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

David A. Zinniker1,3, Monporn Mesdakom4, Tom D. Lorenson5, Paul G. Lillis5, Leslie B. Magoon5, J. Michael Moldowan1,3, Jeremy E. Dahl2,3, and Meng He1

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1Department of Geological and Environmental Sciences, Stanford University, Stanford, CA (dzinniker@gmail.com)
2Department of Material Sciences, Stanford University, Stanford, CA
3Biomarker Technology Company
4Department of Geology, Chulalongkorn University, Thailand
5US Geological Survey, Menlo Park, CA / Lakewood, CO

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.

References


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David Zinniker, Mongporn Mesdakom, Tom Lorenson, Paul Lillis, Les Magoon, J. Michael Moldowan, Jeremy Dahl, Meng He

1 Department of Geological and Environmental Sciences, Stanford University
2 Department of Material Sciences, Stanford University
3 Biomarker Technology Company
4 Department of Geology, Chulalongkorn University, Thailand
5 US Geological Survey, Menlo Park, California / Lakewood, Colorado
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
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 Brodest 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

- **Starting Oil**
- **350°C 24hr**
- **350°C 48hr**
- **400°C 48hr**
- **440°C 24hr**
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

![Graph showing isotopic signatures of various adamantane derivatives, indicating Miocene and Eocene source rocks.](image)
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 diamondoids and in their isomer distributions.
Higher Diamondoid Abundance: Source Specific Markers Retained Through Dry Gas Window

B: San Juan Basin

C: Gulf Coast

Legend:
- Red: Paradox
- Green: Todilto
- Blue: Mancos
- Yellow: Menafee?

Legend for Gulf Coast:
- Black: Smackover
- Orange: Oxfordian (Mexico)
- Blue: Tuscaloosa
- Yellow: Buda
- Green: Eagleford
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

- Vallecitos Grp I
- Vallecitos Grp II
- Oil City / Moreno

[Graph showing line plots for different diamondoid ratios and labels for each line]
Combining diamondoid isotopes and QEDA

pentamantanes (1+2) / triamantane

Miocene Group I: Clay Rich
Miocene Group II: Marls
Cretaceous Oil City
Eocene S. San Joaquin
Cracked Vallecitos
Uncracked Vallecitos
San Joaquin Eocene
San Joaquin Eocene outlier
Vallecitos Groups 1 and 2
Vallecitos w/ cracking
San Joaquin Miocene outliers
San Joaquin Miocene
Coastal Miocene
Salinas Miocene
San Joaquin Cretaceous
Miocene Facies: detrital dominated vs. biogenic dominated

pentamantanes (1+2) / triamantane

$d^{13}$C adamantanes

- Miocene Group I: Clay Rich
- Miocene Group II: Marls

Legend:
- ▲ San Joaquin Miocene outliers
- ▶ San Joaquin Miocene
- □ Coastal Miocene
- □ Salinas Miocene
A Cretaceous cracked source at Vallecitos

pentamantanes (1+2) / triamantane

d$_{13}$C adamantanes vs. d$_{13}$C adamanatanes

- San Joaquin Eocene
- San Joaquin Eocene outlier
- Vallecitos Groups 1 and 2
- Vallecitos w/ cracking
- San Joaquin Cretaceous

Cretaceous Oil City

“Cracked” Vallecitos

Uncracked Vallecitos: Group I and II

Eocene S. San Joaquin

Vallecitos: Group I and II
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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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.