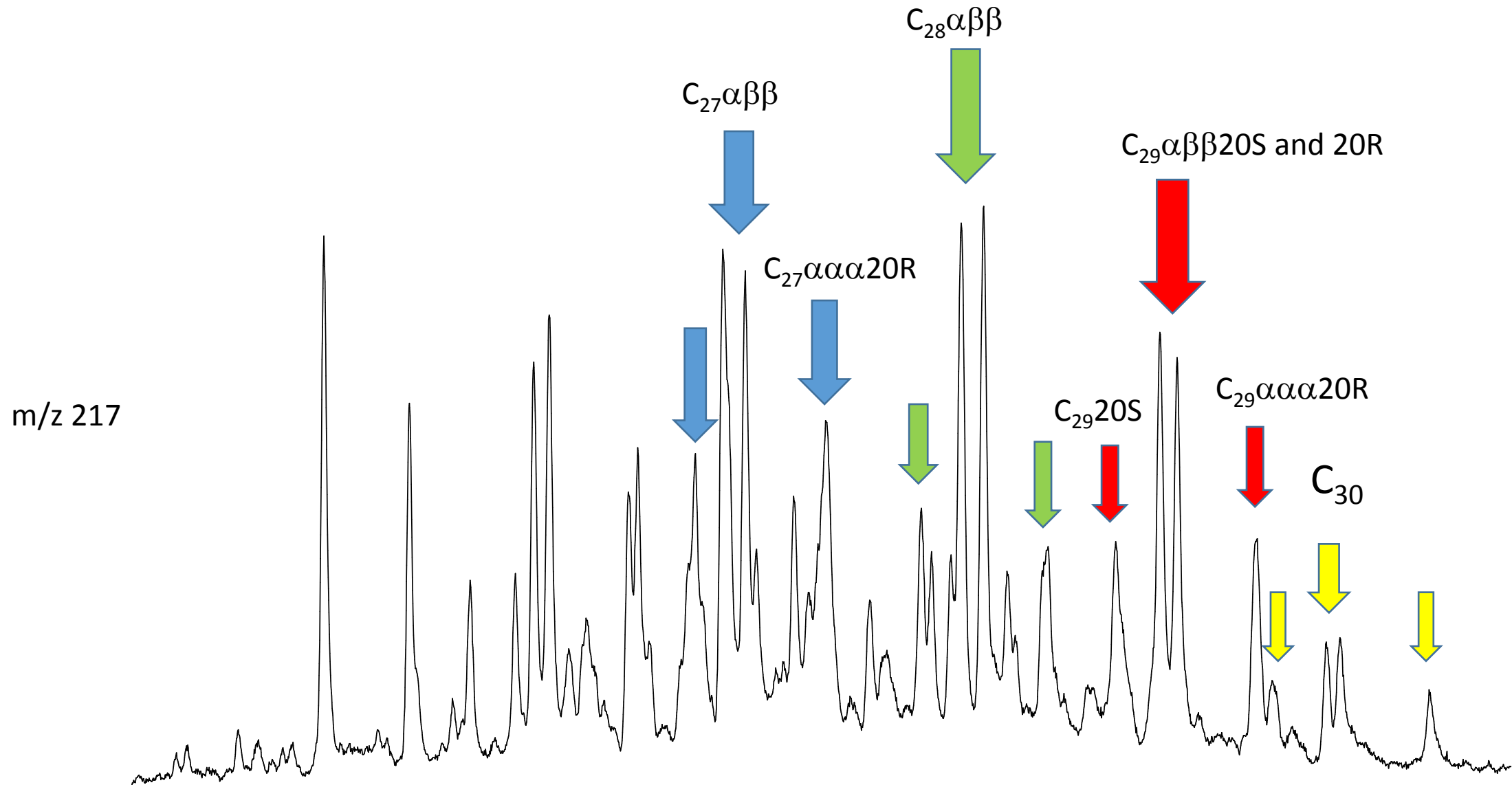
# Correlation of Highly Mature Hydrocarbon Liquids Using Higher Diamondoids

J.E Dahl, J.M. Moldowan and D. Zinniker

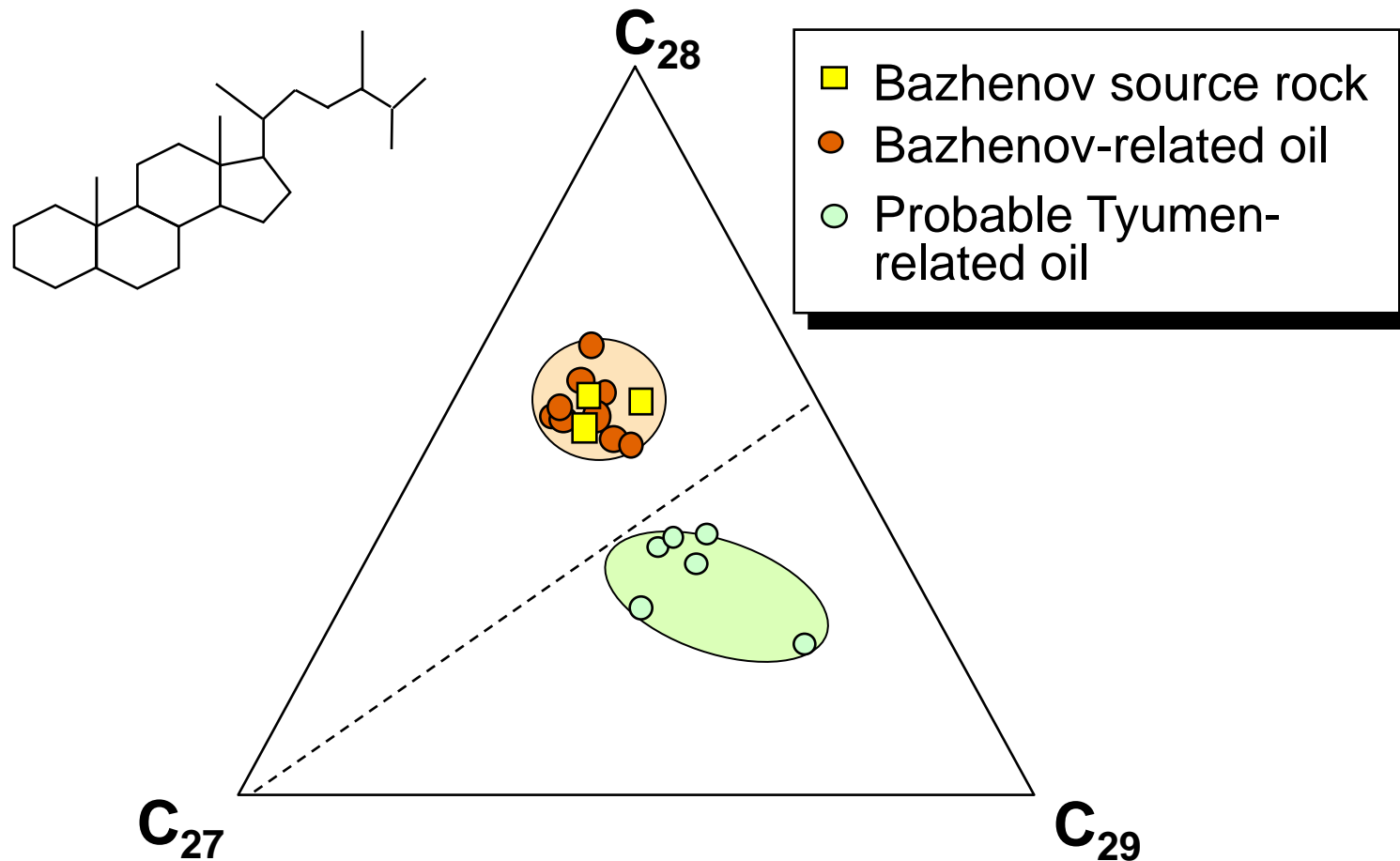
Correlating high-maturity fluids to source rocks  
is a difficult task.



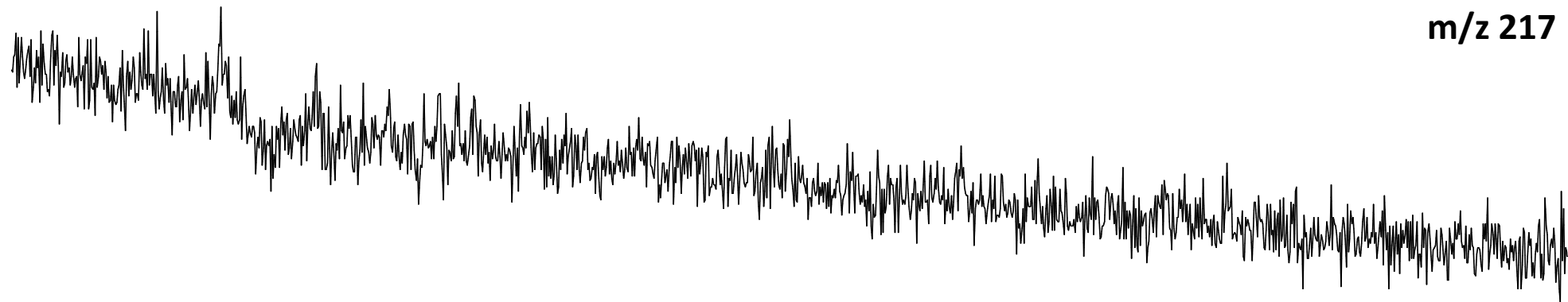
For Oil-Window Maturity Oils, identification of effective source rocks can be done very nicely with Biomarkers



# Sterane Ternary Plot shows oil families.

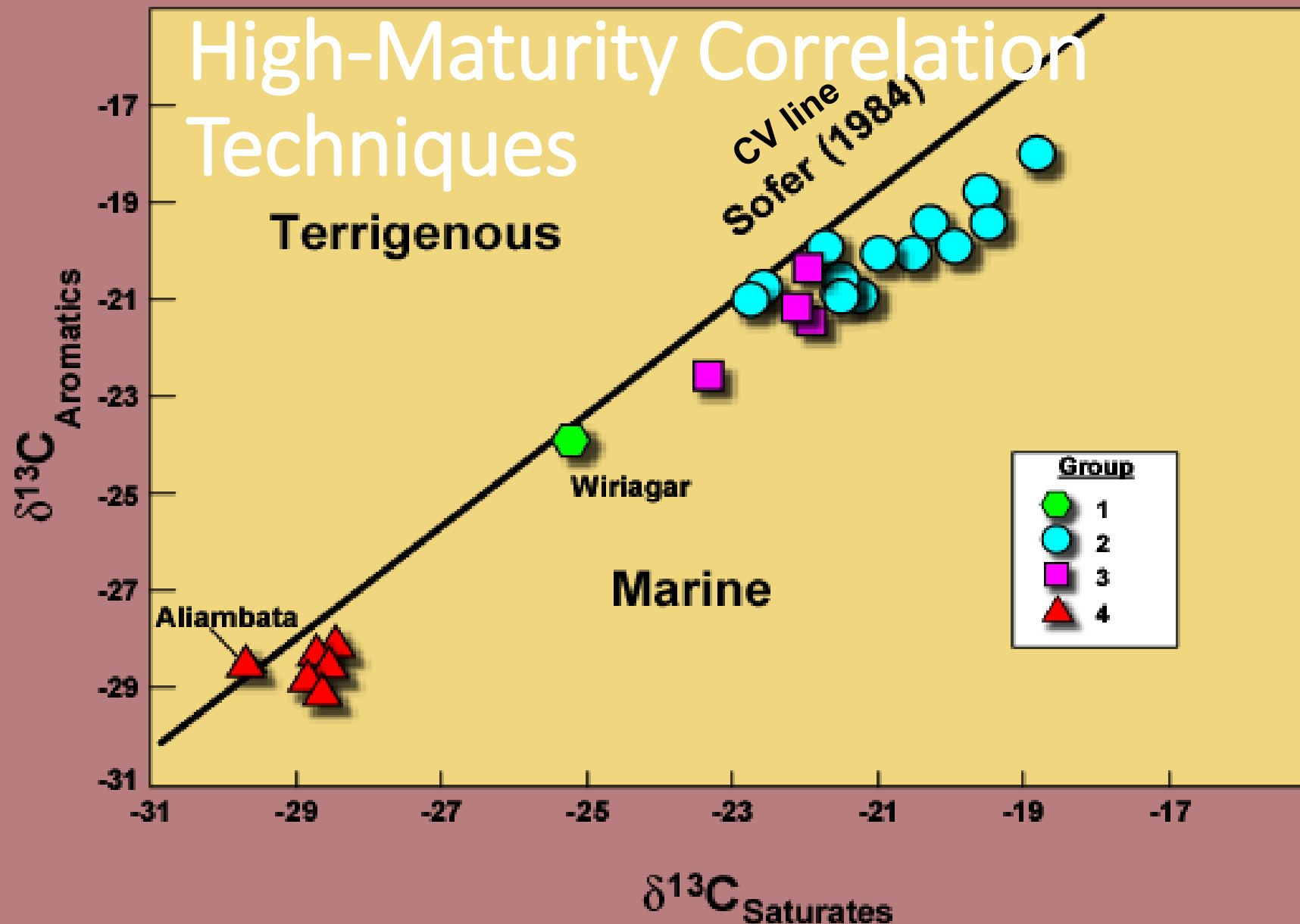


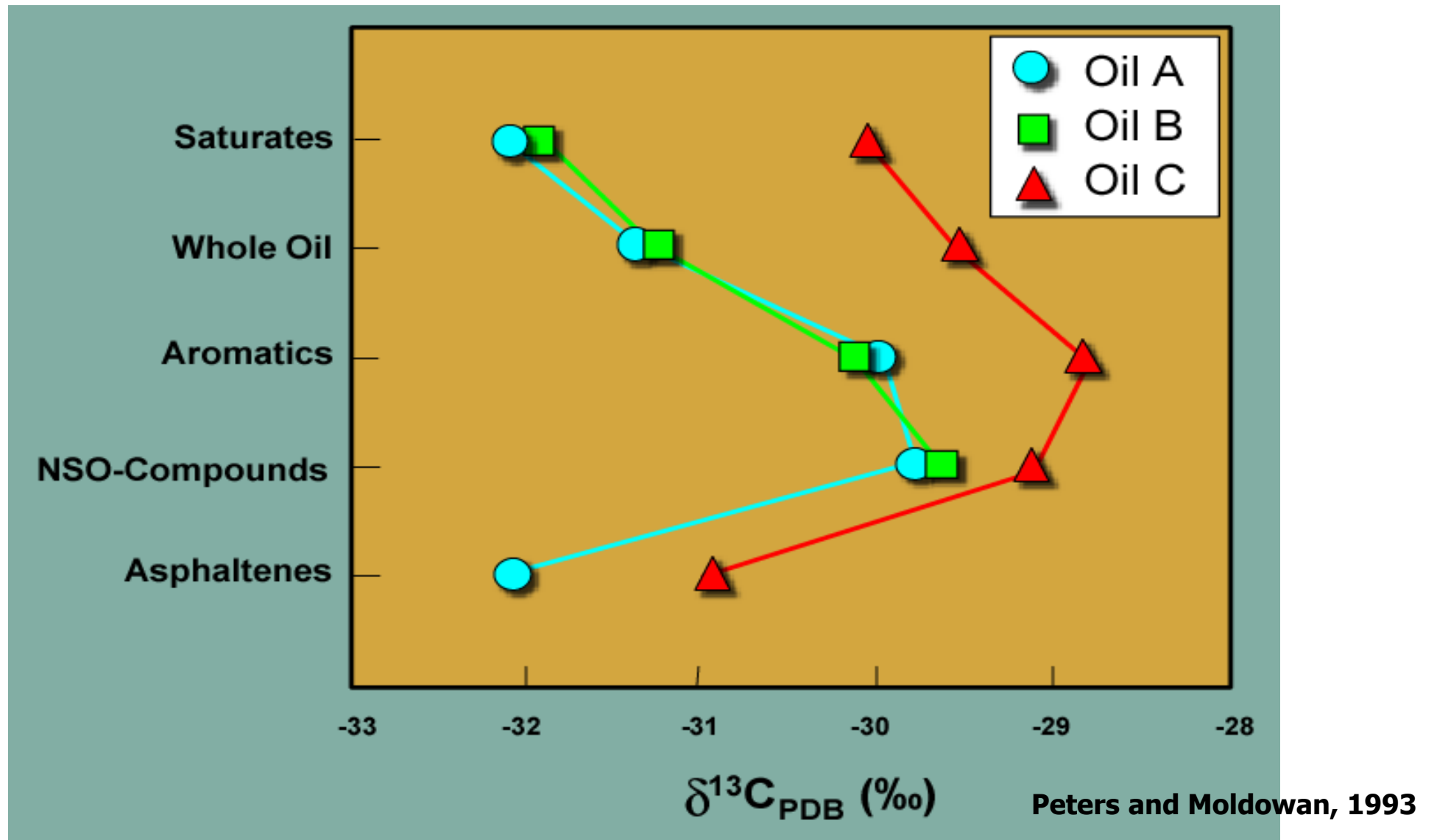
Unfortunately, High-Maturity fluids are generally devoid of biomarkers.



More insidious is when a high-maturity gas condensate contains biomarkers.

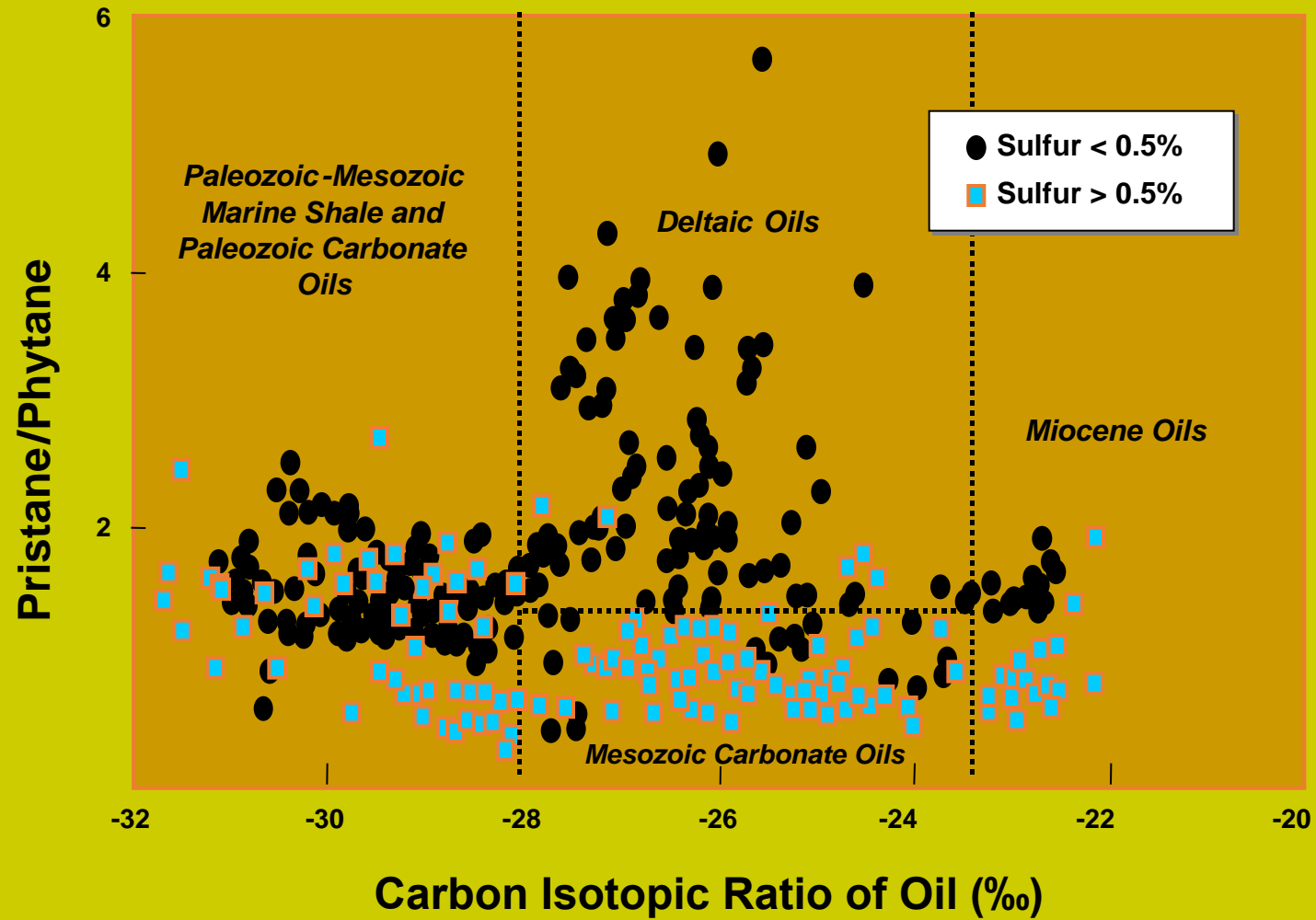
# High-Maturity Correlation Techniques



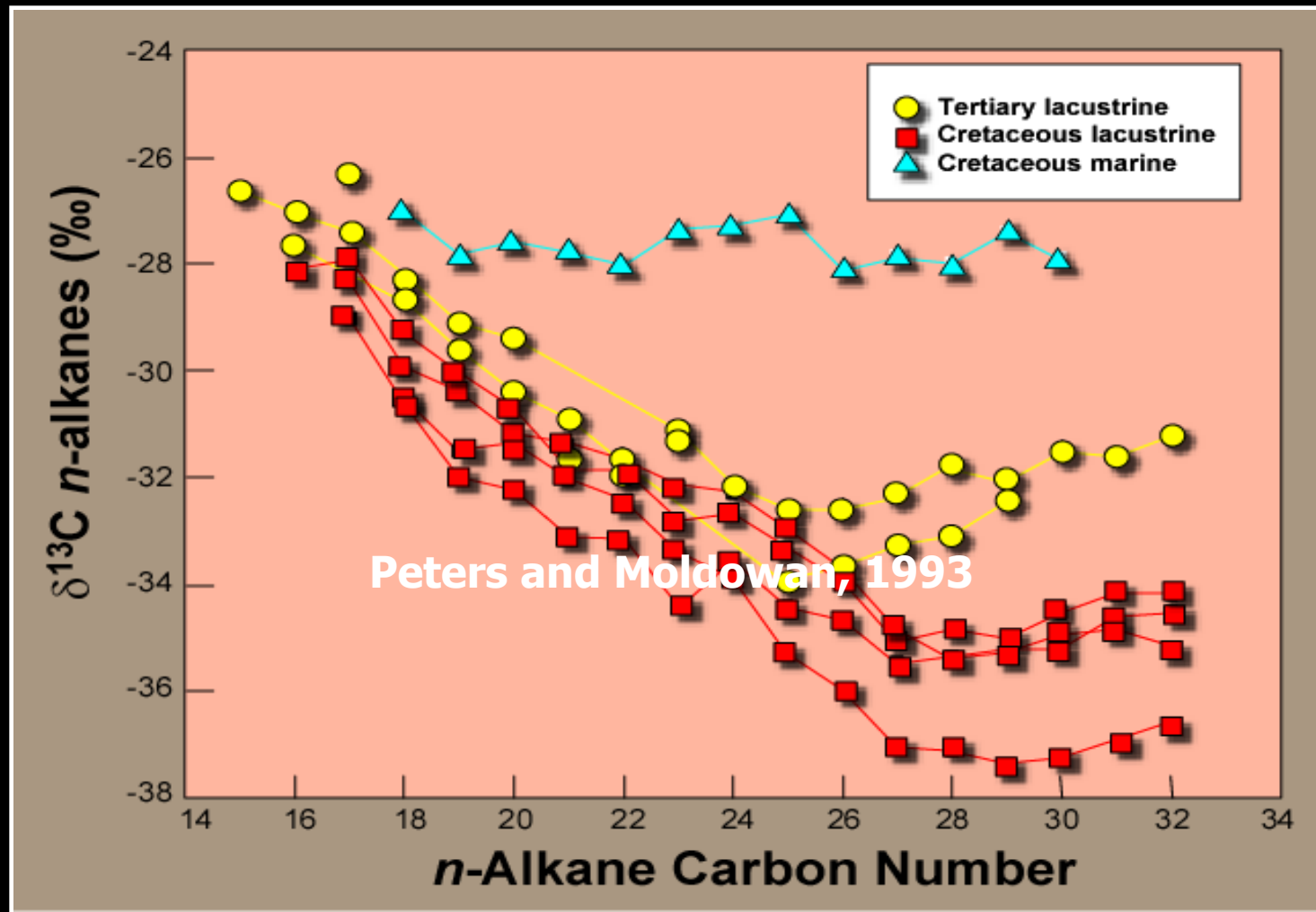


Timan-Pechora Basin, Russia, (Peters and Moldowan, 1993).





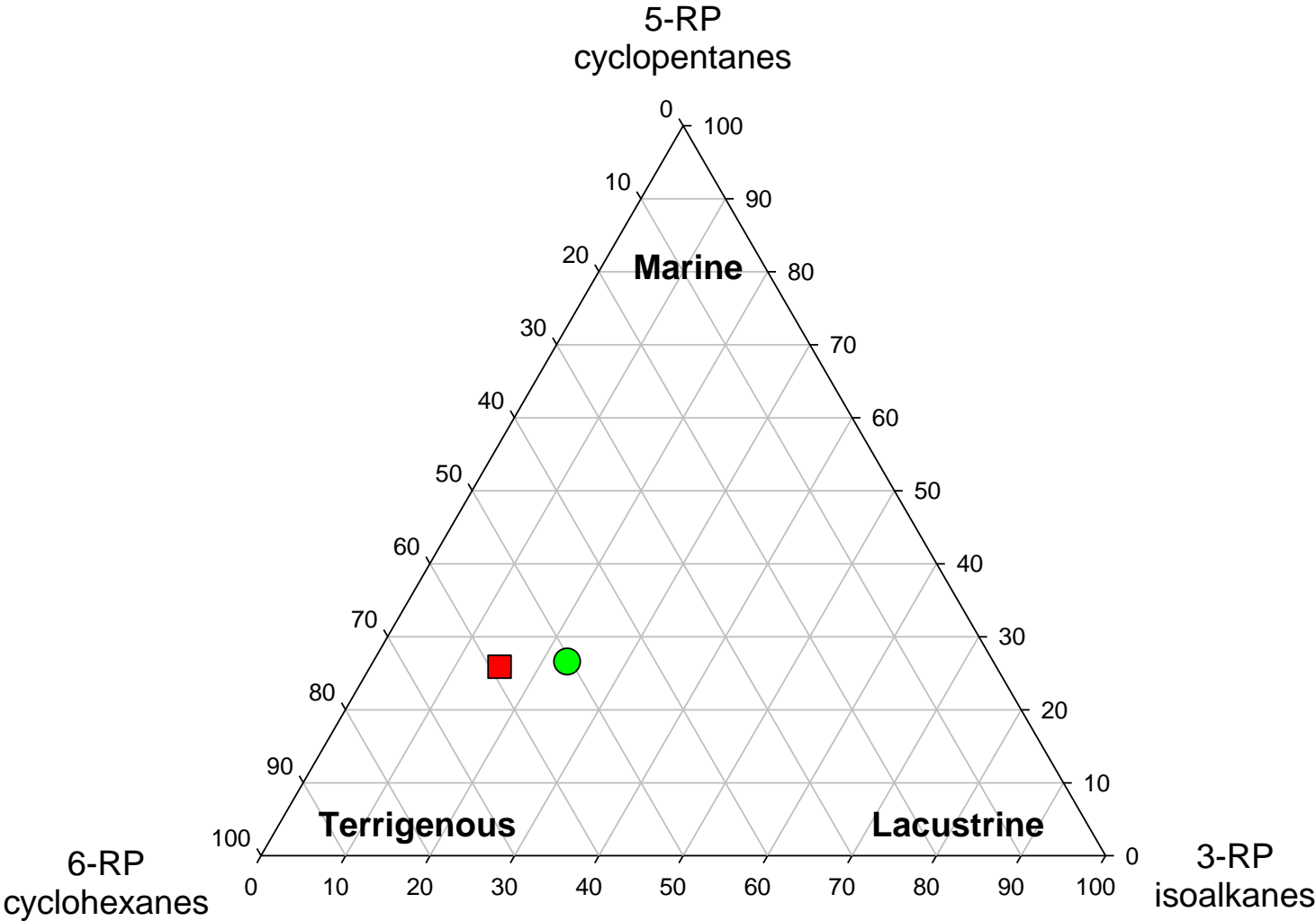
**Peters and Moldowan, 1993**



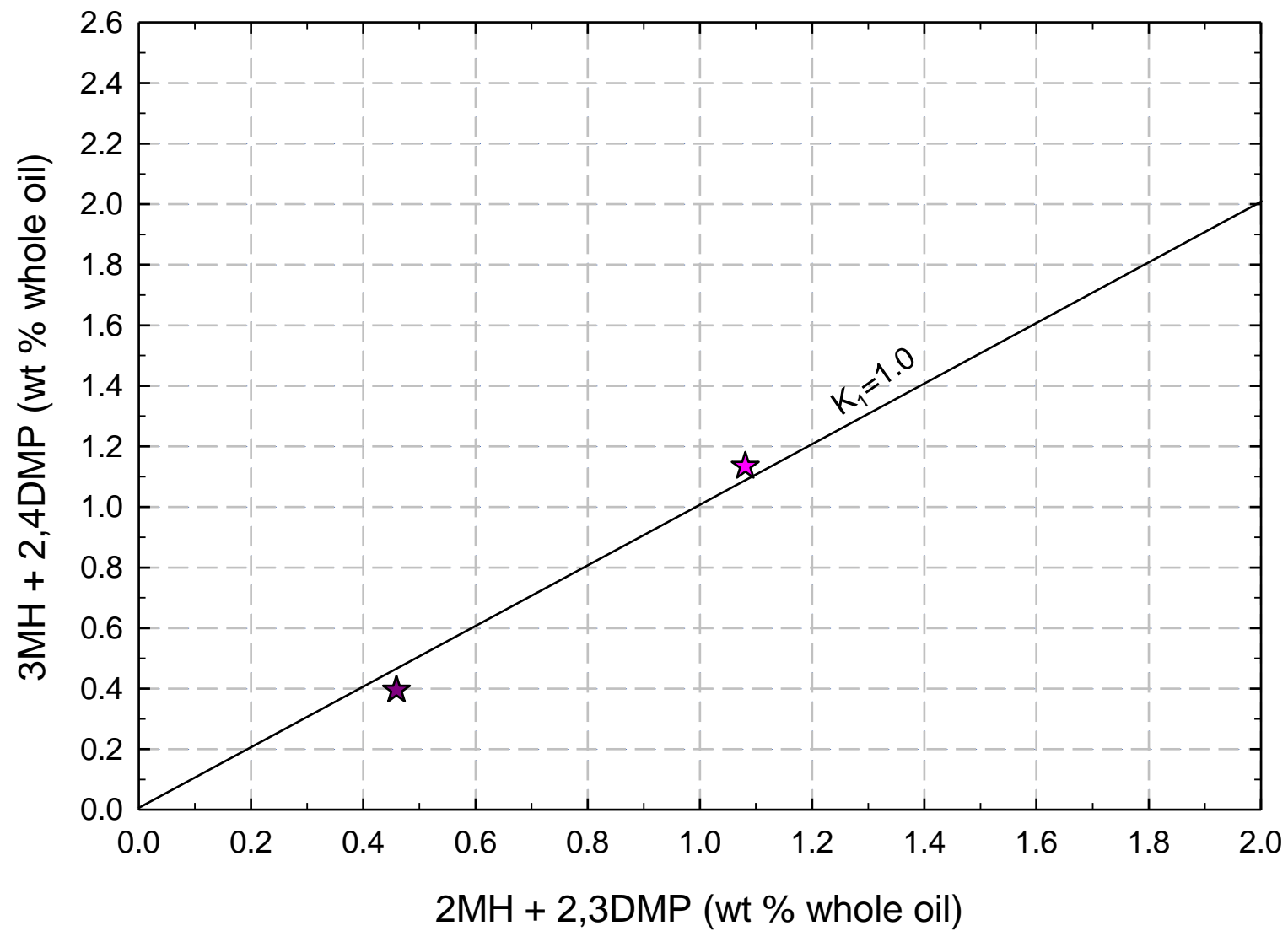
Tertiary marine, and Cretaceous marine organic-rich source rocks in Brazil. (from Guthrie et al., 1996)

Oil – Source Characteristics from GC Data

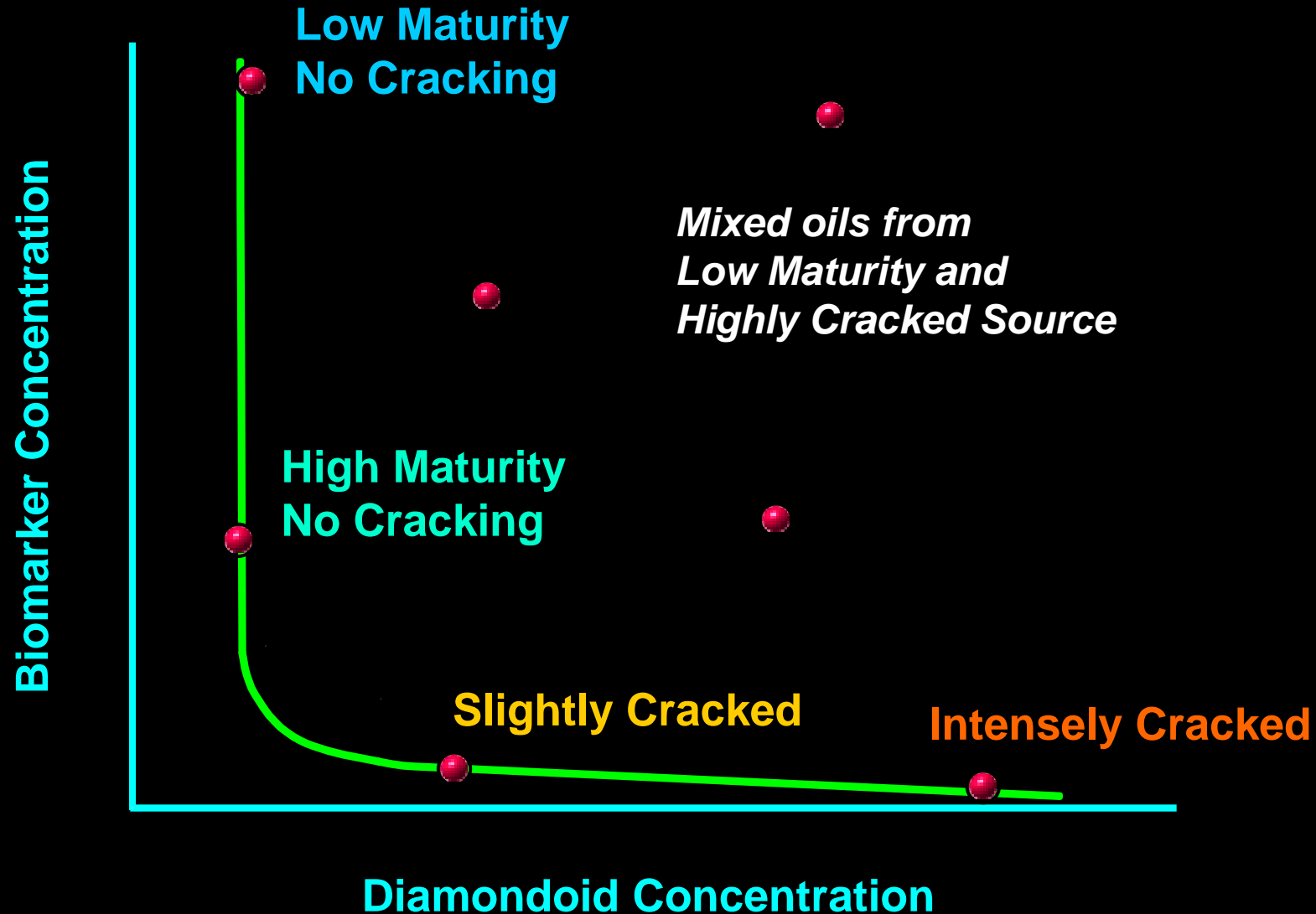
C7 Ternary Plot



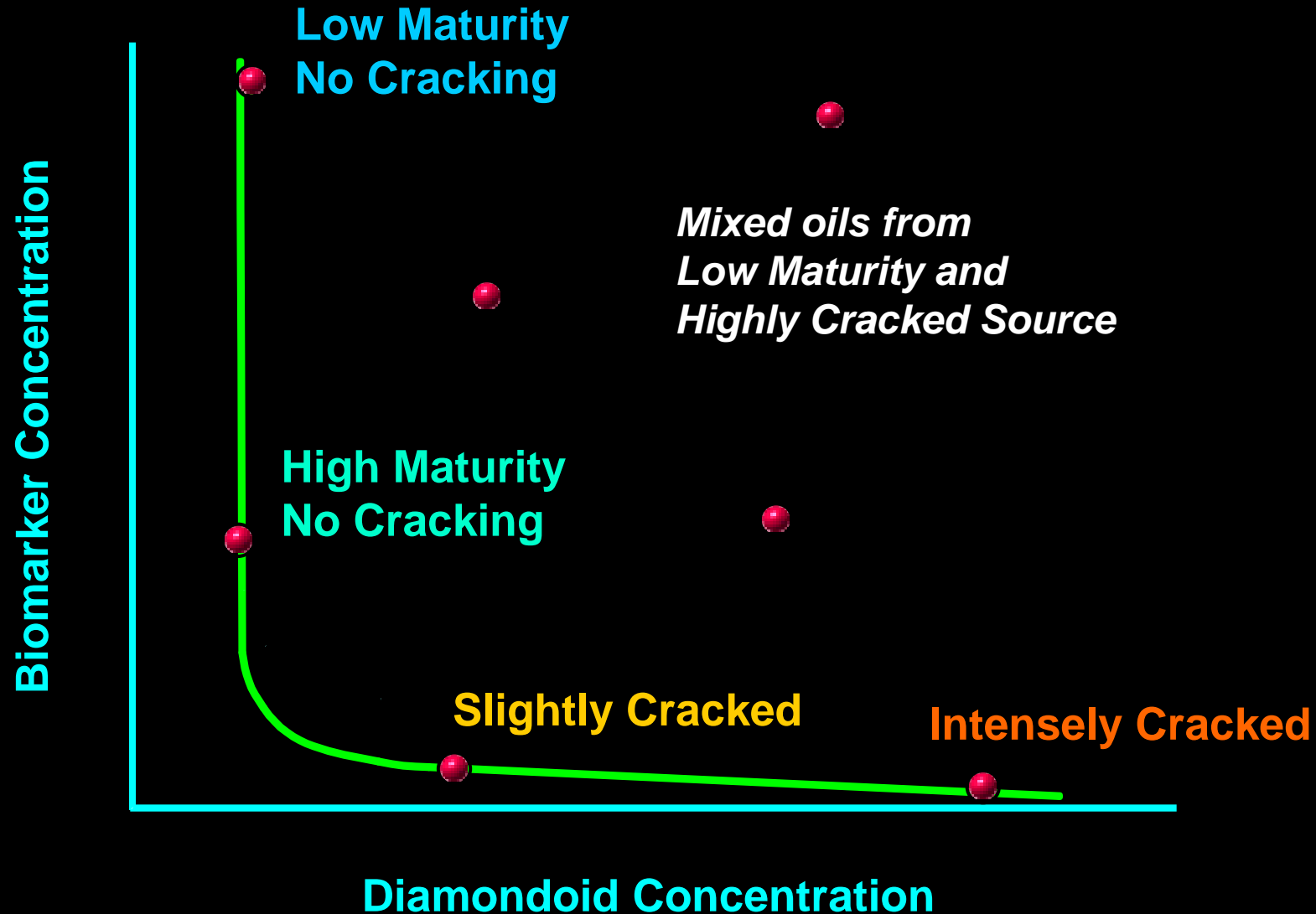
# “Mango” C<sub>7</sub> Parameters for Oil-Oil Correlation



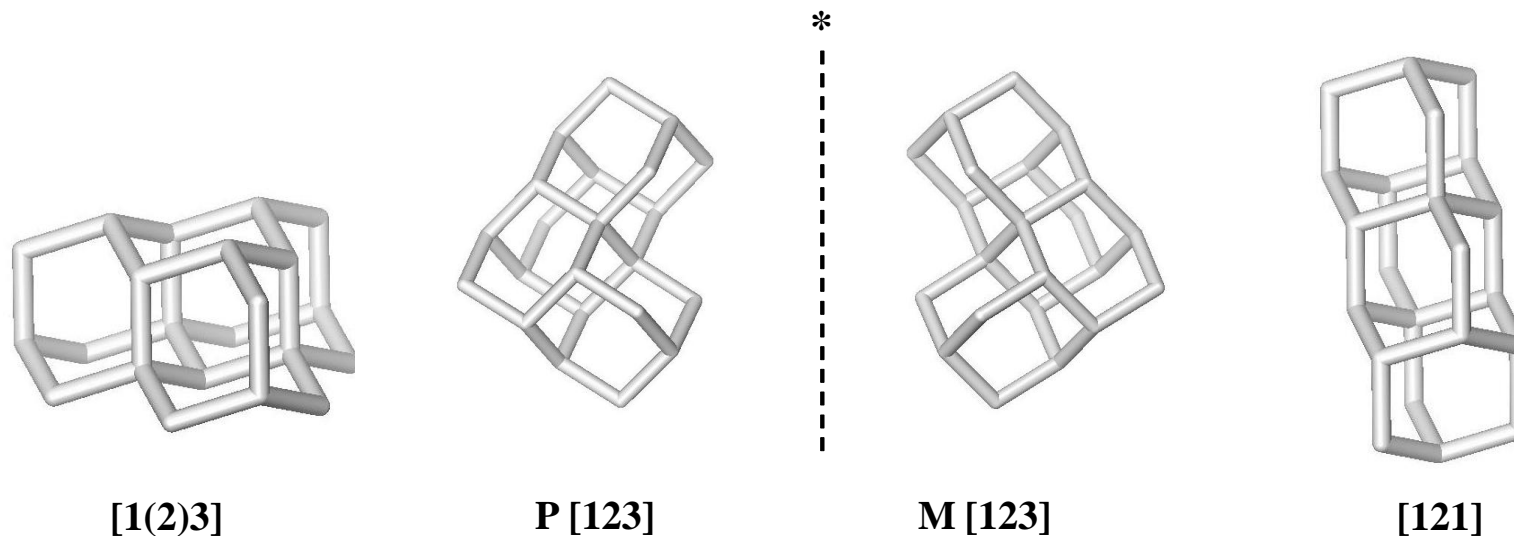
# Problem with biomarkers is illustrated in this diagram



**This diagram also shows a possible solution. Work by Linda Schultz (2001) showed that diamondoids can be used to determine source.**



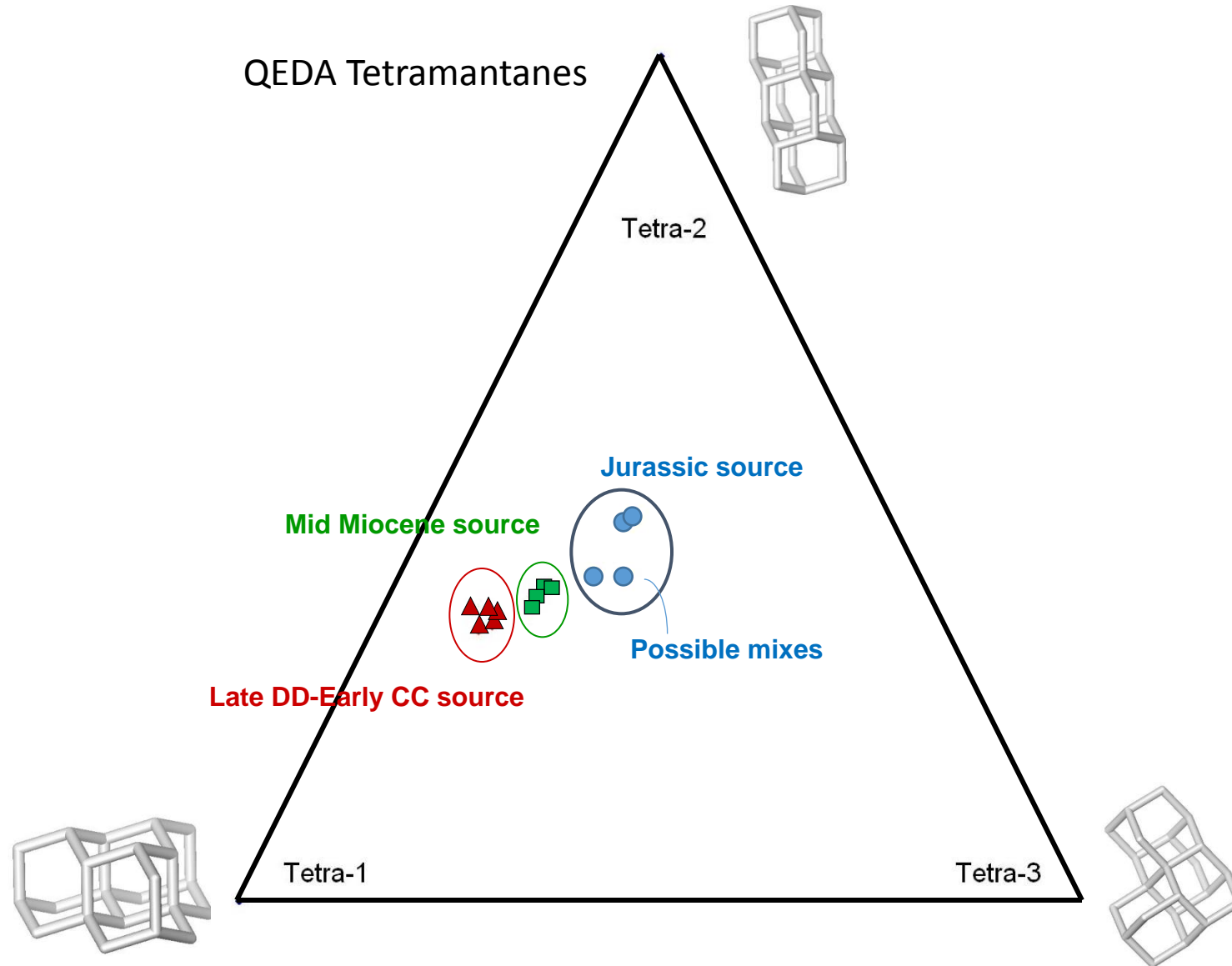
Like biomarkers, higher (4 cages or more) diamondoids come in a variety of isomers.



**Four Tetramantanes**  
– Each With a Different 3-D Shape

**$C_{22}H_{28}$ , MW 292**

## Example from Eastern Europe

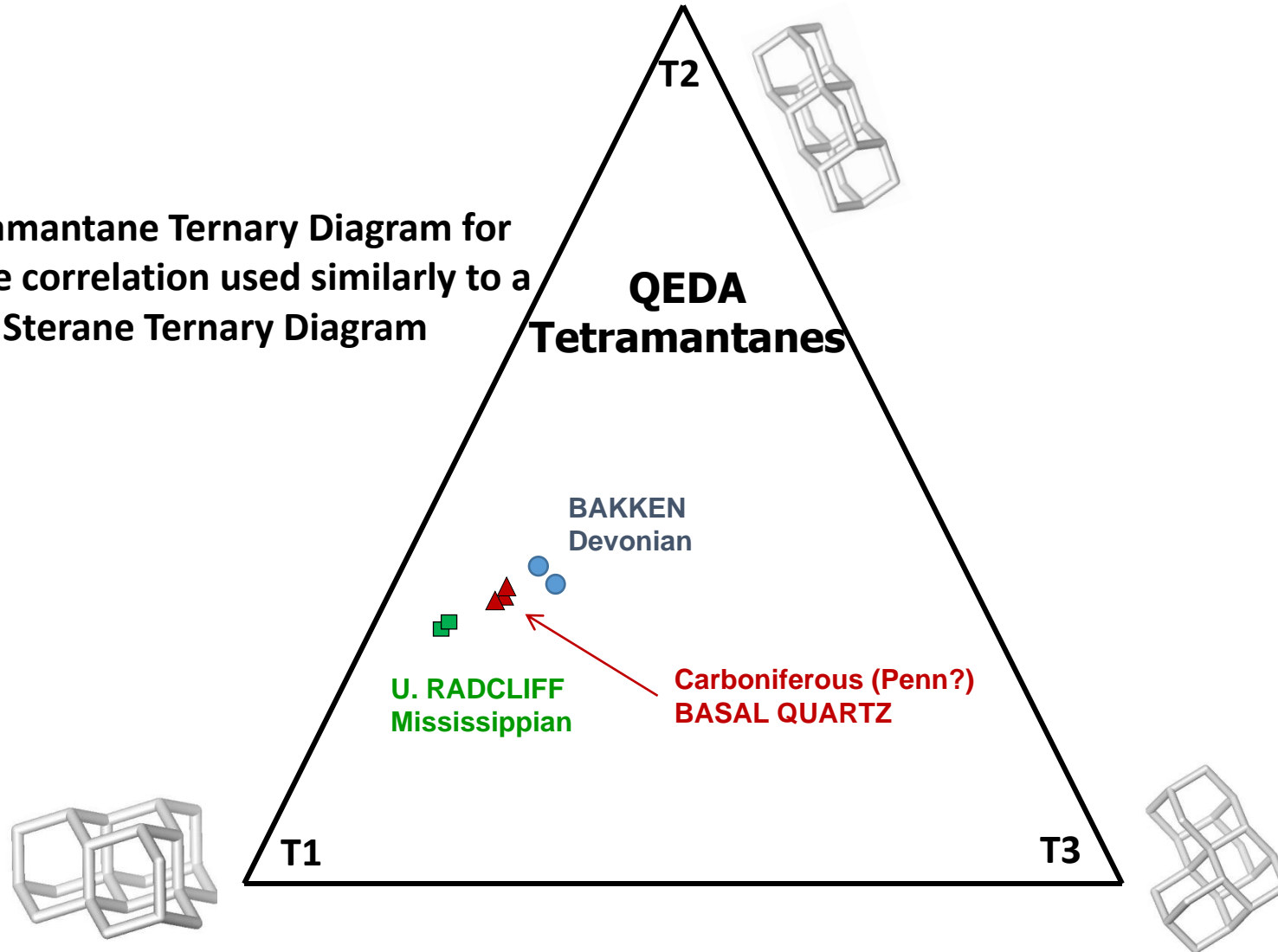




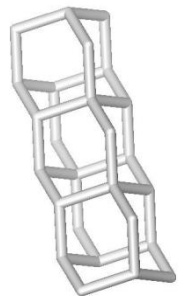
# Use Diamondoids

## Chart for Oil Correlation in Williston Basin

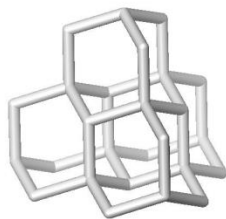
Tetramantane Ternary Diagram for  
source correlation used similarly to a  
Sterane Ternary Diagram



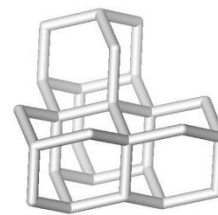
There are Nine Pentamantanes of Molecular Weight 344,  
 $C_{26}H_{32}$  – Each with a Different 3-D Shape



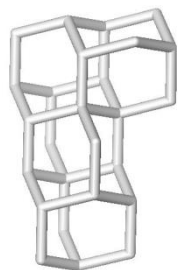
**[1212]**



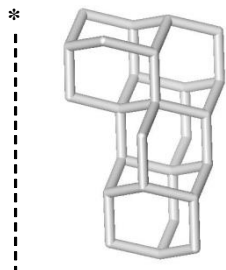
**[1(2,3)4]**



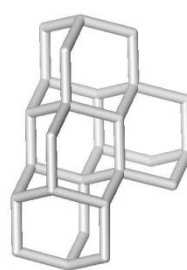
**[12(3)4]**



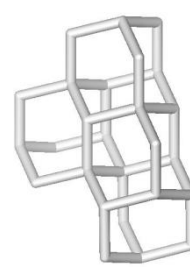
**M[1213]**



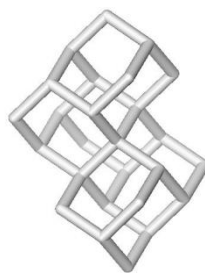
**P[1213]**



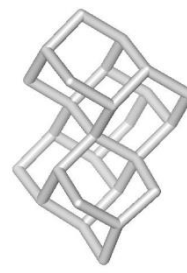
**P[12(1)3]**



**M[12(1)3]**



**P[1234]**

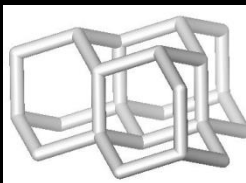


**M[1234]**

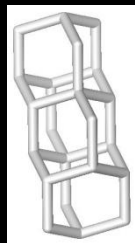
**\*Indicated  
mirror plane**

# QEDA- Structures of extended diamondoids measured in QEDA studies

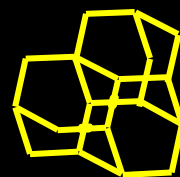
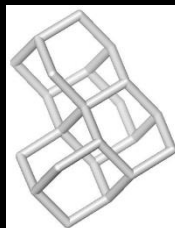
T1



T2



T3



**Triamantane**  
Used for normalization

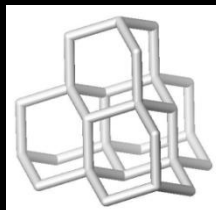
— Tetramantanes —

H1

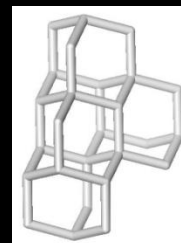


**Cyclohexamantane**

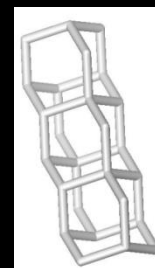
P1



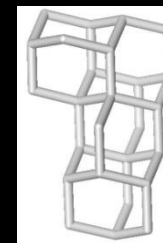
P2



P3

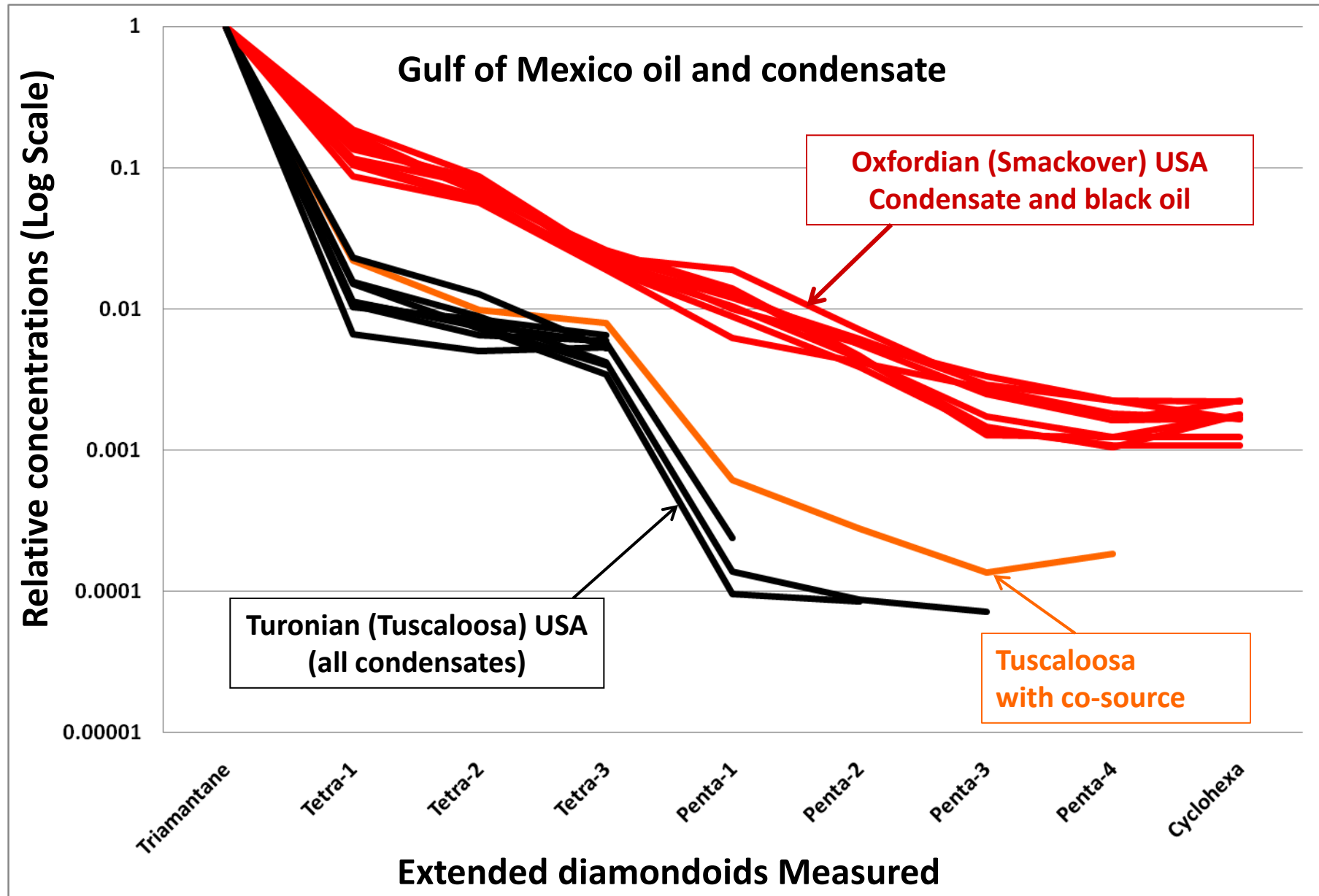


P4



— Pentamantanes —

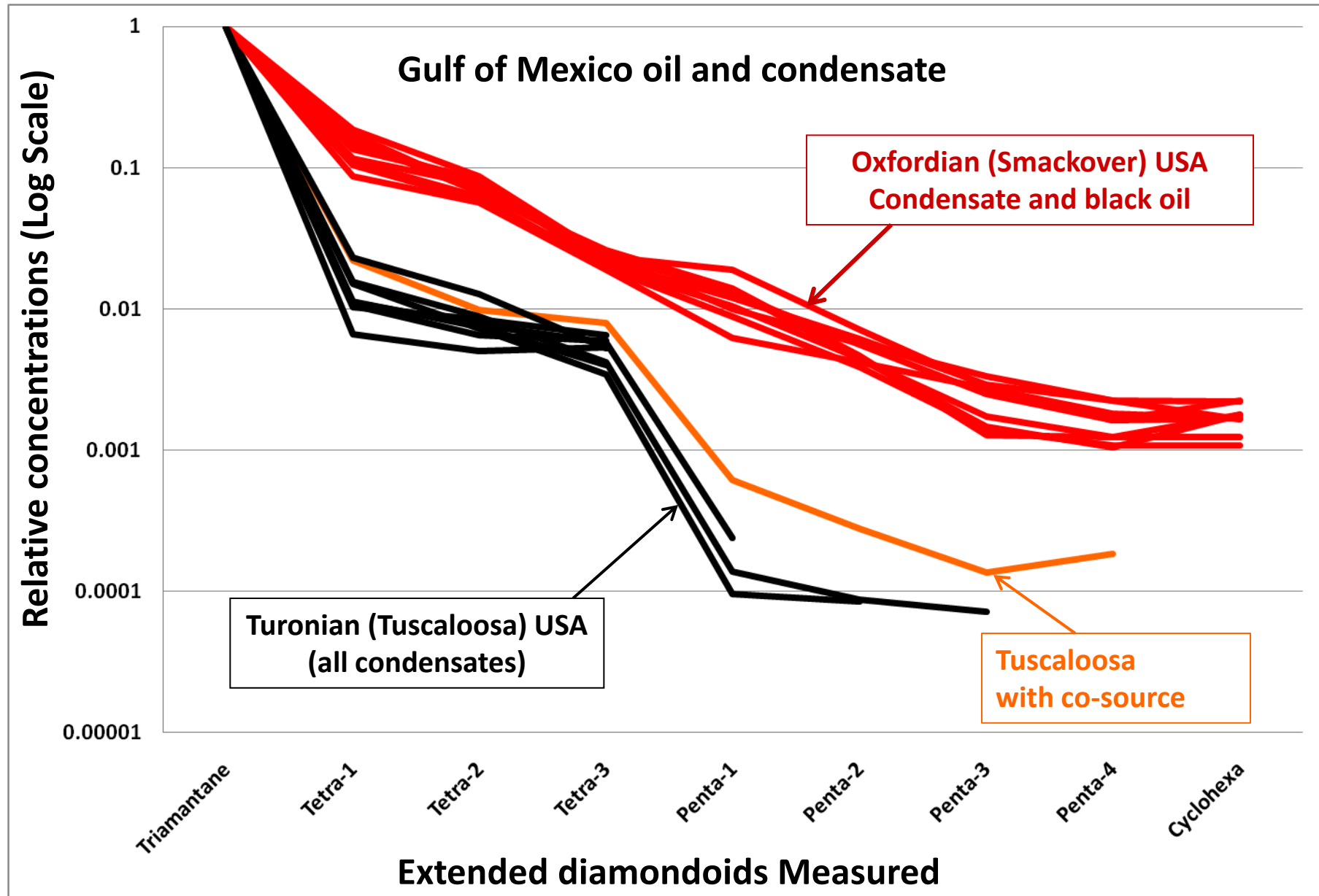
## Diamondoid concentrations can be used to correlate oils



Oils and Condensates in this study are from Smackover and Deep Tuscaloosa Trend, from Claypool and Mancini, 1989 AAPG-Bulletin.

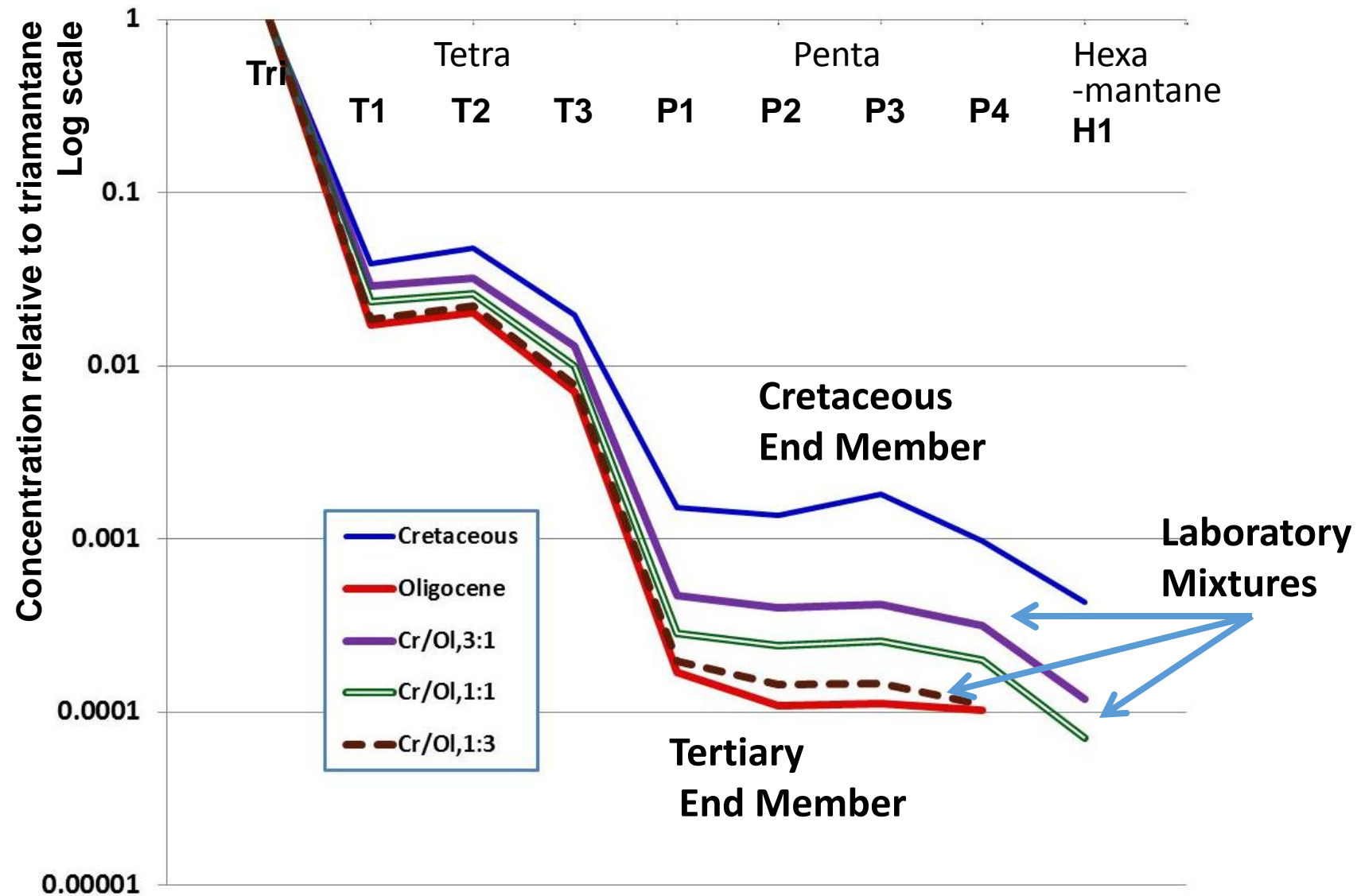
- Source known from geologic control
- Smackover oils range from low-maturity 17°API (Toxey) to over 50°API (Hatters Pond).
- Some Smackover liquids from Mobile Bay are not only highly cracked, they are TSR altered.
- Tuscaloosa Trend condensates have C1/(C1-5) ratios for 0.94 to 0.99

## Diamondoid concentrations can be used to correlate oils

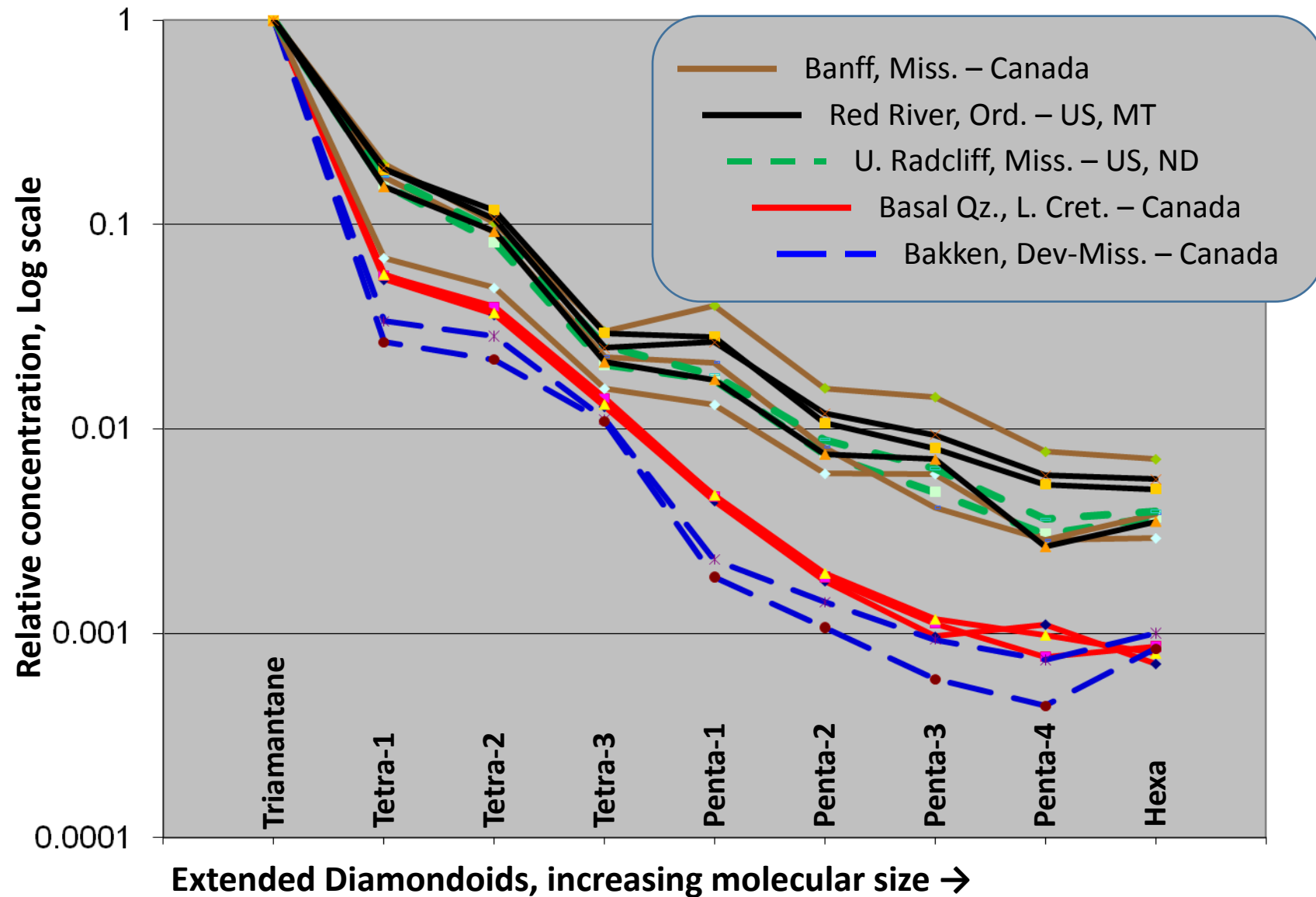


# Selected oil samples from Venezuela differentiated by QEDA

Various mixtures are analyzed to show application to unravel oil-mixtures



**Quantitative extended diamondoid analysis (QEDA)**  
**Williston Basin oil-source correlation for cracked oil, black oil and mixes**



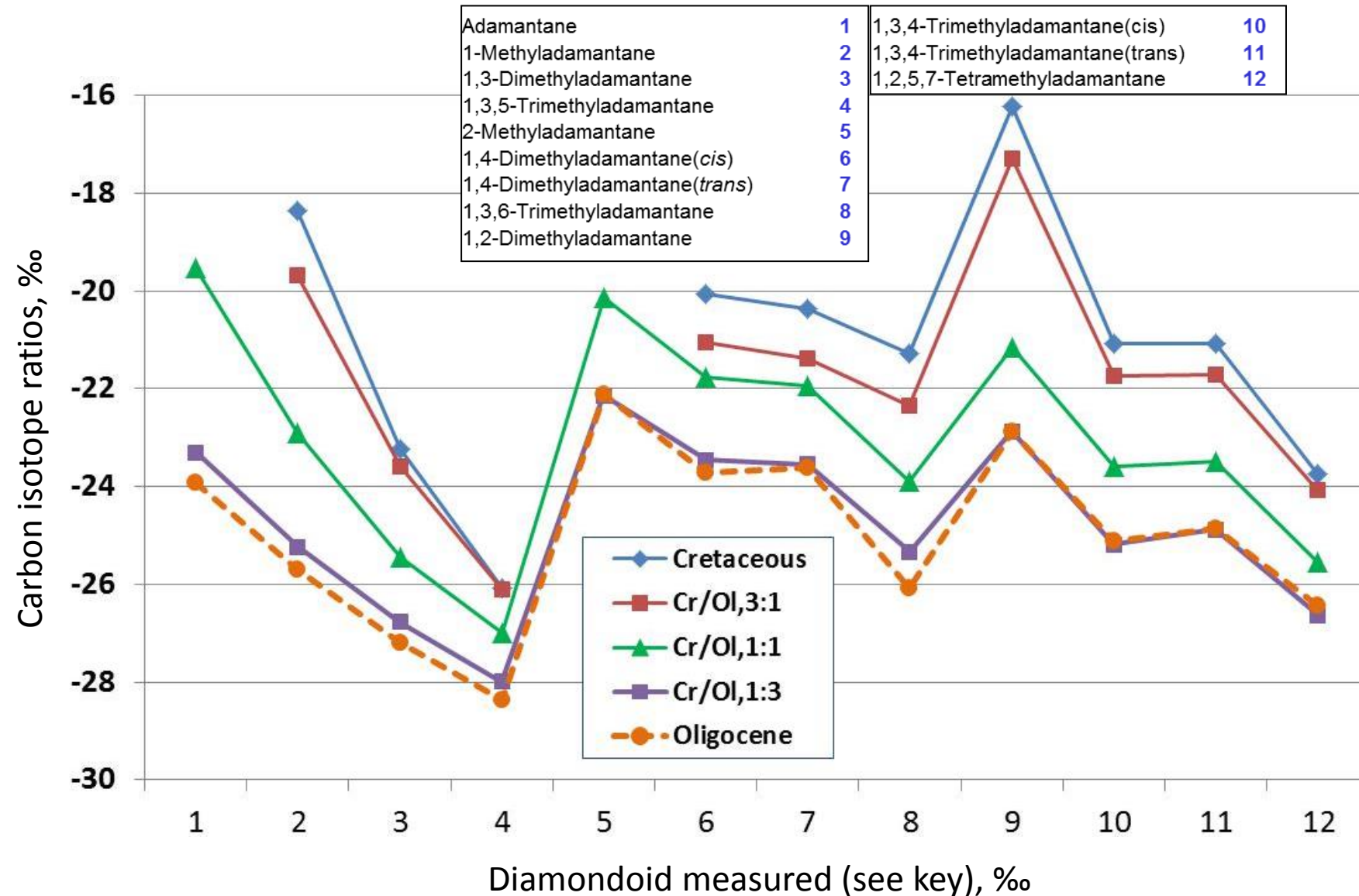


# Isotopic Analysis of Diamondoids

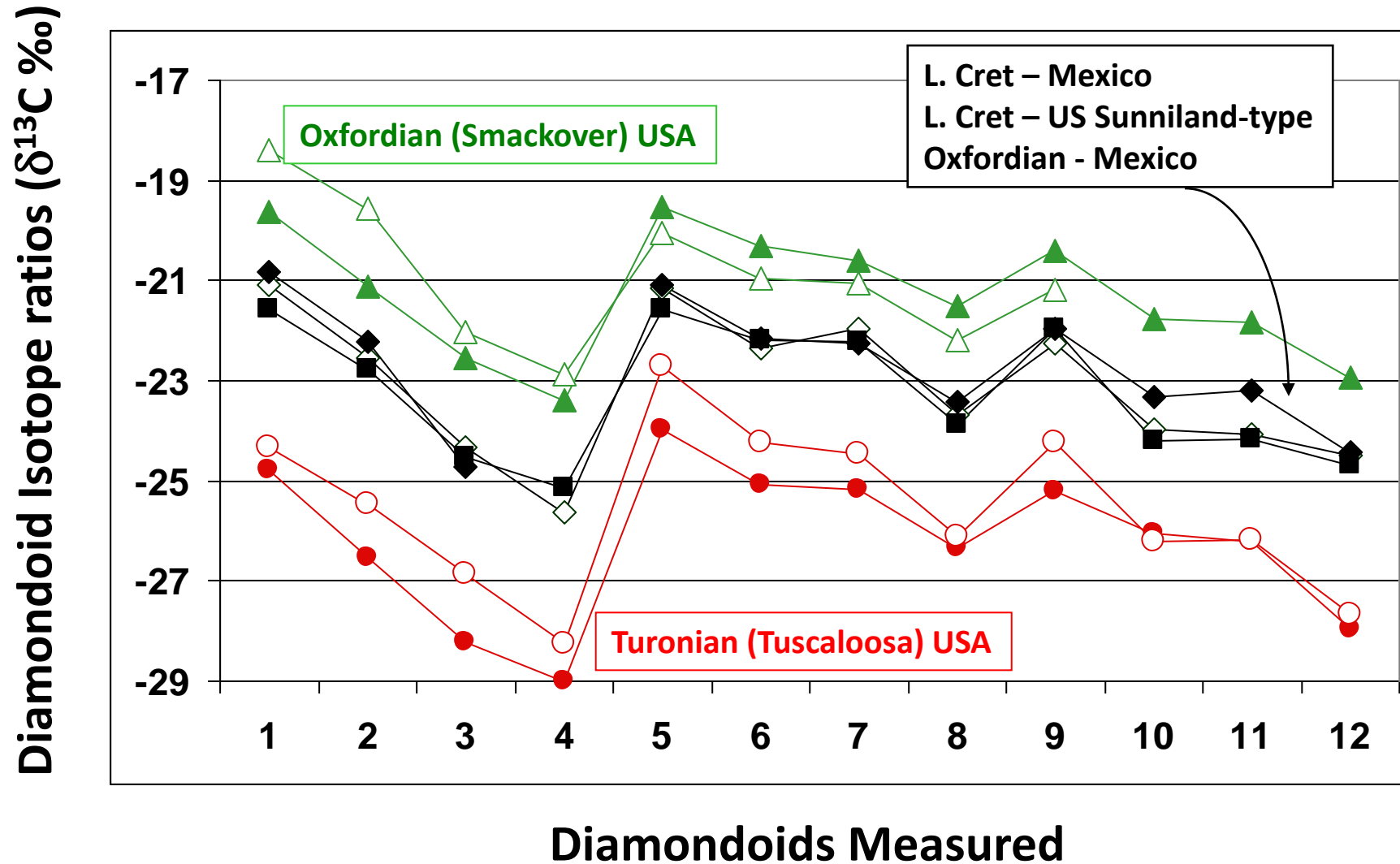
## Key to Diamondoids Measured (X-axis) CSIAD

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

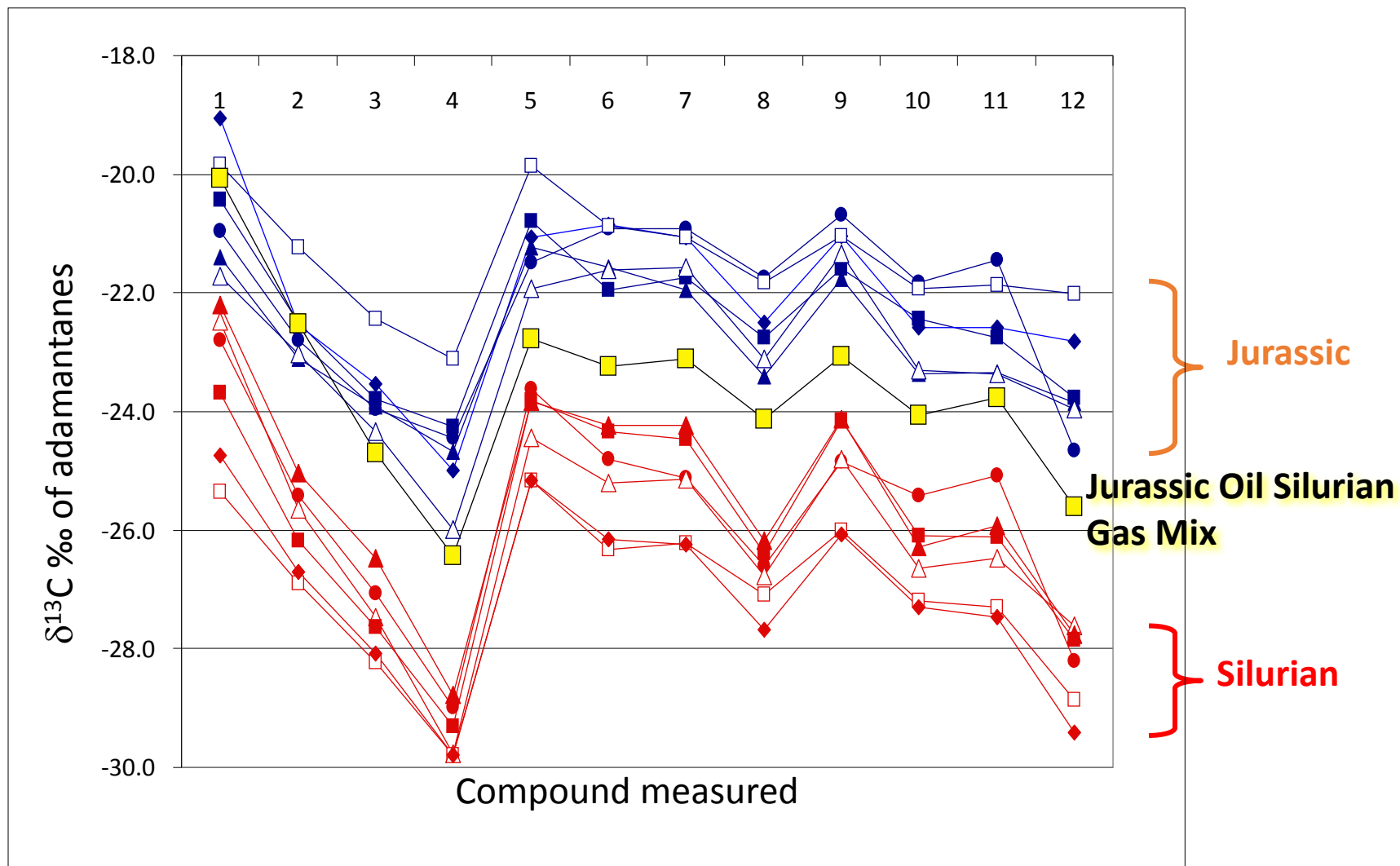
Figure 1. Isotope ratios of diamondoids measured in Cretaceous and Tertiary-oil end-members and their mixtures. Slightly higher diamondoid concentrations in the Oligocene oil result in a weighted distribution favoring Oligocene isotope ratios in the mixtures.



# Diamondoid isotopes distinguish certain oil families in the Gulf of Mexico



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



# Conclusions

- Higher diamondoid (4 cages and larger) distributions can be used to designate oil families and determine liquid hydrocarbon source rocks in much the same way biomarkers are used.
- Unlike biomarkers, higher diamondoids are useful for liquids of any thermal maturity including high-maturity gas condensates. Condensates can be correlated to other condensates, to low maturity oils and/or to source rocks.
- Diamondoid isotopes provide a complementary method of correlating high-maturity fluids.