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## Organofacies and Paleoclimate Controlled Genetic Oil Families in the Onshore/Offshore Santa Maria Basins, California\*

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Search and Discovery Article #11092 (2018)\*\*

Posted August 13, 2018

\*Adapted from oral presentation given at 2018 AAPG Pacific Section Meeting, Bakersfield, CA, April 22-25, 2018 and poster presentation given at 2018 AAPG Annual Convention and Exhibition, Salt Lake City, Utah, May 20-23, 2018

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### Abstract

Chemometric analysis of 21 source-related biomarker and stable carbon isotope ratios for 48 crude oil samples from the onshore and offshore Santa Maria basins identifies six genetic oil families. The data comprise a training set that was used to create a chemometric decision tree to classify newly collected oil samples. The geochemistry and map/stratigraphic distributions of these families reflect different organofacies within the Miocene Monterey Formation source rock controlled by differing oxicity during diagenesis and carbonate versus siliceous-detrital input in ‘carbonate’, ‘marl’, and ‘shale’ organofacies like those in the lower calcareous-siliceous, carbonaceous marl, and clayey-siliceous members of the Monterey Formation found elsewhere in coastal California. The corresponding lithofacies and organofacies appear to be linked to middle Miocene paleoclimatic cooling after ~13.9 Ma, a systematic up-section increase in the stable carbon isotope compositions of the generated oil samples, decreased preservation of calcium carbonate shells from planktic foraminifera and coccoliths, and increased preservation of clay-size siliceous shells of diatoms and radiolarians. Multiple biomarker parameters indicate that the six oil families achieved

early oil-window maturity in the range 0.6-0.7% equivalent vitrinite reflectance despite generally high sulfur content. The results show that organofacies within the Monterey source rock are responsible for many of the geochemical differences between the oil families. This organofacies model for crude oil from the Monterey Formation can be used to enhance future exploration efforts in many areas of coastal California.

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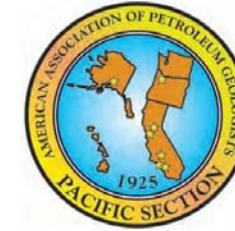
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Vincent E. and W.H. Berger, 1985, Carbon dioxide and polar cooling in the Miocene: the Monterey Hypothesis, *in* E.T. Sundquist and W.S. Broecker, eds., The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations Archean to Present. Geophysical Monographs 32, American Geophysical Union, Washington, D.C., p. 455-468.

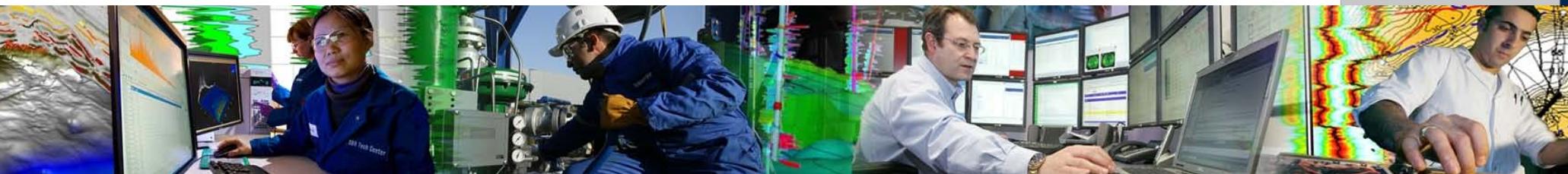


Pacific Section AAPG  
Pacific Exploration: Mature Basins and Prolific Reservoirs



**APRIL 22-25, 2018**  
**BAKERSFIELD, CA**

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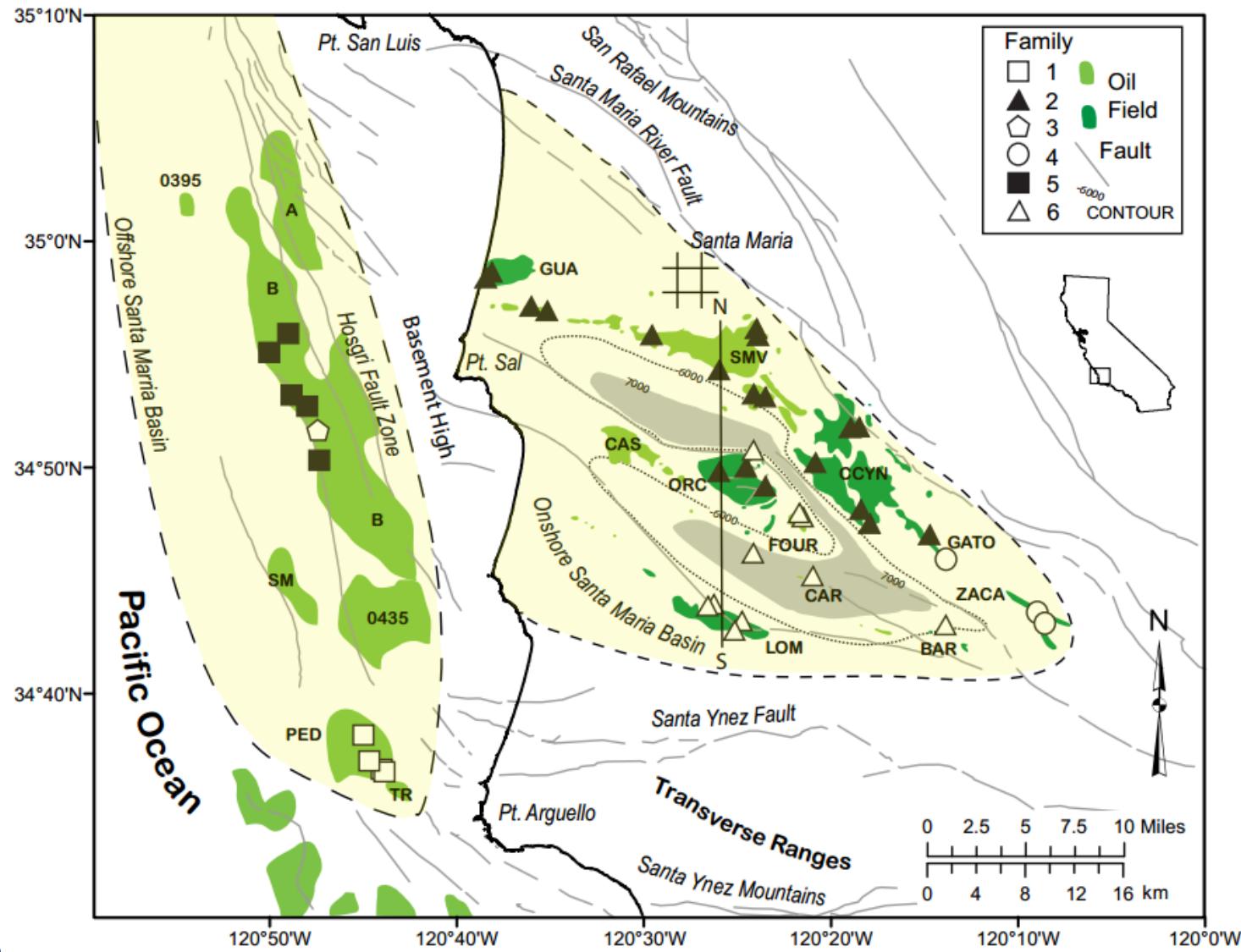


# Purpose of the Study: Offshore/Onshore Santa Maria Basins

- Identify *genetic* oil families using biomarker and carbon isotope data for 48 crude oil samples.
- Create a chemometric (multivariate statistics) decision tree to classify newly collected samples.
- Comment on ‘early’ maturation from sulfur-rich kerogen.
- Evaluate mid-Miocene paleoclimatic cooling as an explanation for distinct oil families.



# A 'Basement High' Separates Onshore/Offshore Basins

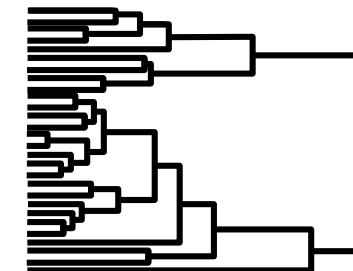


*Oil Families in the  
Ken Peters, Schlumberger and Stanford University*

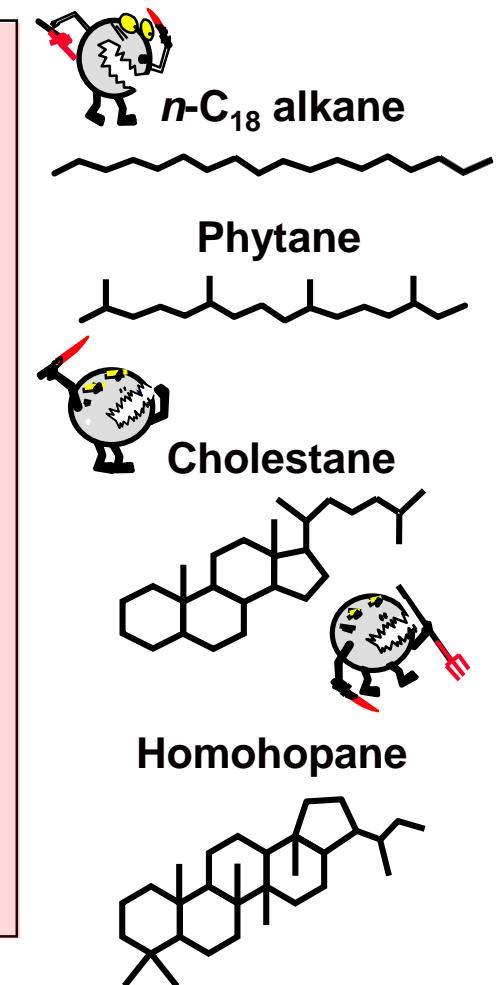
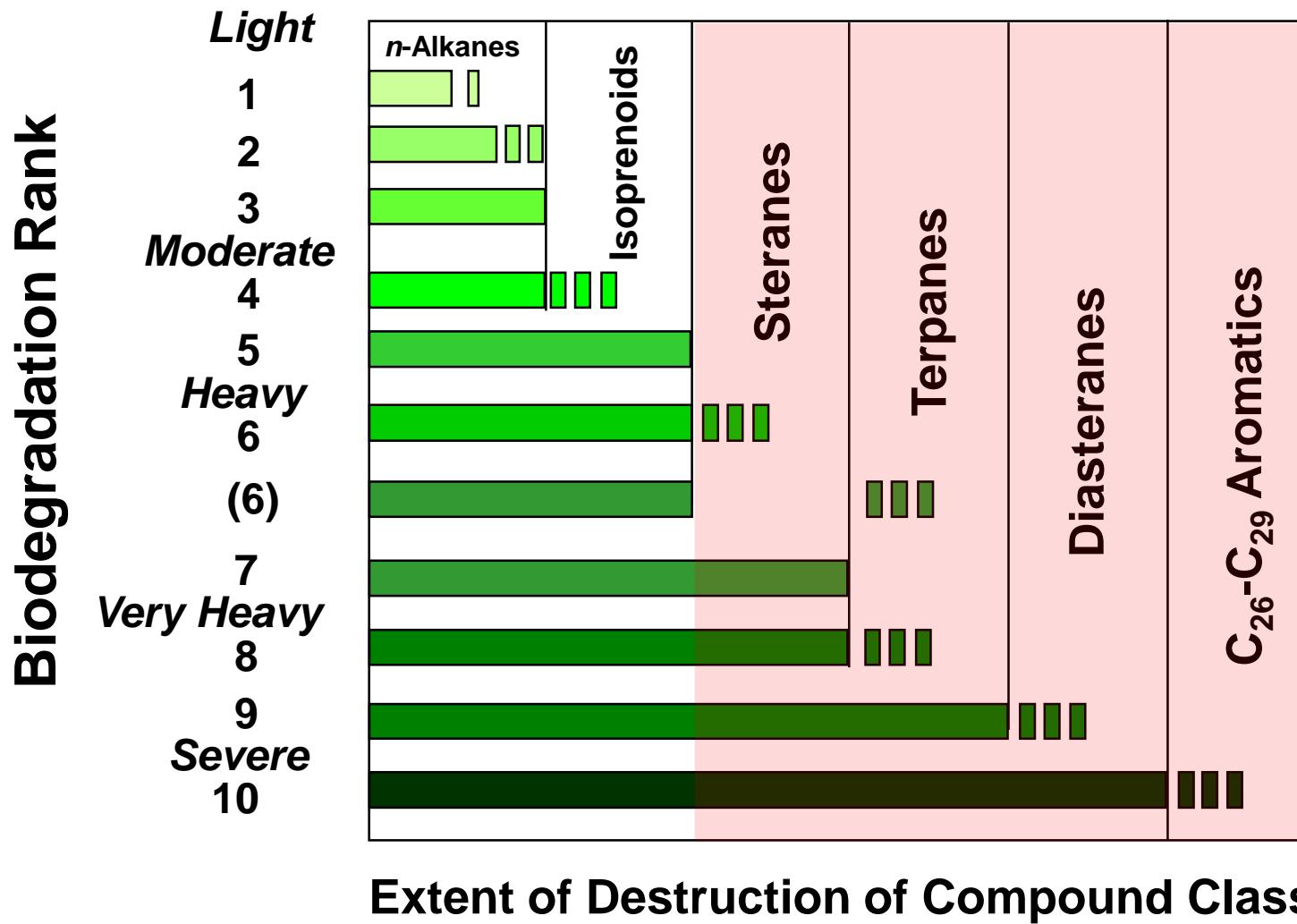


# Keys to Successful Chemometric Classification

- 1) Carefully evaluate the extent of biodegradation, thermal maturation, and data quality for all oil samples.
- 2) Select only good *source-related* ratios; e.g., biomarker homolog ratios and stable carbon isotope ratios.
- 3) Use PCA to discard ratios that represent noise in each data set. Useful parameters differ between basins.
- 4) Use only oil data for the initial discrimination of families. Rock extracts are handled separately after construction of a chemometric decision tree based on the oil data.

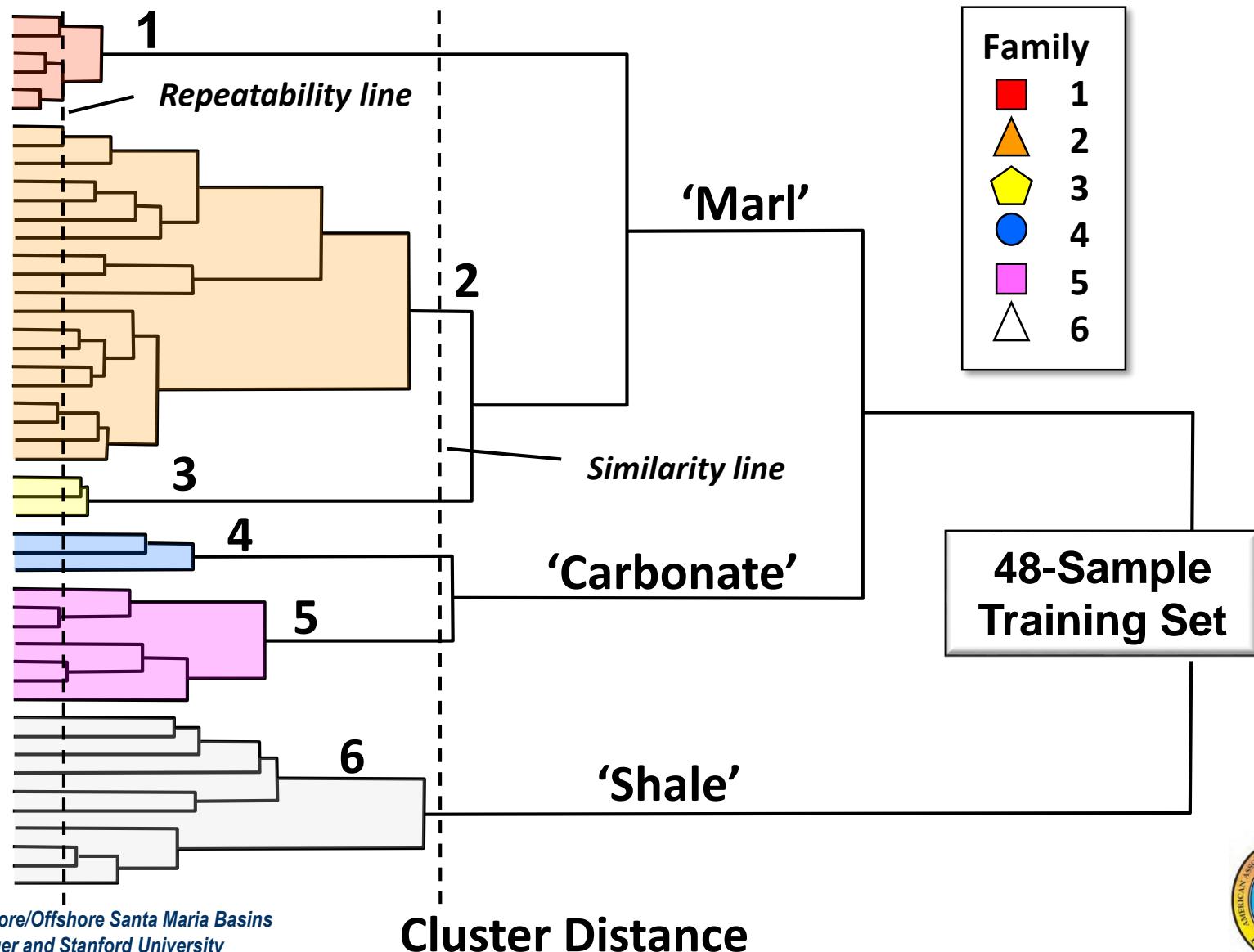


# Biomarkers Bracket Extent of Biodegradation on 'PM' Scale

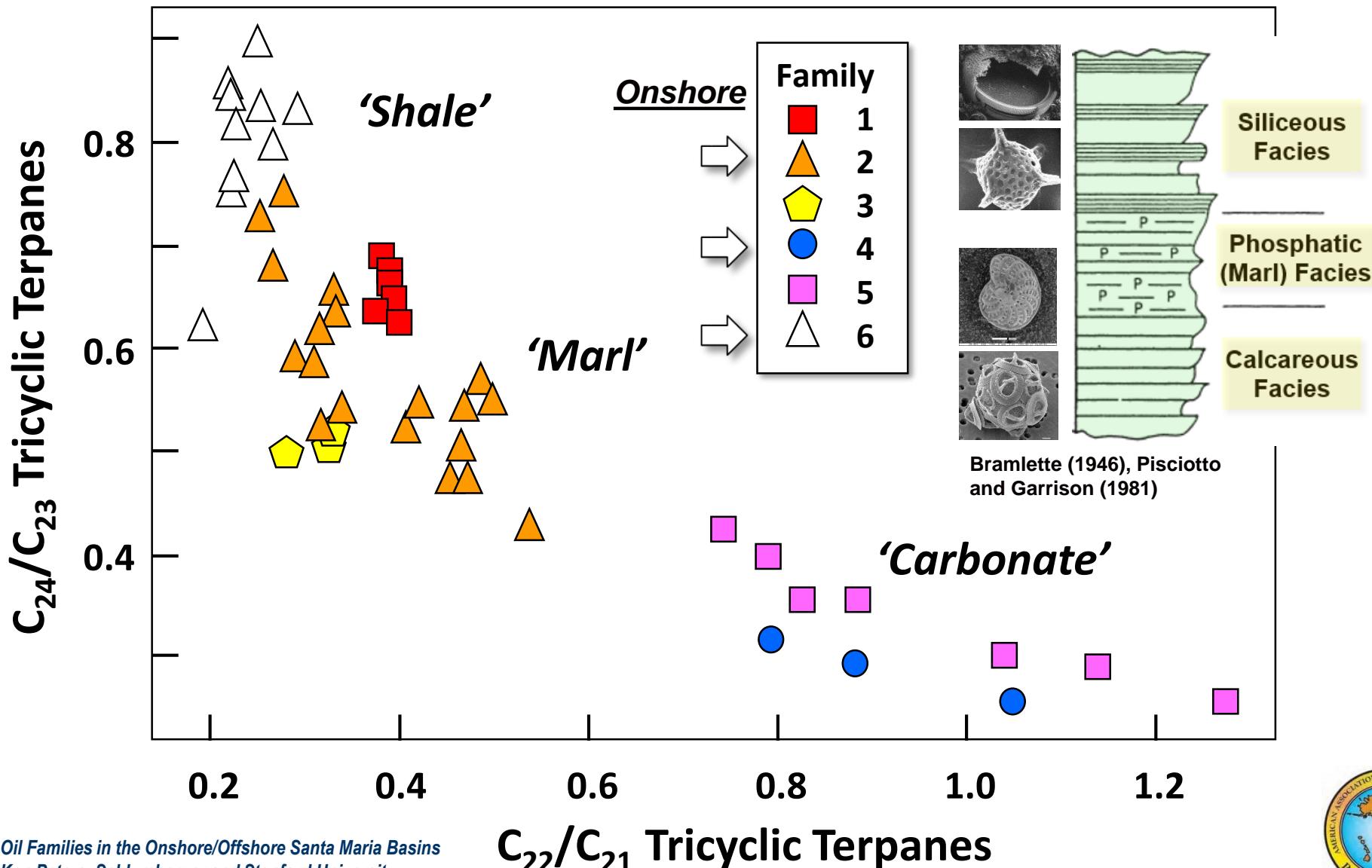


Peters and Moldowan (1993)

# Chemometric Analysis: 21 Biomarker and Isotope Ratios



# Onshore: 'Carbonate', 'Marl', 'Shale' Organofacies (4, 2, 6)



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# Families are Sulfur-Rich, Early Mature, but Not <0.4% R<sub>o</sub>eq

## Crude Oil Family

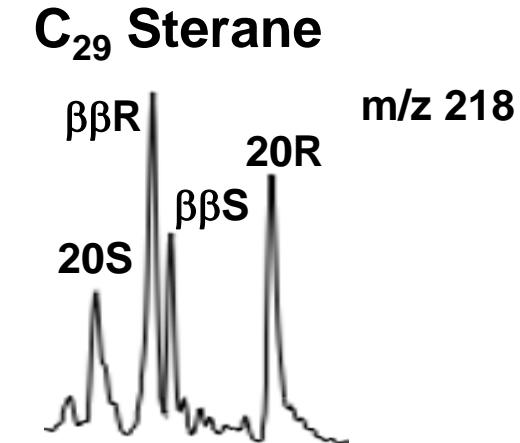
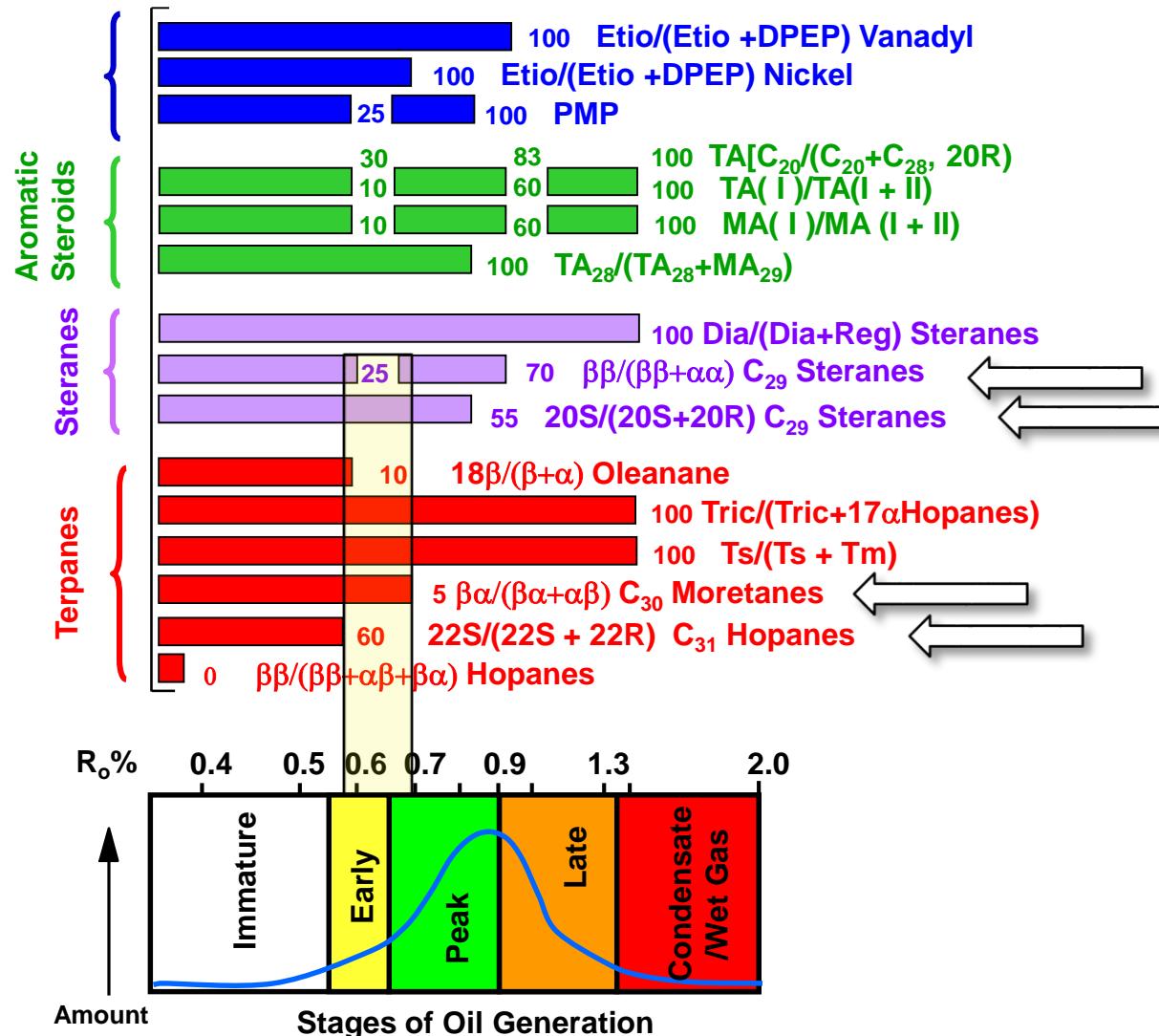
Parameter	1 (6)	'Marl'		'Carbonate'		'Shale'	
		2 (19)	3 (3)	4 (3)	5 (7)	6 (10)	
%Sulfur*	5.0±0.4	3.7±1.7	4.7±0.8	8.2±2.1	7.0±1.3	2.3±2.0	
DBT/P†	1.41±0.25	1.28±0.39	0.52±0.10	3.03±0.10	3.50±0.63	0.62±0.46	
Pristane/phytane*	0.70±0.05	0.86±0.14	1.33±0.05	0.50±0.07	0.44±0.05	0.87±0.06	
Dia/Reg steranes	0.20±0.01	0.30±0.08	0.40±0.03	0.10±0.05	0.09±0.03	0.28±0.16	
C <sub>31</sub> 22S/(S+R)	0.61±0.01	0.62±0.01	0.61±0.01	0.60±0.01	0.60±0.01	0.62±0.03	
C <sub>30</sub> βα/(βα+αβ)	8.3±0.2	9.0±1.1	6.9±0.3	6.6±0.9	7.3±0.5	10.6±1.7	
C <sub>29</sub> 20S/(S+R)	0.37±0.00	0.36±0.02	0.35±0.02	0.34±0.02	0.39±0.02	0.38±0.04	
C <sub>29</sub> ββS/(ββS+ααR)	0.48±0.01	0.45±0.05	0.49±0.01	0.48±0.04	0.54±0.04	0.45±0.11	
TAS3(CR)‡	0.08±0.01	0.10±0.03	0.11±0.01	0.06±0.00	0.06±0.01	0.14±0.08	

\* PM biodegradation rank 0-2; ignore maturity.

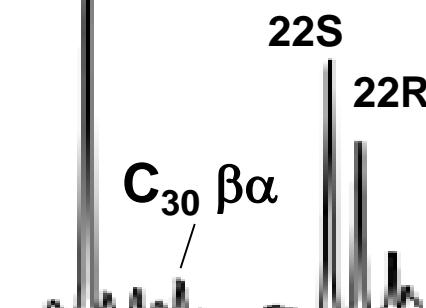
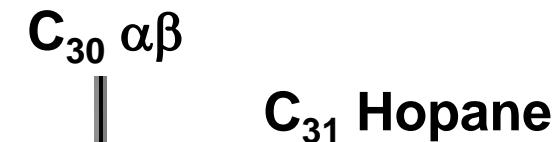
† Dibenzothiophene/phenanthrene

‡ Triaromatic side-chain cracking ratio

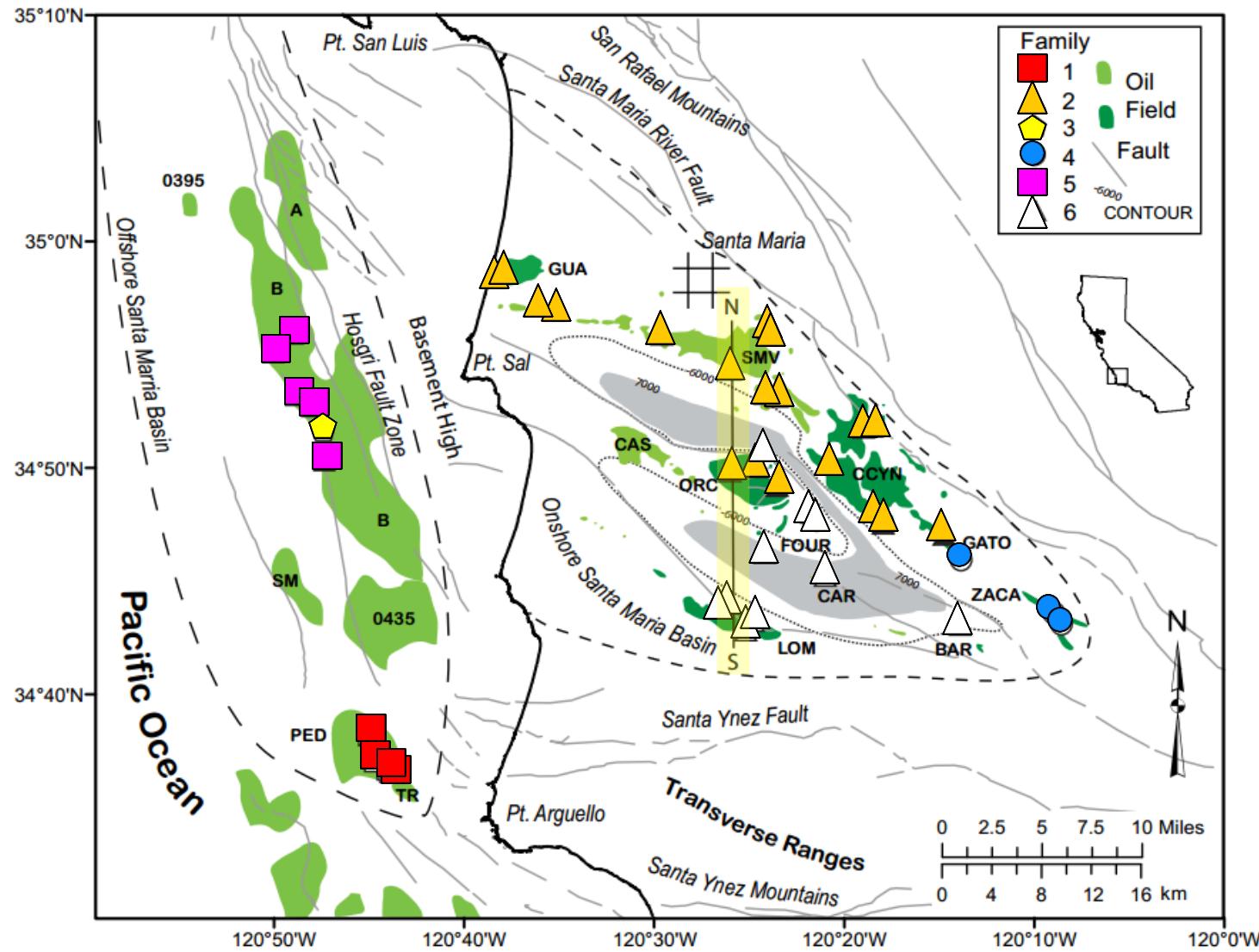
# Biomarker Ratios Bracket Thermal Maturity (0.6-0.7% $R_o$ eq)



m/z 191



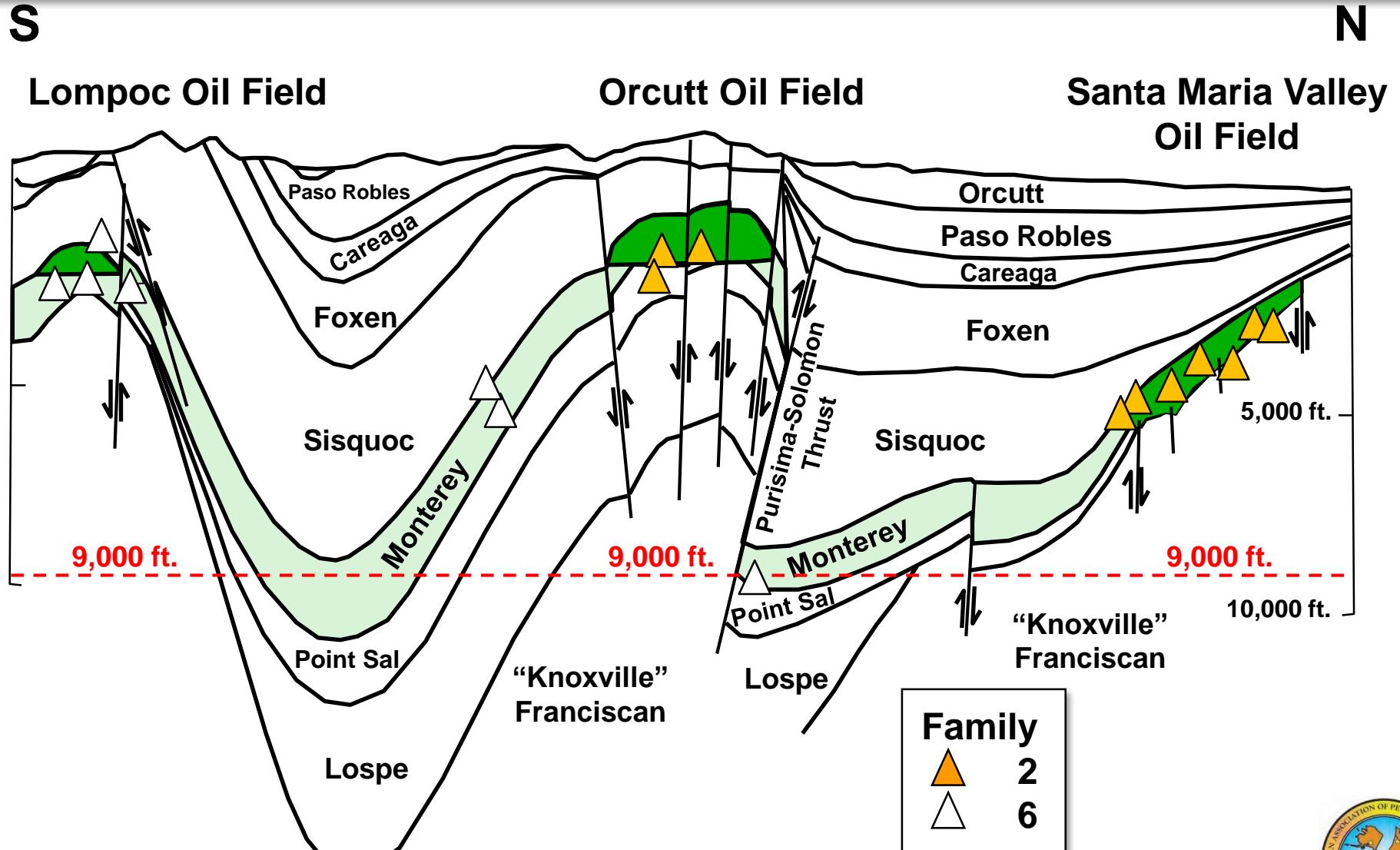
# Genetic Oil Families Show Systematic Distributions



Oil Families in the Onshore/Offshore Santa Maria Basins  
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# Families 2 and 6 Dominate Onshore Santa Maria Basin



*Oil Families in the Onshore/Offshore Santa Maria Basins*  
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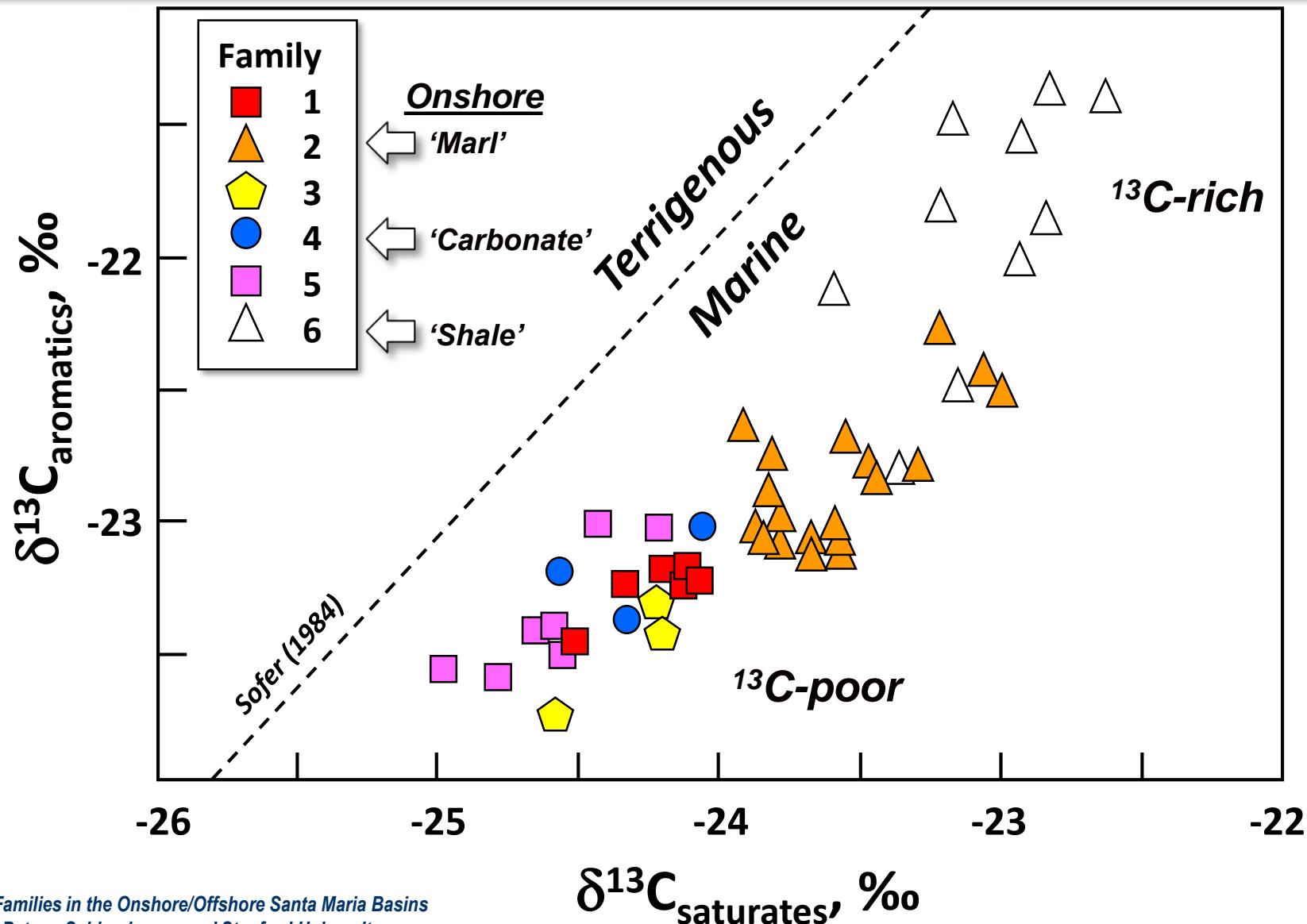


# Chemometric Decision-Tree Classifies New Samples

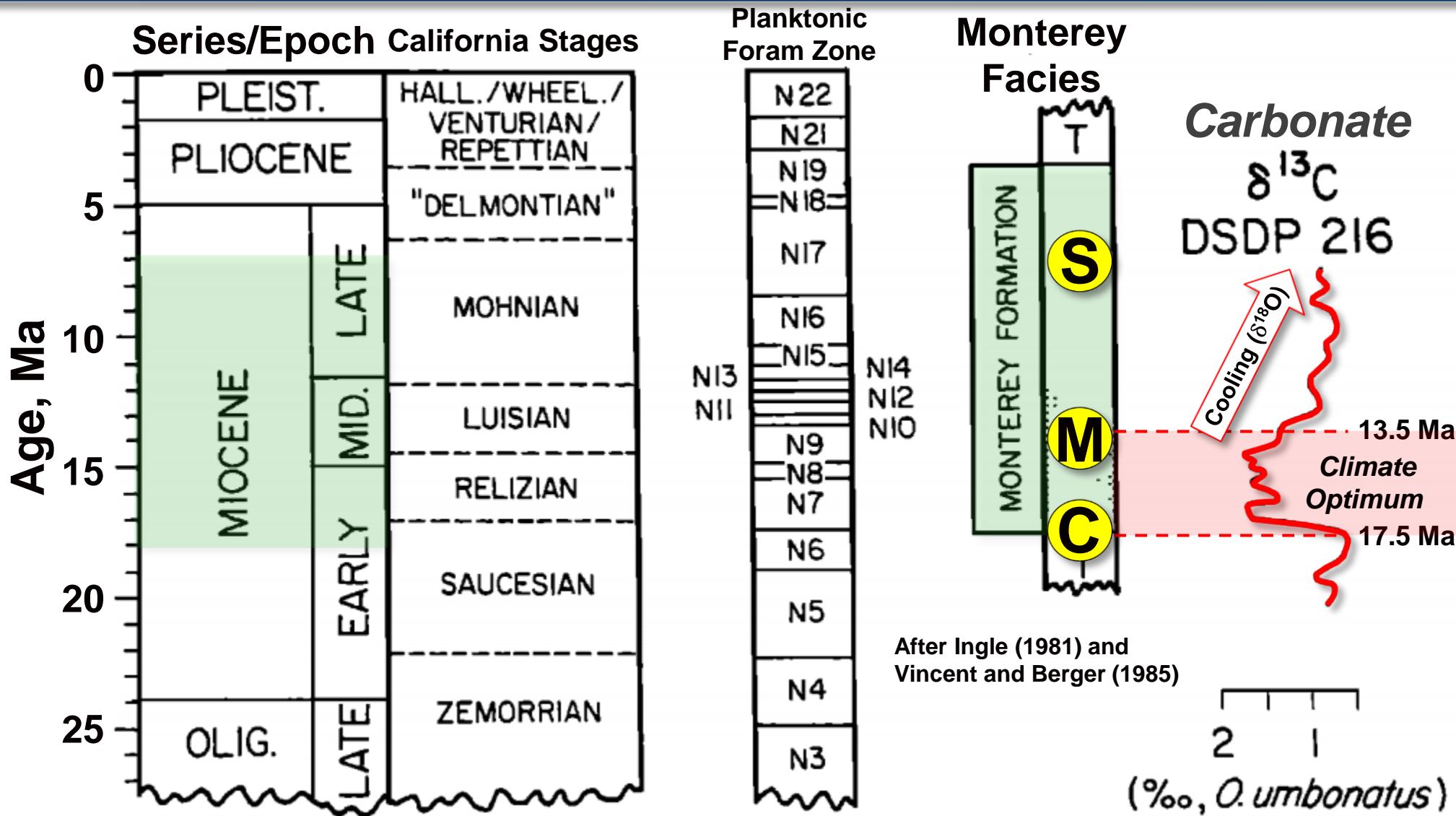
Sample	PM Rank	Field	Assigned Family	Certainty
Unk_733_2	5	East Cat Canyon	2 ▲	Low
Unk_734_2	4	Guadalupe	2 ▲	Moderate
Mai_17_40*	5	Arroyo Grande	No match	NA
409_2_8_27	1	“B” prospect	5 ■	High
Pur_85_818	0	Lompoc	6 △	High
441_1_1043	2	Pt. Pedernales	1 ■	High

\*Outside Santa Maria study area

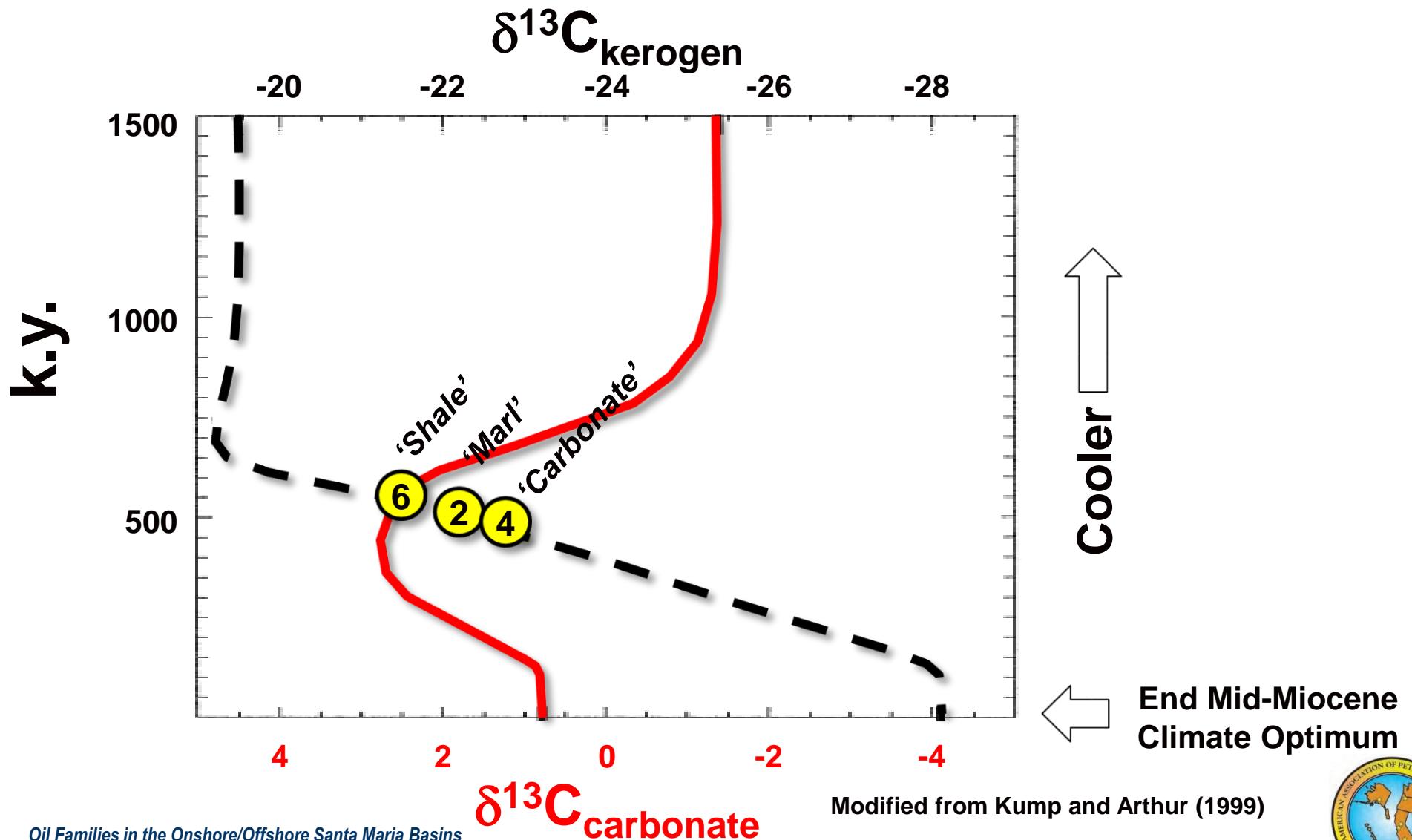
# $^{13}\text{C}$ Increases in ‘Carbonate’, ‘Marl’, ‘Shale’ Families (4, 2, 6)



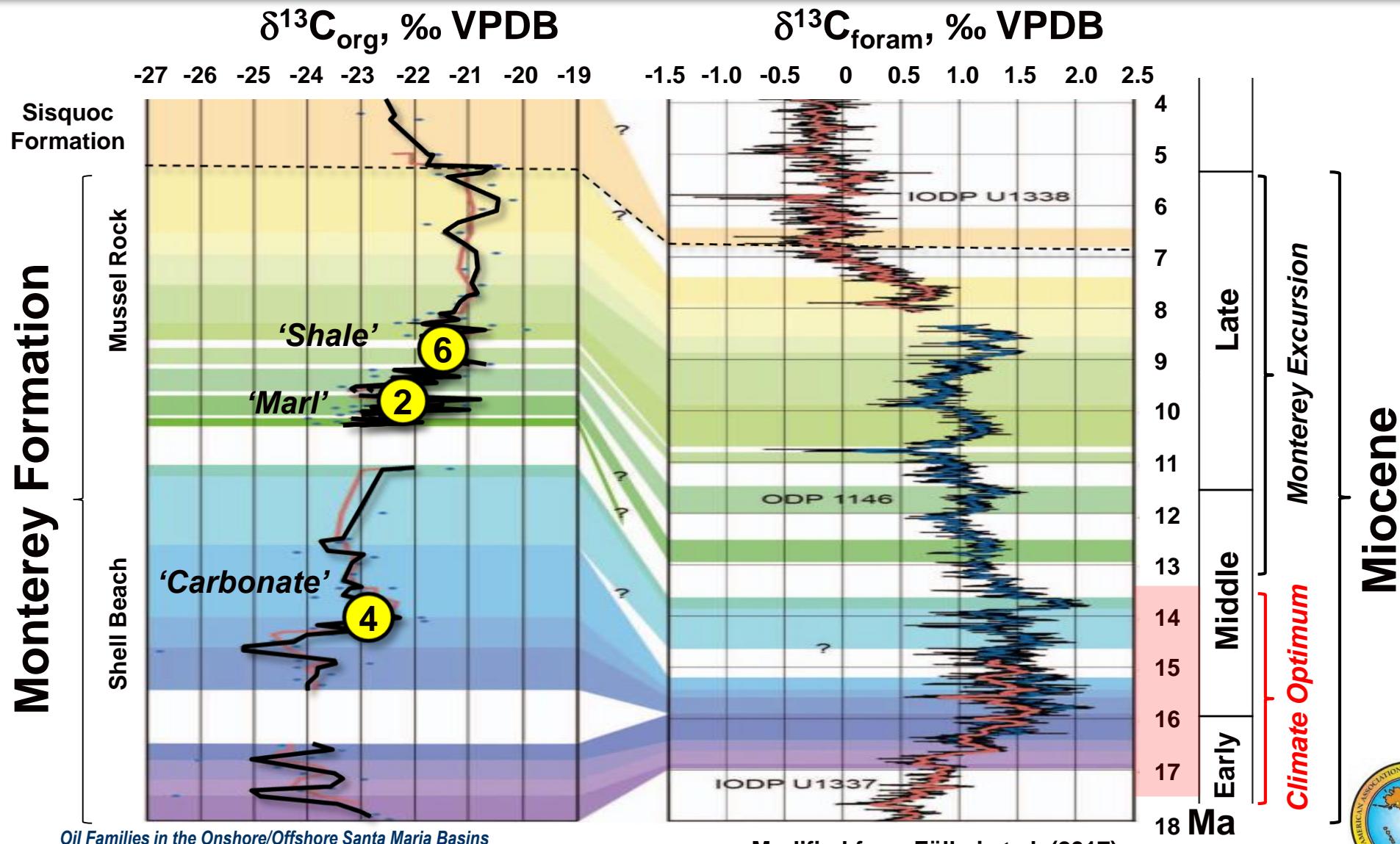
# Cooling After Climate Optimum: Decreased $\delta^{13}\text{C}_{\text{foram carbonate}}$



# Modeled $\delta^{13}\text{C}_{\text{carb}}$ vs. $\delta^{13}\text{C}_{\text{org}}$ Response to Phosphate Increase



# $\delta^{13}\text{C}_{\text{foram}}$ Decreases, $\delta^{13}\text{C}_{\text{org}}$ Increases After Climate Optimum



# Conclusions for Onshore/Offshore Santa Maria Basin Study

- Chemometric analysis of 21 biomarker and carbon isotope ratios for 48 oil samples identifies six genetic families.
- Chemometric decision tree classifies new oils without altering the training set *and* quantifies degree of certainty for each assignment.
- The families show affinities to ‘clayey-siliceous’, ‘carbonaceous marl’, and ‘lower calcareous-siliceous’ members of the Miocene Monterey Formation.
- Maturity for families is ~0.6-0.7%  $R_o$  equivalent; *more* than classic predictions of ‘early’ oil from sulfur-rich kerogen (<0.4%  $R_o$ ).
- Upward changes in organofacies, biomarkers, and isotopes for the oil families are linked to Mid-Miocene paleoclimatic cooling after ~14 Ma, decreased carbonate from forams and coccoliths, and increased silica from diatoms and radiolarians.

# Annual Stanford BPSM Industrial Affiliates Meeting



Santa Maria Basin, California  
November 13-15, 2017



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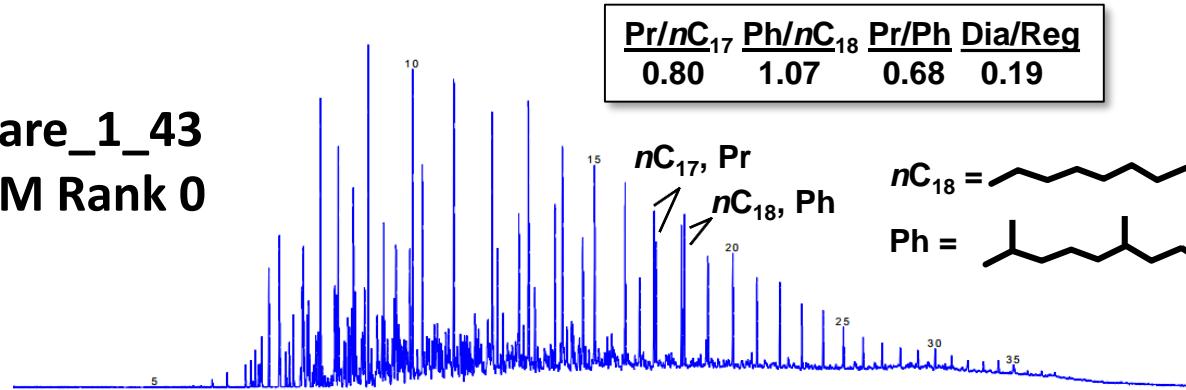
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**Ken Peters**

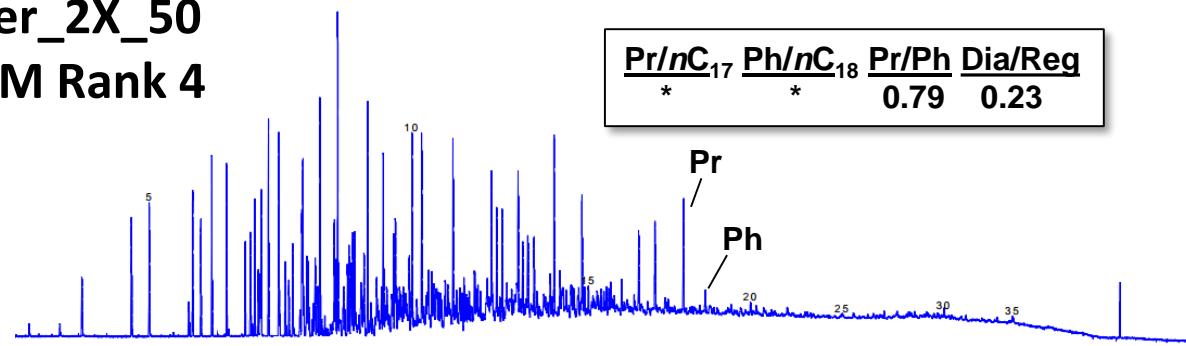
*Geochemistry Advisor, Schlumberger  
Adjunct Professor, Stanford University*

# Reject Heavily Biodegraded Samples (PM >5)

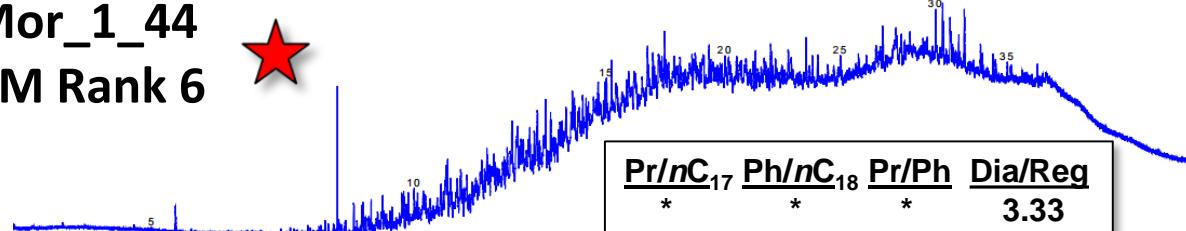
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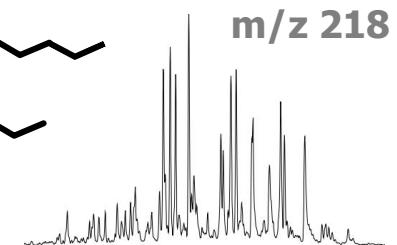
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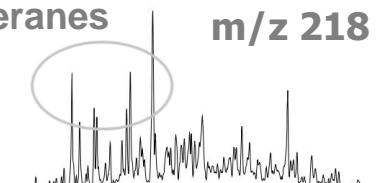
Mor\_1\_44  
PM Rank 6



Steranes



Diasteranes



# About the Speaker: Ken Peters

- 40 years: Chevron, Mobil, ExxonMobil, USGS, Schlumberger, UC Berkeley, Stanford
- ~160 peer reviewed papers in geology, geochemistry, and basin modeling
- *The Biomarker Guide (1993, 2005); Getting Started in Basin and Petroleum System Modeling (2009); Basin Modeling: New Horizons in Research and Applications (2012)*
- Adjunct Professor, Stanford University (BPSM Industrial Affiliates Program)
- Schlumberger NExT Instructor, EAGE Instructor
- Honorary Teaching Fellow (U. of Aberdeen); Visiting Professor (Jacobs U., Bremen)
- Chair Gordon Research Conference on Organic Geochemistry (1998)
- Chair AAPG Research Committee (2007-2010)
- Fellow in The Geochemical Society, AAPG Charles Taylor Fellow; AAPG Distinguished Lecturer (2009 and 2010)
- Associate Editor for *AAPG Bulletin, Journal of Petroleum Geology, and Organic Geochemistry*
- Alfred E. Treibs Medalist (2009); AAPG Honorary Member Award (2013); EAGE Alfred Wegener Award (2016); AAPG Heritage of the Petroleum Geologist Honoree (2017)
- Experience in most basins worldwide

