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


Sofer, Z., 1984, Stable carbon isotope compositions of crude oils; application to source depositional environments and petroleum alteration: AAPG Bulletin, v. 68/1, p. 31-49.

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

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Purpose

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

**AHC**
Ascendant hierarchical cluster analysis – terpane mass chromatograms

**PCA**
Principal components analysis – 17 source-related biomarker and isotope ratios

*Peters et al., 2012 in press, AAPG Bulletin.*  
AHC Oil Families are Based on Terpane Chromatograms

- Miocene Monterey
- Eocene Tumey
- Eocene Kreyenhagen

- Sierra Nevada
- Coalinga
- Kettleman
- North Dome
- Raisin City
- Chico
- Martinez
- Kern River
- South Belridge
- Elks Hills
- Midway-Sunset
- Buena Vista
- Yowlumne
- Paloma
- Tejon
- Devil’s Den
- Kern River

Terpanes (m/z 191)

- C_{32} Hopanes 22S and 22R

Retention time, min.
Terpanes Resist Secondary Processes and Describe Source

Biodegradation Ranik

Biodegradation

---

Terpanes

---

Diasteranes

C<sub>26</sub>-C<sub>29</sub> Aromatics

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Extent of Destruction of Compound Class

Peters and Moldowan (1993)

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Thermal Maturity

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Peters et al. (2005)
How Similar are Samples? Calculate in Two or $n$-Dimensions

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

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

Measurement X

Measurement Y

a $(x_1, y_1)$

b $(x_2, y_2)$
A simple example with 2 measurements on 7 samples.
Calculate the Distance Between Points
Calculate the Distance Between Points
Calculate the Distance Between Points
Calculate the Distance Between Points
Calculate the Distance Between Points
AHC Dendrograms are Based on Cluster Distance in $n$-Space
Ascendant Hierarchical Cluster Analysis (AHC): 22 Families

Cluster Distance

165 Samples

AHC Oil Families

- Miocene Monterey
- Eocene Tumey
- Eocene Kreyenhagen

Terpanes

Response

Retention time, min.

30 40 50 60 70 80

Repeatability
AHC Families Provide Geologic Insight into Compartments

Miocene Monterey
Eocene Tumey
Eocene Kreyenhagen

*Replicates

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)
17 Geochemical Ratios Characterize the Training Set Oils

<table>
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<th>AHC Family</th>
<th>C18/C23</th>
<th>C22/C21</th>
<th>C24/C23</th>
<th>C26/C25</th>
<th>C27/Tet/C23</th>
<th>C28/HC29/C</th>
<th>O/H</th>
<th>C31/R/H</th>
<th>S1/S6</th>
<th>S/H</th>
<th>%C27</th>
<th>%C28</th>
<th>%C29</th>
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Carbon Isotopes Distinguish Many San Joaquin Oil Samples

- $\delta^{13}C_{\text{aromatics}}$, %0
- $\delta^{13}C_{\text{saturates}}$, %0

**Terrigenous**
- Family 1
- Family 2
- Family 3
- Family 4
- Family 5

**Marine**
- Family 8
- Family 10

**AHC Families**
- BA304E
- DD276E

**Sofer (1984)**

**Mixtures**
- Miocene Monterey
- Eocene Tumey
- Eocene Kreyenhagen

BA304E

Family 5
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

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

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
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

AHC Families

More Reducing

More Oxic

C_{28}/H vs. C_{35}S/C_{34}S

C_{27}T/C_{27}
Generative Kitchens are Separated by the Bakersfield Arch
Miocene Oil Families are from N or S of the Bakersfield Arch

<table>
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<tr>
<th>Source Rock</th>
<th>Buttonwillow (North)</th>
<th>North Flank Arch</th>
<th>Bakersfield Arch</th>
<th>South Flank Arch</th>
<th>Tejon (South)</th>
<th>AHC Family</th>
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Source Rock:
- Buttonwillow (North)
- Tejon (South)

Oil Pools:
- NW
- SE

Depocenters:
- Buttonwillow Depocenter (North)
- Tejon Depocenter (South)
Filling History in Elk Hills Field is Tied to Oil Family Maturity

Base map after Zumberge et al. (2005)

Mainly turbidite
Mainly porcelanite
Mixed

Stevens Reservoirs

Lease boundary
North Coles Levee

Asphalto
Midway-Sunset

24Z Sand
26R Sand
29R Anticline
31S Anticline

14
15
16
17.1
17.2
18
20
21
22

EH241M
Filling History in Elk Hills Field is Tied to Oil Family Maturity
Elk Hills Families 15 and 16 Have Different Bulk Properties

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)
    o North of Bakersfield Arch (one family)
    o South of Bakersfield Arch (five families)
  ✓ Upper Miocene Monterey Formation (eight families)
    o North of Bakersfield Arch (four families)
    o 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