Advances in Analytical Technologies for Correlation of All Hydrocarbon Fluids, Oil Mixtures and Extracts*

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Search and Discovery Article #41401 (2014)**
Posted July 24, 2014

*Adapted from oral presentation given at 2014 AAPG Annual Convention and Exhibition, Houston, Texas, April 6-9, 2014

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Abstract

Classical geochemical technology developed decades ago retains value, but in most cases, applications simply retrace previous conclusions and do not open new opportunities. New technologies that deliver the resolving power necessary to distinguish hydrocarbon sources in greater detail and delineate co-sourced petroleum mixtures open new vistas in basin modeling. Here we reveal novel compound specific isotope analysis (CSIA) parameters to accomplish those goals. In order to perform CSIA the targeted compound classes must first be isolated from the petroleum. CSIAs of steranes, hopanes, C12-C40 isoprenoids and C7-C30+ alkanes, terrestrial terpanes (e.g. bicadinane and oleanane), naphthalenes, phenanthrenes and diamondoids are illustrated and examples from worldwide applications to perform source-differentiation are depicted. Laboratory mixtures from different end-member oils from Venezuela, Colombia and the US Gulf of Mexico, respectively, were prepared. Analyses of these mixtures show the power of those new methods for (1) recognition of mixes, (2) determination of all sources, and (3) determination of the relative input from each source. Methods to utilize asphaltenes for biodegraded-oil correlation are also revealed. Asphaltenes preserve original biomarkers and alkanes. Those compounds can be generated by hydrous pyrolysis and used for correlation. While fingerprints of these generated compounds might not match related non-biodegraded oil, the generated biomarkers and alkanes retain isotopic signatures from the kerogen and can be used for correlation by using CSIA methods. Diamondoids are a universal compound class for correlation. With a few exceptions, diamondoids are recalcitrant or inert to alteration by biodegradation and can be used to correlate severely biodegraded oil. They can be sequestered even from severely biodegraded oil or thermally altered condensate and used for correlation with any other petroleum liquids or extracts both by CSIA-D and by fingerprints of large diamondoid molecules (tria-, tetra-, pentamantanes, etc.), termed quantitative extended diamondoid analysis (QEDA).

Reference Cited

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.

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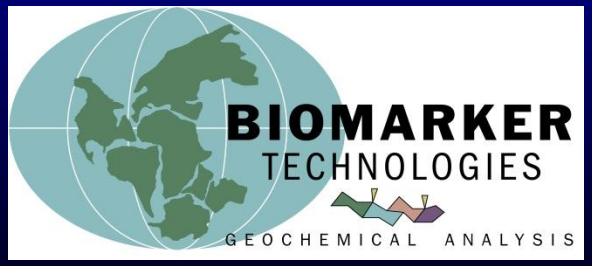

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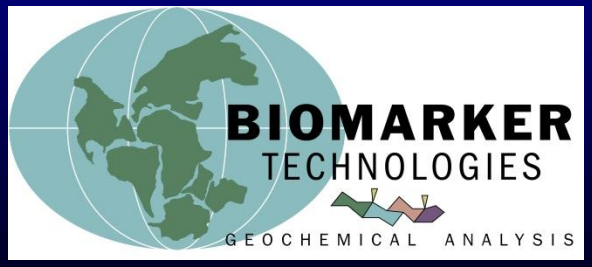


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The magic bullet for correlation of all hydrocarbon fluids must…

- Be ubiquitous in thermal hydrocarbon fluids
- Form prior to expulsion from the source rock
- Carry a source-specific chemical signature
- Not be altered by secondary effects

Diamondoids are the magic bullet!!!

Facts About Diamondoids

Ubiquitous in thermal hydrocarbon fluids:

> 5000 samples analyzed: all crude oil, condensate, seepage oil, biodegraded oil, source rock, and tight shale.

Form prior to expulsion from the source rock:

Originate from organic matter at super-acid sites in the source rock.

Diamondoids are the magic bullet!!!

Facts About Diamondoids

Carry a source-specific chemical signature:

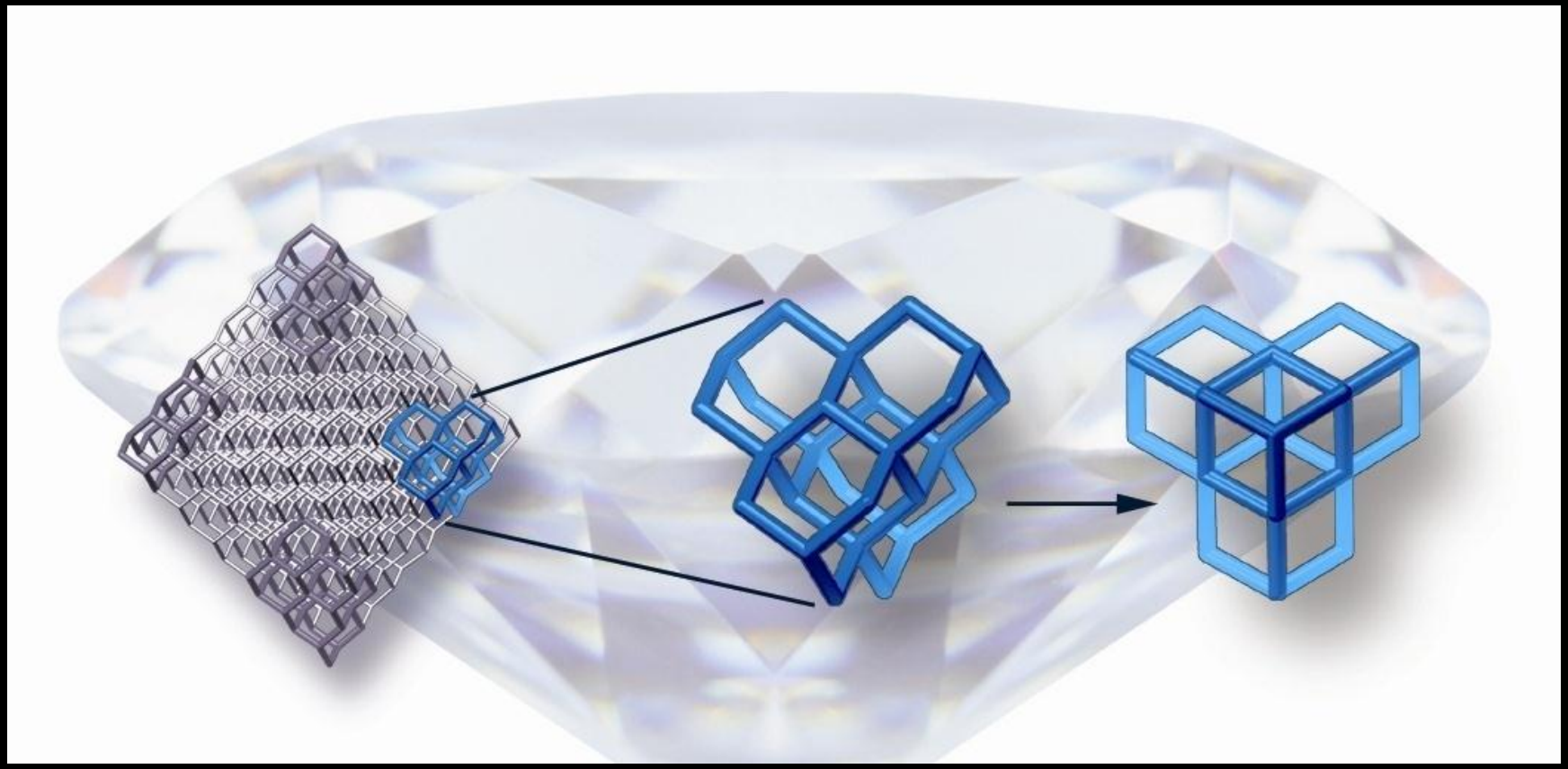
Isotopically and structurally related to the organic matter from which they are formed.

Not altered by secondary effects:

Unaltered to at least 4.0 % Ro.
Quantifiable in severely biodegraded oil.

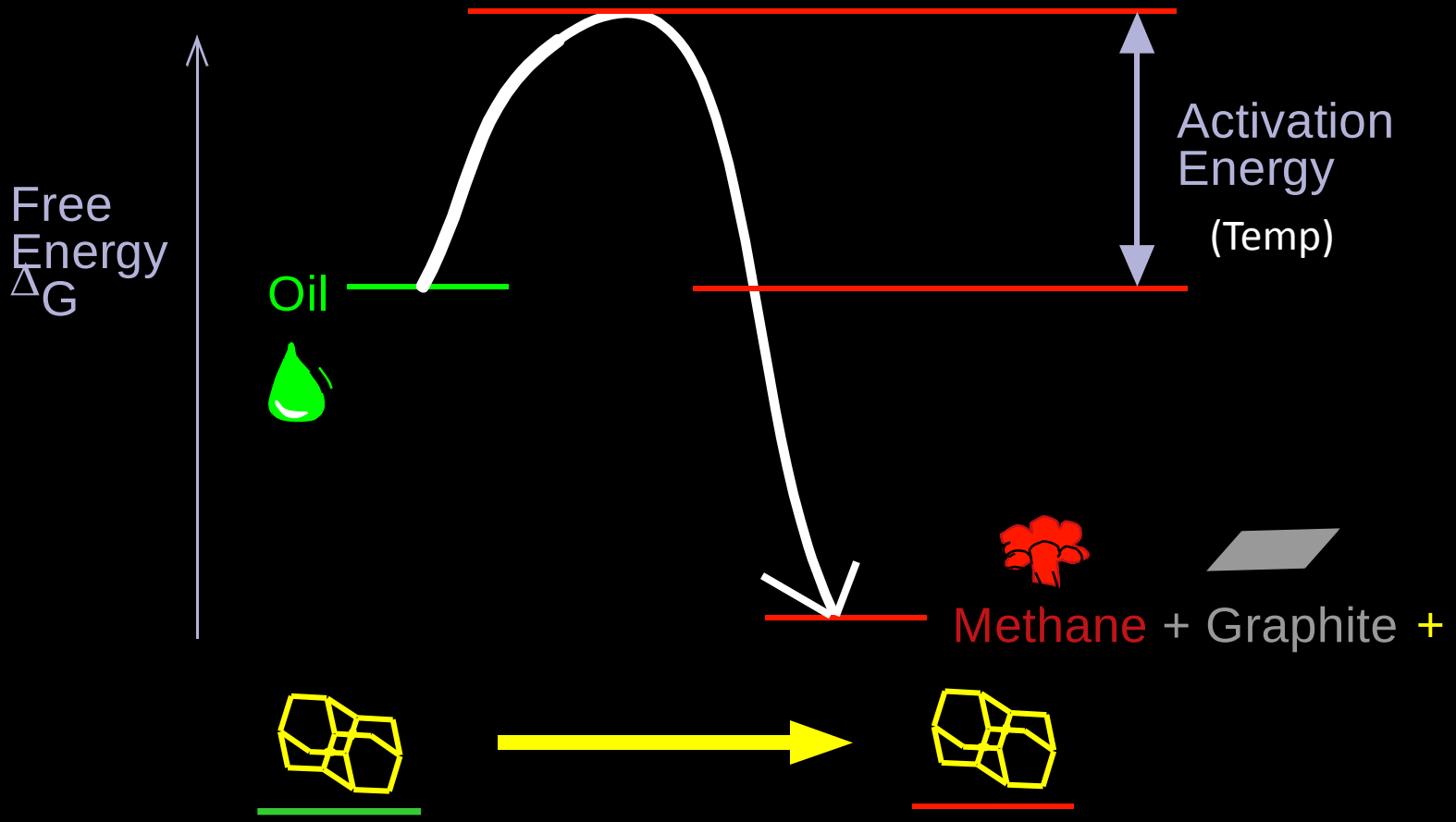
Diamondoids are the magic bullet!!!

Diamondoids are the Ultimate Oil-Field Nanosensors



They are Extremely Stable Oil Components.
All Petroleums Contain Diamondoids.

What happens to diamondoids during oil cracking?

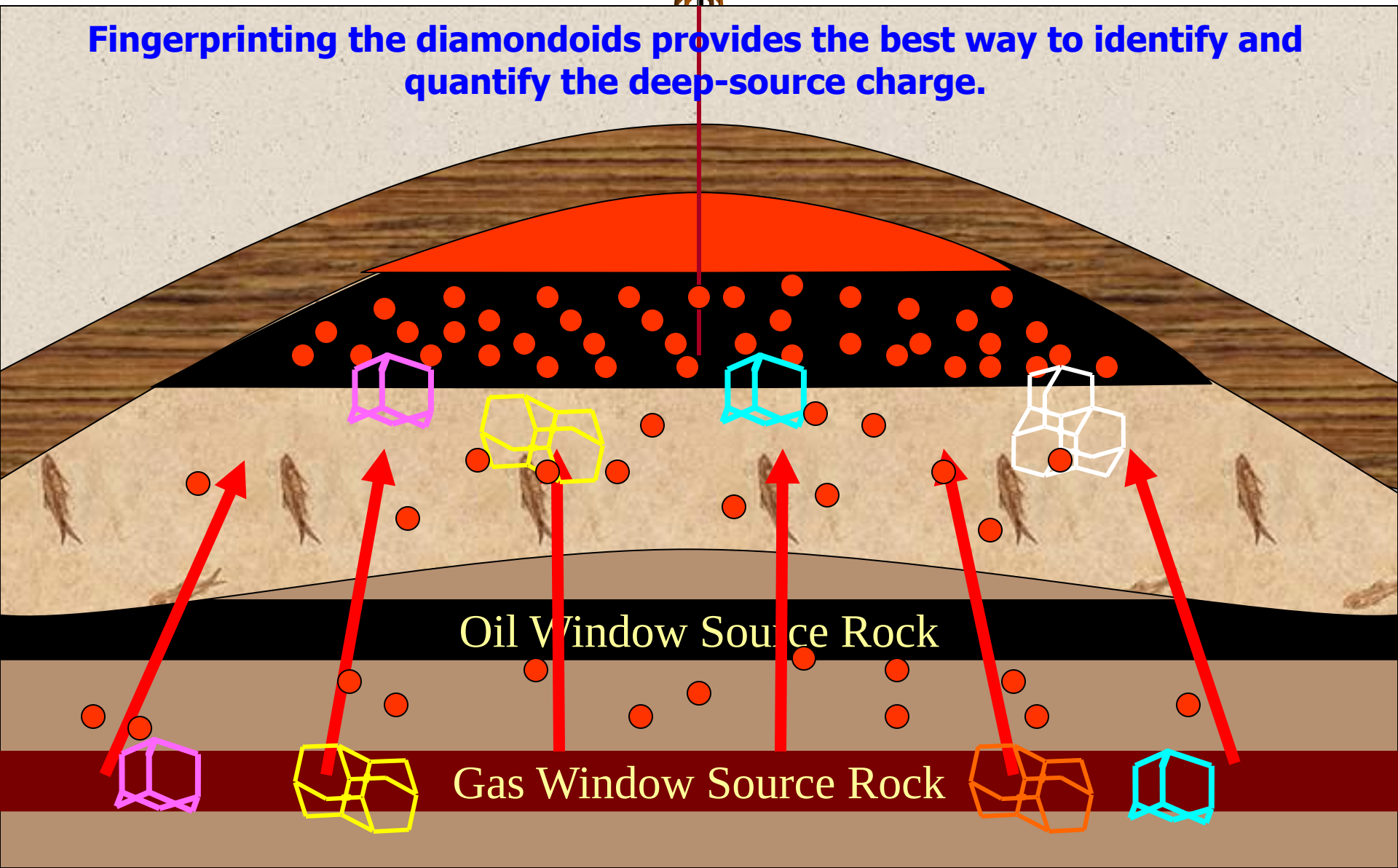


They undergo no chemical or physical change!

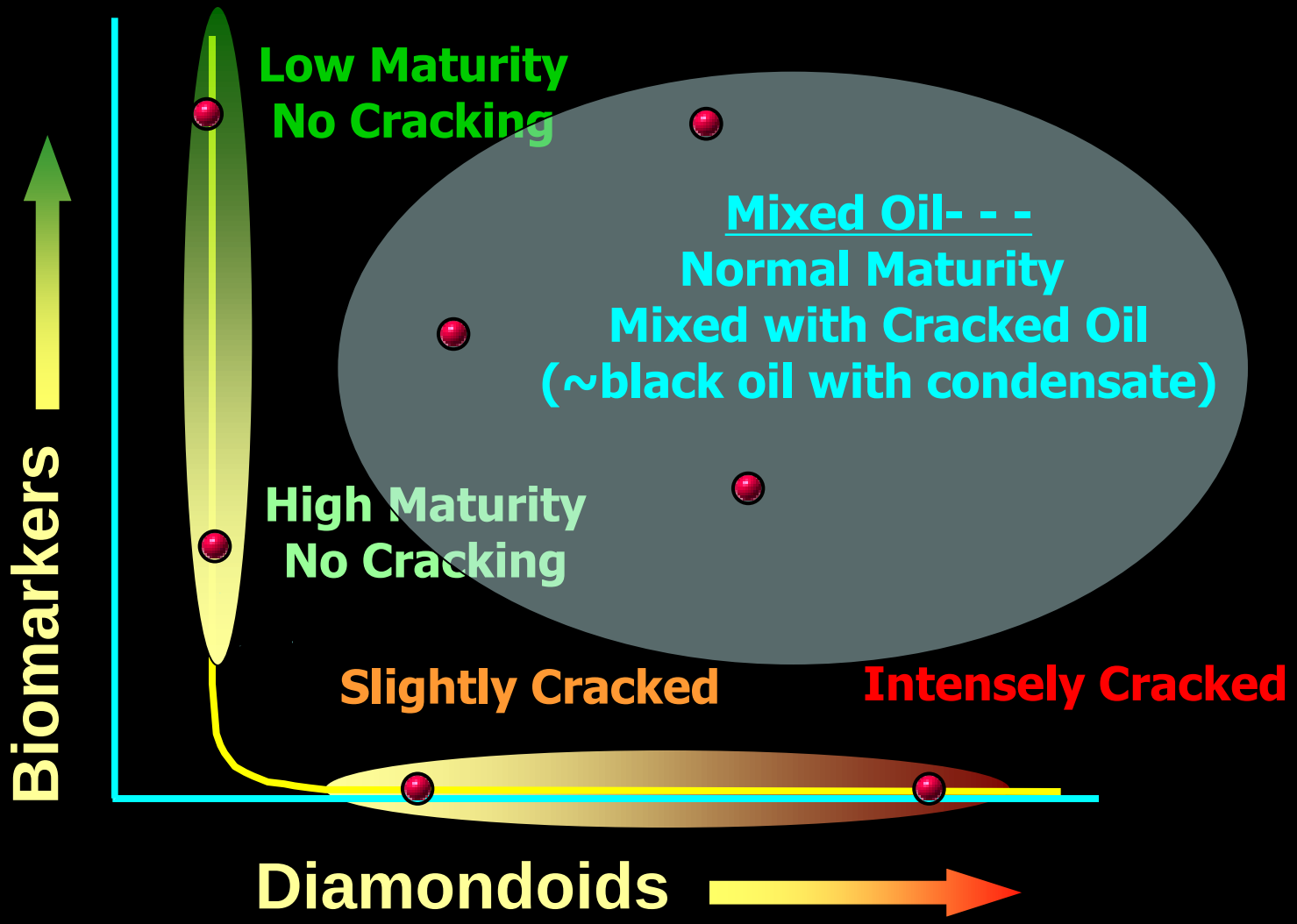
They become more concentrated in the remaining cracked oil or bitumen

Deep gas and condensate bubble up through the reservoir.

Gas may move on while diamondoids remain in the reservoir.



Recognition of Cracked/Mixed Oil by Quantitative Diamondoid Analysis (QDA)



Dahl et al., 1999

GEOCHEMICAL PARAMETERS FOR UNRAVELING MIXTURES

and/or

WHEN BIOMARKER DATA ARE COMPROMISED

AND NEED SOME HELP

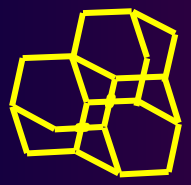
Black Oil, Condensate, Biodegraded Oil, etc.

TECHNOLOGIES TO DETERMINE THE DEEP SOURCE

(1) COMPOUND SPECIFIC ISOTOPE ANALYSIS of DIAMONDOIDS (CSIA-D)

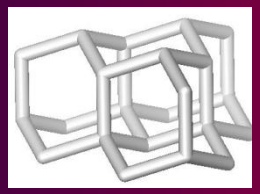
(2) QUANTITATIVE EXTENDED DIAMONDOID ANALYSIS (QEDA)

Structures of diamondoids in QEDA studies

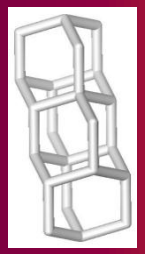


Triamantane
Used for normalization

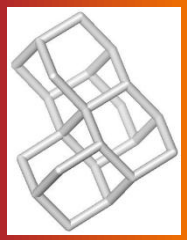
T1



T2

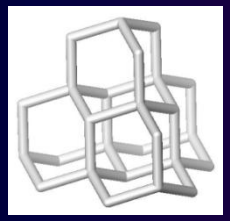


T3



Tetramantanes

P1



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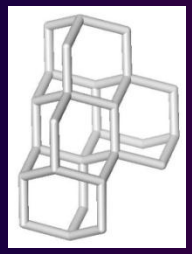

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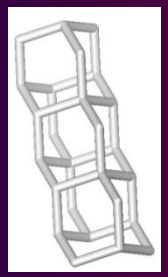
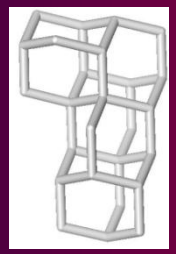


P4

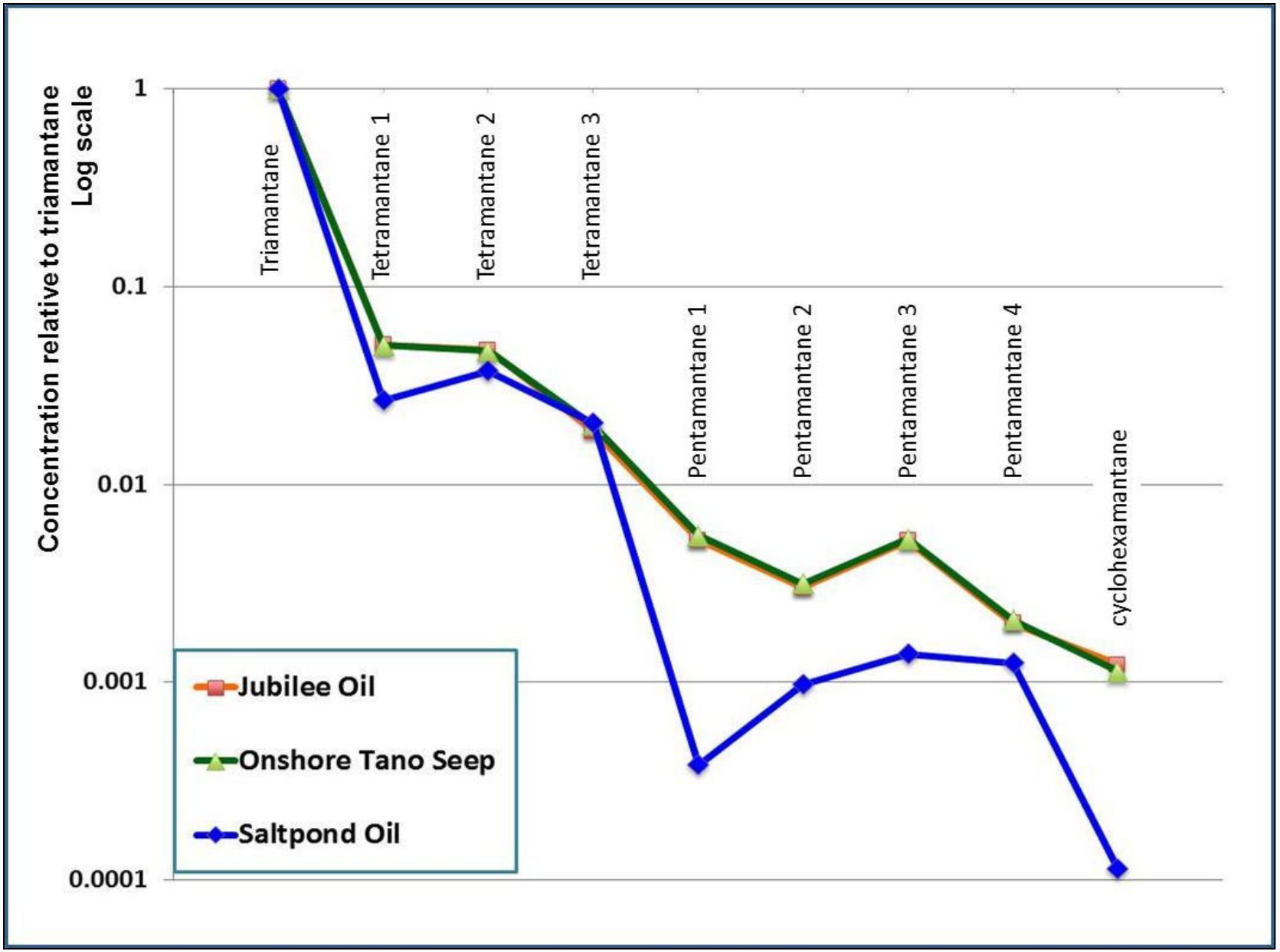


H1

Cyclohexamantane

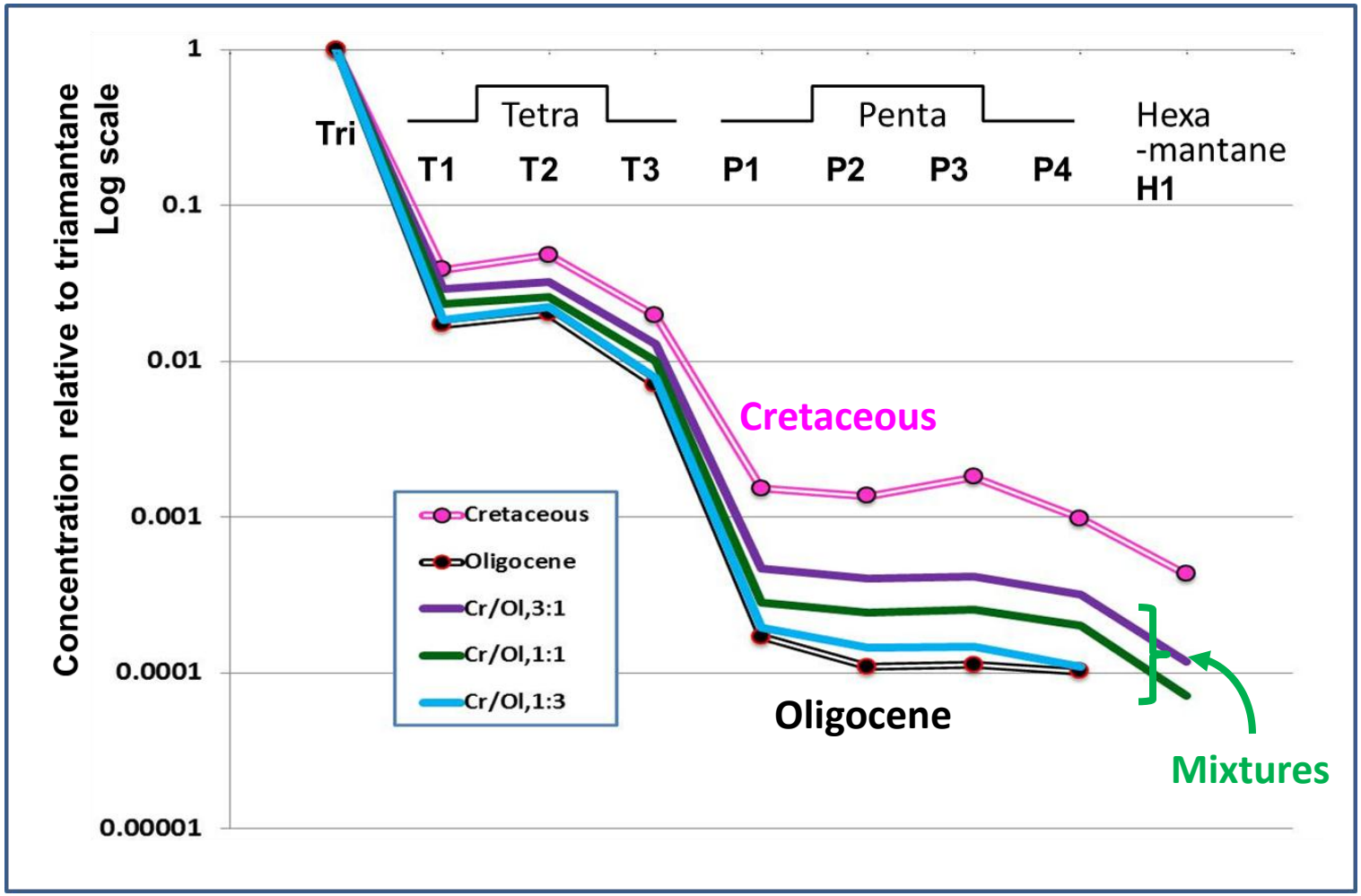
Pentamantanes

EXAMPLE Correlation of oil samples from Ghana

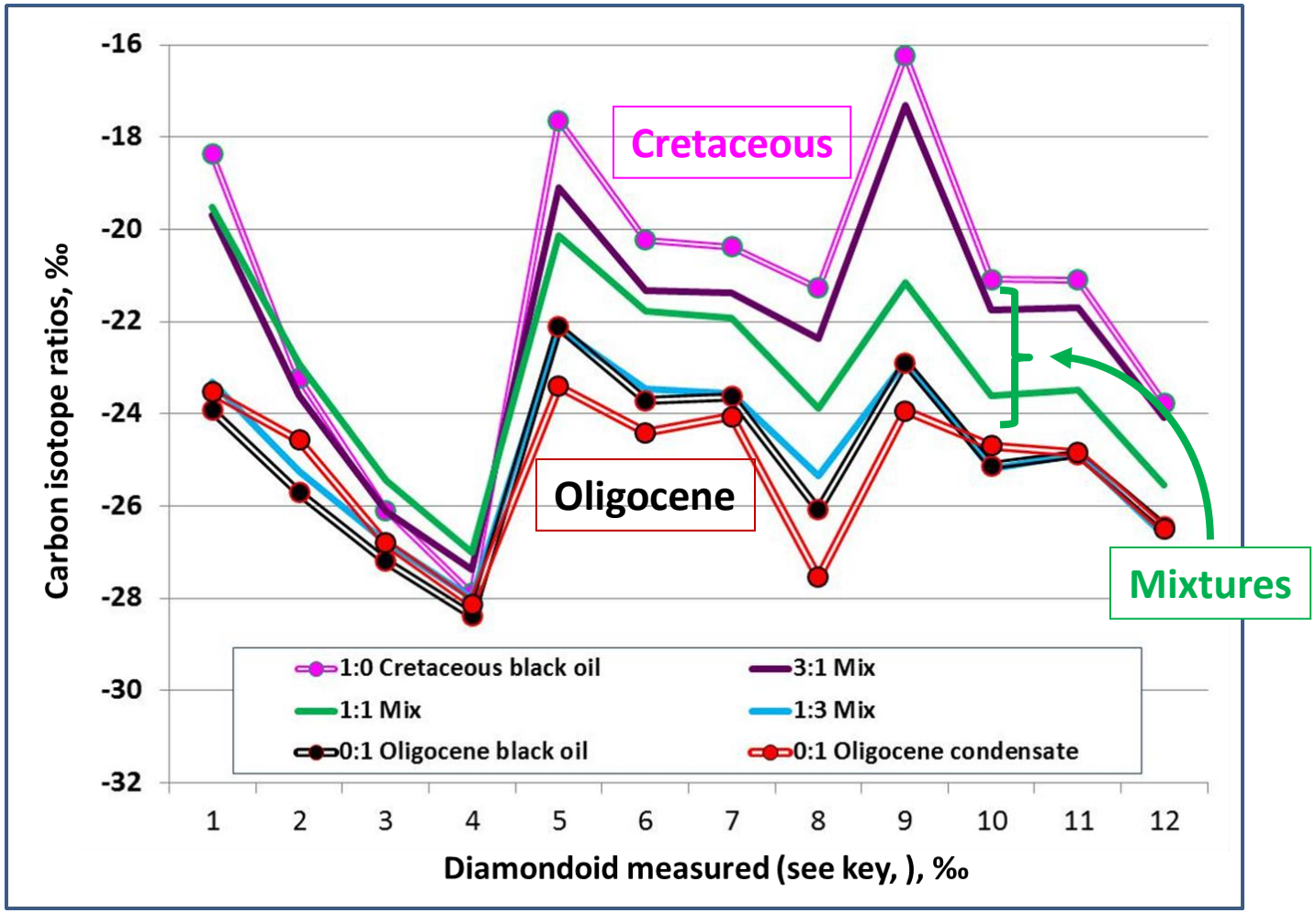


Cretaceous and Oligocene oil samples from Venezuela differentiated by QEDA

Various mixtures shown



Isotope ratios of diamondoids measured in Cretaceous and Tertiary-oil end-members oils from Venezuela, and their mixtures.

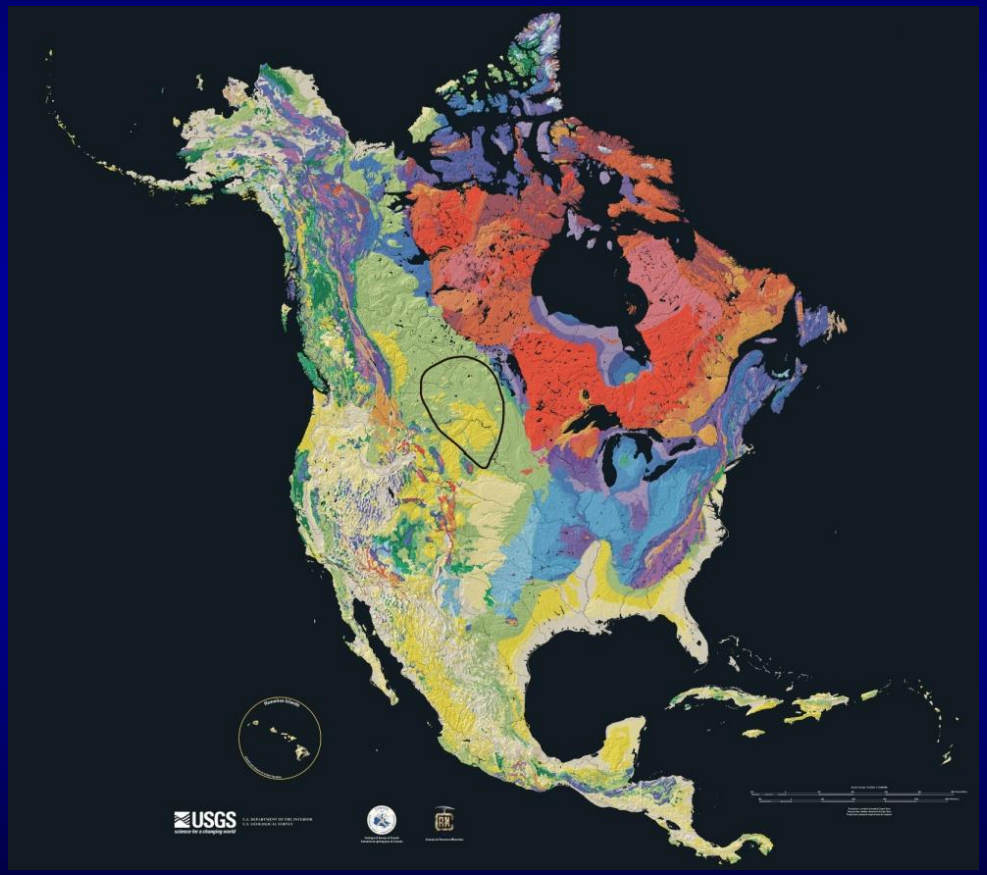


GEOCHEMICAL PARAMETERS FOR UNRAVELING MIXTURES

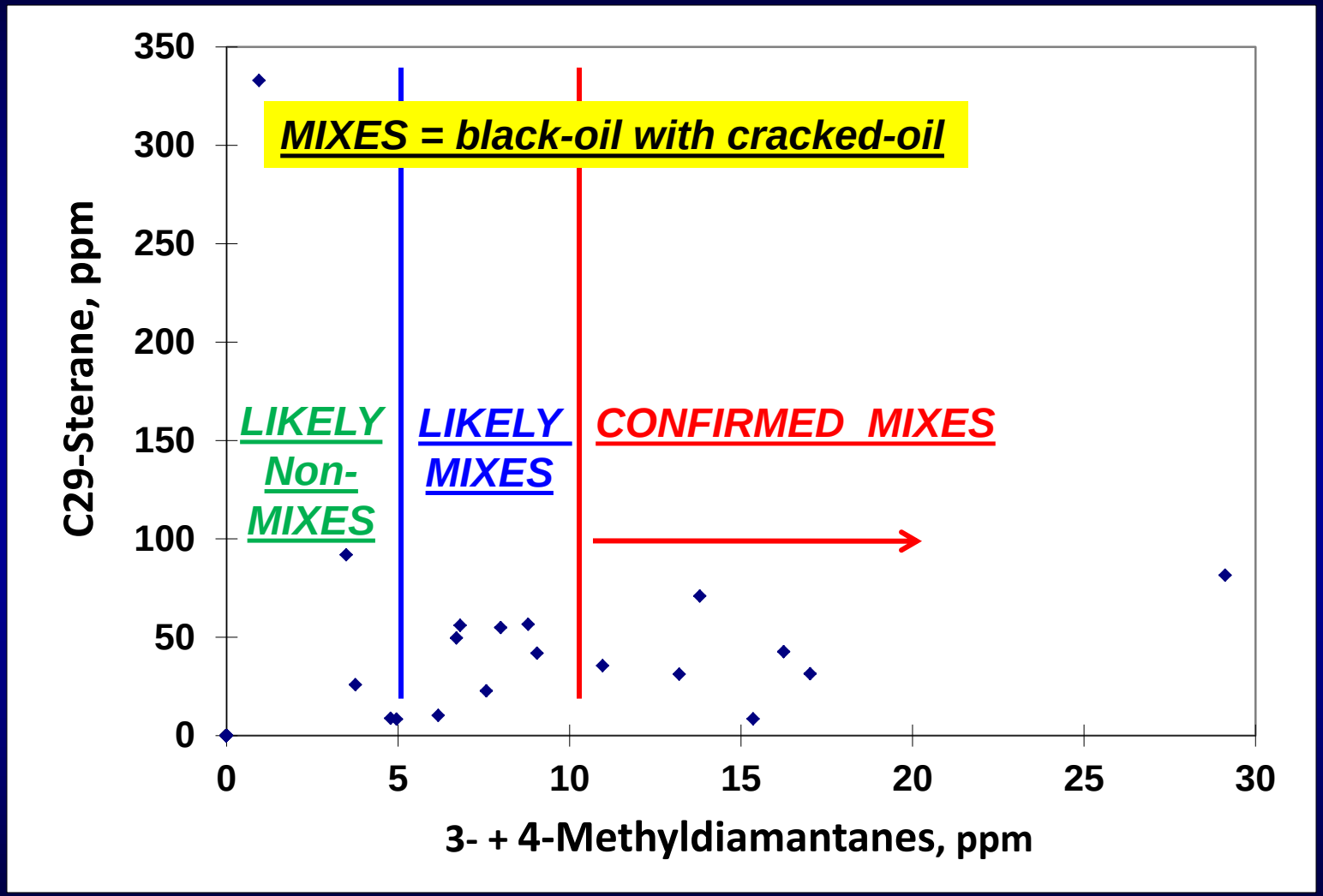
Example from

WILLISTON BASIN

Williston Basin: A frontier for oil and gas production from tight shale

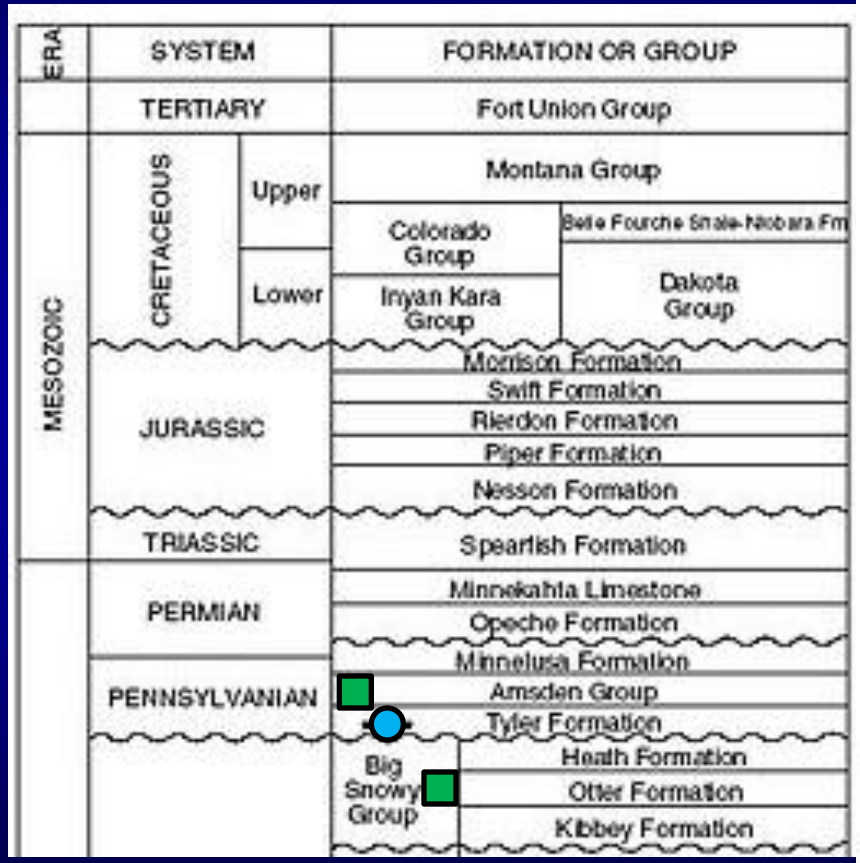


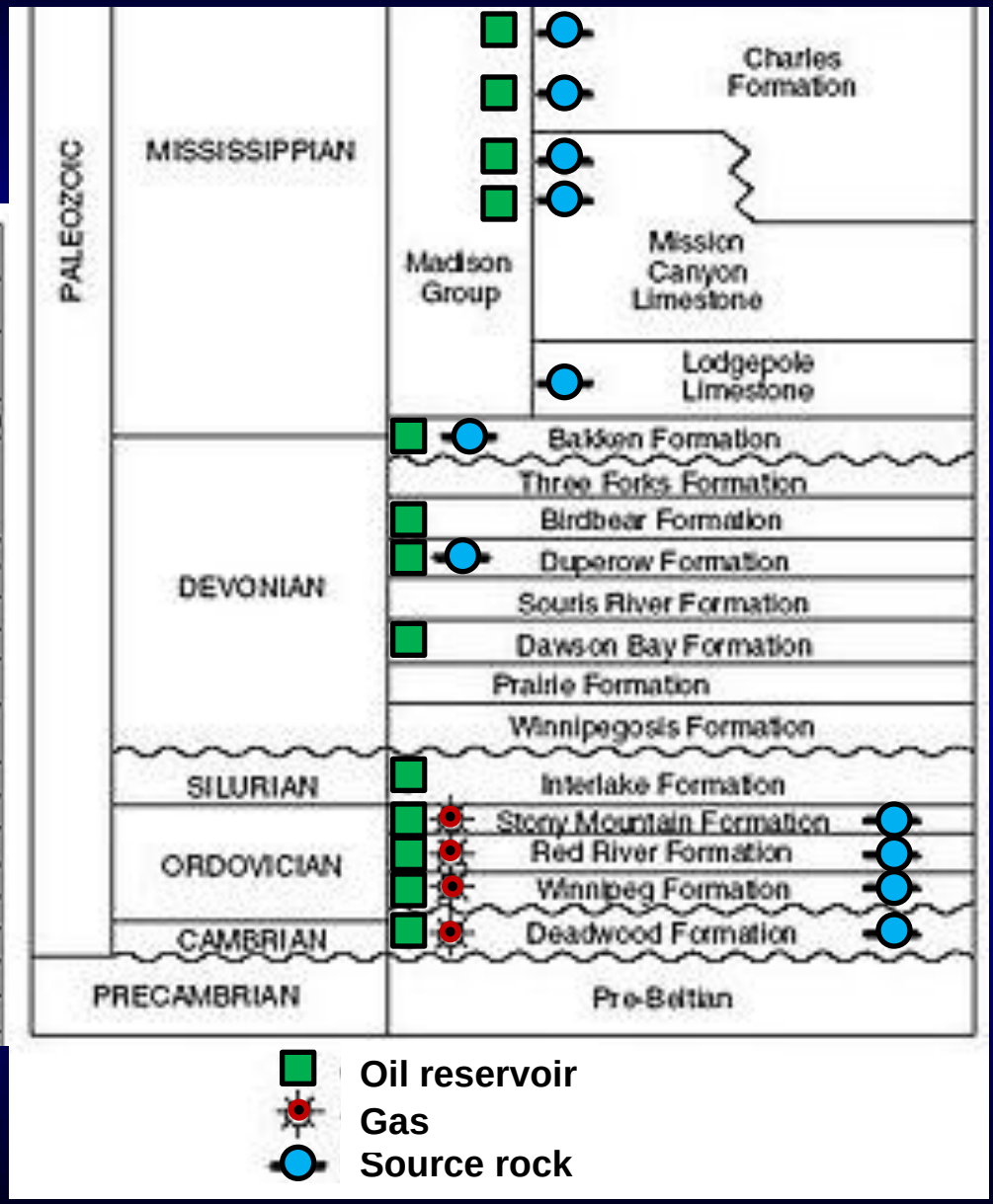
Quantitative Diamondoid Analysis (QDA)
Black-oil/Cracked-oil mixes occur commonly in the Williston Basin



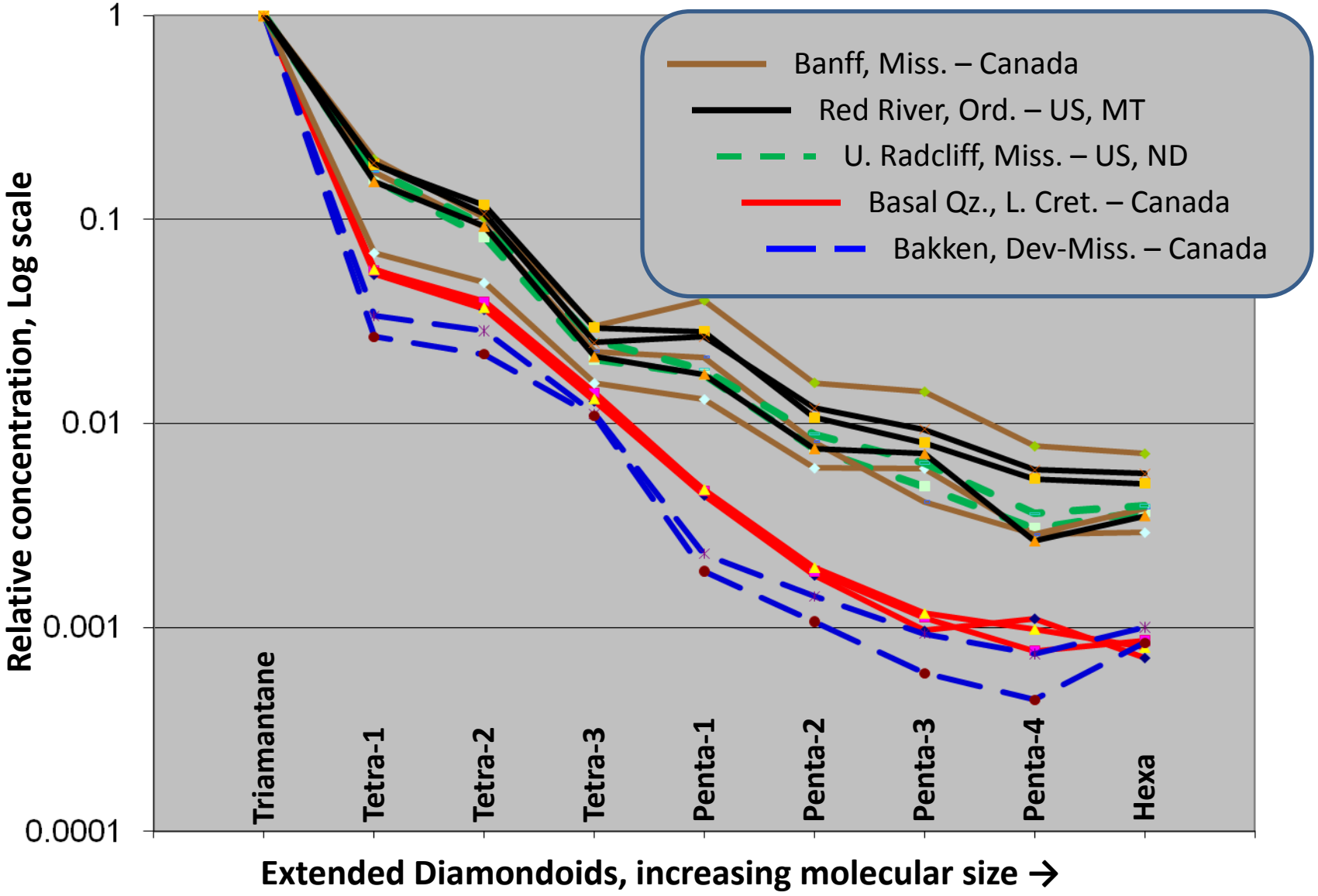
All oil samples in this set appear as black oil.
The high-maturity cracked-oil cannot be detected by a light color.

Twelve proven and potential source rocks of the Williston Basin

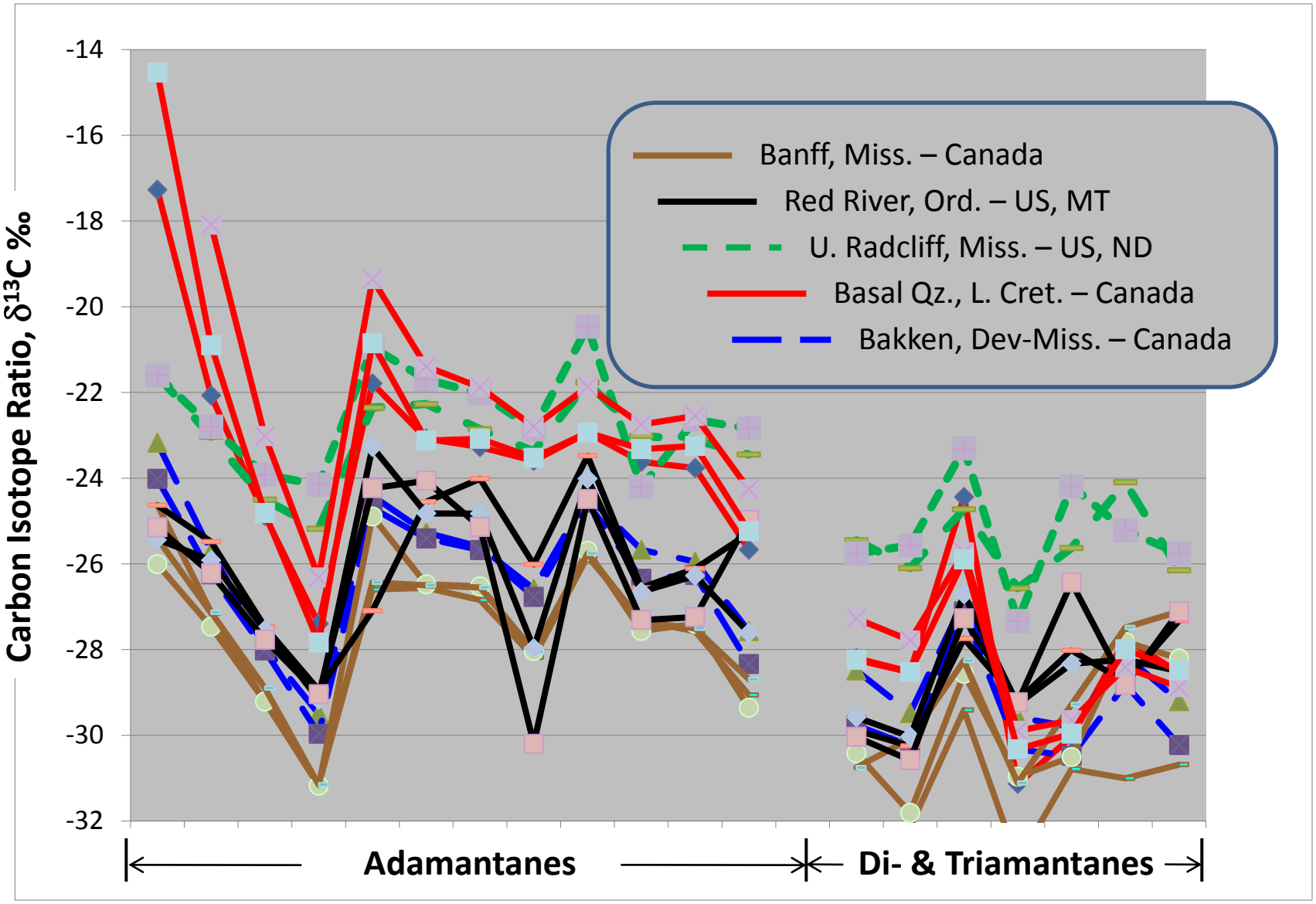




Quantitative extended diamondoid analysis (QEDA)
Williston Basin oil-source correlation for cracked oil, black oil and mixes



Compound specific isotope analysis of diamondoids (CSIA-D)
Williston Basin oil-source correlation for cracked oil, black oil and mixes



GEOCHEMICAL PARAMETERS FOR UNRAVELING MIXTURES and INFERRING GAS SOURCES

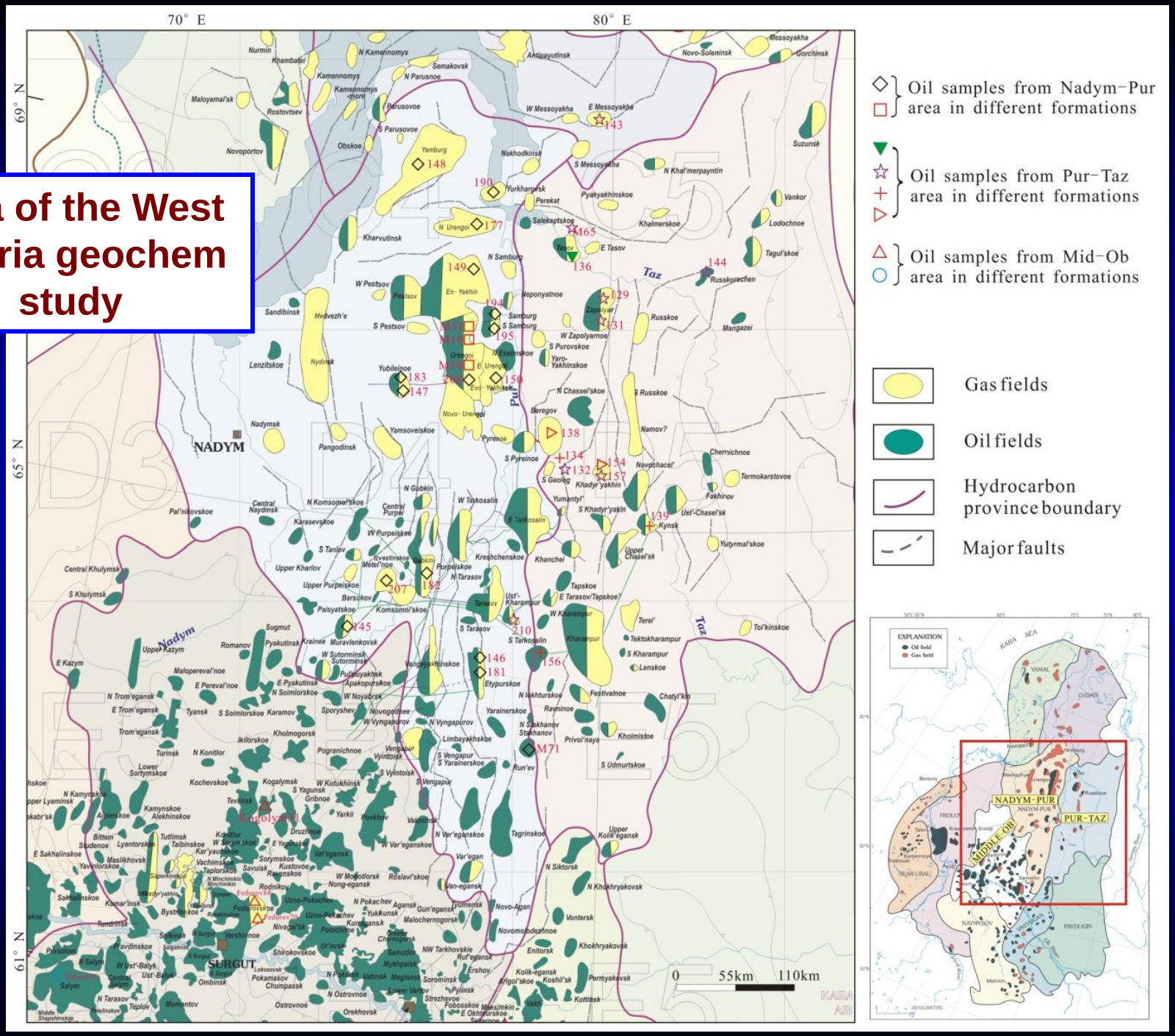
Example from

NORTH CENTRAL WEST SIBERIA

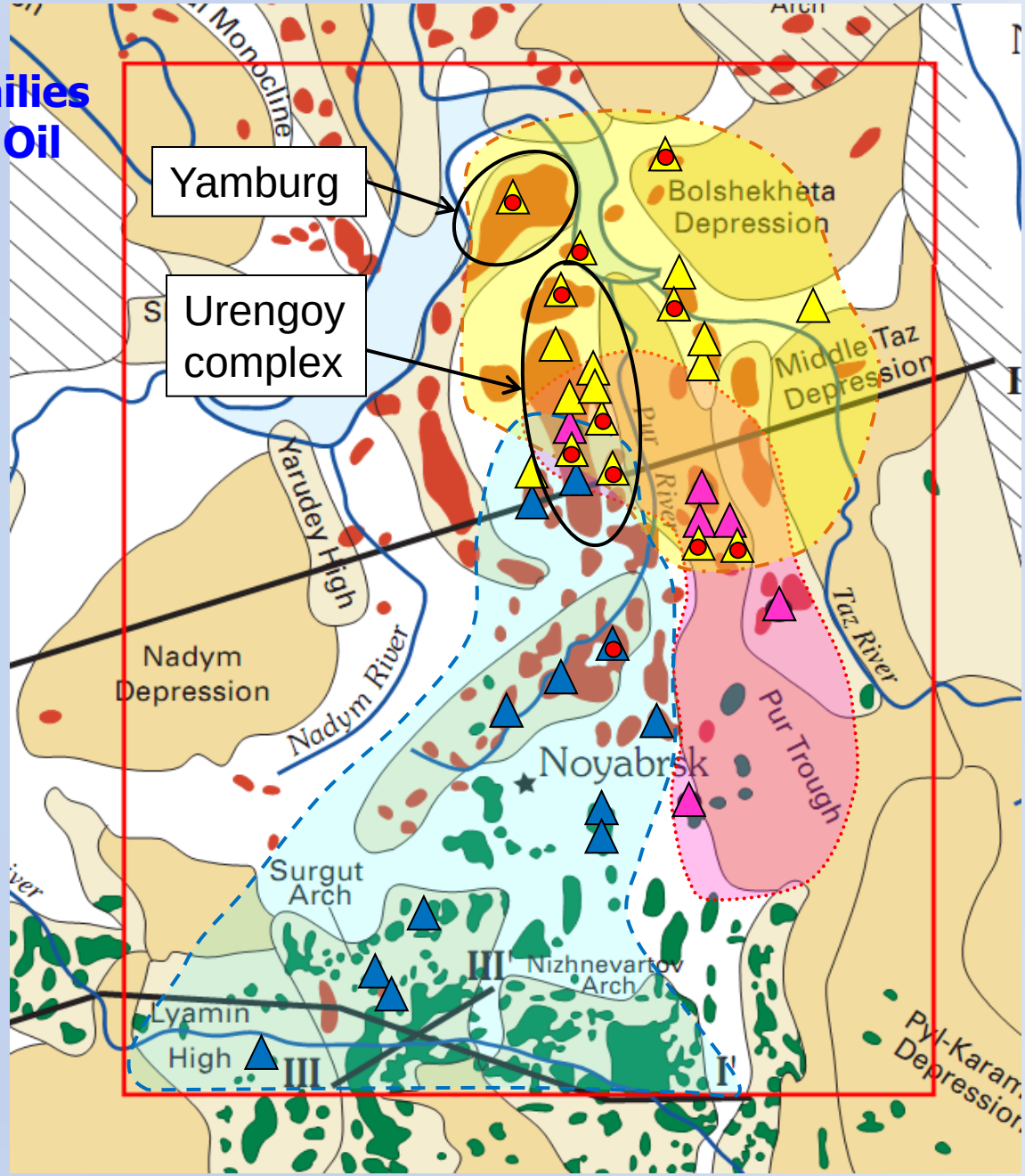
BIOMARKER TECHNOLOGIES
GEOCHEMICAL ANALYSIS

LELAND STANFORD JUNIOR UNIVERSITY
ORGANIZED 1891

Area of the West Siberia geochem study



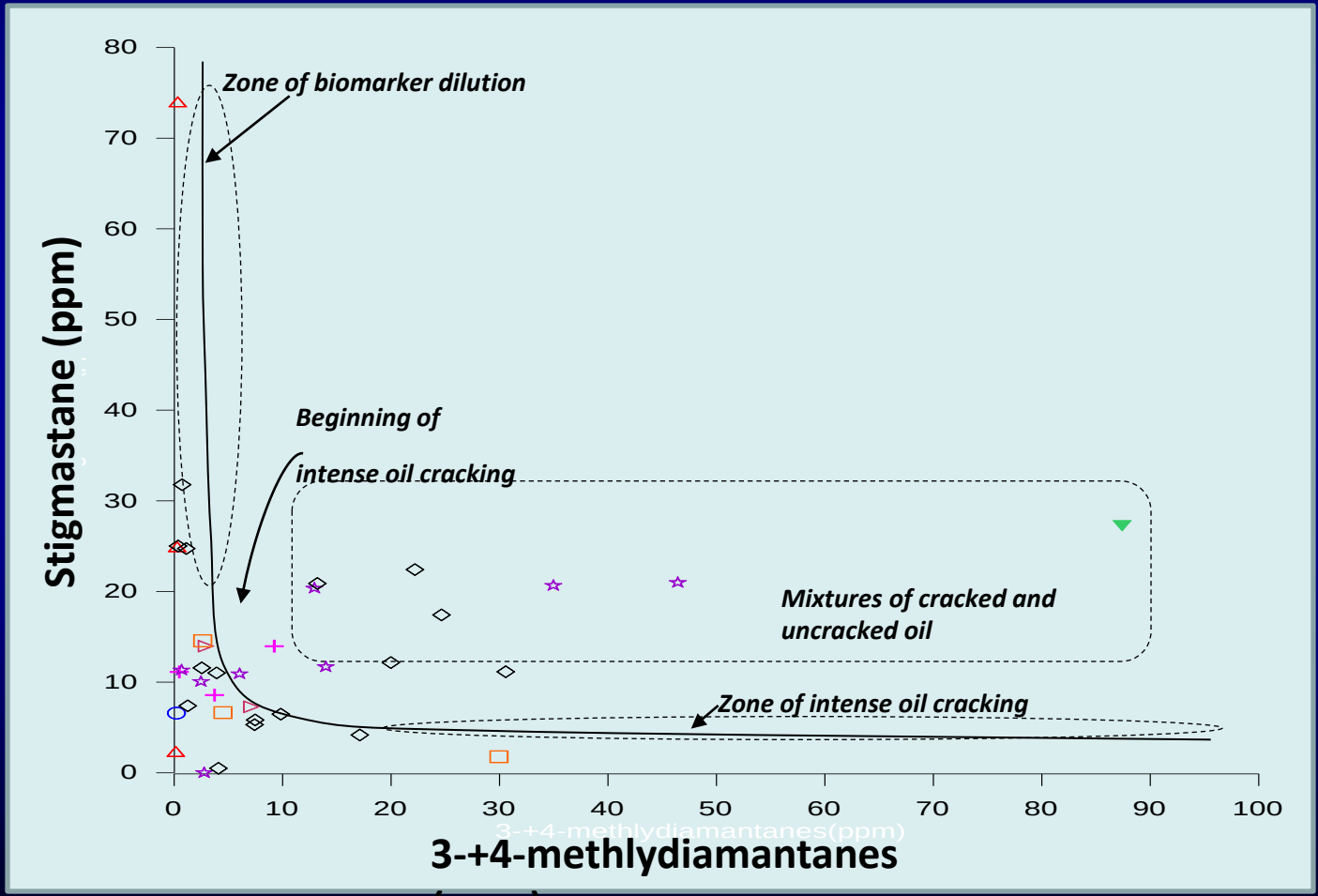
Map Showing Study Area, Distributions of the Oil Families and Occurrence of Cracked Oil



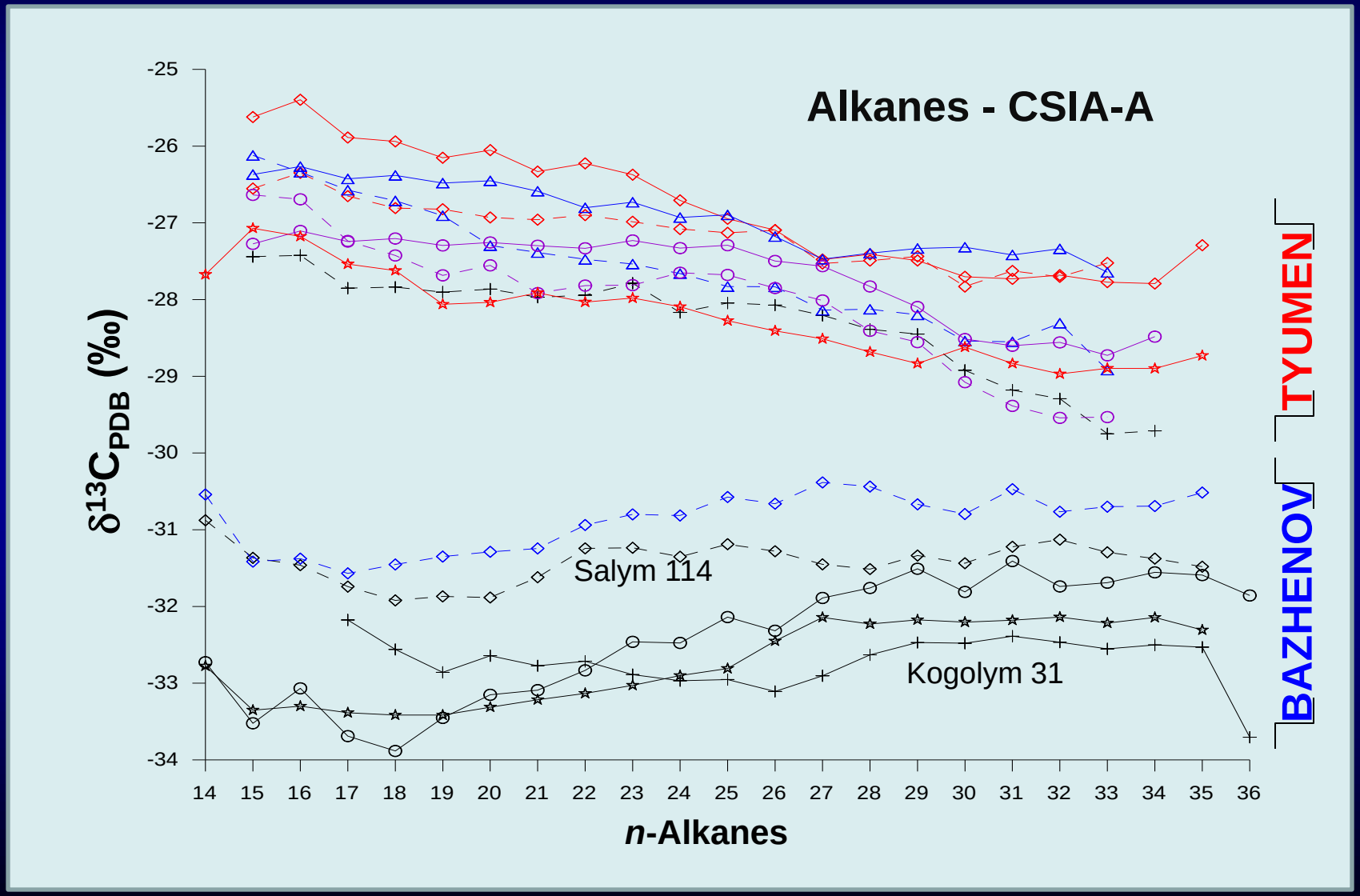
- Basin boundary
- Gas field
- Source-Mixed area
- High diamondoids
- Study area
- Oil field
- Family I sample
- Structural high
- Family area
- Family II sample
- Structural low
- Family II area
- Mixed sample

0 100 200 300 400 500 km

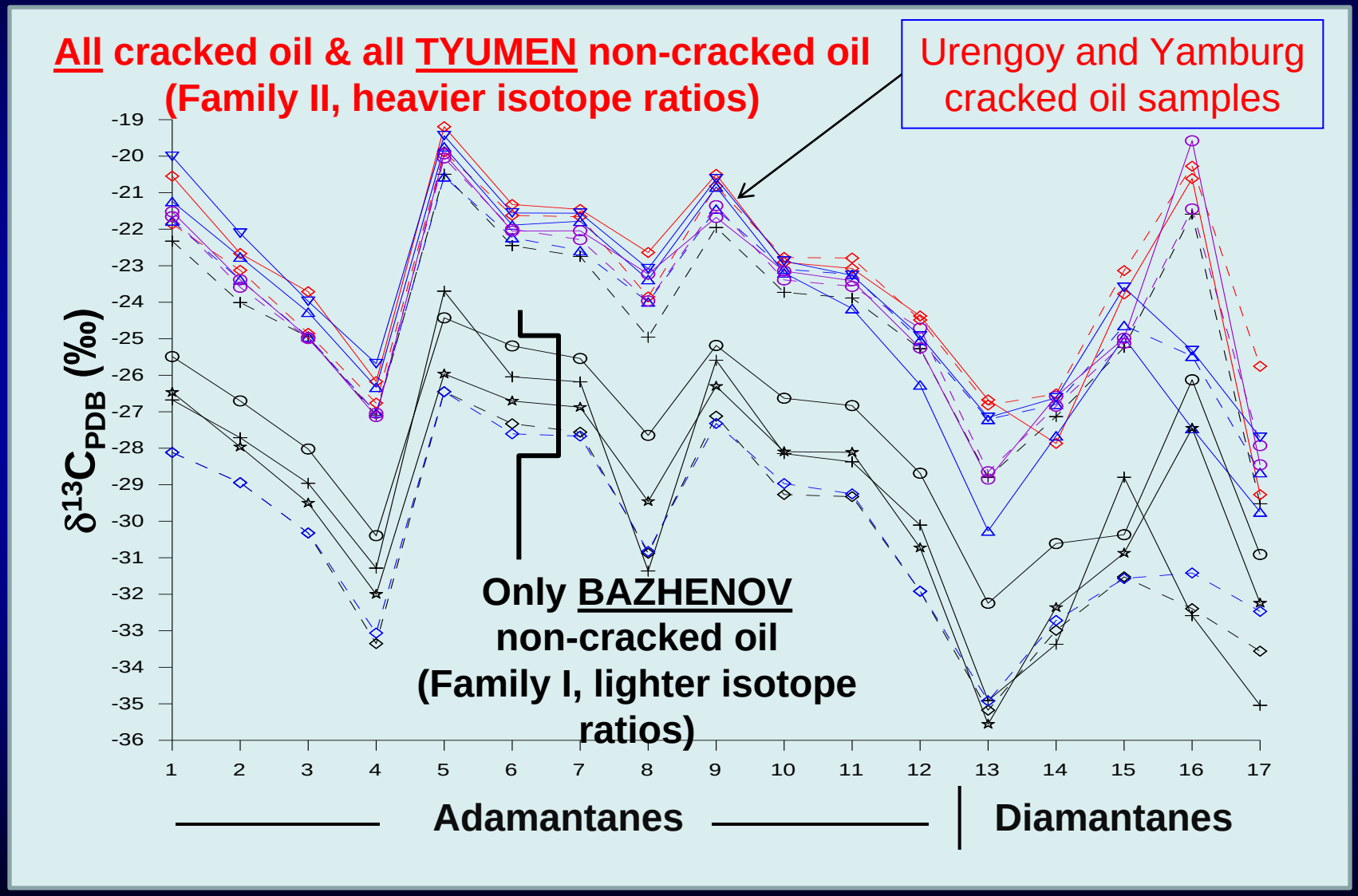
The Diamondoid-Biomarker Cracking Chart Shows Many Cracked and Mixed-Maturity Oil Samples



Isotopes of the n-Alkanes distinguish End-member Oil Families I & II
Mixed-Oil Family IIIa Is Dominated By Source II
Mixed-Oil Family IIIb Is Dominated by Source I



Diamondoid isotopes by CSIA-D distinguish oil families. All cracked oil samples show diamondoids in Family II.



CONCLUSIONS – North Central West Siberia Oil Systems

- ⇨The Upper Jurassic Bazhenov Source that dominates the Middle Ob Region (South Central West Siberia) fades in importance toward the north, replaced by a (putative) Lower-Middle Jurassic Deltaic source such as Togur-Tyumen

- ⇨ Liquids from the giant gas fields (i.e., Urengoy & Yamburg) are dominated by the L-M Jurassic source signature

- ⇨ Cracked oil found in those northern oil and gas fields correlates by diamondoid isotopes (CSIA-D) with the L-M Jurassic CSIA-D signature

- ⇨ The occurrence of cracked oil from the deeper L-M Jurassic source in the giant gas fields suggests they contain thermal gas and tentatively assigns the primary gas source as the Togur-Tyumen formation

CONCLUSION

Diamondoids are the magic bullet to investigate all types of challenging correlation problems

Thank you!!

Deep/cracked-oil source?
Mixed oil?
Biodegraded oil

Thank you!!

Thank you!!