New Techniques for Recognizing and Understanding High-Maturity Petroleum Systems in California*

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Abstract

Deep petroleum systems are little understood components of California's sedimentary basins. Condensates, high API gravity admixtures to black oils, and thermogenic gas represent new and difficult plays for exploration. Our work is aimed at recognizing these systems, their source rocks, their thermal history and migration. It involves surveying extensive sample libraries for the occurrence of ultra-stable markers (diamondoids, simple aromatics, triaromatic steroids, etc.) in cracked or mixed oil and mapping out their contributions to known reservoirs. Previous work in California focused on less stable molecular markers (i.e. biomarkers) and was blind to these high maturity contributions.

Ultra-stable components can be fingerprinted and correlated with petroleum source rocks using higher diamondoid distributions, diamondoid isotopes, aromatic isotopes, and light hydrocarbon isotopes. Newly defined petroleum systems can be modeled and potential hydrocarbon contributions considered during exploration.

A growing database of more than 100 petroleum samples from the San Joaquin, Salinas, Santa Barbara, Los Angeles, and the Eel River basins are being collected. High maturity contributions have already been recognized in many San Joaquin, Santa Barbara, and

Eel River fields as part of this work. Preliminary fingerprinting of ultra-stable markers indicates deep highly-cracked sources from the Cretaceous, Eocene, and Miocene in California's sedimentary basins. Most deep contributions are found as mixes with black oils where they dominate the distribution of ultra-stable markers but contribute little to the distribution of biomarkers. Unique fingerprints for both biomarkers and ultra-stable markers helps point toward the source rock for these independent components and provide a fuller view of petroleum systems.

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Leifer, I., and D. Culling, 2010, Formation of seep bubble plumes in the Coal Oil Point seep field: GeoMarine Letters, v. 30/3-4, p. 339-353.

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biomarker technology

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High-Maturity Petroleum Systems

Fundamental to modeling of petroleum systems is determining that the correct source (and all potential sources) are being modeled.

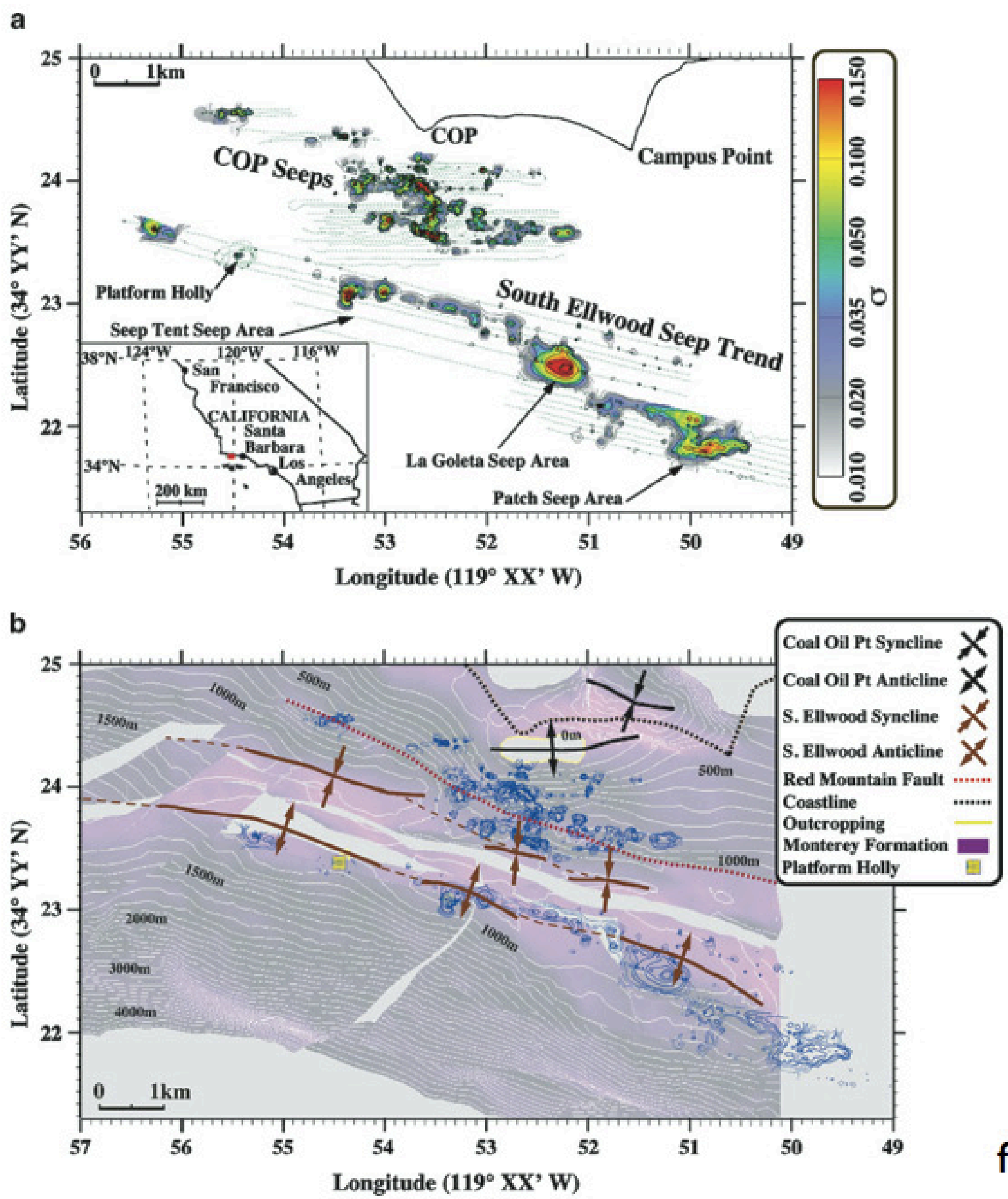
Ultra-stable molecular markers provide us with molecular and isotopic fingerprints to **source** high maturity liquids -- alone or in mixtures

A growing knowledge of these compounds, their genesis, and destruction may provide more detailed information concerning both source and evolution of petroleum systems.

Understanding high-maturity systems sheds light on **Unidentified Sources**, **Causes for API variability**, **GOR**, and **sources of thermogenic gas**.

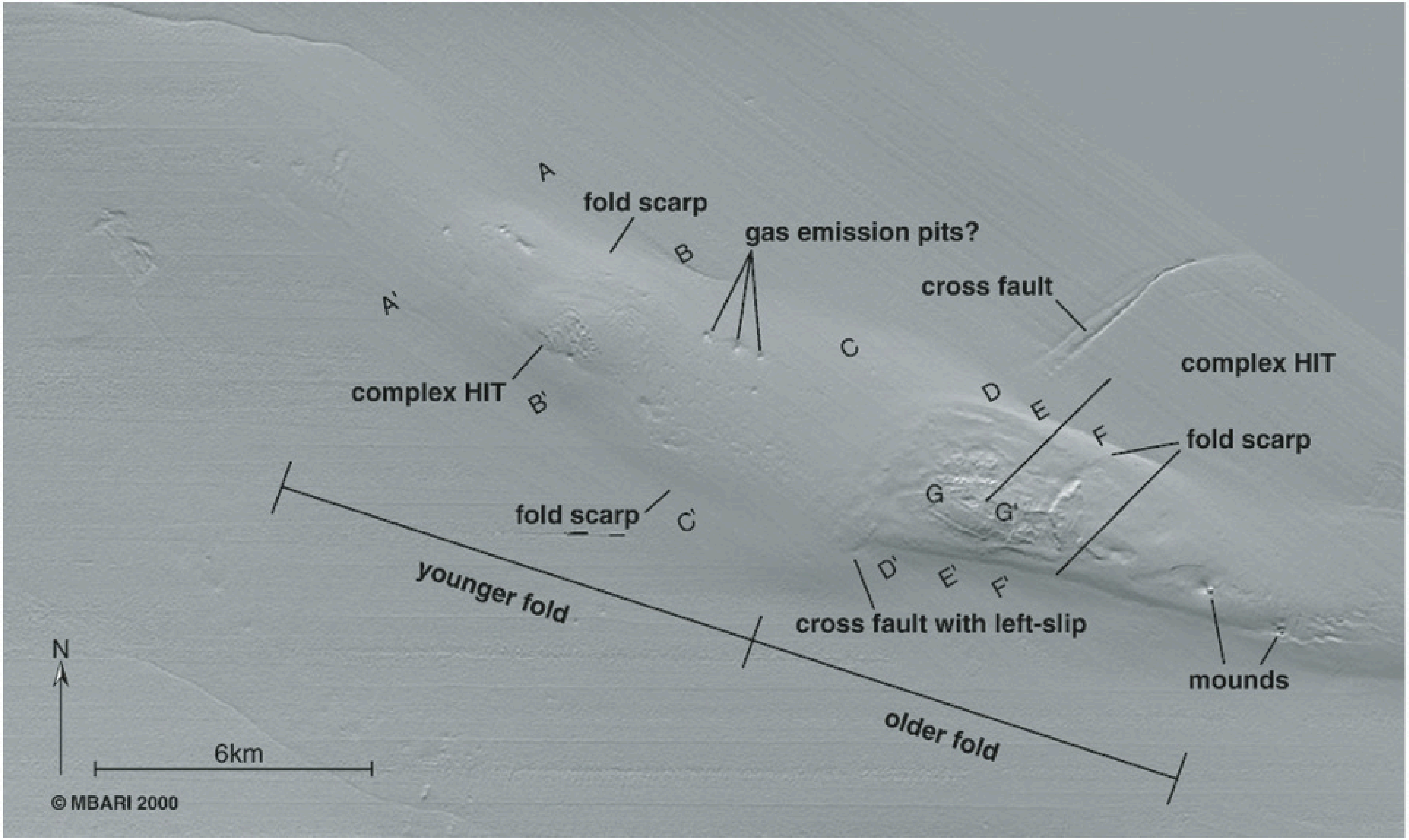
California Deep Source Study:
Focusing on Accessible Produced Oil Samples and Seeps -- a Joint USGS / Stanford

Visualizing Santa Barbara Seeps with Bubble Streams



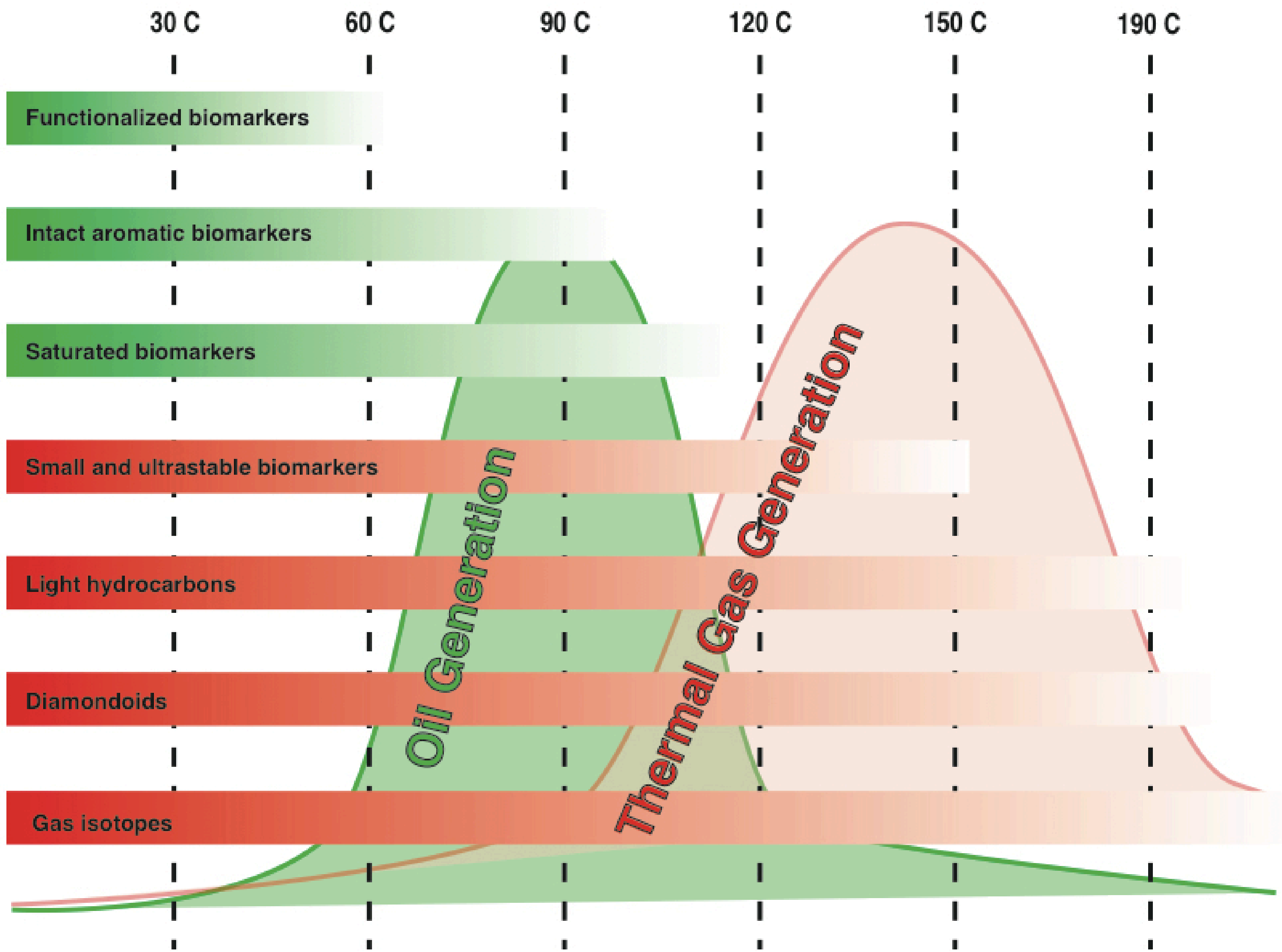
from Leifer et al, 2010

Santa Barbara Basin -- Hydrocarbon Induced Topography



from Keller et al., 2007

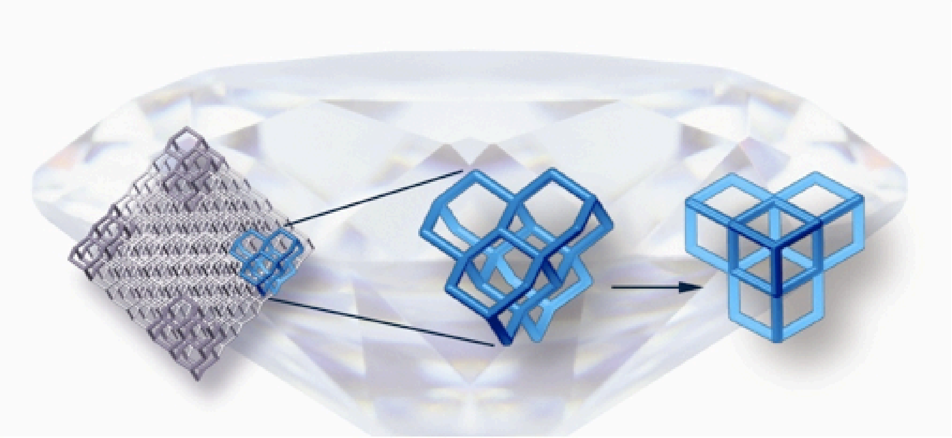
Most widely used source parameters have limited utility at high maturity



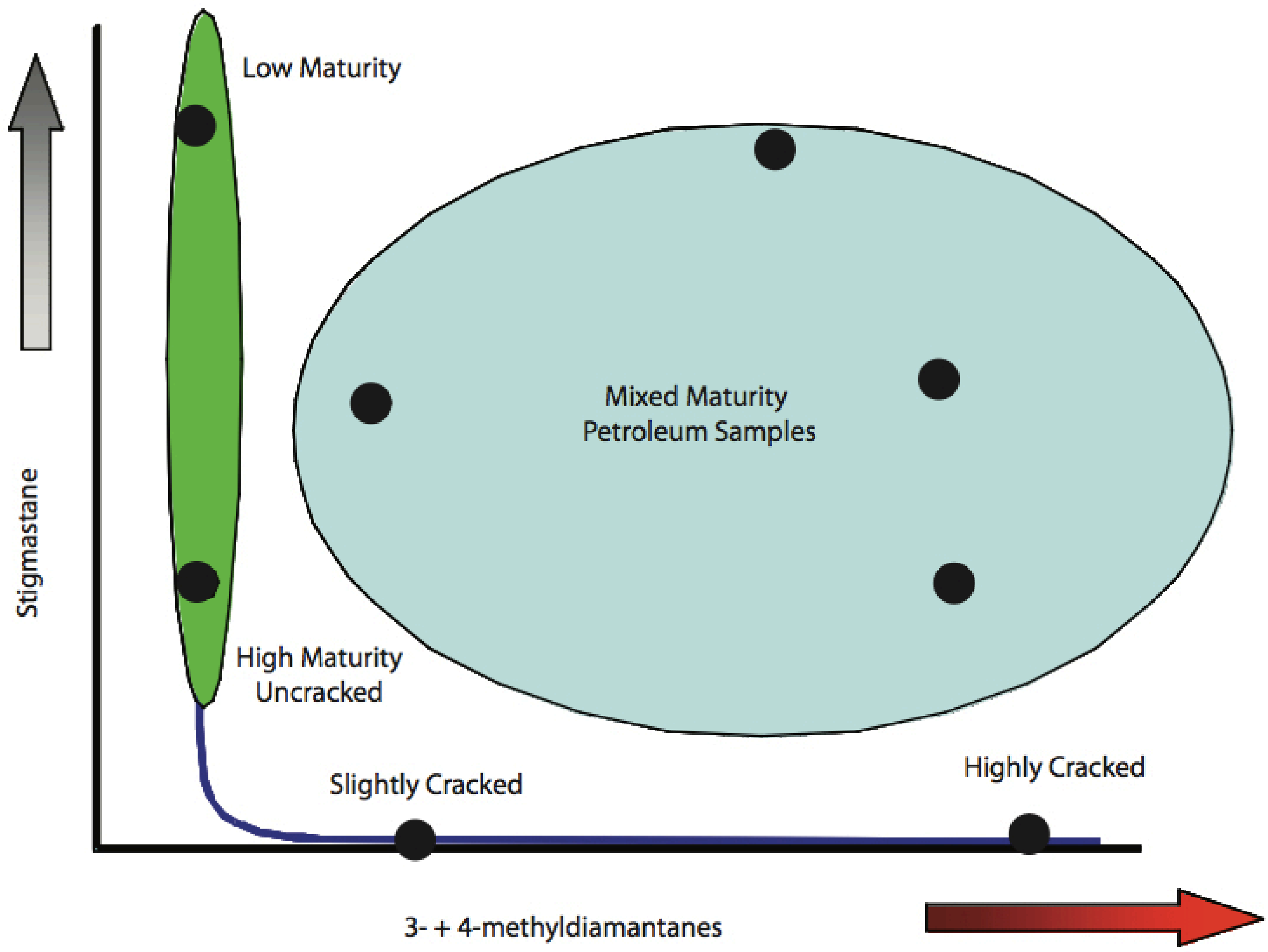
Today's Focus: Diamondoids

Conservative Compounds Present Throughout Oil and Gas Windows

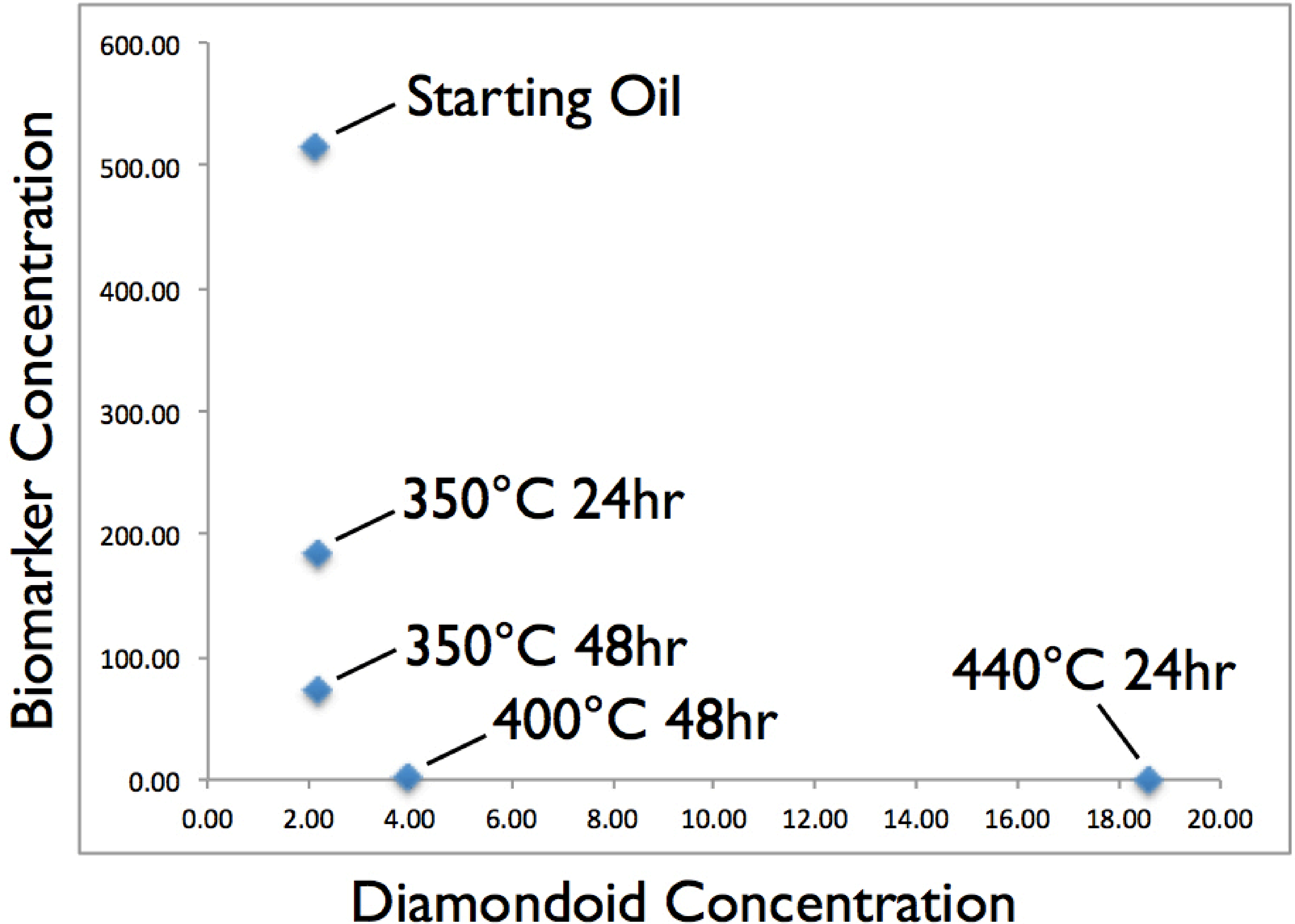
- **Quantitative Cracking Estimates**
- **Identification of "Stealth" Condensate Contributions**
- **Correlations across the Broadest Possible Range of Maturities**
- **Vapor phase transport and evaporative fractionation**
- **Thermochemical Sulfate Reduction studies**
- **Tight Shales: % Cracking, Gas Pressure, Oil Properties, Diffusive Gas Loss**



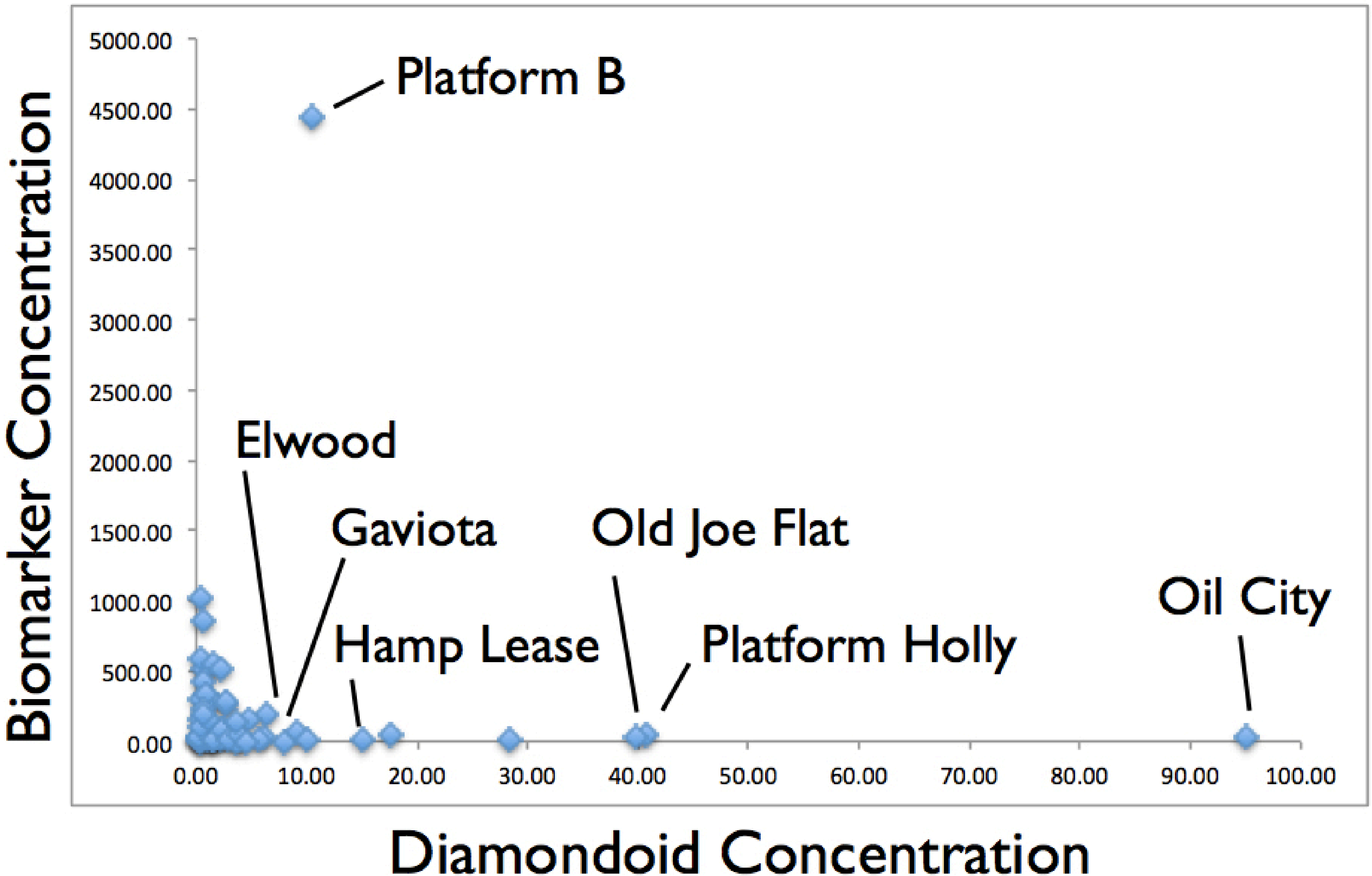
Identifying mixed petroleum samples based on quantitative diamondoid analysis



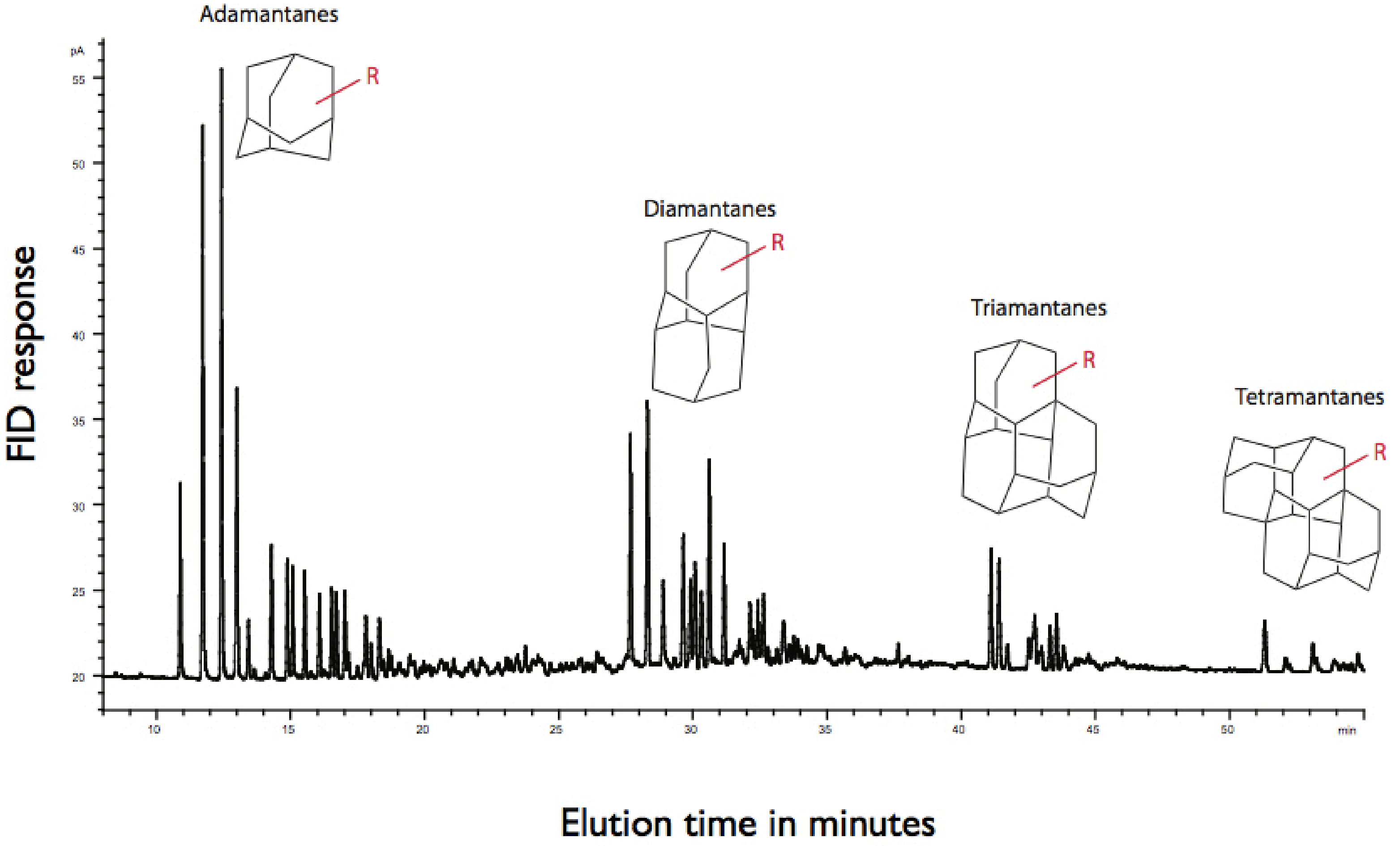
Artificial Cracking of a Kreyenhagen-Sourced Oil



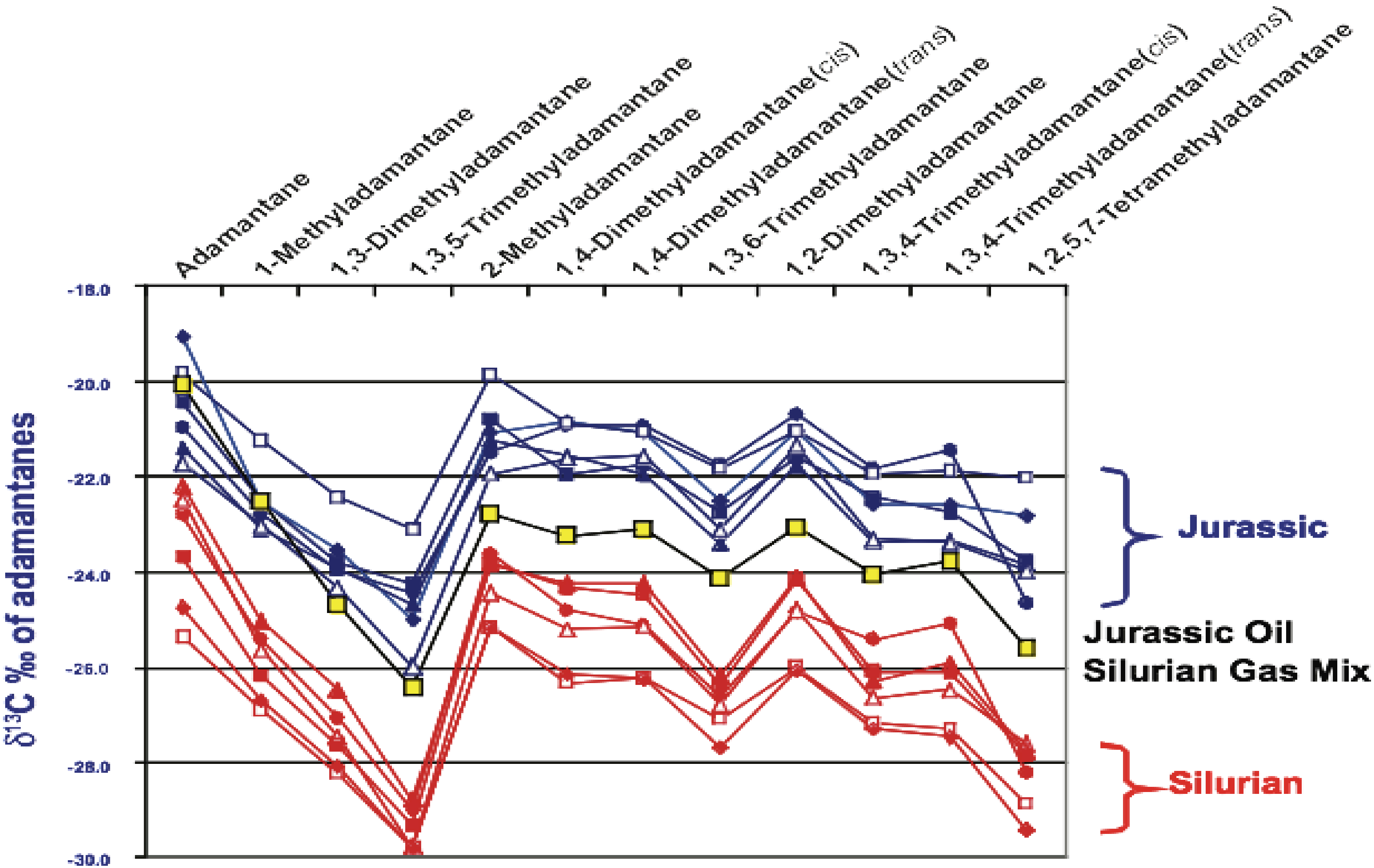
Approximately One Third of California Oils Studied show Evidence of Cracking



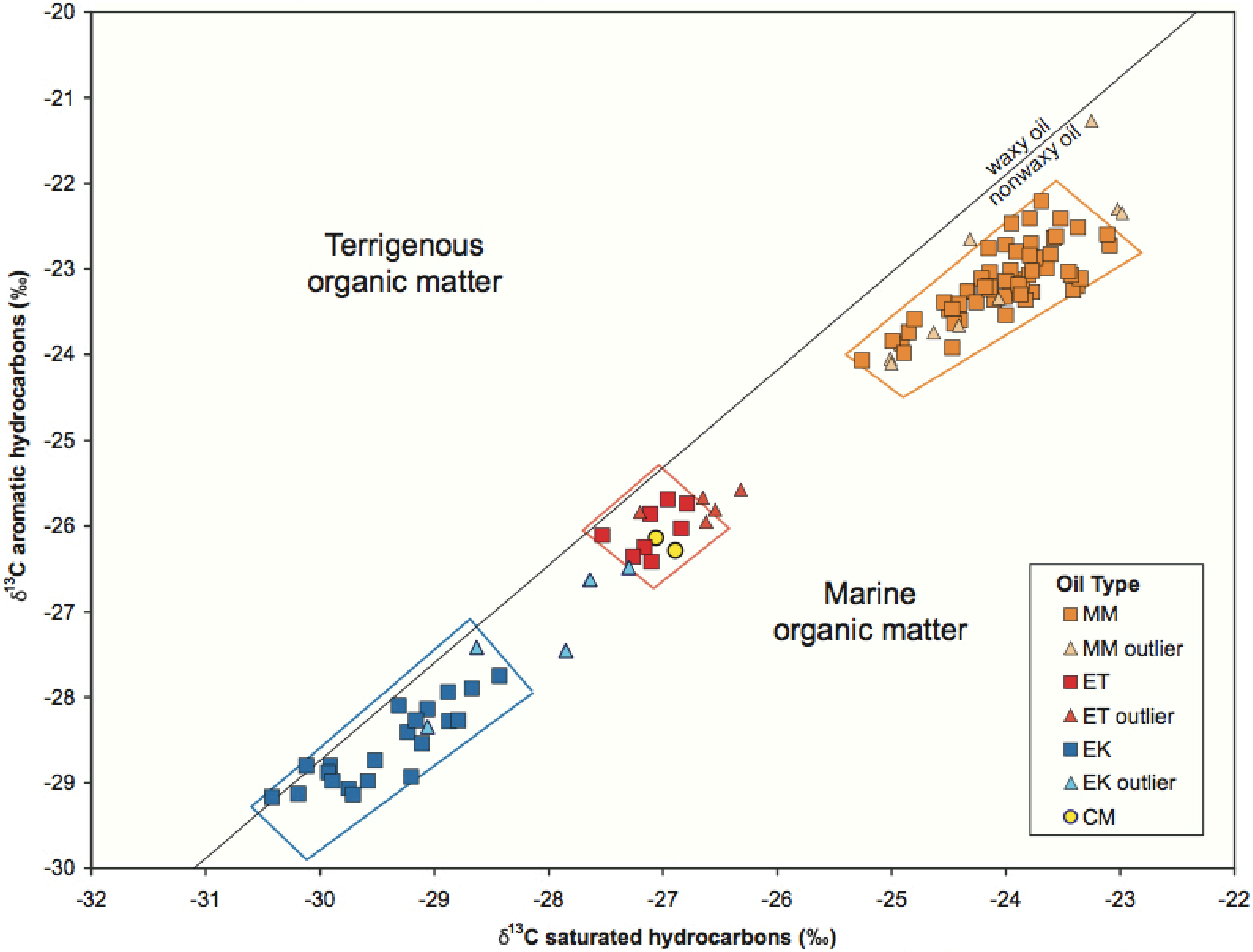
Pure diamondoid fraction isolated from crude oil (useful for isotope analysis or higher diamondoid quantification)



Identification of mixed oils based on diamondoid isotopes

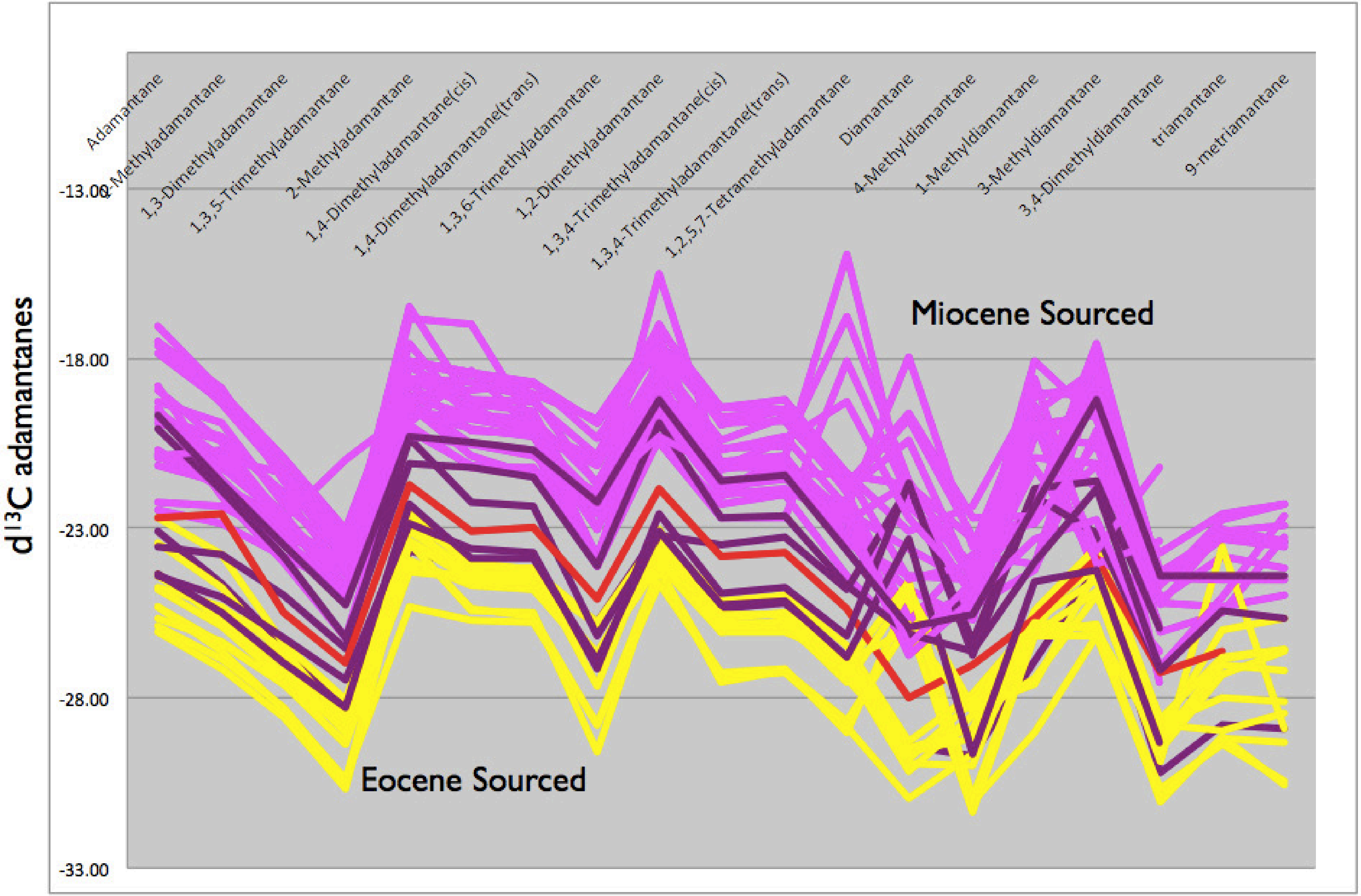


Diamondoid Isotopes are expected to mirror bulk isotopes of the high-maturity contribution in mixtures

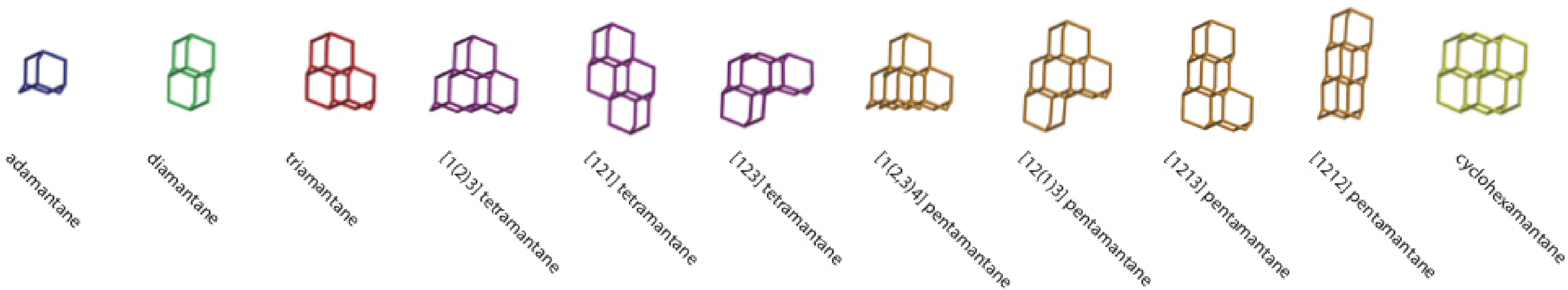


From Lillis and Magoon, 2007

Diamondoid isotopes:
Distinguishing Cretaceous, Eocene, and Miocene Source Rocks



Higher Diamondoids: A Source Signature?

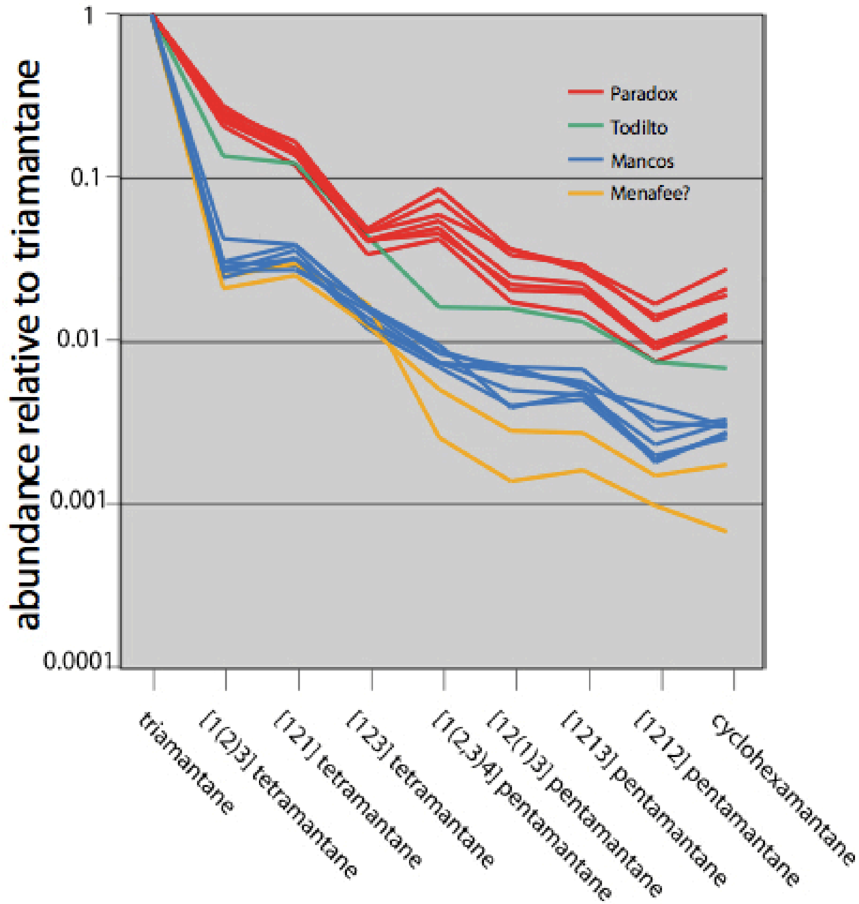


During early maturation diamondoids are formed by catalytic processes in source rocks. They grow via a molecular "snowball" process to larger and larger diamondoids depending on catalytic conditions in source rocks.

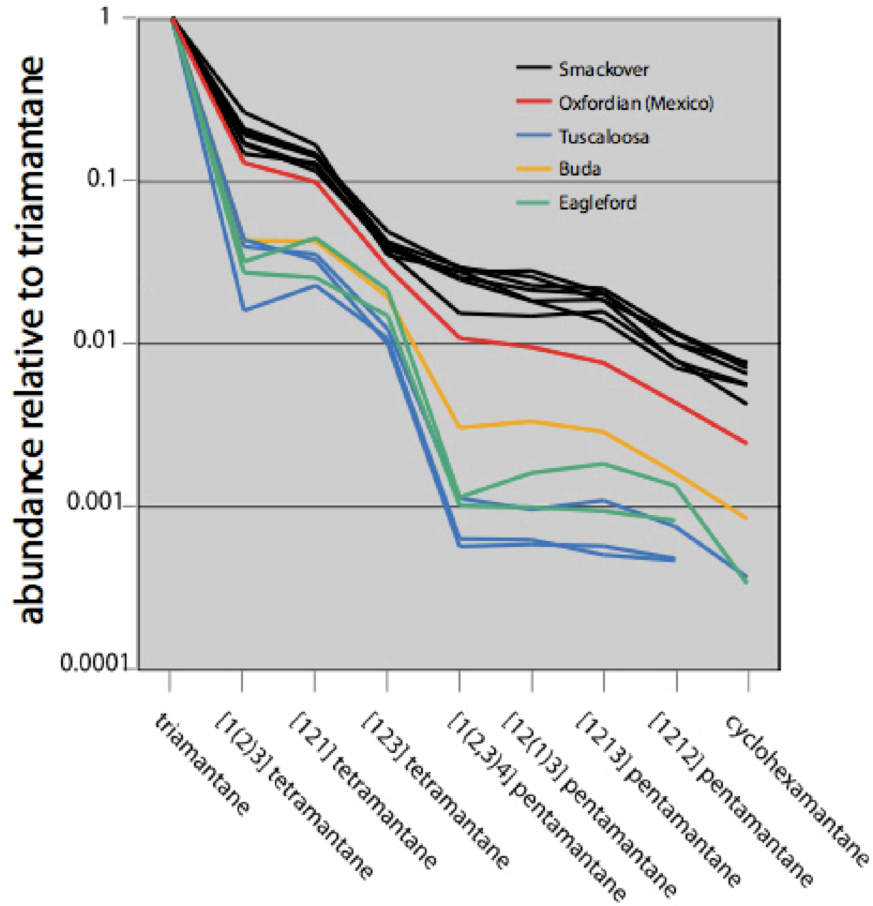
New work on higher diamondoids (1,000 to 1,000,000 times less abundant than adamantane) indicates the possibility of a robust source signature hidden in their ratios to lower diamodoids and in their isomer distributions.

Higher Diamondoid Abundance: Source Specific Markers Retained Through Dry Gas Window

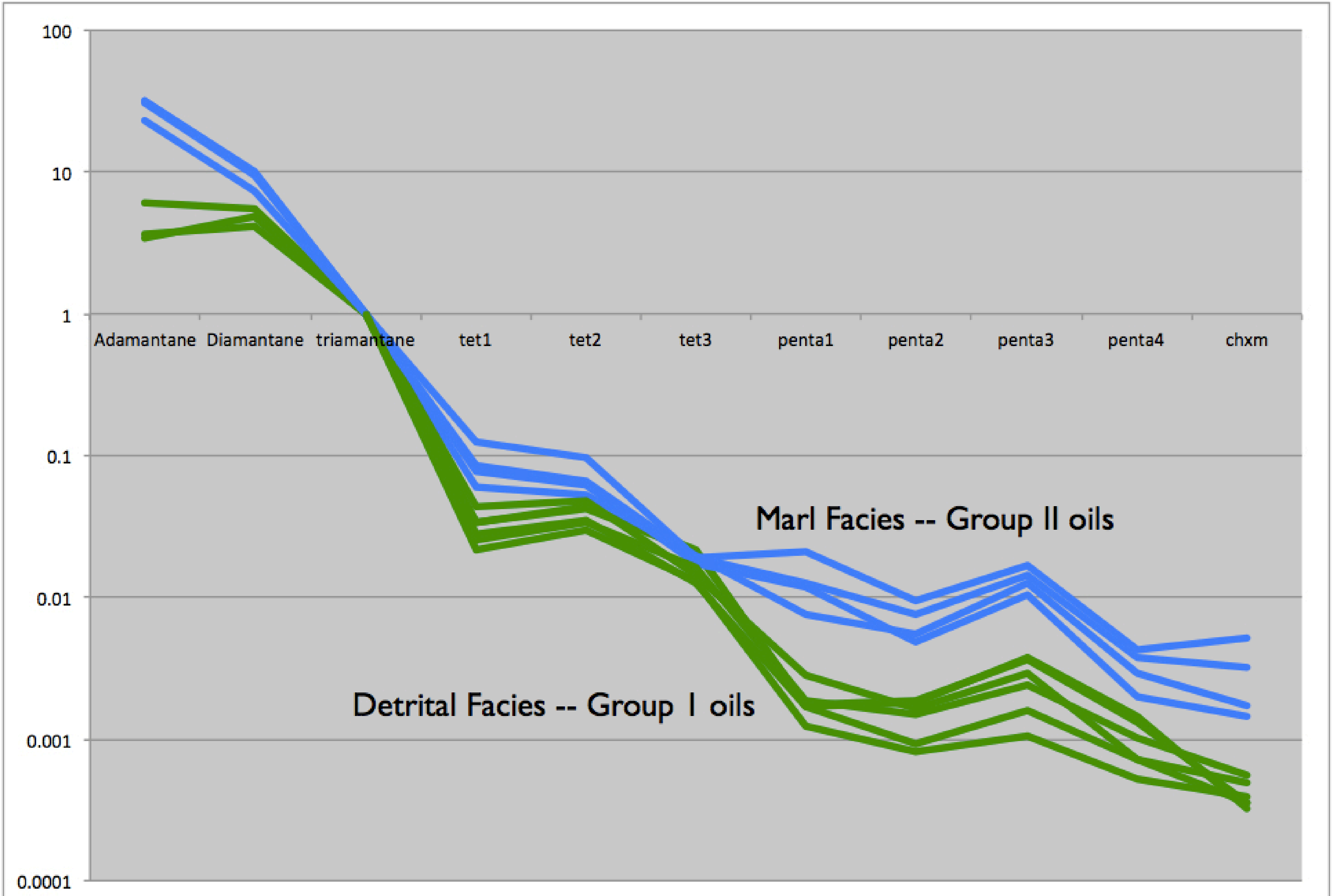
B: San Juan Basin



C: Gulf Coast

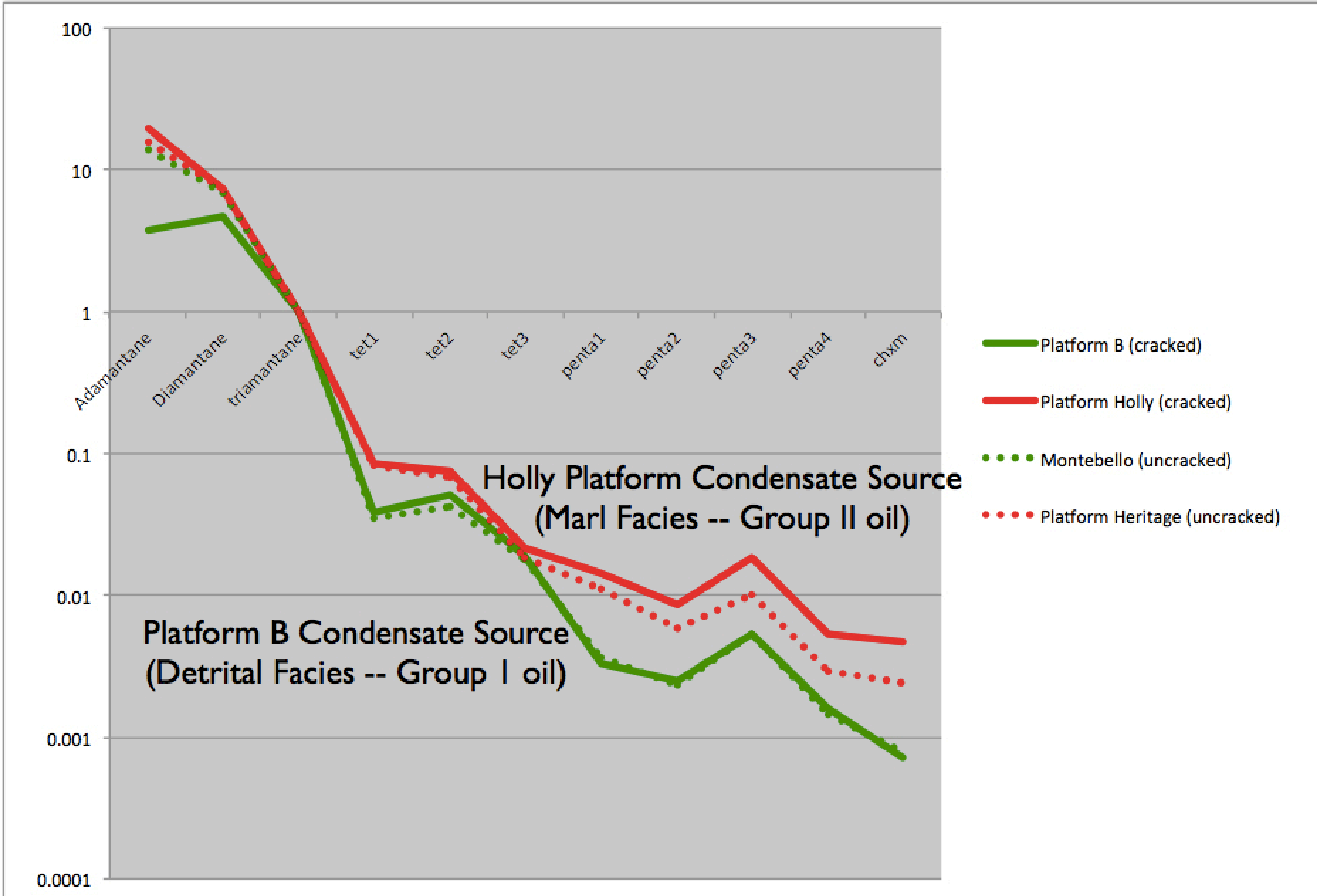


Higher Diamondoid Ratios: Distinguishing Miocene Facies in Coastal Basins

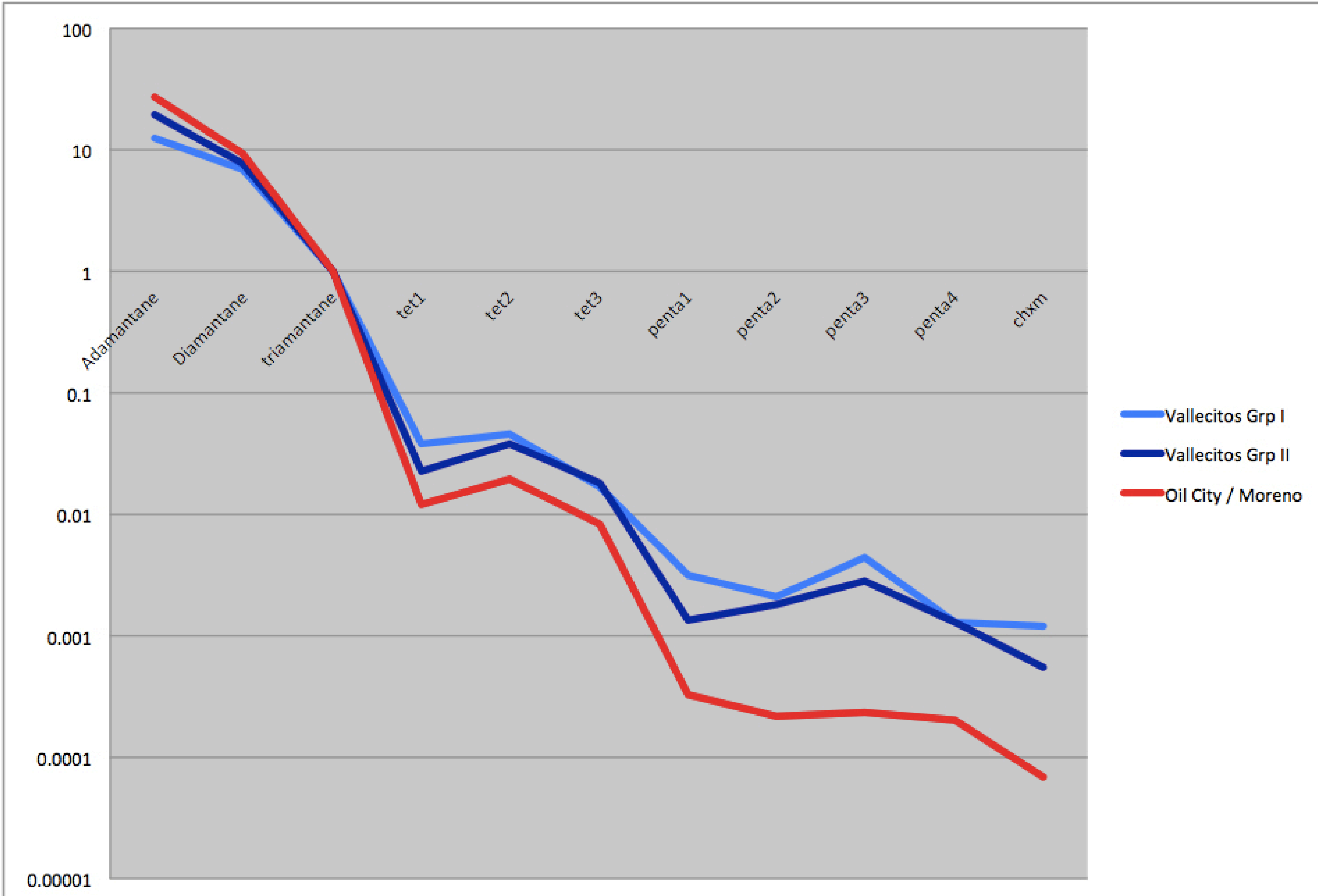


Higher Diamondoid Ratios:

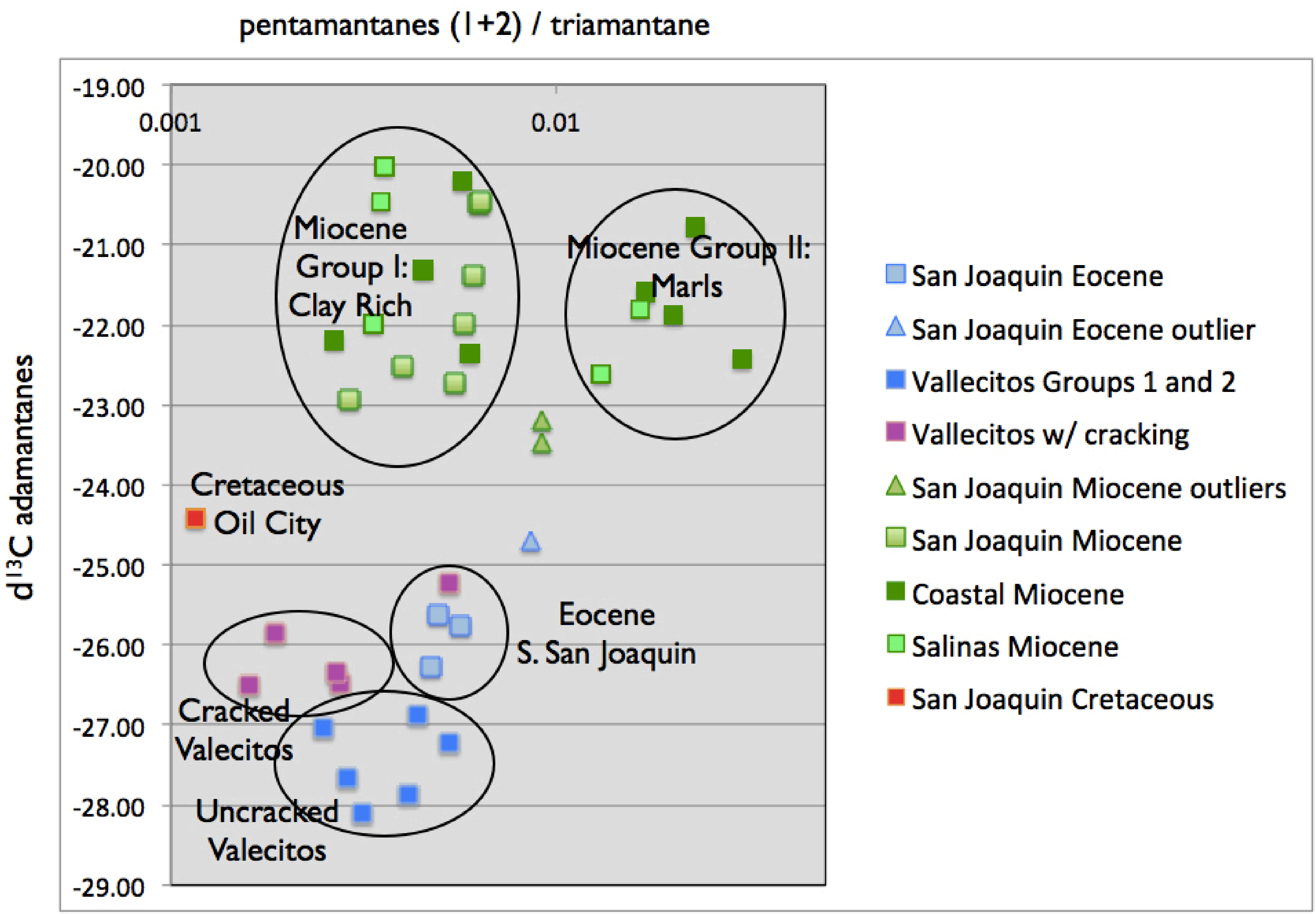
Two Types of Miocene Condensates in the Santa Barbara Basin



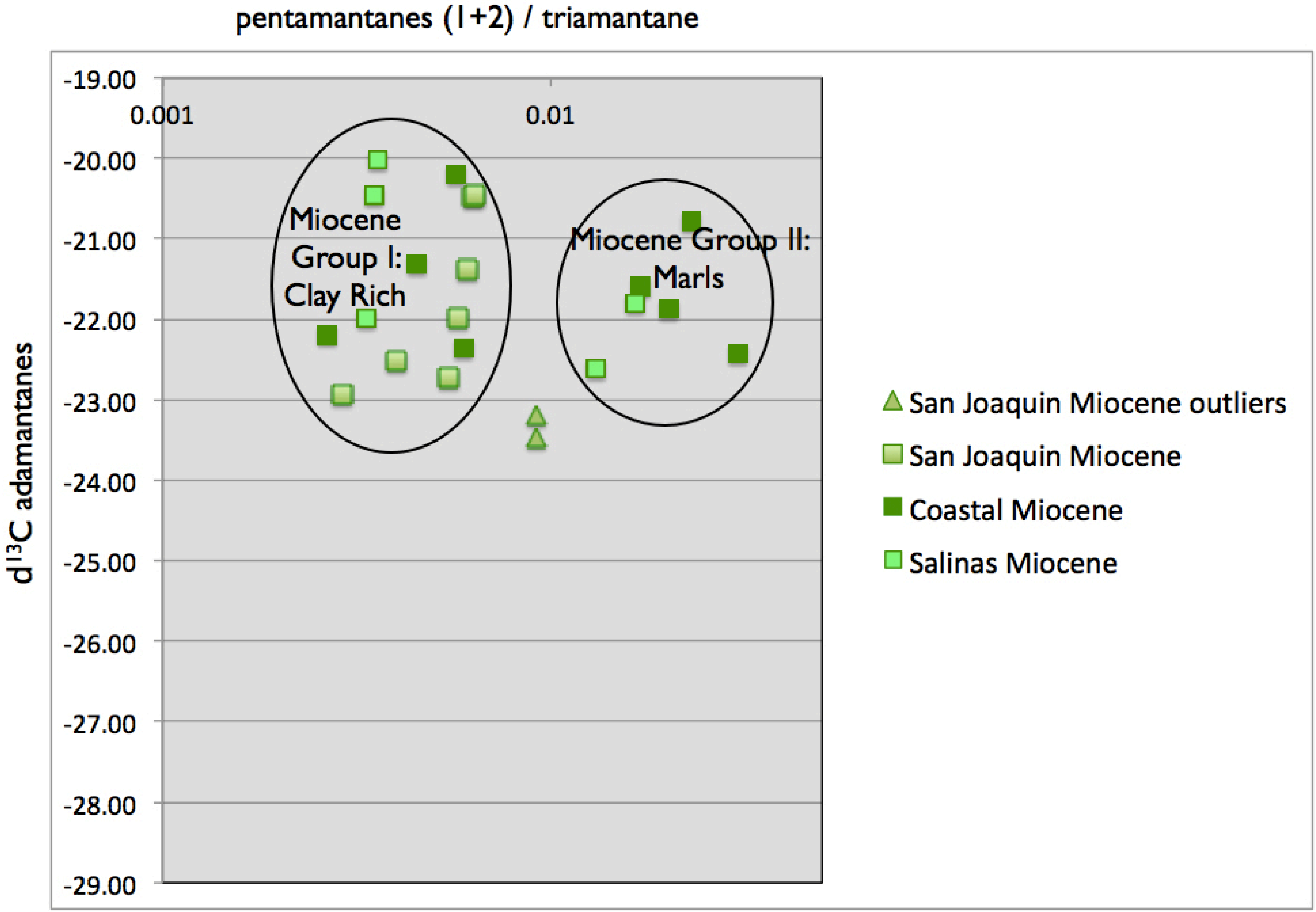
Higher Diamondoid Ratios: Distinguishing Vallecitos Condensate Sources



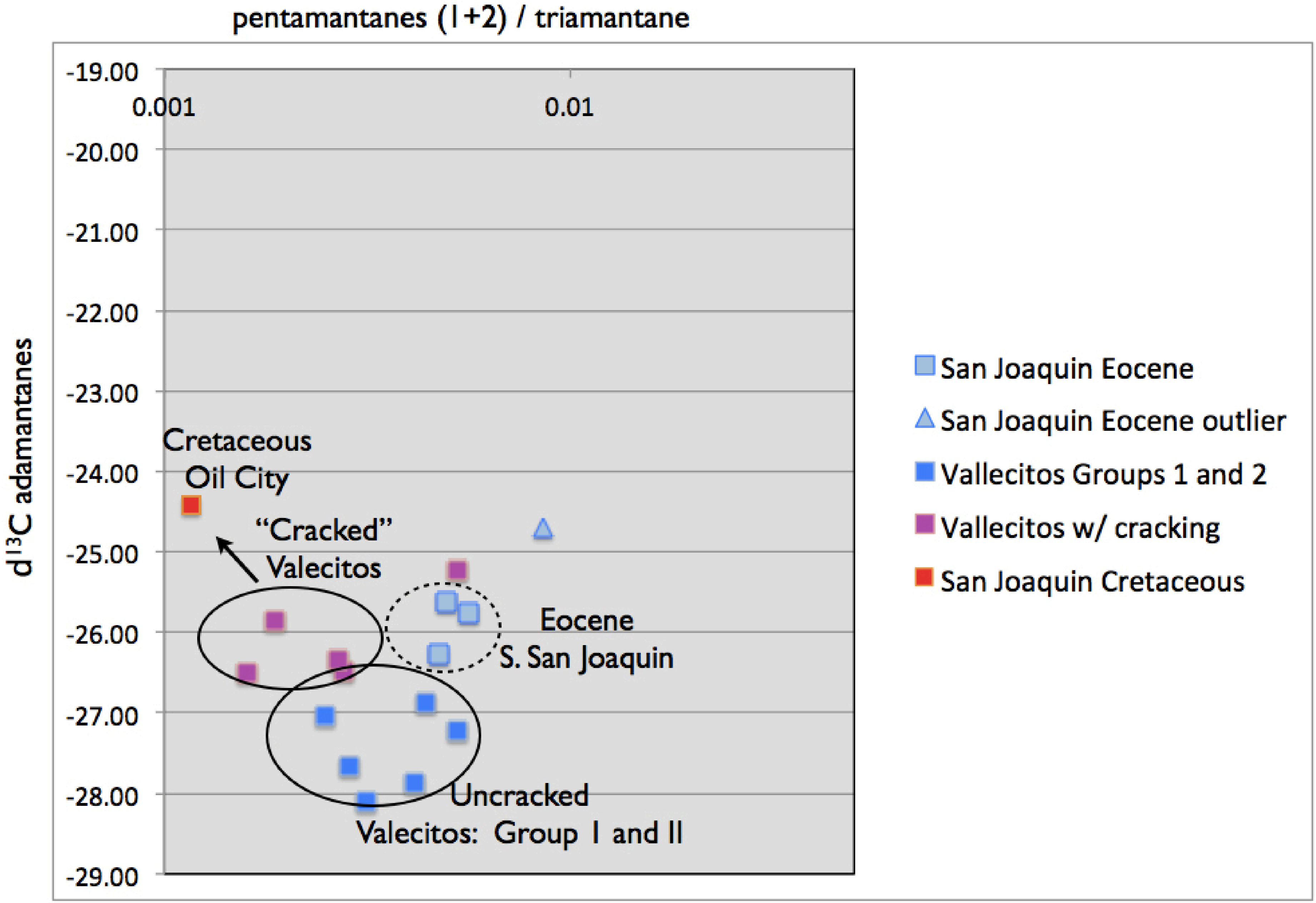
Combining diamondoid isotopes and QEDA



Miocene Facies: detrital dominated vs. biogenic dominated



A Cretaceous cracked source at Valecitos



Conclusions

•Over 100 petroleum samples from the San Joaquin, Salinas, Santa Barbara, Los Angeles, and the Eel River basin have been analyzed.

•High maturity contributions have been recognized in many San Joaquin, Santa Barbara, and Eel River fields. This includes approximately 1/3 of studied samples. Most are mixtures with immature components.

•Fingerprinting of ultra-stable markers indicates deep cracked sources include the Cretaceous, Eocene, and Miocene source rocks.

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Stanford's School of Earth Sciences

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Our Future Goals

1) Complete analysis of ultra-stable markers (isotopes and molecular signatures) on select samples in study.

2) Increase the geographic distribution of sampling in California to other sites where thermogenic gas, API gravity variability, or geology point to the possible migration of hydrocarbons from deep cracked source rocks. In particular we are interested in samples from the western San Joaquin Basin, Los Angeles Basin, and California Borderland.

3) Extend quantitative diamondoid analysis (cracking studies) to **seeps** where water washing, biodegradation, and evaporation may alter oil volume and composition. This work will include higher diamondoids and diamondoid acids.