New Geochemical-Chemometric Evidence for Multiple Miocene and Eocene Oil Families in the San Joaquin Basin, California*

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Abstract

Chemometric analyses of geochemical data for 165 crude oils allowed identification of genetically distinct oil families and their inferred source rocks and provided insights into migration pathways, reservoir compartments, and filling histories in the San Joaquin Basin. In the first part of the study, 17 source-related biomarker and stable carbon isotope ratios were evaluated using principal components analysis (PCA) to identify genetic families. In the second part of this study, ascendant hierarchical clustering (AHC) based on the Ward aggregation method was applied to the terpane (m/z 191) fingerprints for the oil samples in order to compare with the PCA results. The results for the two chemometric methods are remarkably similar, despite differing data input and assumptions. Recognized source rocks for the oil families include the (1) Eocene Kreyenhagen and Tumey formations, (2) Miocene Monterey Formation (Buttonwillow depocenter), and (3) Miocene Monterey Formation (Tejon depocenter).

AHC identifies 22 oil families in the basin as corroborated by independent data, such as stable isotope ratios, sample location, reservoir unit, and thermal maturity maps from a three-dimensional basin and petroleum system model. Eight oil families originated from Eocene source rock in the basal Kreyenhagen Formation (five families) and the overlying Tumey Formation (three families) in the Buttonwillow depocenter. Fourteen Miocene families are from upper and lower Monterey Formation source rocks and migrated from the Buttonwillow and Tejon depocenters north and south of the Bakersfield Arch, respectively. Both the Eocene and Miocene families show little cross-stratigraphic migration due to seals within the source rocks. The results help to explain the different filling histories of the oil families in Elk Hills and other fields and improve understanding of migration paths and potential zones of bypassed oil in the San Joaquin Basin. They also show the value of chemometrics applied to large petroleum databases where all samples are analyzed using the same procedures and instrumentation.

References

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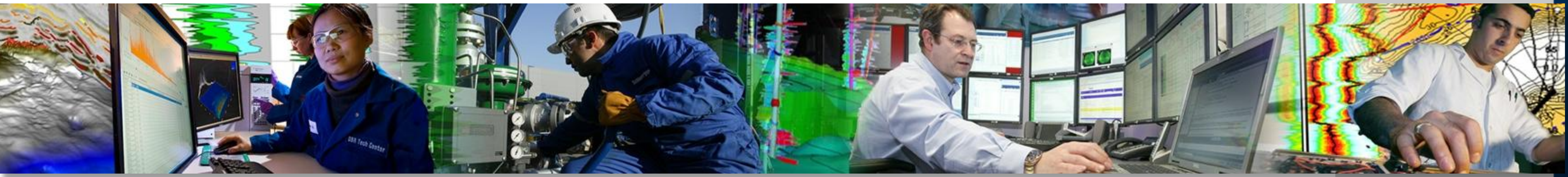
New Geochemical-Chemometric Evidence for Multiple Miocene and Eocene Oil Families in the San Joaquin Basin, CA



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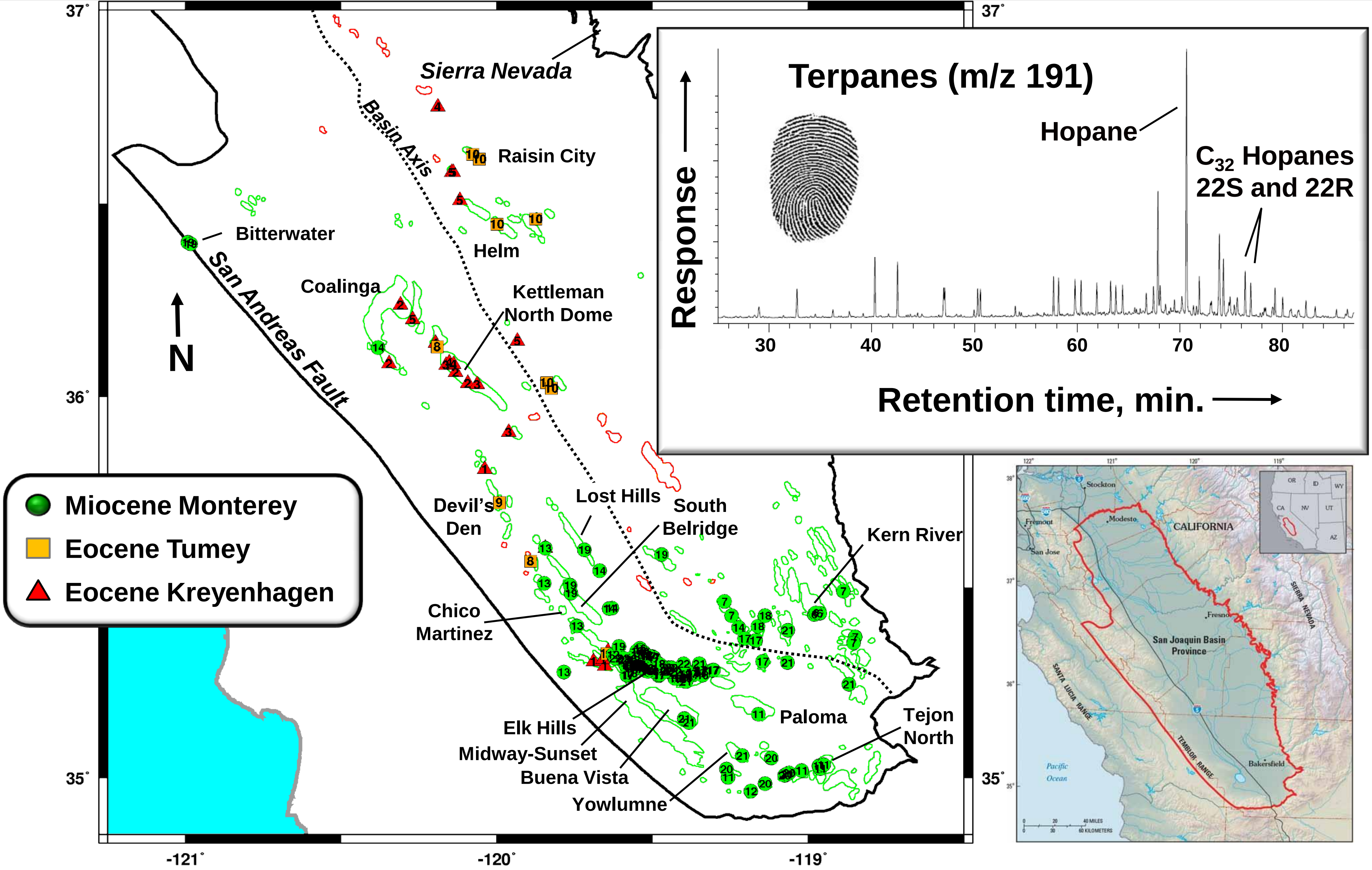
Chemometrics (Multivariate Statistics) of San Joaquin Oils

Purpose

- **Use two chemometric methods to classify 165 crude oil samples and identify petroleum systems**

AHC	**PCA**
Ascendant hierarchical cluster analysis **– terpane mass chromatograms**	***Principal components analysis*** **– 17 source-related biomarker and isotope ratios**
Peters et al., 2012 in press, AAPG Bulletin.	***Peters et al., 2007, AAPG Bulletin, v. 91, p. 877-913.***

AHC Oil Families are Based on Terpane Chromatograms

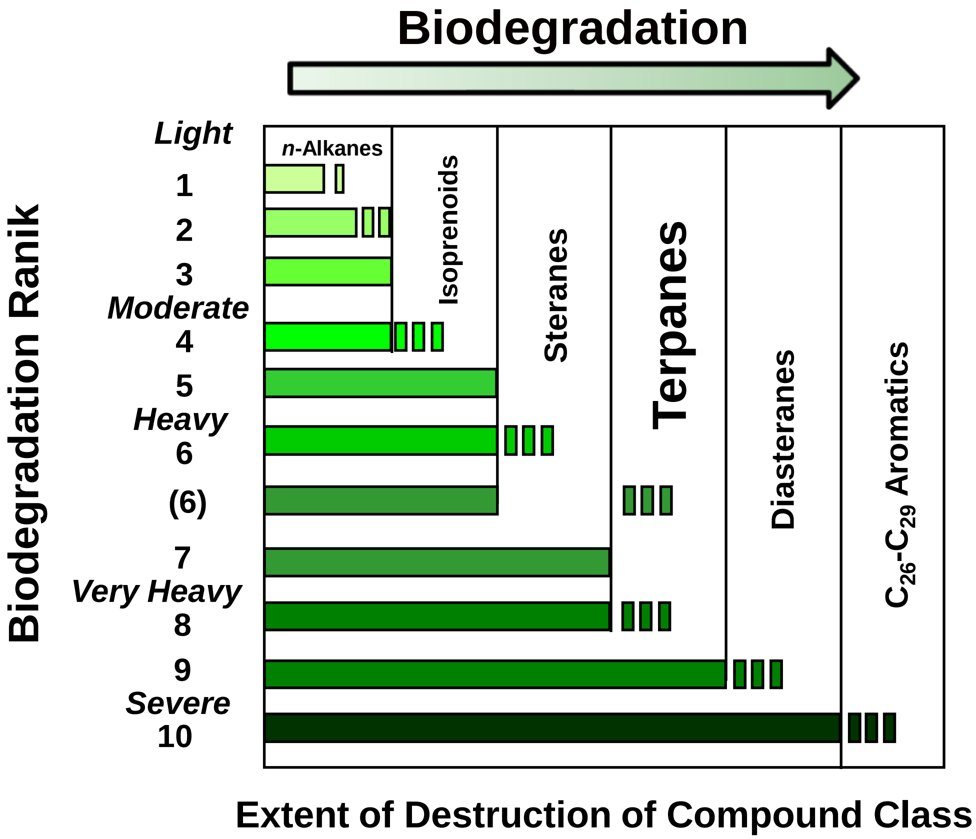


● Miocene Monterey

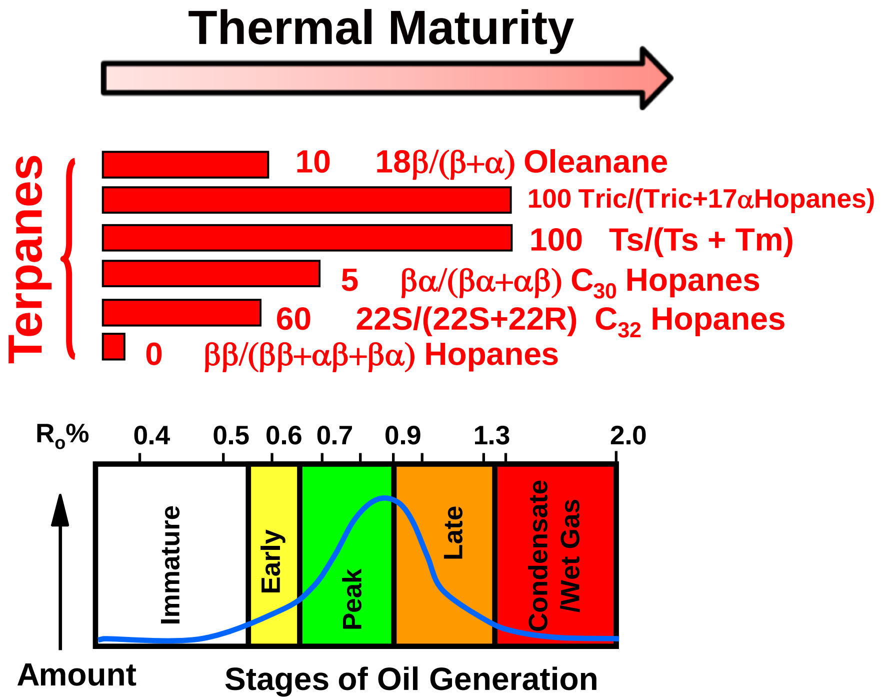
■ Eocene Tumey

▲ Eocene Kreyenhagen

Terpanes Resist Secondary Processes and Describe Source

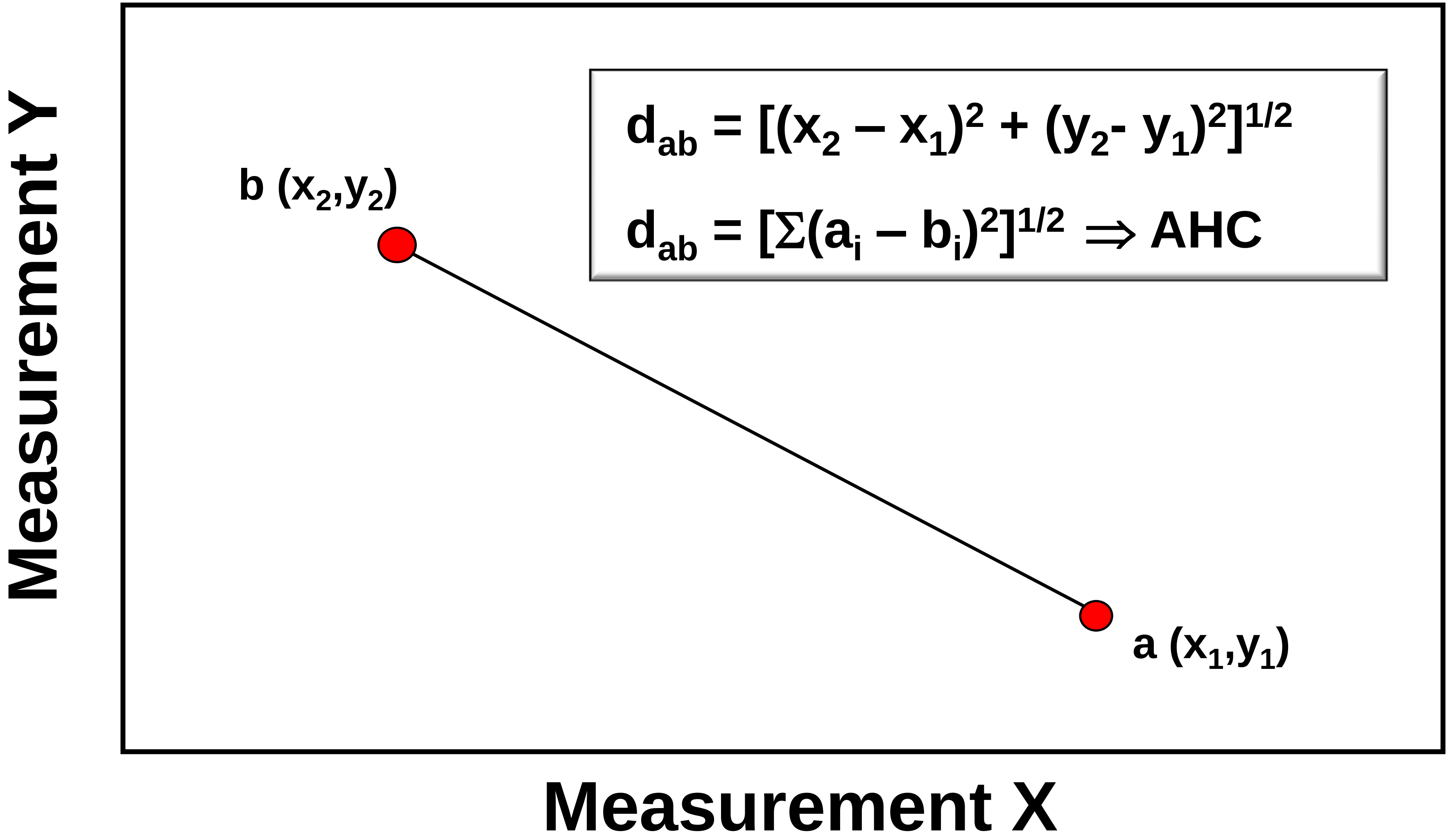


Peters and Moldowan (1993)



Peters et al. (2005)

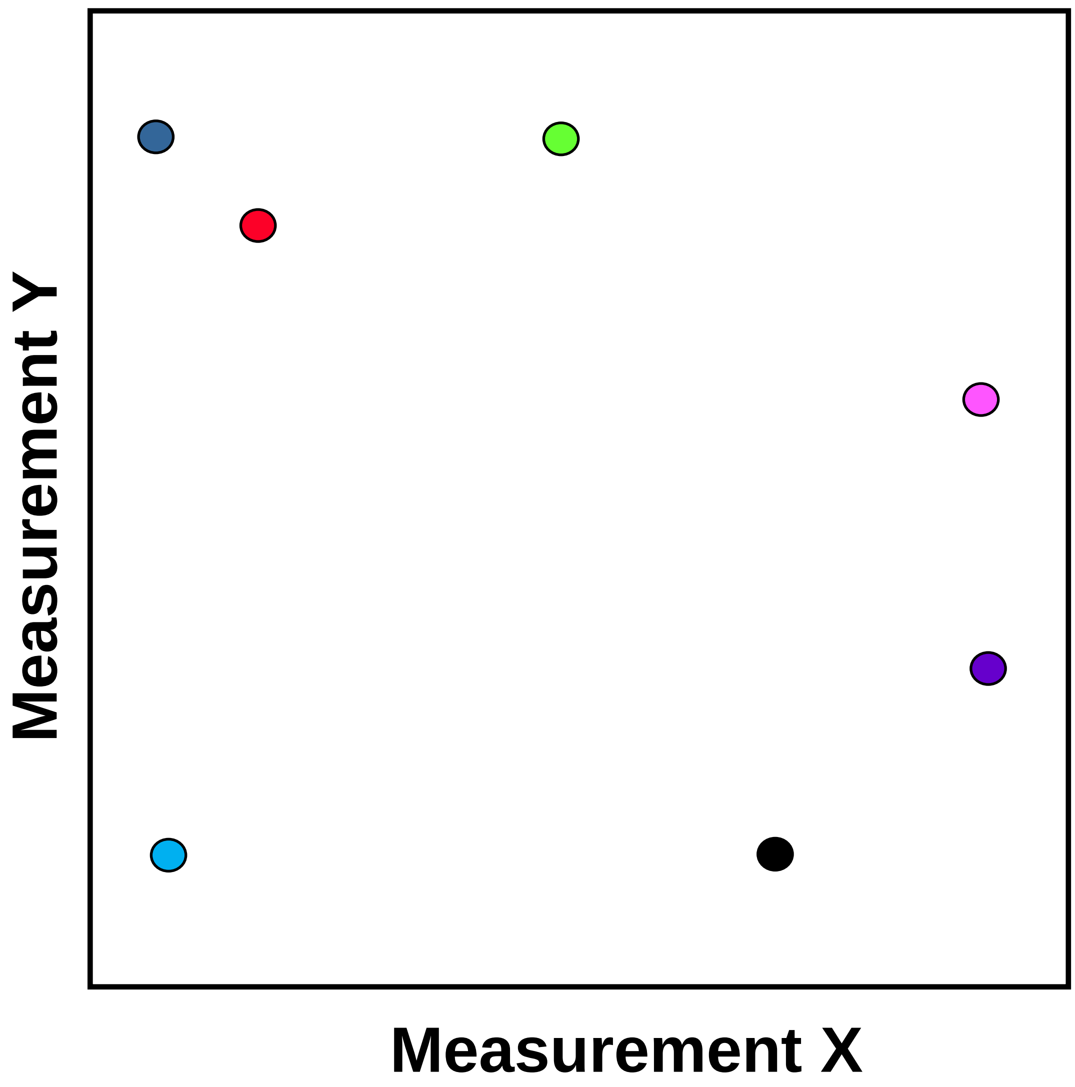
How Similar are Samples? Calculate in Two or *n*-Dimensions



$$d_{ab} = [(x_2 - x_1)^2 + (y_2 - y_1)^2]^{1/2}$$

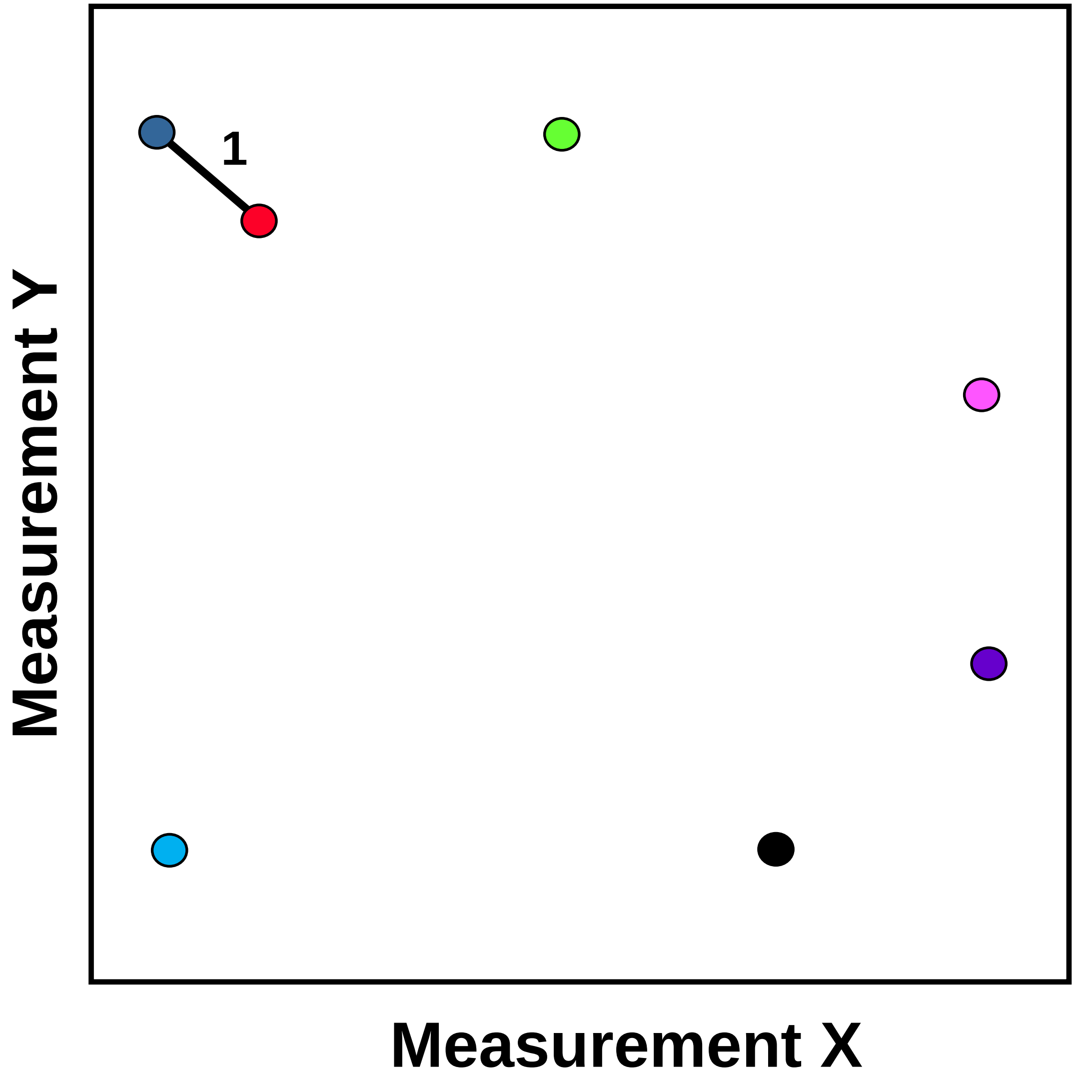
$$d_{ab} = [\Sigma(a_i - b_i)^2]^{1/2} \Rightarrow \text{AHC}$$

Calculate the Distance Between Points

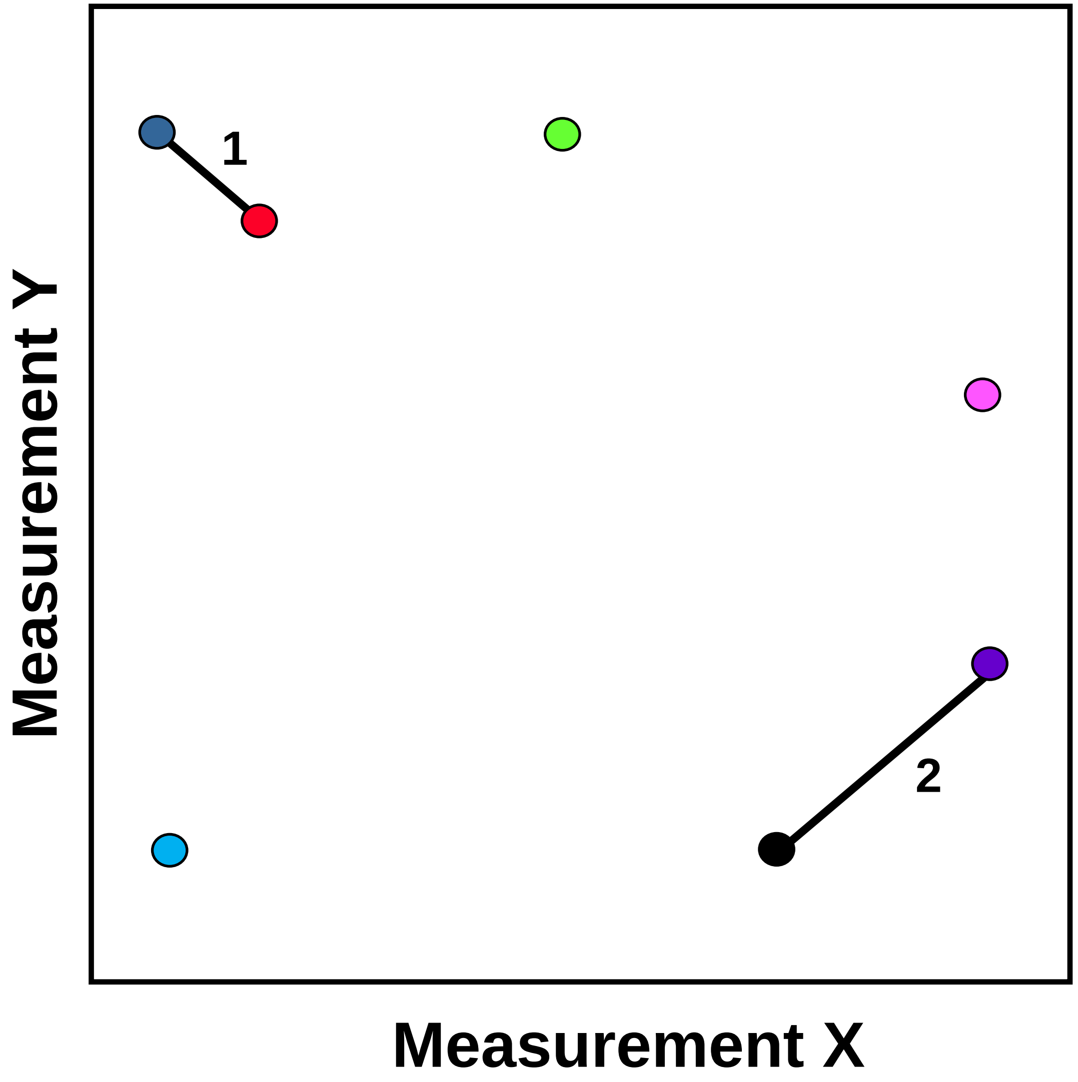


A simple example with 2 measurements on 7 samples.

Calculate the Distance Between Points



Calculate the Distance Between Points



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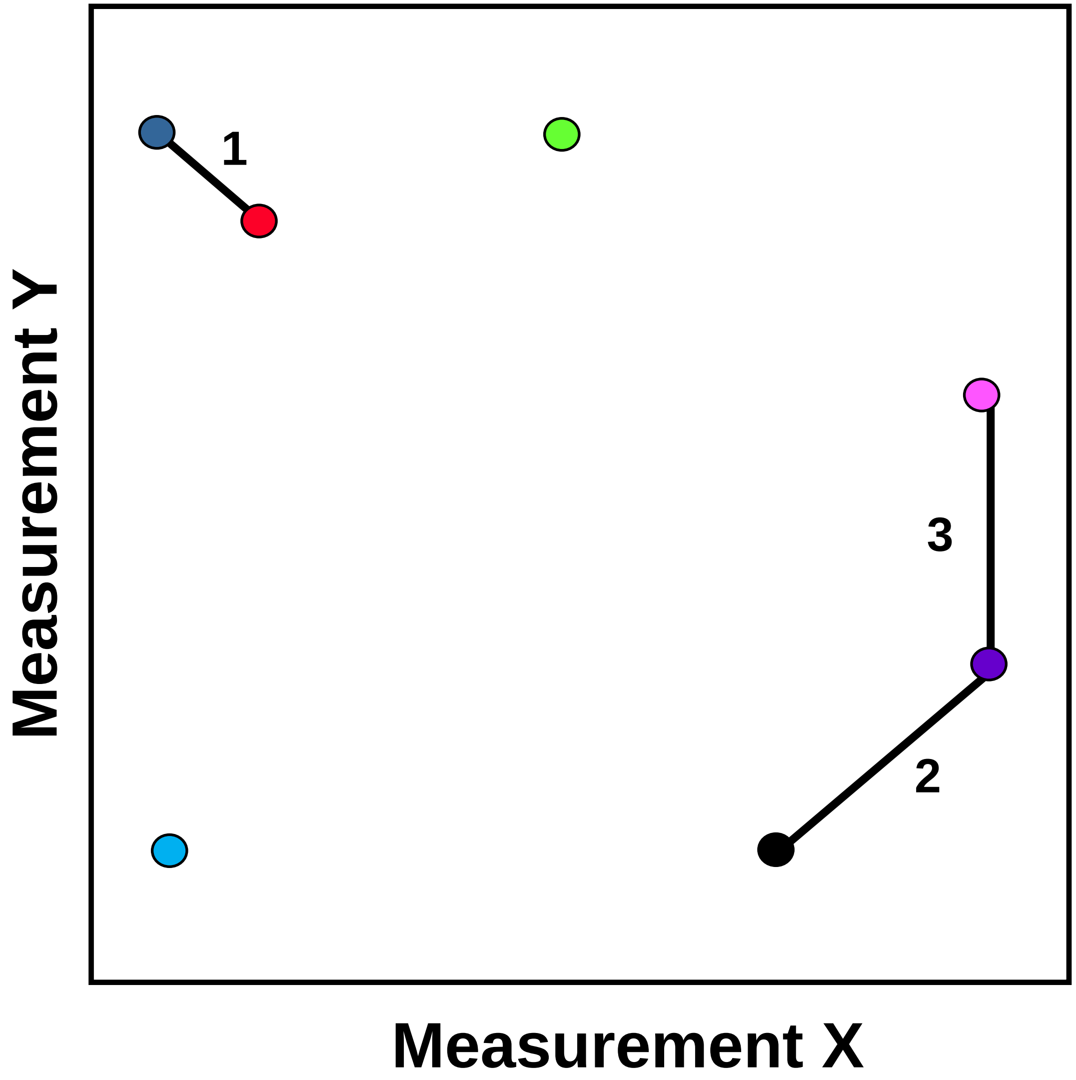

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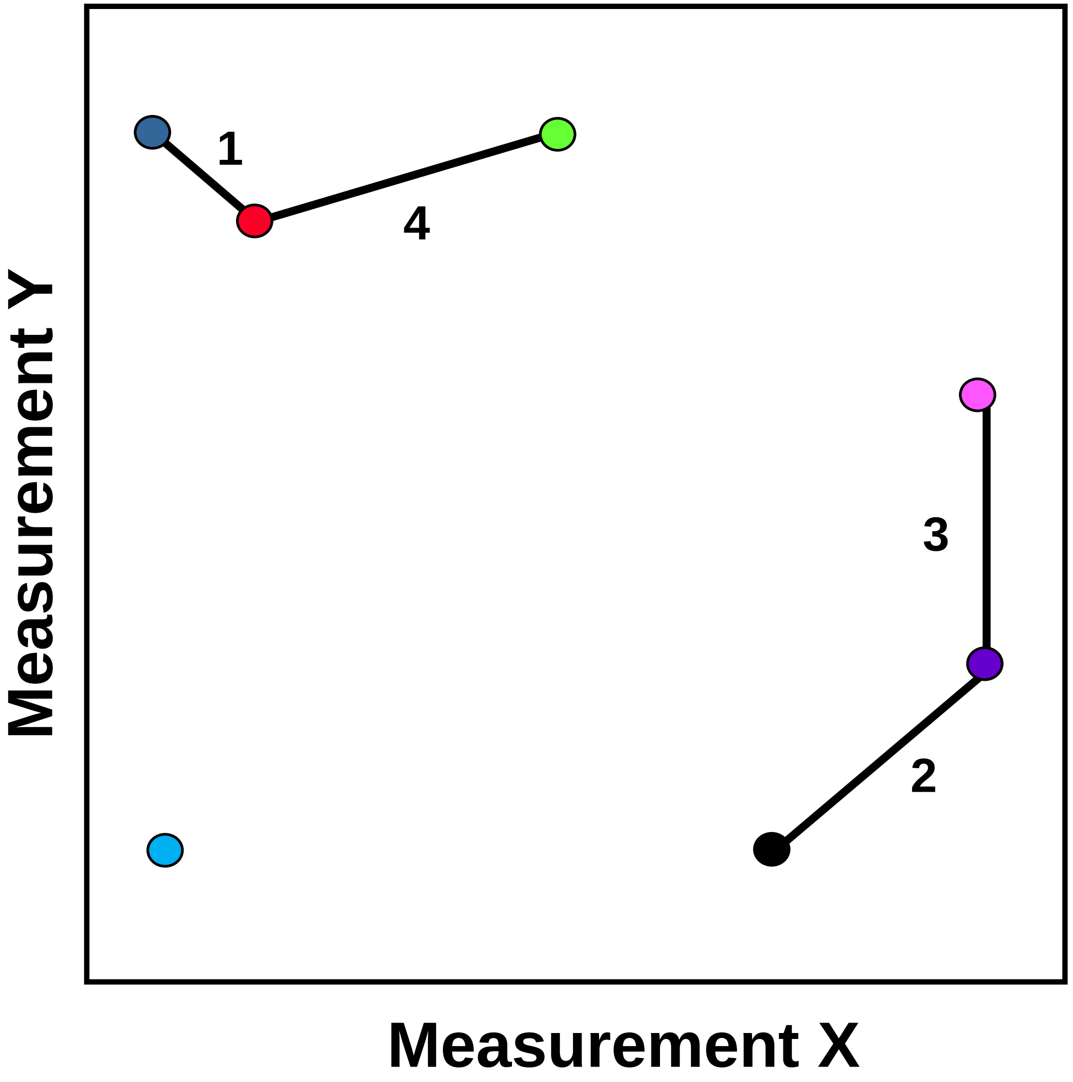
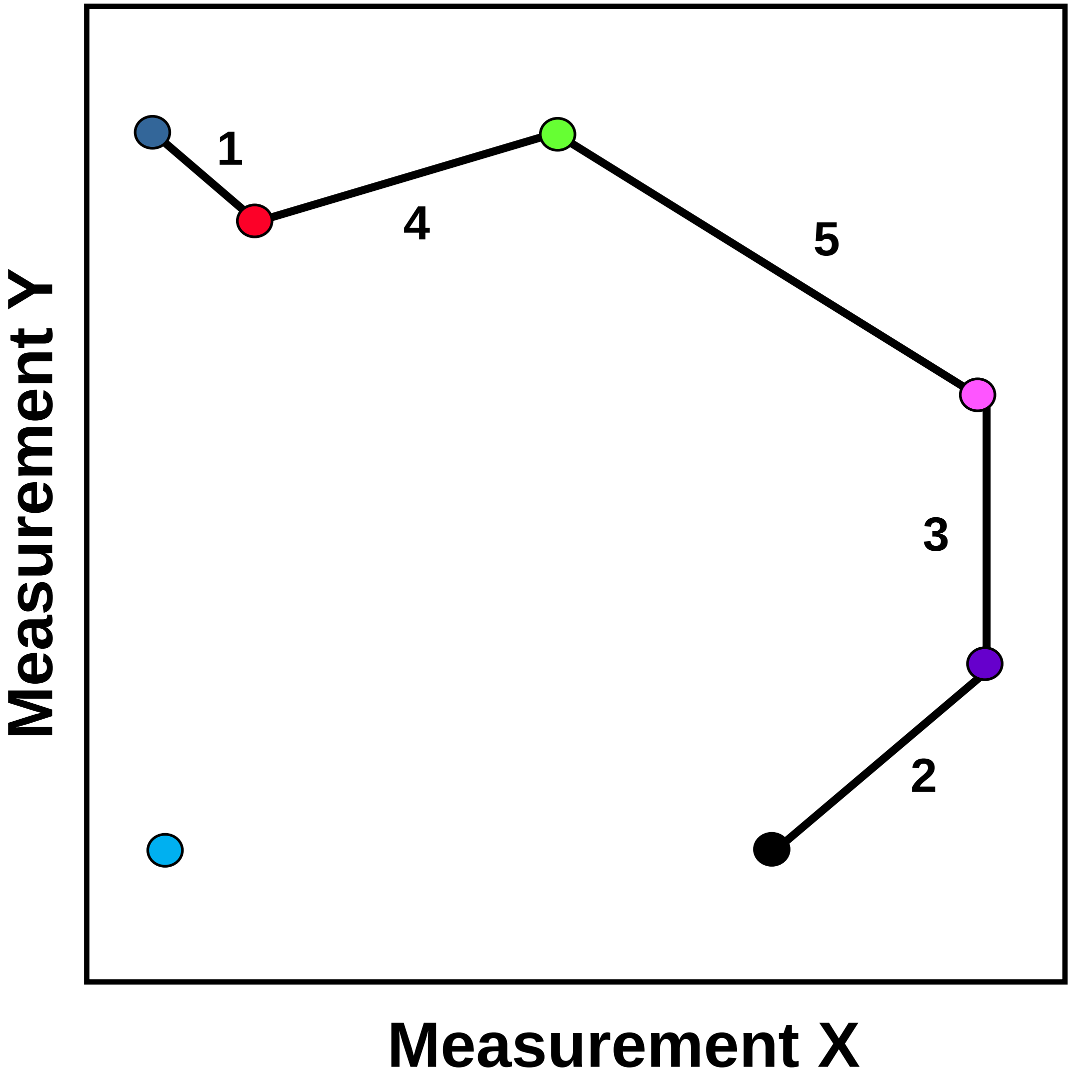
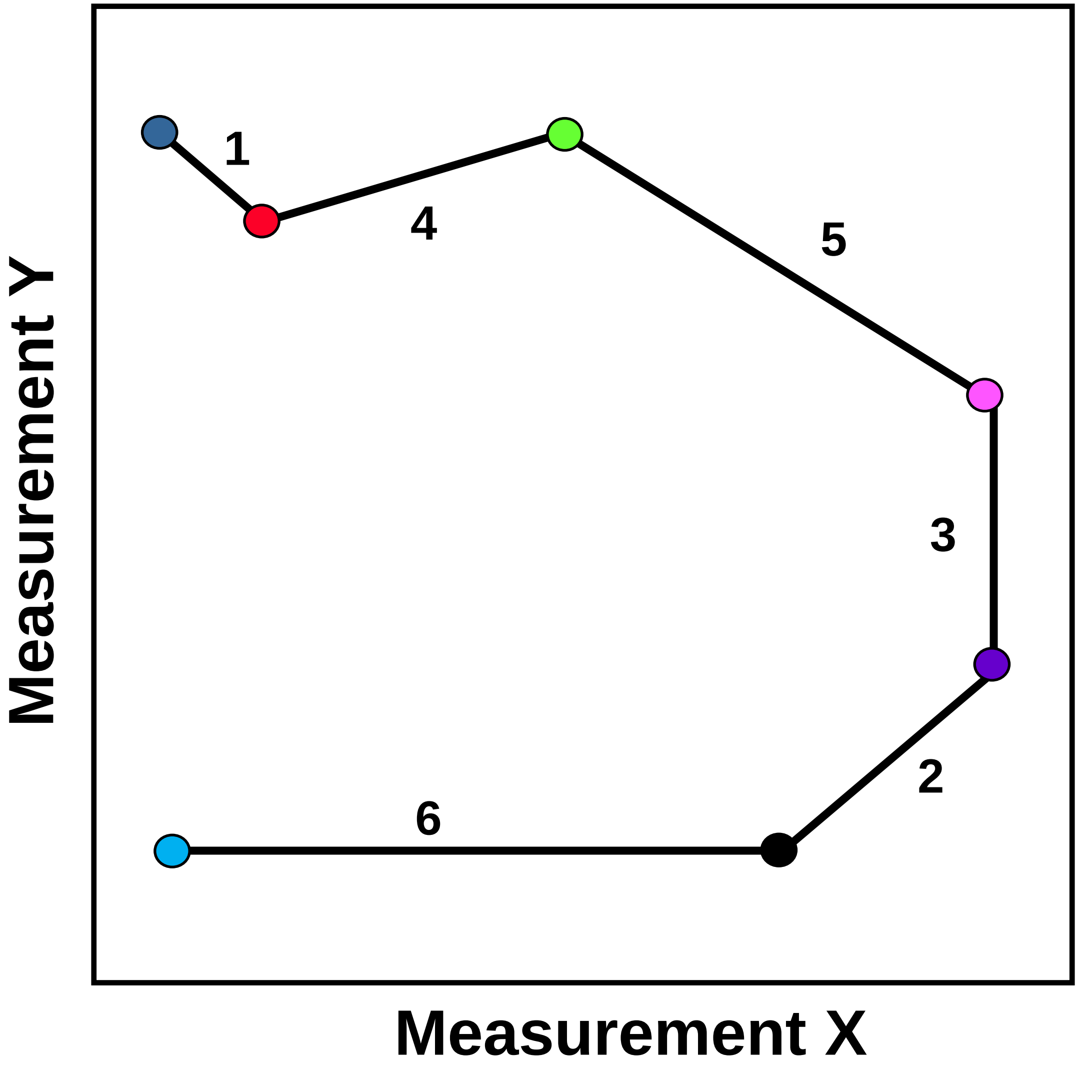
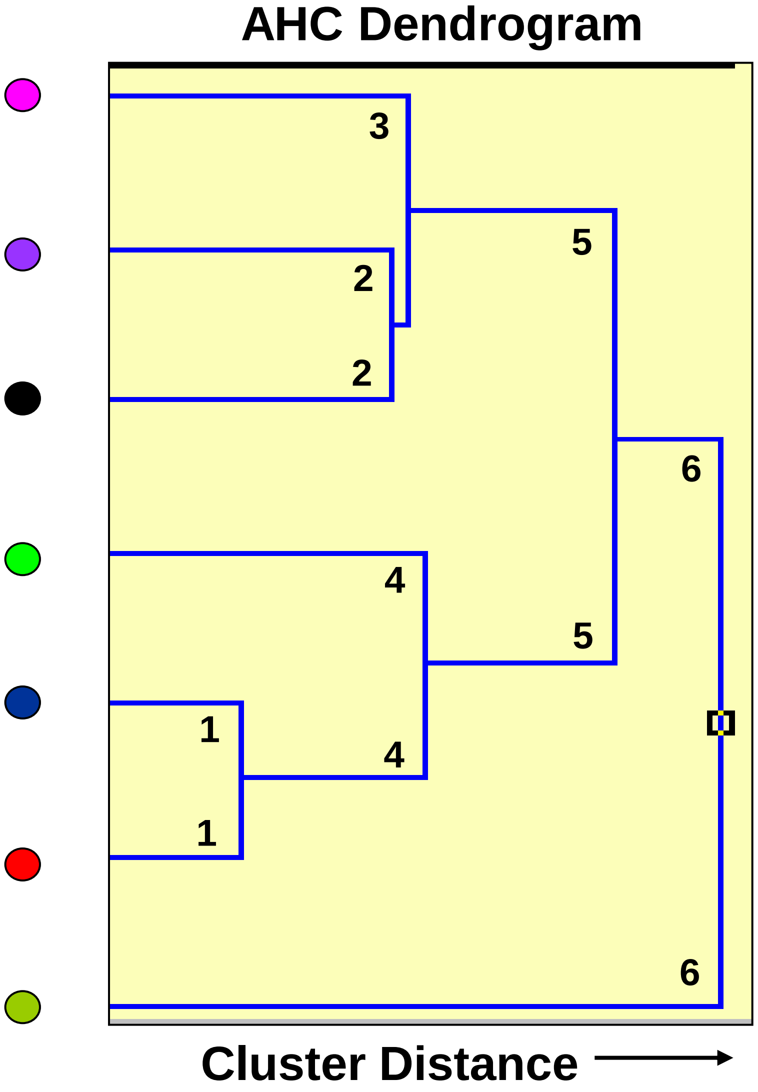


Calculate the Distance Between Points

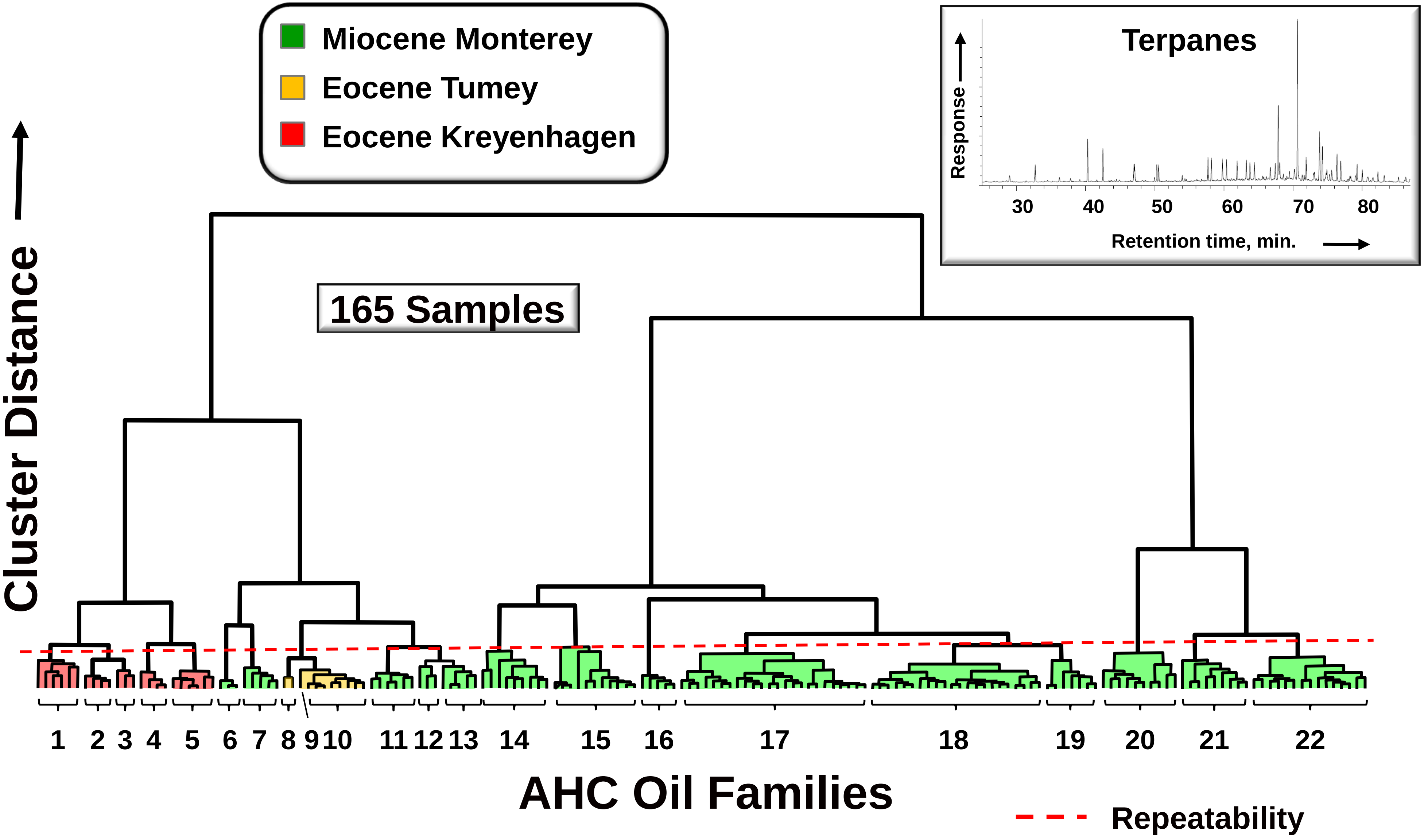


AHC Dendrograms are Based on Cluster Distance in *n*-Space

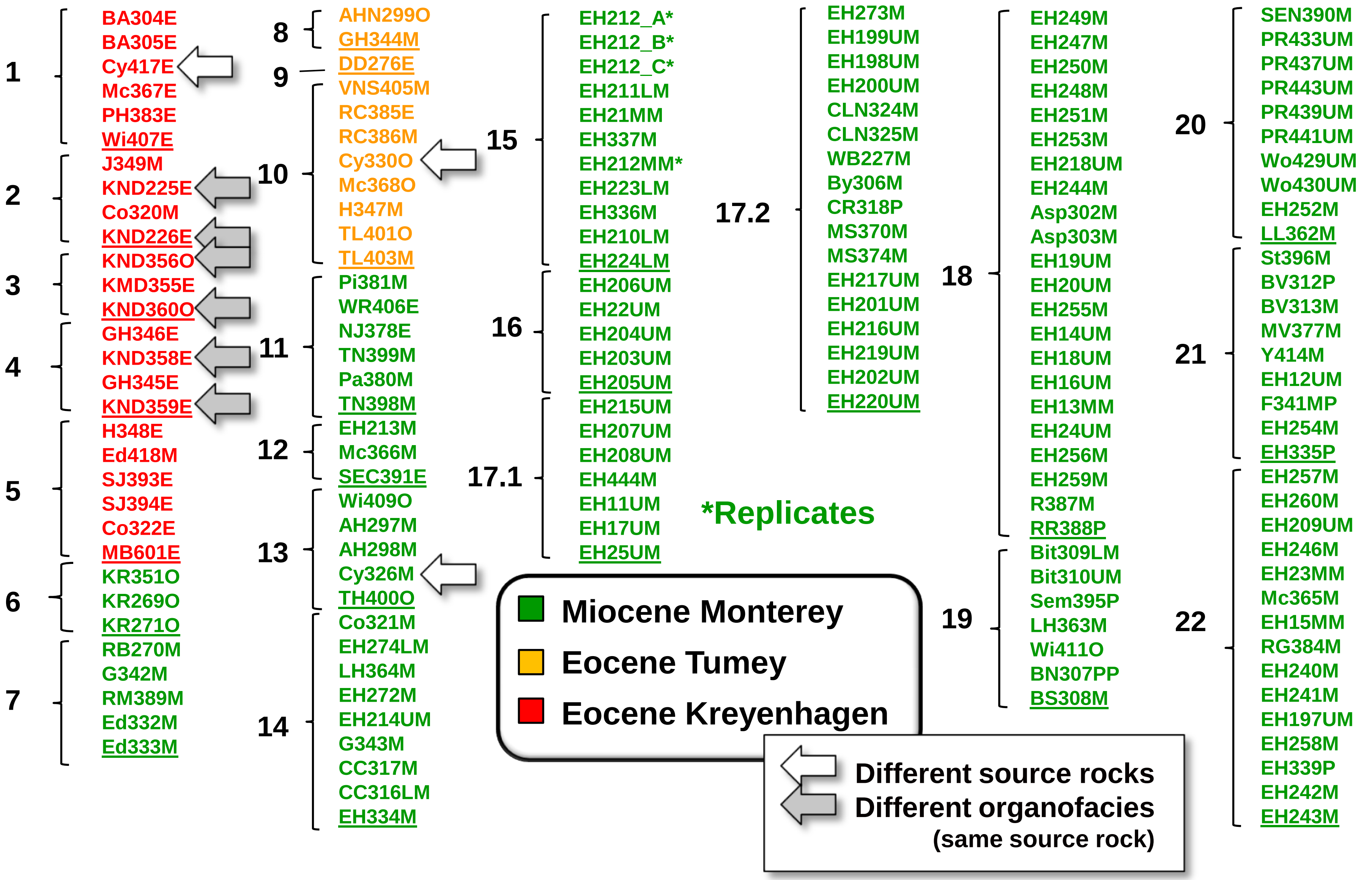




Ascendant Hierarchical Cluster Analysis (AHC): 22 Families



AHC Families Provide Geologic Insight into Compartments



1
BA304E
BA305E
Cy417E
Mc367E
PH383E
Wi407E

2
J349M
KND225E
Co320M
KND226E

3
KND356O
KMD355E
KND360O

4
GH346E
KND358E
GH345E
KND359E

5
H348E
Ed418M
SJ393E
SJ394E
Co322E
MB601E

6
KR351O
KR269O
KR271O

7
RB270M
G342M
RM389M
Ed332M
Ed333M

8
AHN299O
GH344M

9
DD276E

10
VNS405M
RC385E
RC386M
Cy330O
Mc368O
H347M
TL401O
TL403M

11
Pi381M
WR406E
NJ378E
TN399M
Pa380M
TN398M

12
EH213M
Mc366M
SEC391E

13
Wi409O
AH297M
AH298M
Cy326M
TH400O

14
Co321M
EH274LM
LH364M
EH272M
EH214UM
G343M
CC317M
CC316LM
EH334M

15
EH212_A*
EH212_B*
EH212_C*
EH211LM
EH21MM
EH337M
EH212MM*
EH223LM
EH336M
EH210LM
EH224LM

16
EH206UM
EH22UM
EH204UM
EH203UM
EH205UM

17.1
EH215UM
EH207UM
EH208UM
EH444M
EH11UM
EH17UM
EH25UM

17.2
EH273M
EH199UM
EH198UM
EH200UM
CLN324M
CLN325M
WB227M
By306M
CR318P
MS370M
MS374M
EH217UM
EH201UM
EH216UM
EH219UM
EH202UM
EH220UM

18
EH249M
EH247M
EH250M
EH248M
EH251M
EH253M
EH218UM
EH244M
Asp302M
Asp303M
EH19UM
EH20UM
EH255M
EH14UM
EH18UM
EH16UM
EH13MM
EH24UM
EH256M
EH259M
R387M
RR388P

19
Bit309LM
Bit310UM
Sem395P
LH363M
Wi411O
BN307PP
BS308M

20
SEN390M
PR433UM
PR437UM
PR443UM
PR439UM
PR441UM
Wo429UM
Wo430UM
EH252M
LL362M

21
St396M
BV312P
BV313M
MV377M
Y414M
EH12UM
F341MP
EH254M
EH335P

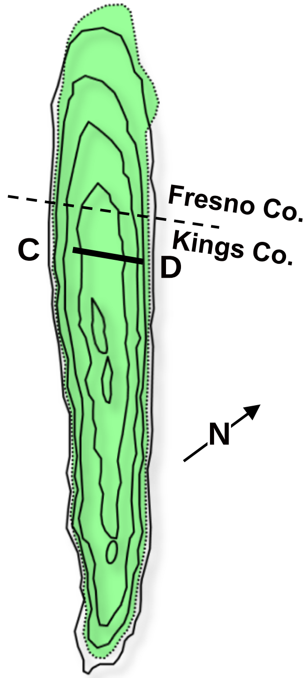
22
EH257M
EH260M
EH209UM
EH246M
EH23MM
Mc365M
EH15MM
RG384M
EH240M
EH241M
EH197UM
EH258M
EH339P
EH242M
EH243M

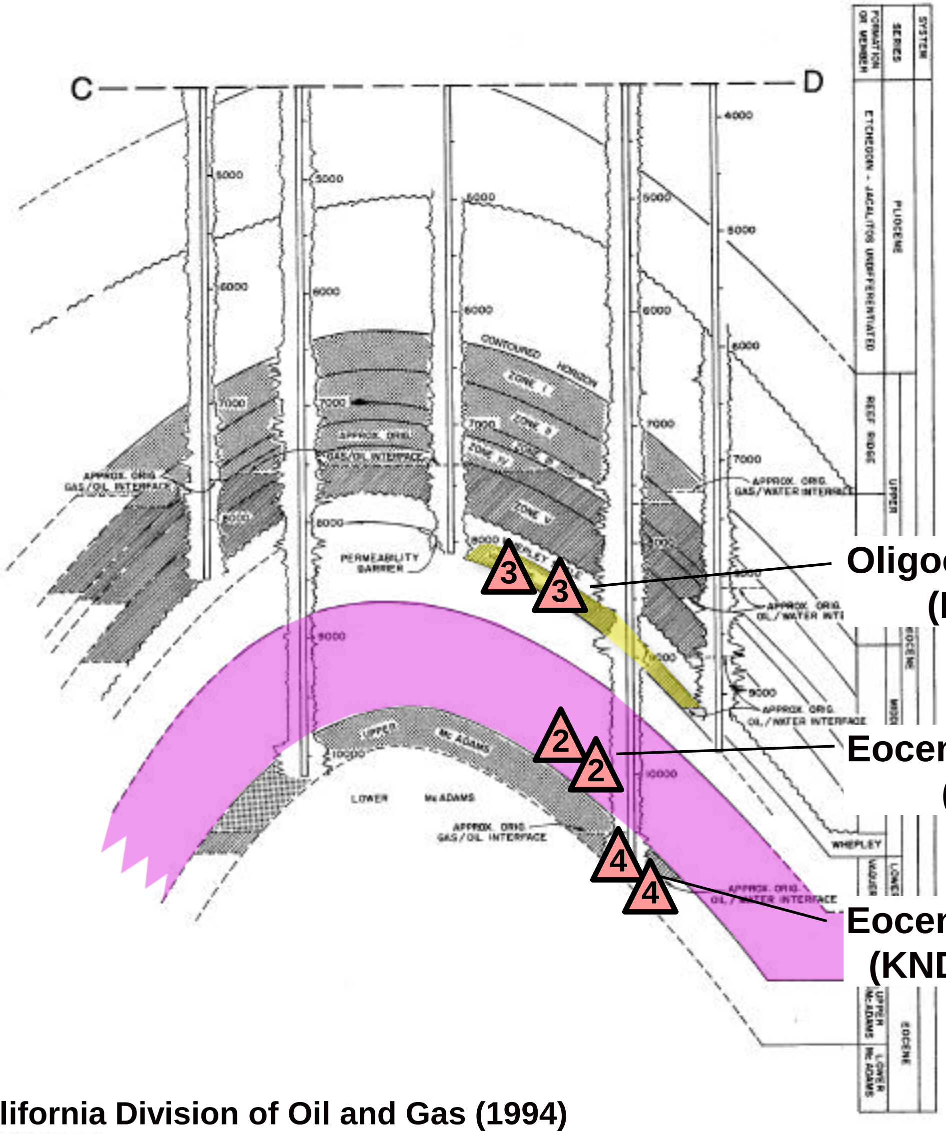
*Replicates

🟩 Miocene Monterey
🟨 Eocene Tumey
🟥 Eocene Kreyenhagen

Different source rocks
Different organofacies
(same source rock)

Kettleman N. Dome Includes Three Kreyenhagen Oil Families





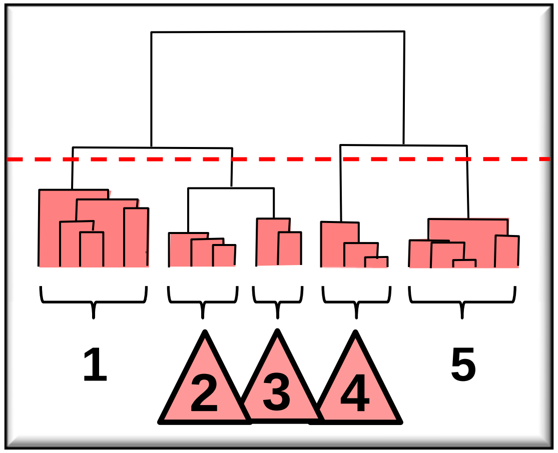
Oligocene Vaqueros Formation
(KND356O, KND360O)

Eocene Kreyenhagen Formation
(KND225E, KND226E)

Eocene Lodo Formation
(KND358E, KND359E)

California Division of Oil and Gas (1994)

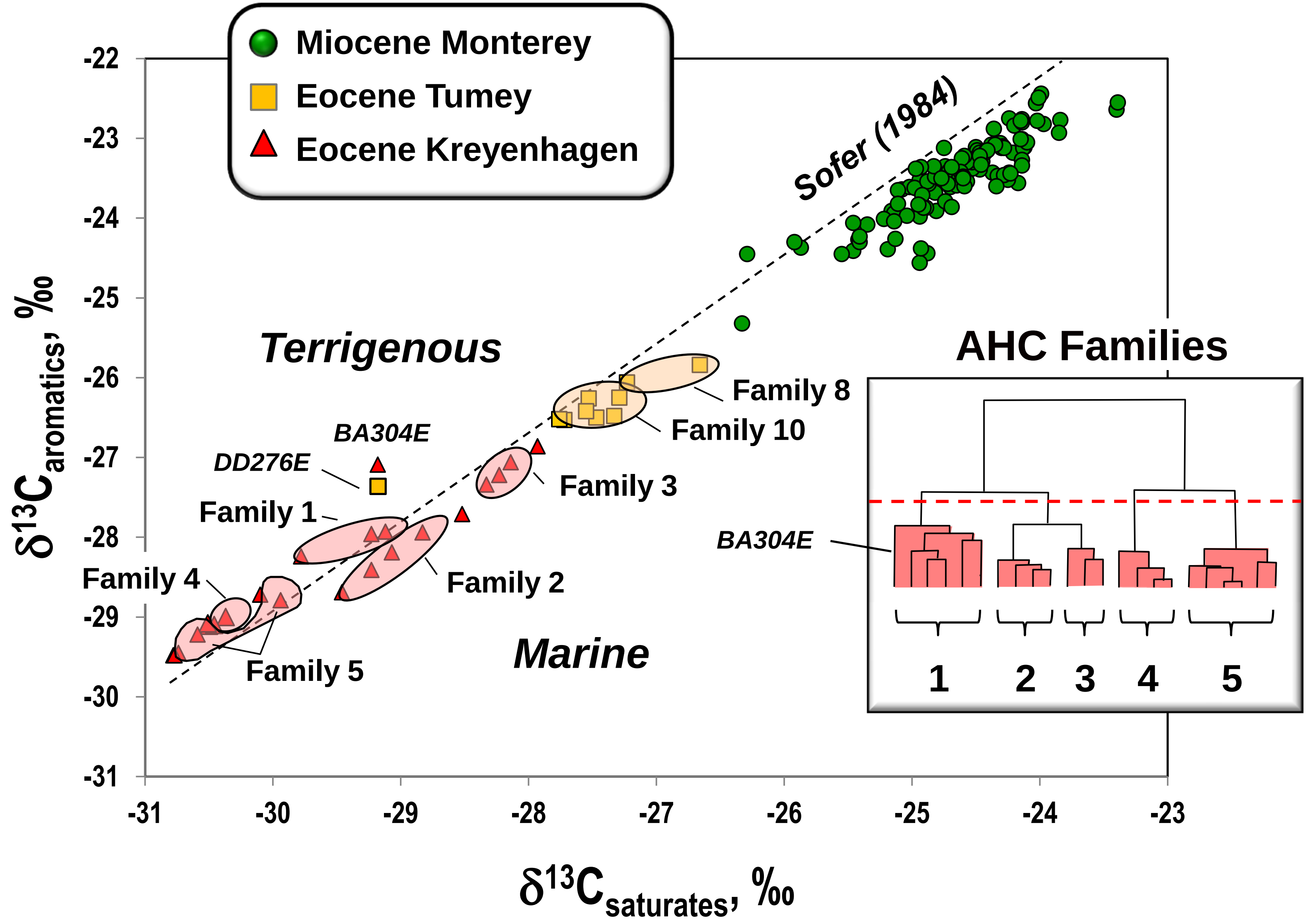
AHC Families



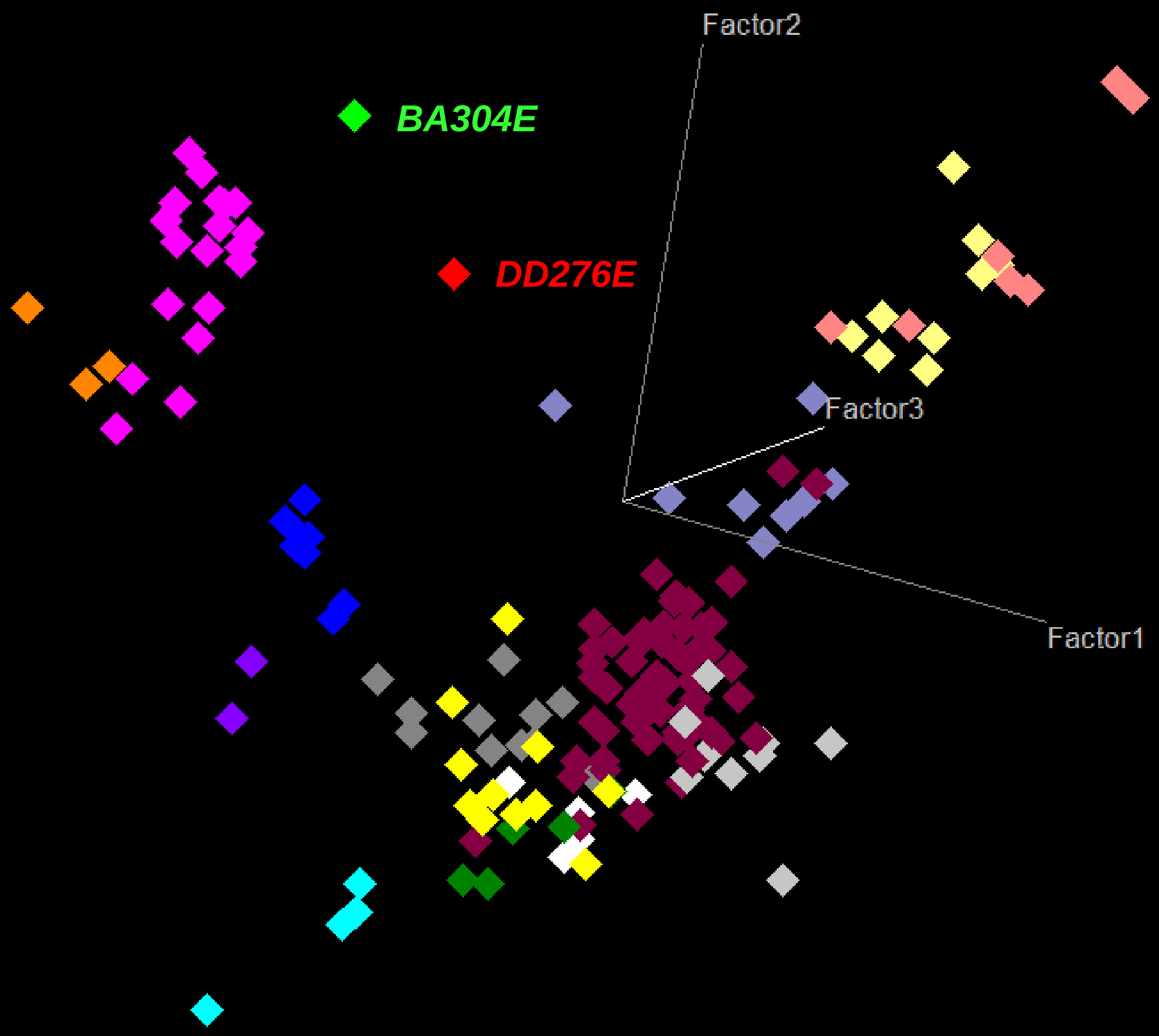
17 Geochemical Ratios Characterize the Training Set Oils

AHC Family	Terpanes										Steranes					Isotopes	
	C_{19}/C_{23}	C_{22}/C_{21}	C_{24}/C_{23}	C_{26}/C_{25}	Tet/C_{23}	$C_{27}T/C_{27}$	C_{28}/H	C_{29}/H	Ol/H	$C_{31}R/H$	S1/S6	S/H	$\%C_{27}$	$\%C_{28}$	$\%C_{29}$	$\delta^{13}C_{sat}$	$\delta^{13}C_{aro}$
1	0.07 ±0.05	0.32 ±0.01	0.67 ±0.05	0.92 ±0.09	0.22 ±0.05	0.02 ±0.04	0.02 ±0.01	0.46 ±0.05	0.15 ±0.04	0.24 ±0.01	1.19 ±0.54	1.06 ±0.20	32.62 ±0.58	36.59 ±1.62	30.79 ±1.37	-28.96 ±0.64	-27.63 ±0.54
2	0.03 ±0.01	0.34 ±0.02	0.60 ±0.05	0.84 ±0.05	0.21 ±0.01	0.09 ±0.04	0.10 ±0.05	0.53 ±0.03	0.12 ±0.01	0.25 ±0.01	0.81 ±0.11	1.10 ±0.14	30.94 ±0.40	38.57 ±1.20	30.50 ±1.59	-29.15 ±0.27	-28.31 ±0.32
20	0.07 ±0.02	0.21 ±0.02	0.57 ±0.06	0.92 ±0.08	0.14 ±0.01	3.46 ±1.52	0.62 ±0.27	0.45 ±0.04	0.17 ±0.06	0.20 ±0.01	0.18 ±0.04	2.29 ±0.30	27.24 ±1.61	44.28 ±1.28	28.49 ±0.78	-24.96 ±0.24	-23.95 ±0.34
21	0.08 ±0.07	0.22 ±0.02	0.65 ±0.07	0.98 ±0.06	0.13 ±0.02	1.19 ±0.43	0.24 ±0.04	0.47 ±0.05	0.18 ±0.07	0.21 ±1.01	0.26 ±0.10	1.56 ±0.24	29.89 ±1.32	42.17 ±0.77	27.93 ±1.03	-24.60 ±0.37	-23.53 ±0.22
22	0.02 ±0.01	0.26 ±0.03	0.63 ±0.06	0.84 ±0.05	0.10 ±0.01	0.81 ±0.27	0.22 ±0.04	0.51 ±0.03	0.11 ±0.01	0.24 ±0.03	0.27 ±0.04	1.80 ±0.23	32.42 ±1.17	39.87 ±0.67	27.70 ±1.12	-25.34 ±0.42	-24.15 ±0.29

Carbon Isotopes Distinguish Many San Joaquin Oil Samples

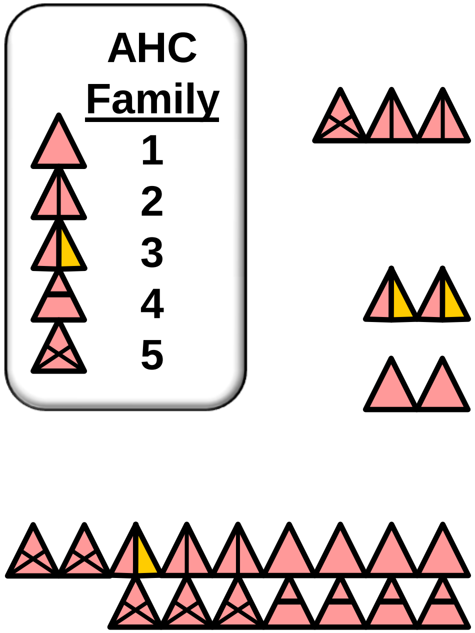


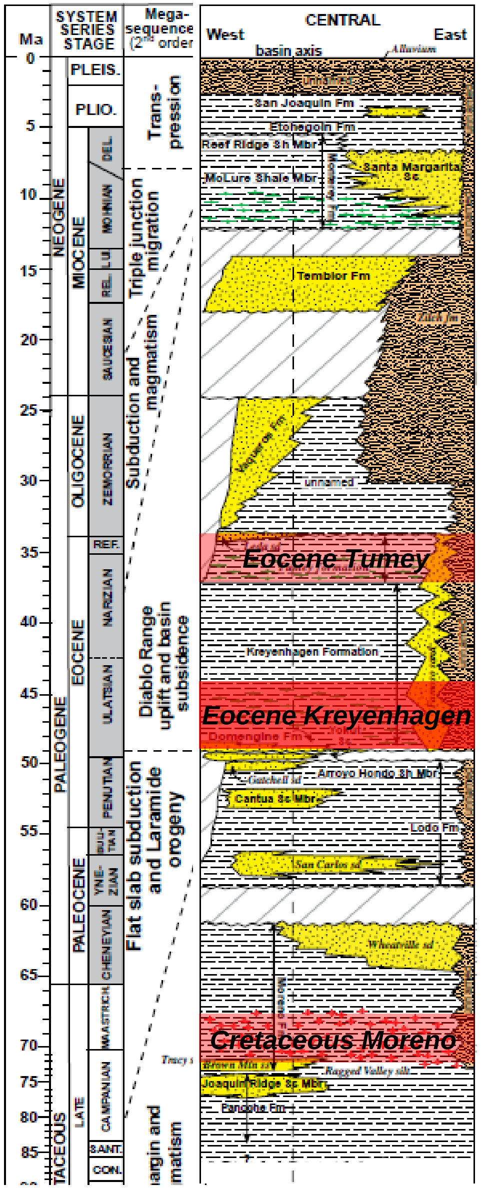
PCA and AHC Results are Very Similar



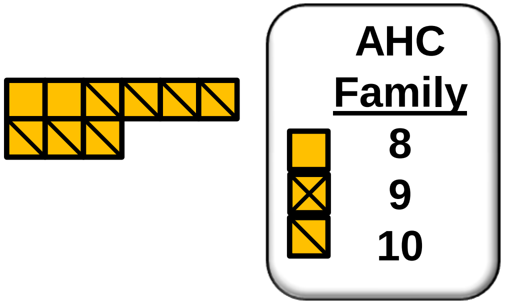
Eocene Oil Families are from Kreyenhagen or Tumey Source

Families 1-5: Kreyenhagen Source, Mostly Eocene Pools

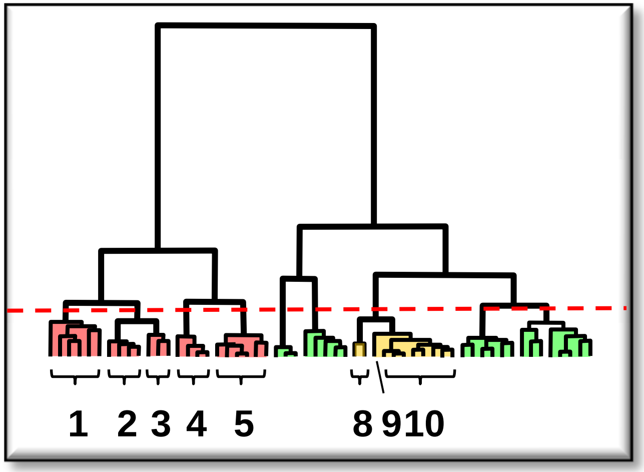




Families 8-10: Tumey Source, Mostly Miocene Pools



AHC Families



The oil families retain the geochemical fingerprint of organofacies variations in their source rocks.

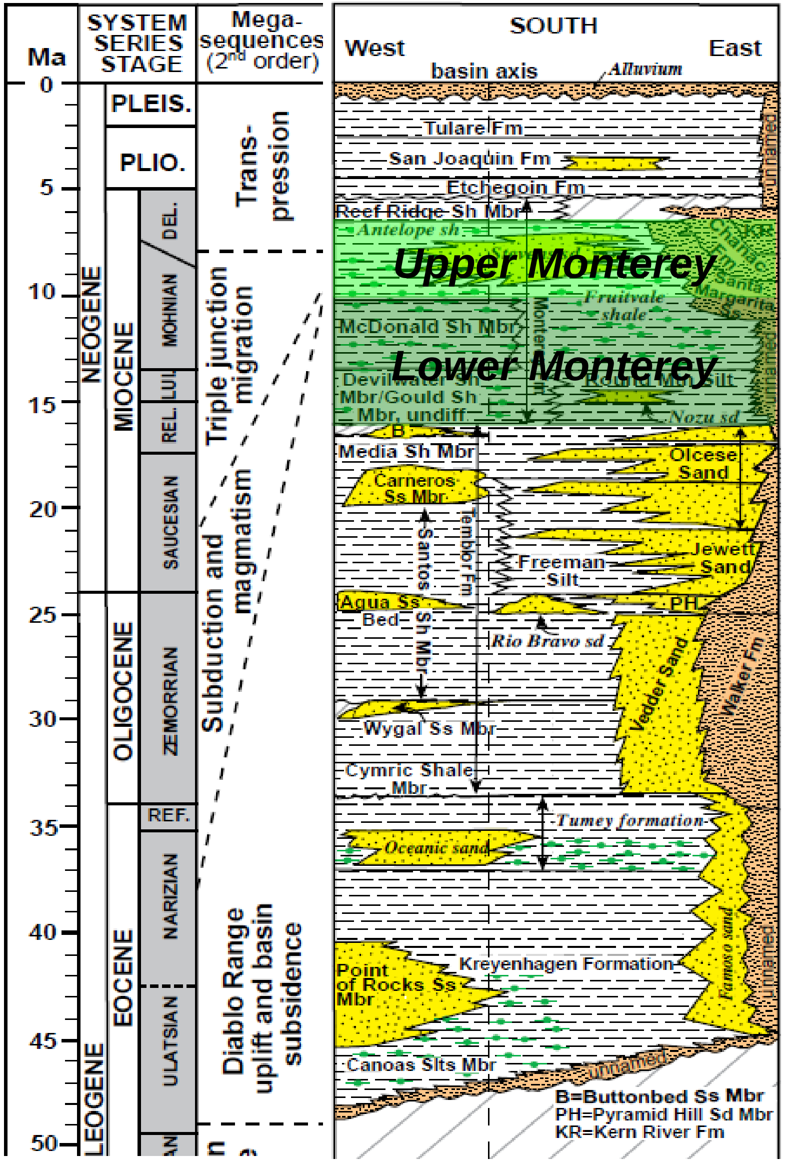
Miocene Oil Families are from Upper or Lower Monterey

Families 6, 7: Lower Monterey (or Temblor) Source, Pre-Monterey Pools

Lower Miocene-Oligocene Pools

⊖⊖⊖⊖⊖

⊘⊘⊘



B=Buttonbed Ss Mbr
PH=Pyramid Hill Sd Mbr
KR=Kern River Fm

Families 20-21: Upper Monterey Source, Stevens, Reef Ridge, Chanac Pools

🟢🟢🟢🟢🟢🟢🟢🟢

🟢⚫⚫⚫⚫⚫

⚫⚫?

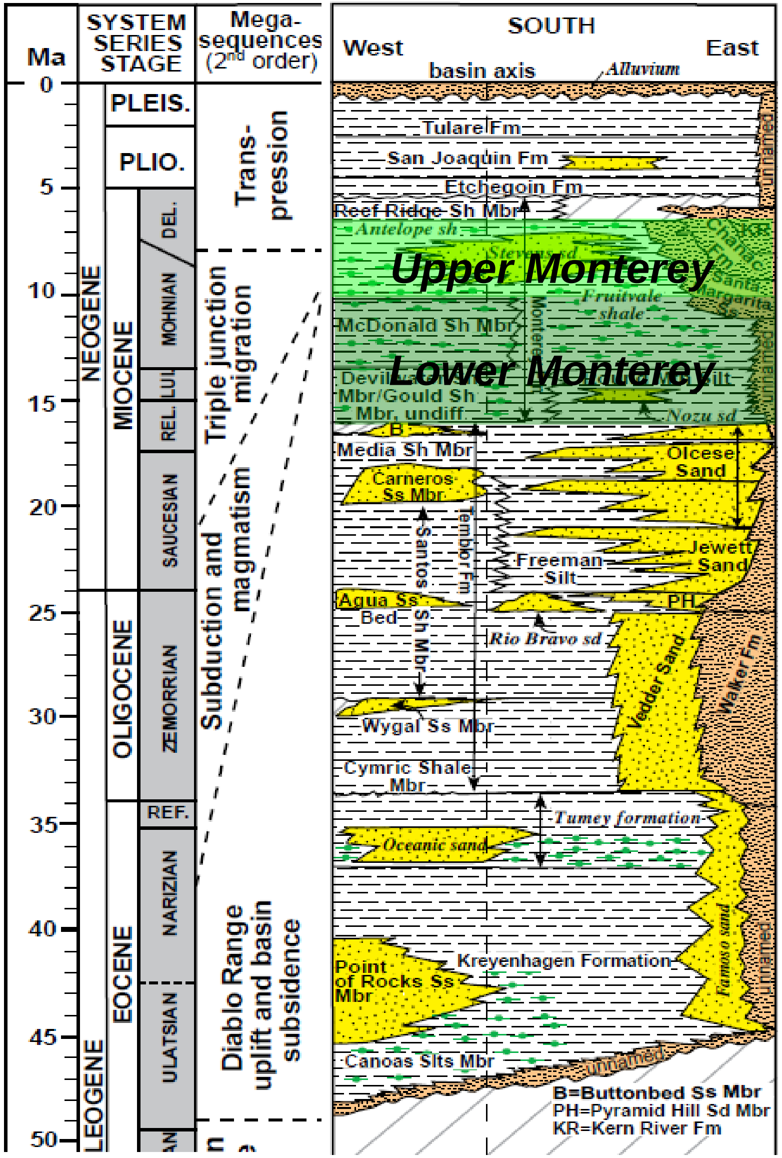
⚫

AHC
Family

⊘ 6
⊖ 7
🟢 20
⚫ 21

Stratigraphy of Families Helps to Identify their Source Rocks

Families 11-13: Lower Monterey Source(?), Mostly Pre-Monterey Pools



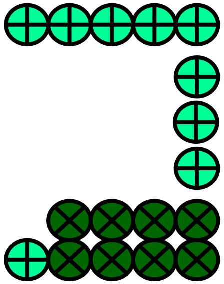
Family 22: Upper Monterey Source, Mostly Stevens, Reef Ridge, Etchegoin Pools

AHC
Family

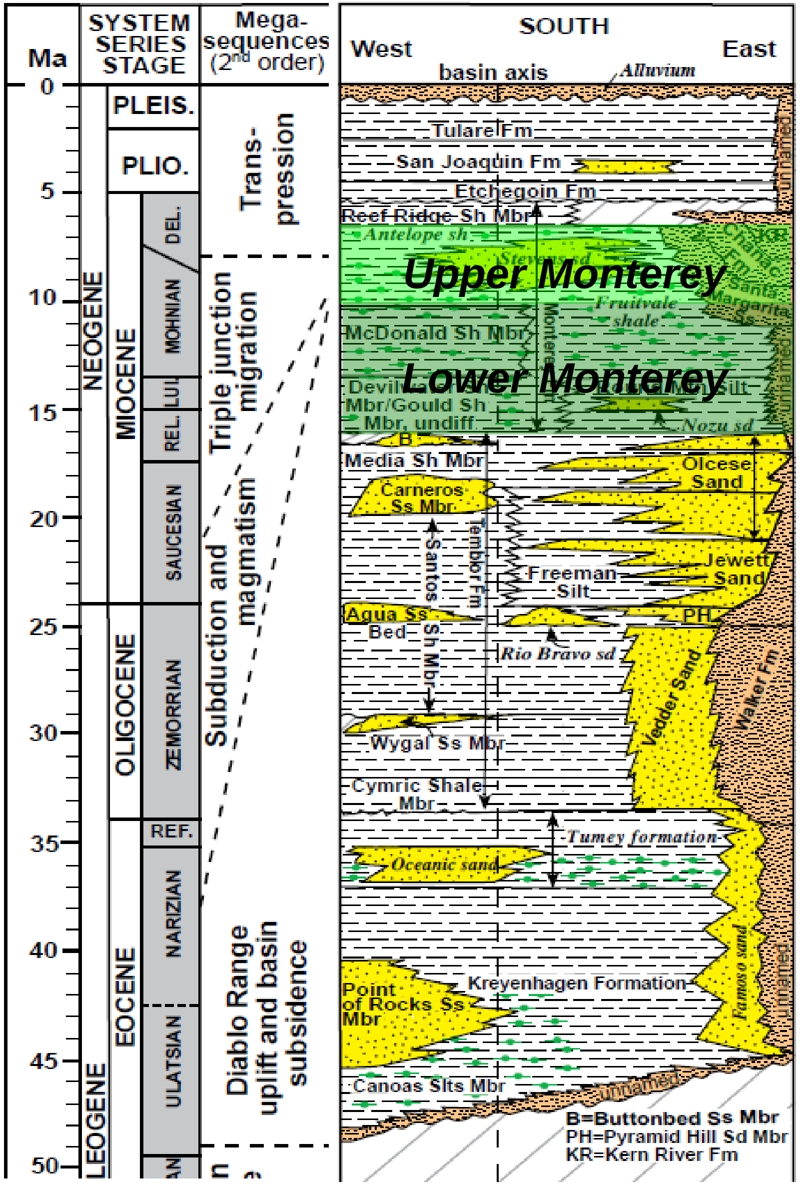
- ⦶ 11
- ⦸ 12
- ⊘ 13
- ● 22

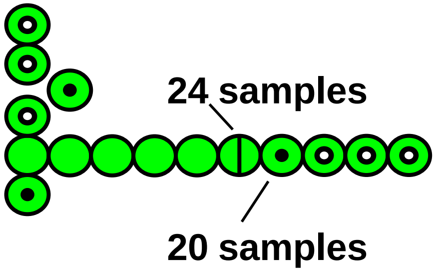
Stratigraphy of Families Helps to Identify their Source Rocks

Family 14: Upper Monterey Source, Mostly "Monterey" Pools



Family 15: Lower Monterey Source (No Access to Stevens Sand) Pre-Monterey Pools

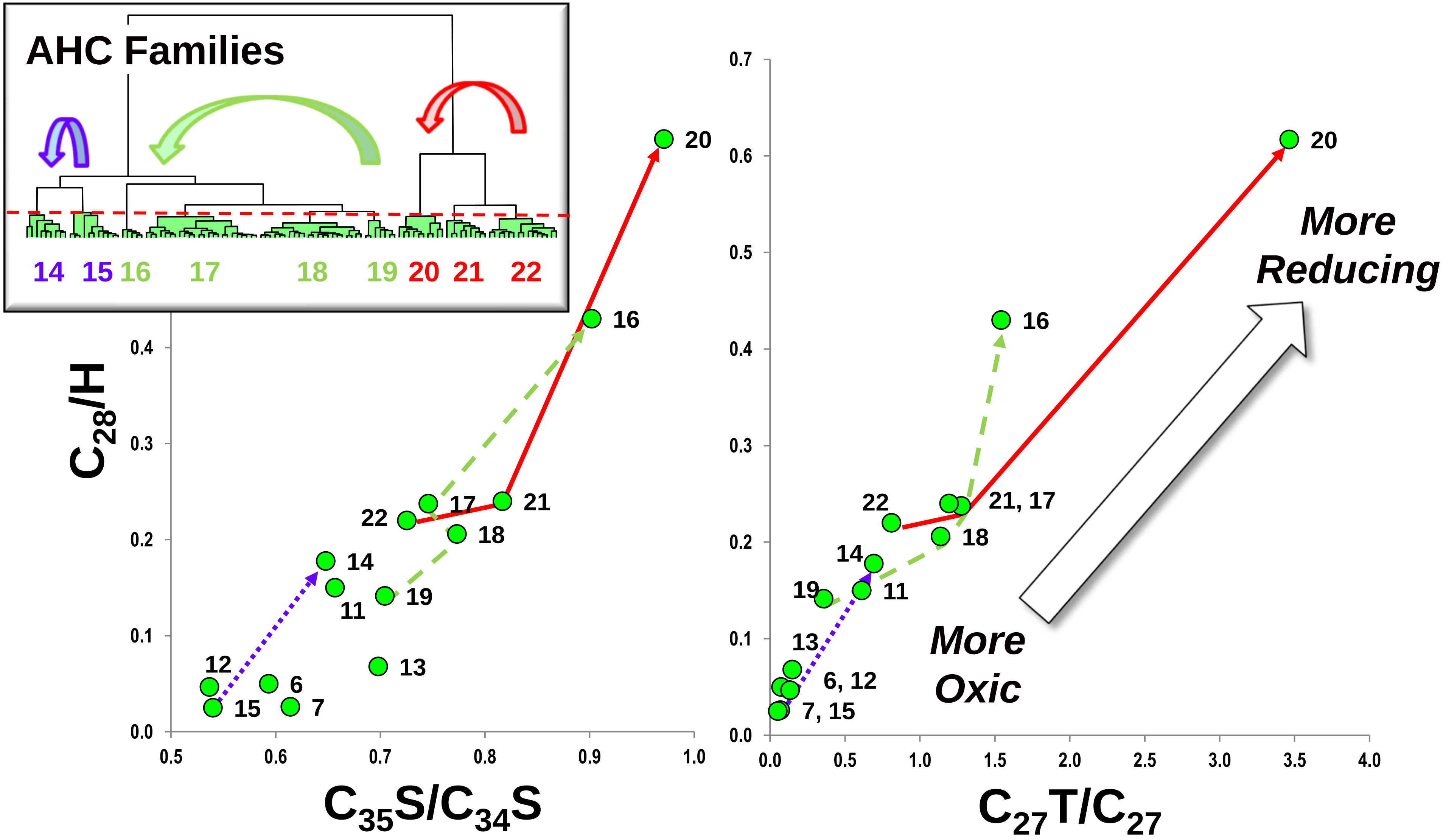




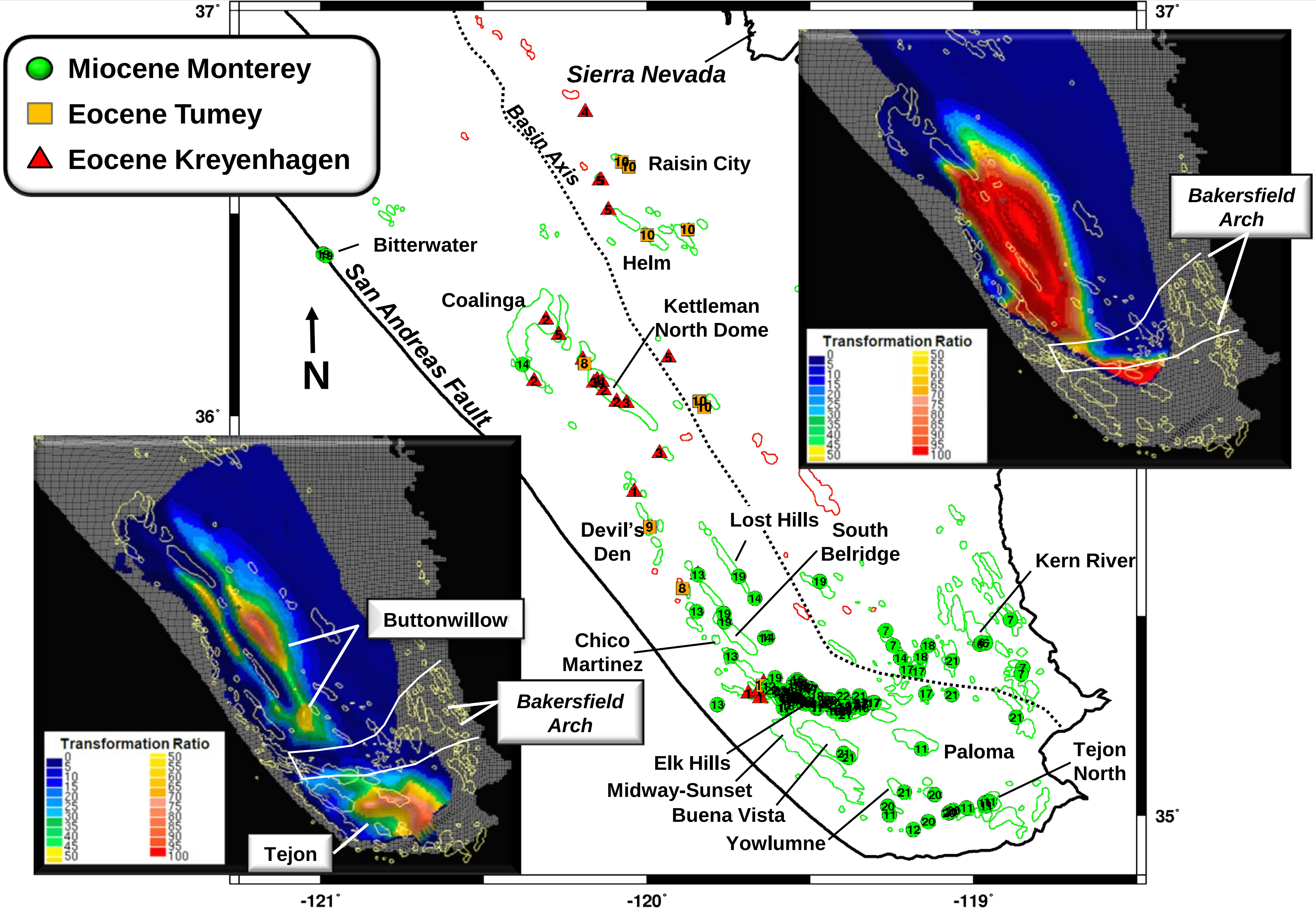
Families 16-19: Upper Monterey Source, Mostly Stevens Sand Pools

AHC Family	
⊕	14
⊗	15
●	16
⦶	17
⊙	18
◎	19

Terpanes in Oils Show Differences in Source Rock Oxicity

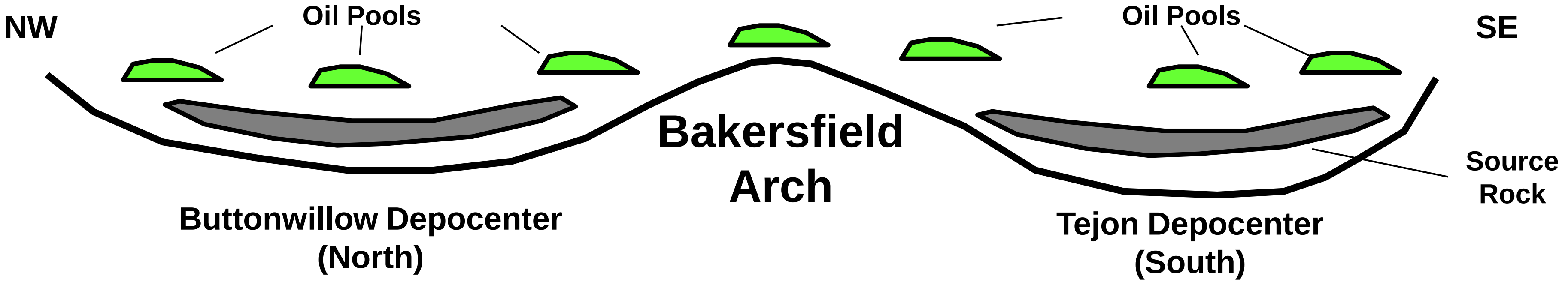


Generative Kitchens are Separated by the Bakersfield Arch

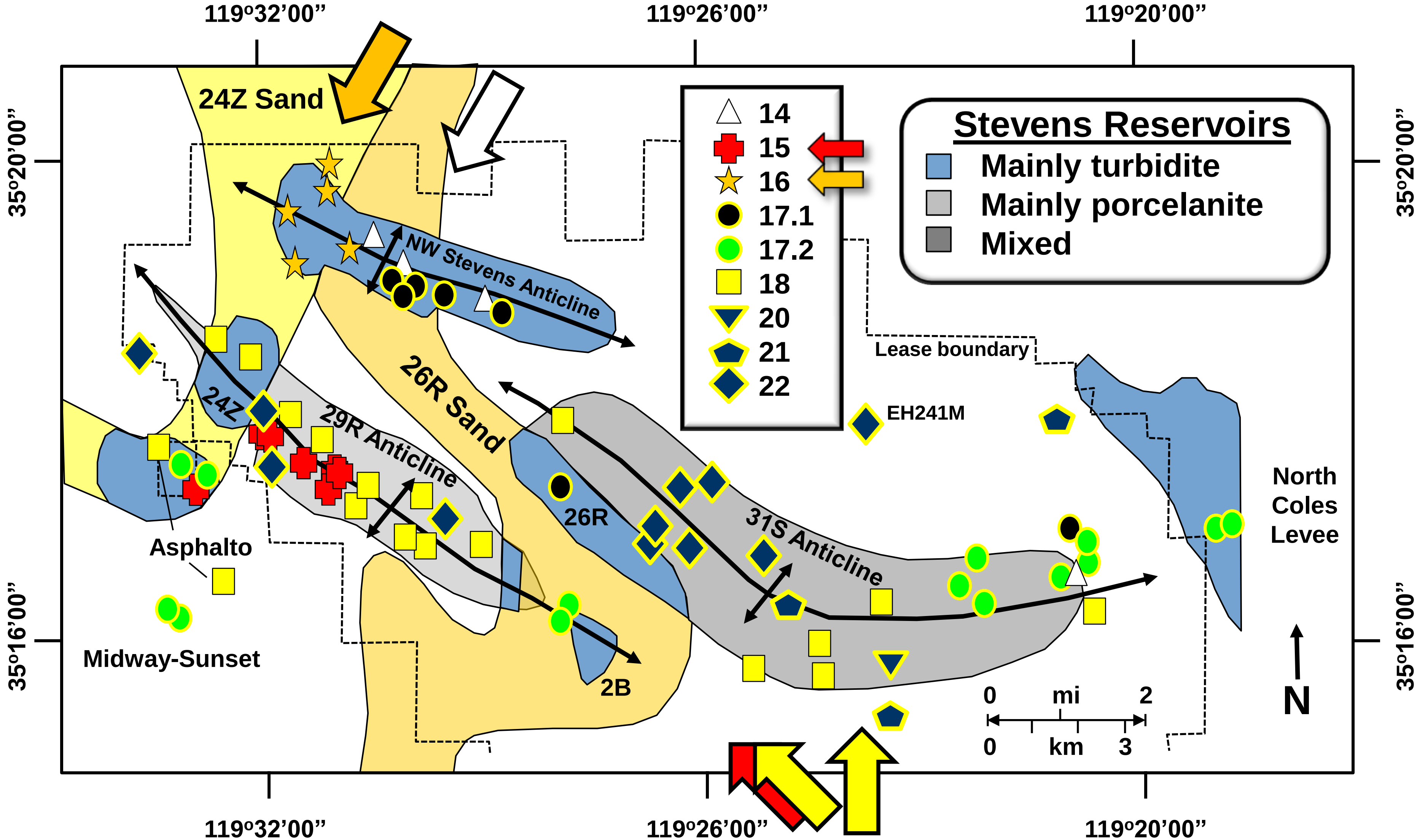


Miocene Oil Families are from N or S of the Bakersfield Arch

Source Rock	Buttonwillow (North)	North Flank Arch	Bakersfield Arch	South Flank Arch	Tejon (South)	AHC Family
Upper Monterey	4	4	1			14
		5				16
		6	1			17.1
			15	2		17.2
			22			18
	7					19
					10	20
		1	2	2	4	21
		1	14			22
Lower Monterey			3			6
			3	2		7
					6	11
			2		1	12
	3		2			13
			7	1		15

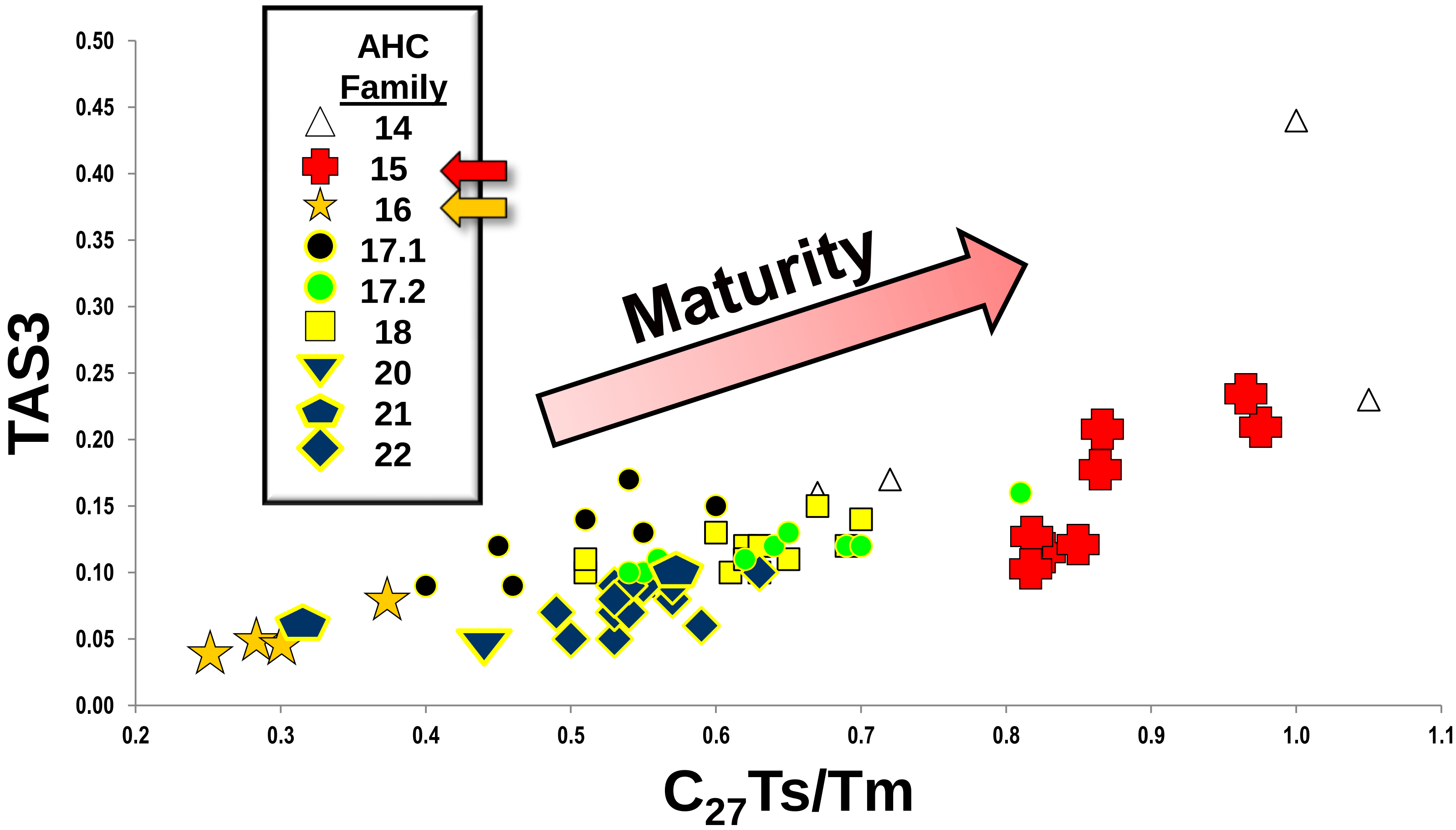


Filling History in Elk Hills Field is Tied to Oil Family Maturity

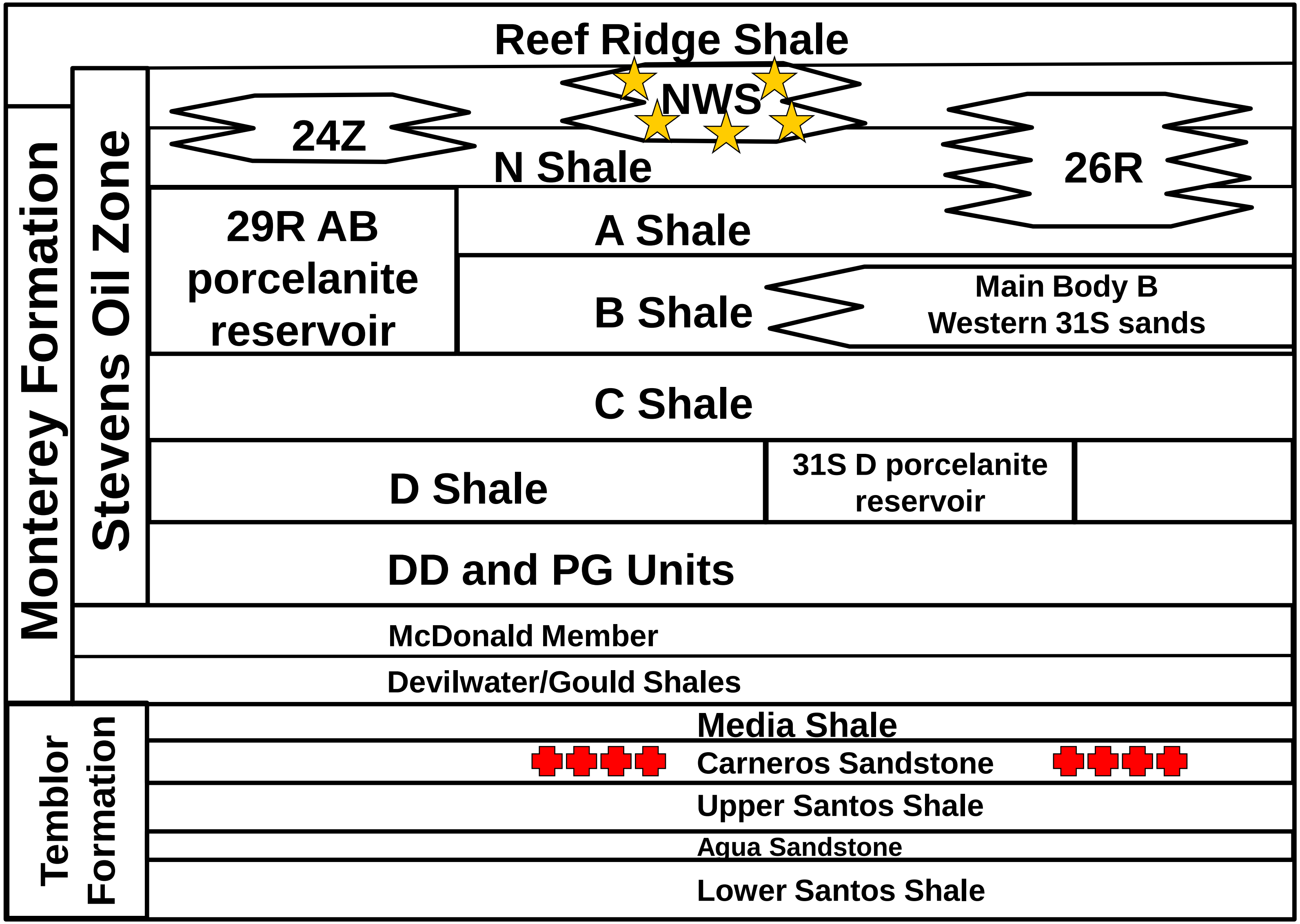


Base map after Zumberge et al. (2005)

Filling History in Elk Hills Field is Tied to Oil Family Maturity



Elk Hills Families 15 and 16 Have Different Bulk Properties



Reef Ridge Shale

Monterey Formation

Stevens Oil Zone

NWS

24Z

N Shale

26R

29R AB porcelanite reservoir

A Shale

B Shale

Main Body B
Western 31S sands

C Shale

D Shale

31S D porcelanite reservoir

DD and PG Units

McDonald Member

Devilwater/Gould Shales

Temblor Formation

Media Shale

Carneros Sandstone

Upper Santos Shale

Aqua Sandstone

Lower Santos Shale

Family 16

26^{o}API
1.1% sulfur
129 ppm V+Ni

Family 15

30^{o}API
0.39% sulfur
35 ppm V+Ni

Stratigraphy from Reid and McIntyre (2001)

Conclusions: San Joaquin Geochemistry and Modeling

- **22 AHC oil families retain the geochemical fingerprint of vertical and lateral organofacies variations in their source rocks:**
  - ✓ **Eocene Tumey Formation (two families)**
  - ✓ **Eocene Kreyenhagen Formation (five families)**
  - ✓ **Lower part of Miocene Monterey or Temblor Formation (six families)**
    - ○ **North of Bakersfield Arch (one family)**
    - ○ **South of Bakersfield Arch (five families)**
  - ✓ **Upper Miocene Monterey Formation (eight families)**
    - ○ **North of Bakersfield Arch (four families)**
    - ○ **South of Bakersfield Arch (four families)**

- **Eocene oil families originated in one depocenter north of the Arch**
- **Miocene oil families originated from upper and lower Monterey source rock in two depocenters north and south of the Arch**
- **Principal components analysis (PCA) and ascendant hierarchical cluster analysis (AHC) offer independent means to identify oil families, each with their own advantages**

Exposed Monterey Formation at Chico Martinez Creek

Courtesy R. Behl