

Evolution of Molecular Geochemistry in Petroleum Exploration and Development*

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Abstract

Organic geochemistry is a young science ([Kvenvolden](#), 2006). Alfred Treibs (1899-1983) is recognized as the father of organic geochemistry based on his milestone paper showing the link between chlorophyll in plants and porphyrins in petroleum, thus providing the first strong evidence for the organic origin of petroleum (Treibs, 1936). The Alfred E. Treibs Award is presented annually by the Organic Geochemistry Division of the Geochemical Society for major achievements in organic geochemistry. Treibs and 16 of the 32 Treibs medalists are underlined in the following discussion. Early applications of organic geochemistry were mainly molecular geochemistry, which is a hybrid of natural product chemistry, analytical chemistry, synthetic organic chemistry, physical organic chemistry, and geology. Little progress was made in molecular geochemistry for >30 years after [Treibs](#) (1936), until the development of computerized gas chromatography-mass spectrometry. Today, molecular geochemistry and its repertoire of analytical tools are vital components in the exploration and production departments of the major oil companies and at many universities and government organizations. Some textbooks that discuss molecular geochemistry include [Tissot](#) and [Welte](#) (1984), [Moldowan](#) et al. (1992), [Hunt](#) (1996), [Peters](#) et al. (2005), and Dembicki (2017). This paper focuses on conceptual milestones in the application of molecular geochemistry to petroleum exploration and development. (Clifford Walters will discuss analytical milestones in another paper from this conference.) Cited publications for each conceptual milestone listed below are examples and are not meant to be comprehensive.

Past-Present Conceptual Milestones

- Biomarkers as molecular fossils (Eglinton et al., 1964; Philippi, 1965; Eglinton and Calvin, 1967)
- Petroleum system concept, direct oil-source correlation (Hunt and Jamieson, 1956; Dow, 1974; Williams, 1974; Seifert and Moldowan, 1978, 1981; Perrodon, 1992; Magoon and Dow, 1994)
- Source-related biomarker ratios, indirect oil-source correlation (Didyk et al., 1978; Huang and Meinschein, 1979; Seifert and Moldowan, 1978; Moldowan et al., 1985; Sinninghe Damsté et al., 1995; Koopmans et al., 1996a; Grice et al., 1998)
- Chemometrics of biomarker and isotopic data for correlation, deconvoluting mixtures (Peters et al., 1986, 2007, 2008; Zumberge, 1987)
- Compound-specific isotope analysis (CSIA) for correlation: alkanes, biomarkers, diamondoids (Matthews and Hayes, 1978; Hayes et al., 1990; Schoell et al., 1992; Peters and Craenay, 2004; Amrani et al., 2009; Greenwood et al., 2015; Moldowan et al., 2017)
- Age-related biomarker ratios (Grantham and Wakefield, 1988; Moldowan et al., 1994; Holba et al., 1998, 2001; Moldowan and Jacobson, 2000)
- Maturity assessment using biomarkers and other compounds (Seifert and Moldowan, 1980; Mackenzie and Maxwell, 1981; Mackenzie et al., 1981; Radke and Welte, 1983; Boreham et al., 1988)
- Biomarkers to assess biodegradation (Seifert and Moldowan, 1979; Volkman et al., 1983, 1984; Peters et al., 1996; Bennett and Larter, 2008)
- Gas geochemistry for source, maturity, biodegradation, thermochemical sulfate reduction (Schoell, 1983; Chung et al., 1988; Berner and Faber, 1996; Manzano et al., 1997; Tang et al., 2000; Zumberge et al., 2012; Milkov and Etiope, 2018; Xia and Gao, 2018)
- Diamondoids for extent of oil cracking, mixed charge (Dahl et al., 1999; Wei et al., 2007)
- Light aromatics (BTEX) for proximity of accumulations (Hunt, 1979; Burtell and Jones, 1996)
- Carbazoles for migration distance (Larter et al., 1996)

Present-Future Conceptual Milestones

- Time-lapse reservoir geochemistry (Milkov et al., 2007; Liu et al., 2017)
- Fluid inclusion biomarkers (Kvenvolden and Roedder, 1971; Karlsen et al., 1993; Jones and Macleod, 2000)

- Aromatics for correlation, terrigenous systems (Schwark and Püttmann, 1990; Koopmans et al., 1996b; Van Aarssen et al., 2007;)
- Petroleomics (Mullins et al., 2007)
- Fluid residence time in reservoirs (Larter and Adams, 2010; Larter et al., 2012; Zhao, 2017)
- Clumped isotopes for temperature assessment (Eiler, 2007; Stolper et al., 2014, 2017)
- Genomics for enhanced production, surfactants (Pal et al., 2017)
- Biomarker precursors in living organisms (Fischer et al., 2005; Summons et al., 1999)

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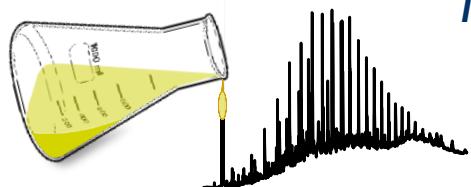
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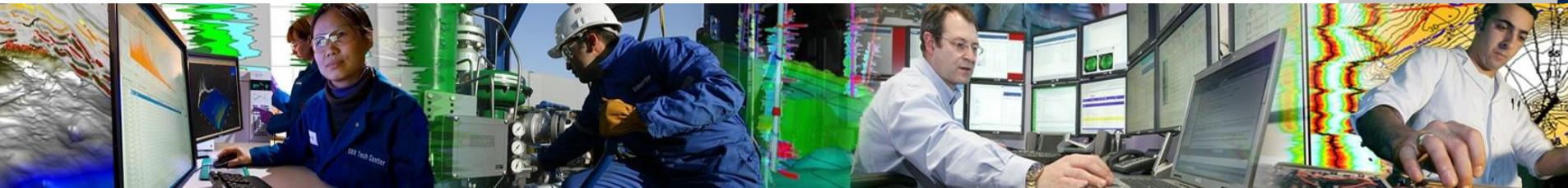
The Evolution of Petroleum Systems Analysis



Alfred E. Treibs

**MARCH 4, 2019
HOUSTON TEXAS**

Evolution of Molecular Geochemistry in Petroleum Exploration and Development



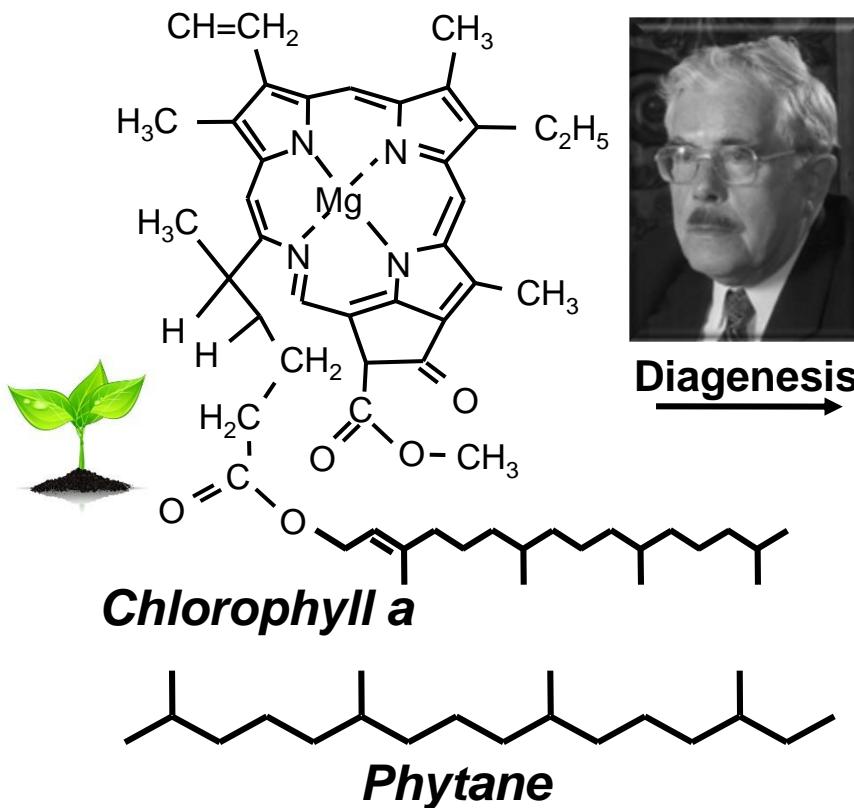
Dr. Ken Peters

*Geochemistry Advisor, Schlumberger
Adjunct Professor, Stanford University*



Schlumberger

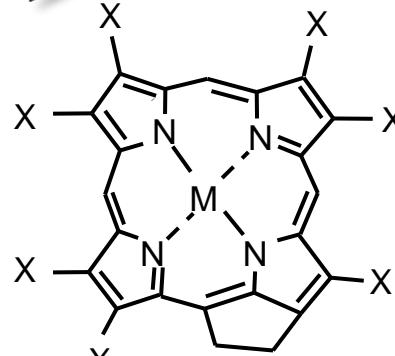
Alfred E. Treibs: The First Molecular Geochemist



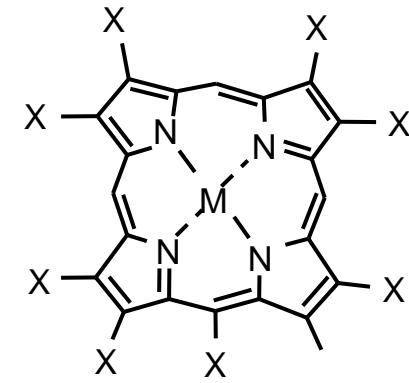
X = H or Alkyl Group

M = Vanadyl [$V = O(II)$] or Nickel [$Ni(II)$] Ion

1936



DPEP



etio



Pristane

Biomarker Guide, p. 67

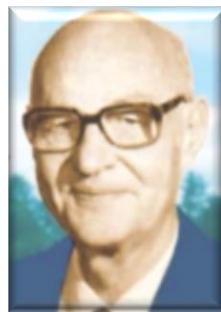
Versus abiogenic hypothesis....

1899-1983



Treibs

1979



Philippi

1980



Tissot

1981



Eglinton

1982



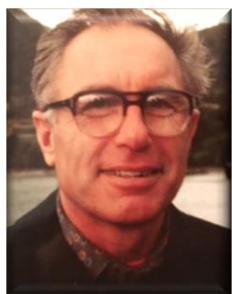
Hunt

1983



Welte

1984



Seifert

1985



Albrecht

1987



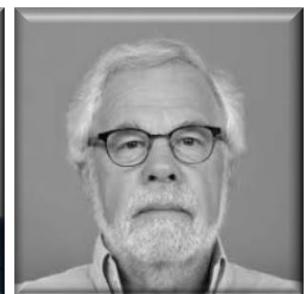
Hoering

1989



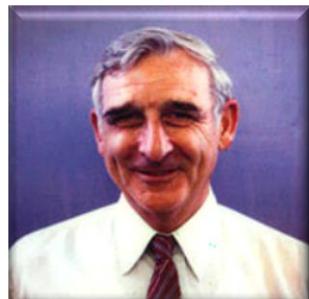
Maxwell

1991



de Leeuw

1993



3

Kaplan

1995



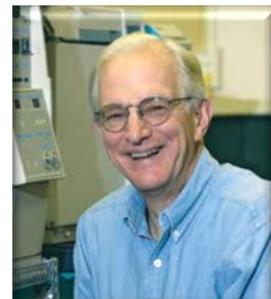
Kvenvolden

1996



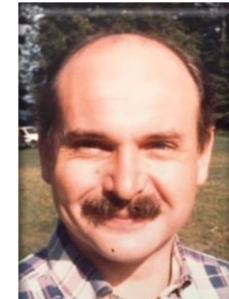
Parker

1997



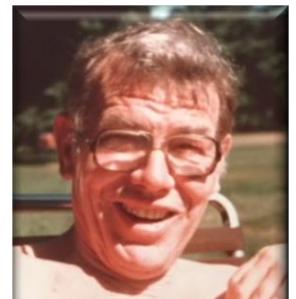
Hayes

2000



Hedges

2001



Smith

2002



Douglas

2003



Summons

2004



Galimov

2005



Damst  

2006



Simoneit

2007



Michaelis

2008



Schoell

2009



Peters

2010



Volkman

2011



Moldowan

2012



Des Marais

2013



Fogel

2014



Larter

2016



Hatcher

2017



Freeman

2018



Schouten

2019



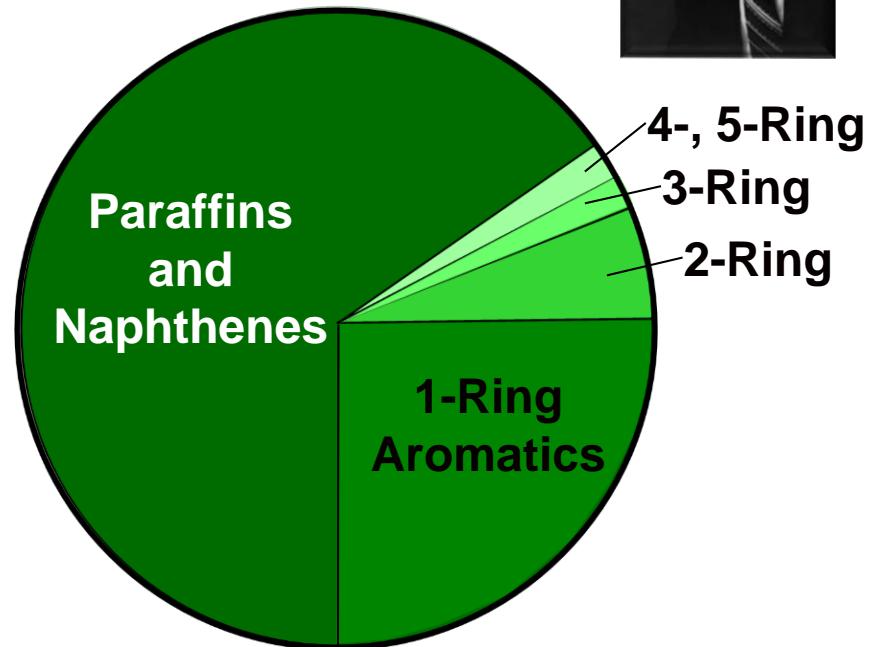
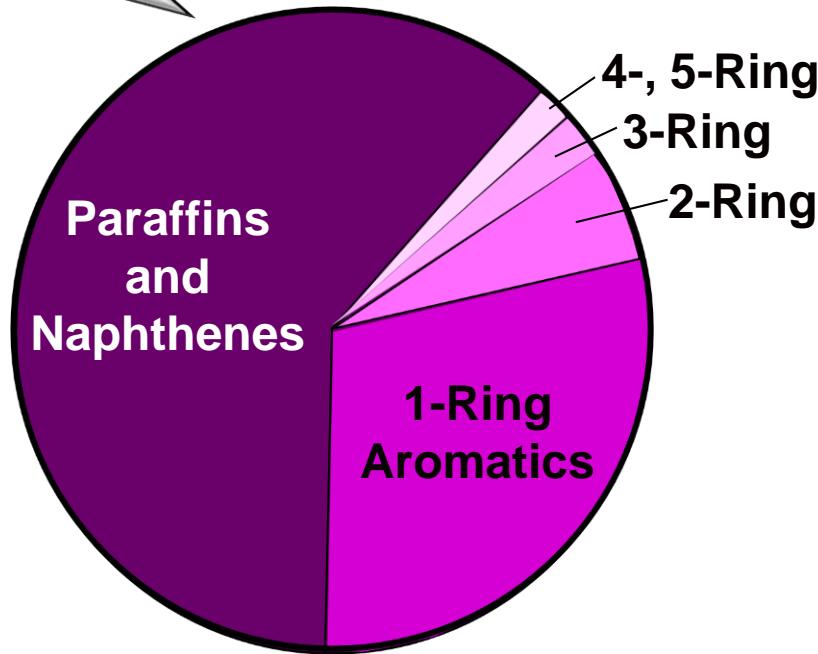
Derenne

Milestone: The First *Direct* Oil-Source Rock Correlation

Column distillation.....before GC, biomarkers

1956

Hydrocarbon type distribution >400°F



Frontier Shale Extract

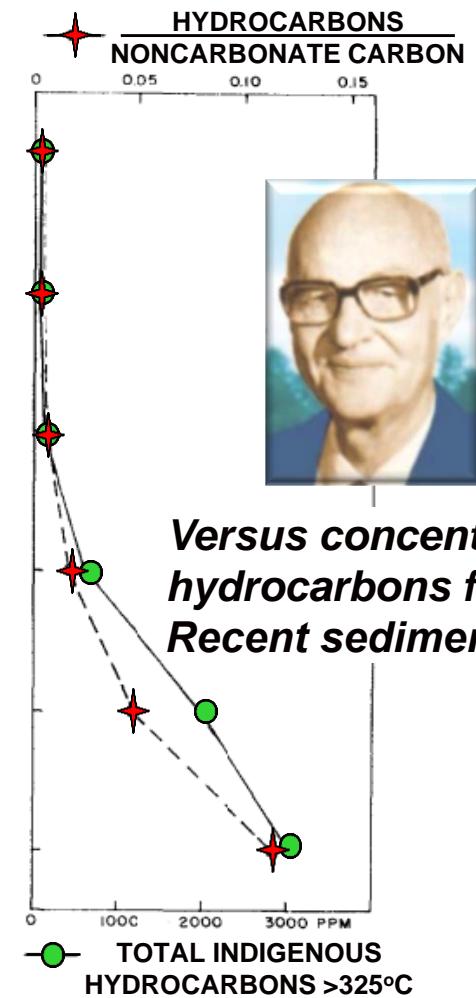
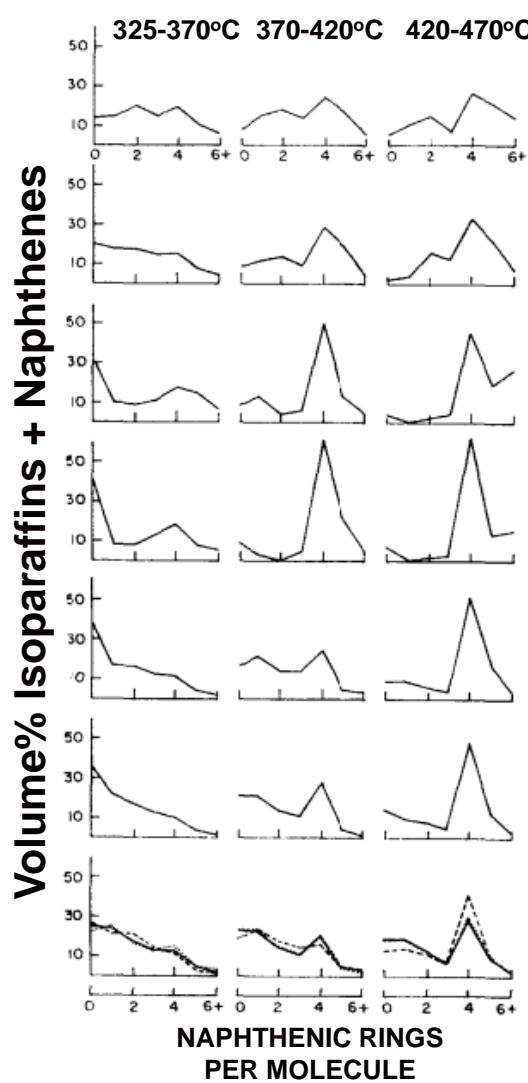
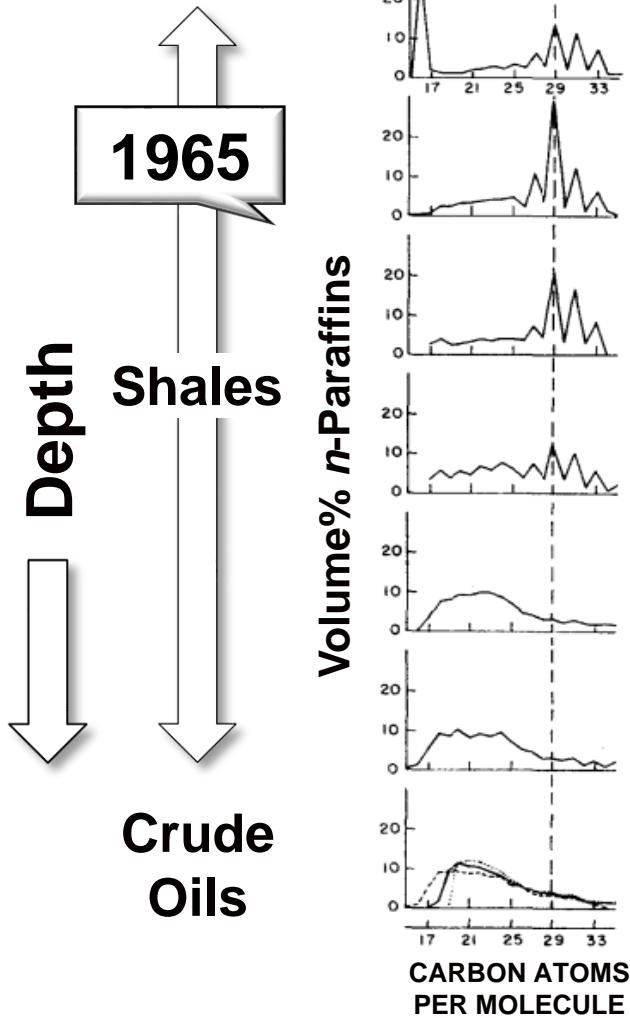
Wall Creek Sandstone Oil

Hunt and Jamieson (1956)

Schlumberger

Maturation of Organic-Rich Shales Yields Petroleum

Los Angeles Basin

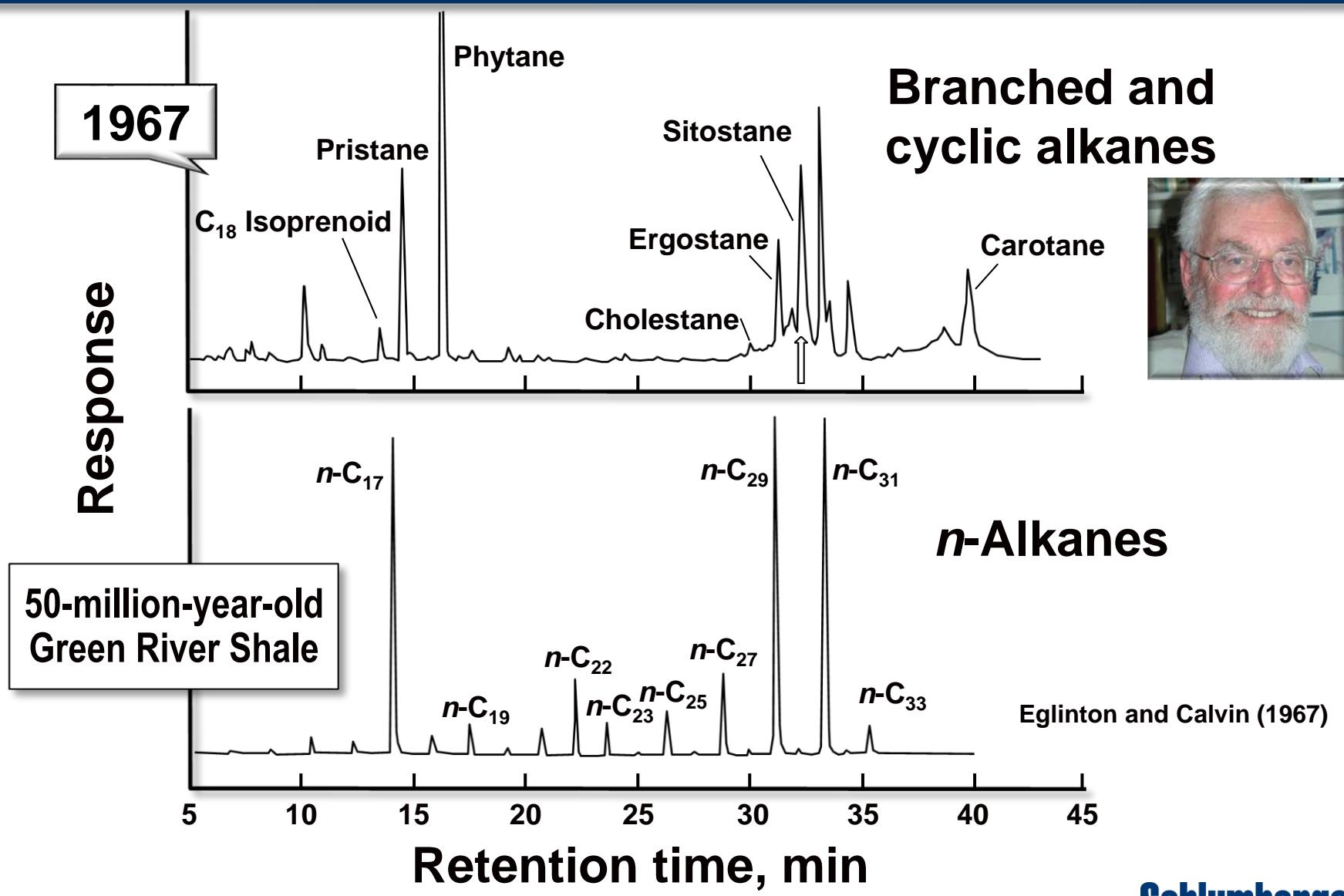


Versus concentrated hydrocarbons from Recent sediments....

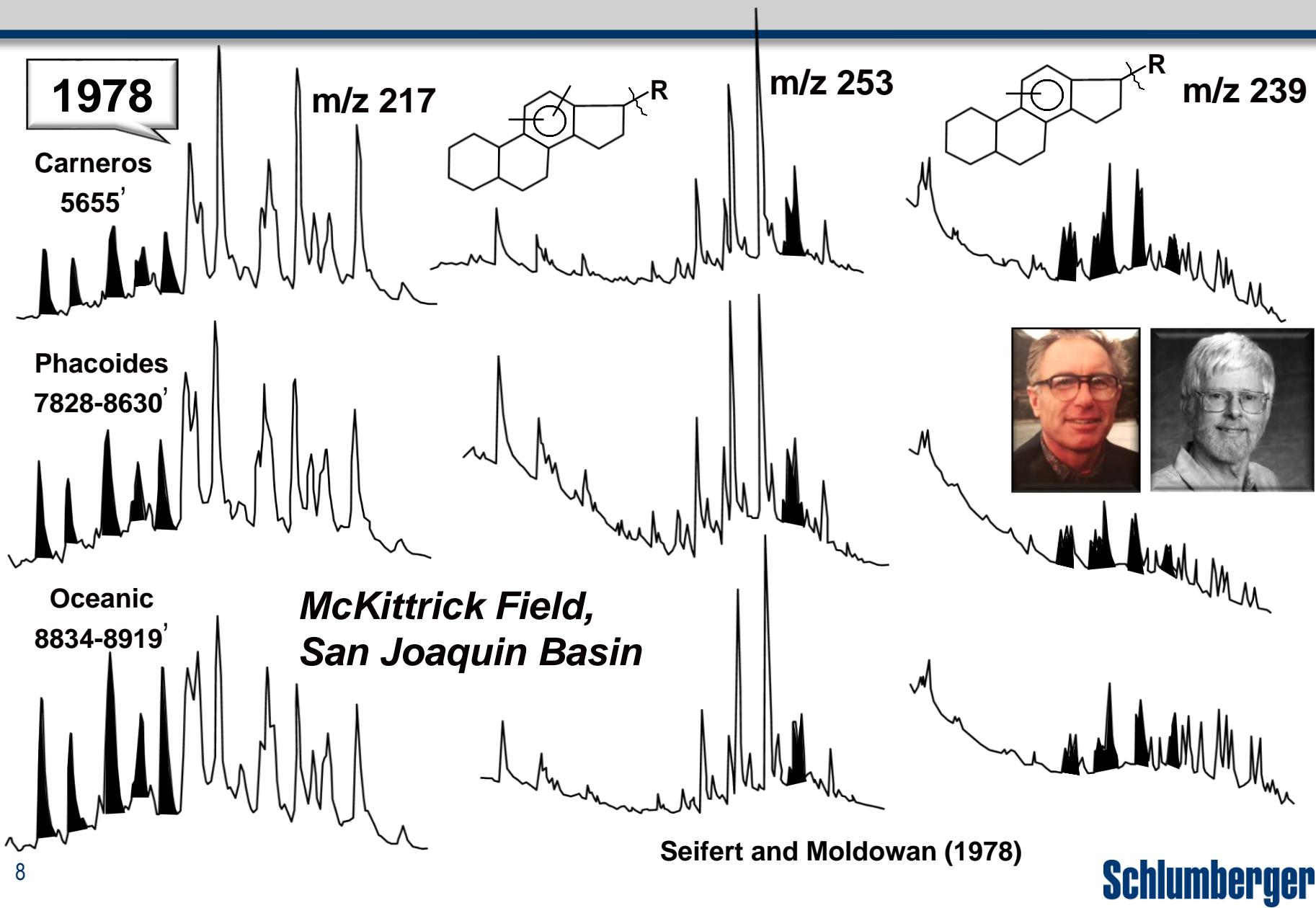
Philippi (1965)

Schlumberger

'Biomarkers' Describe Early Life Without Macrofossils



Direct Oil-Oil Correlation: Similarity Through Heritage

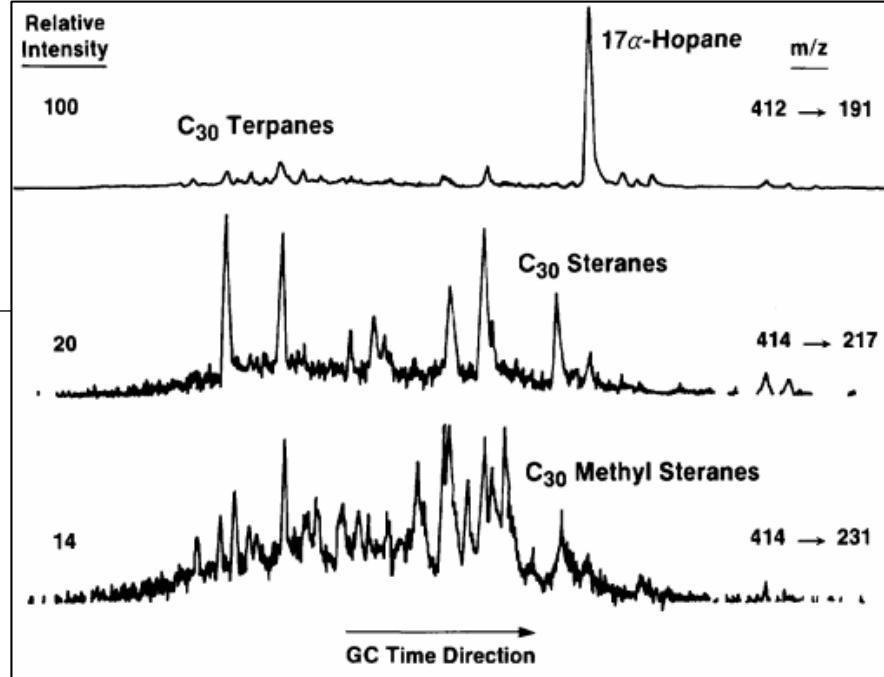


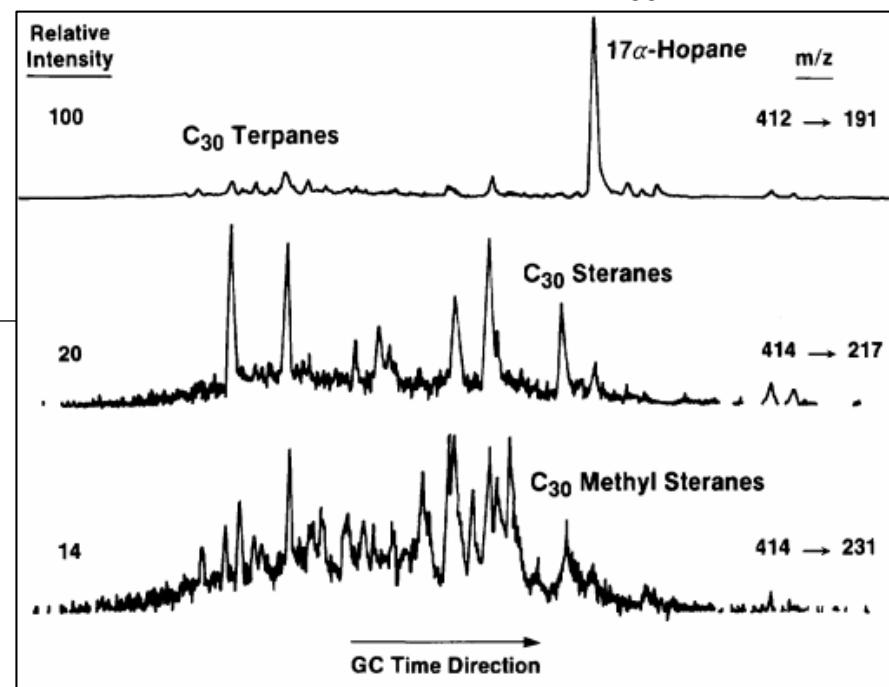
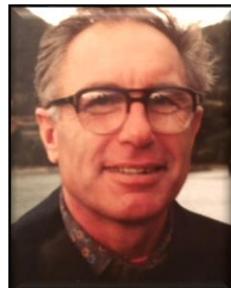
Indirect Oil-Source Rock Correlation: Key Parameters

1985

Relationship Between Petroleum Composition and Depositional Environment of Petroleum Source Rocks

J. MICHAEL MOLDOWAN, WOLFGANG K. SEIFERT and EMILIO J. GALLEGO

	Nonmarine vs. Marine	Nonmarine vs. Marine Shale	Nonmarine vs. Marine Carbonate	Marine Shale vs. Carbonate	
C ₃₀ steranes	++++	++++	++++	--	
Sulfur (%)	++	++	+++	++	
MA-steroids	++	++	Sadlerochit, Alaska Crude (C ₃₀ steranes)		
High-MW paraffins	++	++			
CPI	--	--			
Pristane/phytane	--	--			
Steranes/hopanes	+	+			
Carbon isotopes	--	--			
Gammacerane index	--	--			



Oil-Oil and Oil-Source Correlation Using Chemometrics

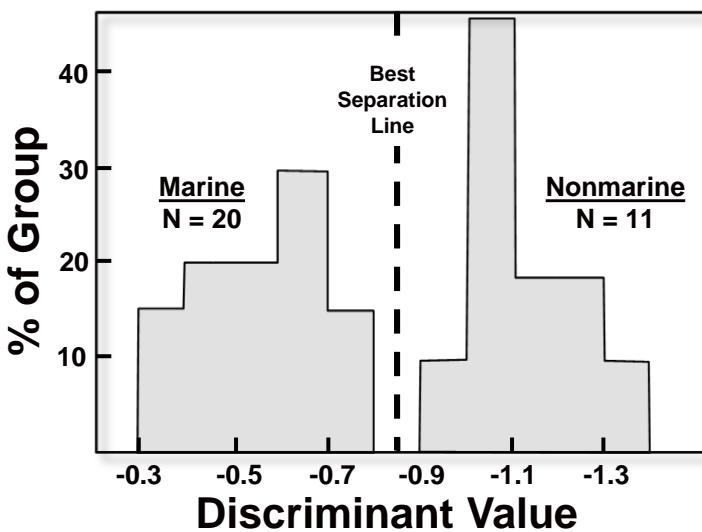
Petroleum Isotopic and Biomarker Composition Related to Source Rock Organic Matter and Depositional Environment

K.E. PETERS, J.M. MOLDOWAN, M. SCHOELL, and W.B. HEMPKINS



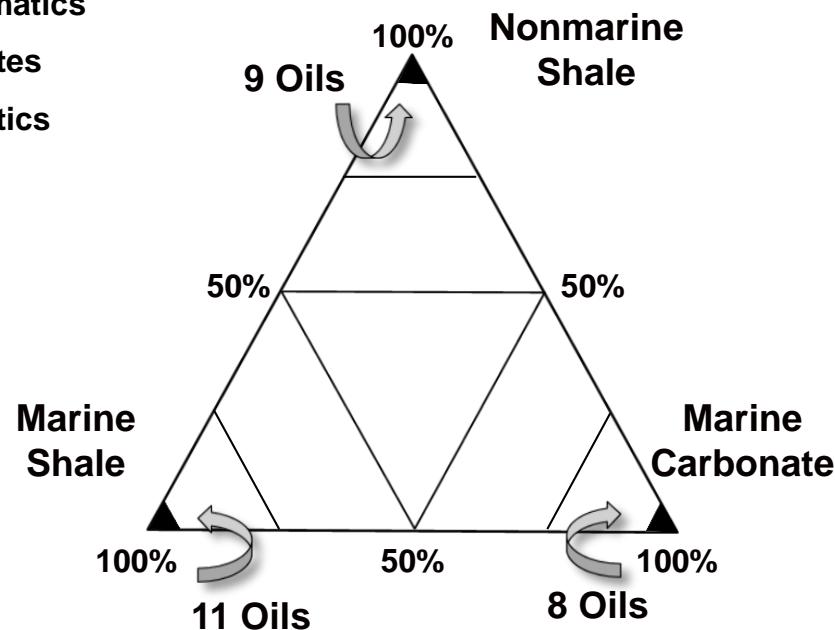
1986

Two-Group Discriminant Analysis



- C₃₀ sterane ratio
- MA-steroid ratio
- δ¹³C_{saturates}
- δ¹³C_{aromatics}
- δD_{saturates}
- δD_{aromatics}

Three-Group Discriminant Analysis

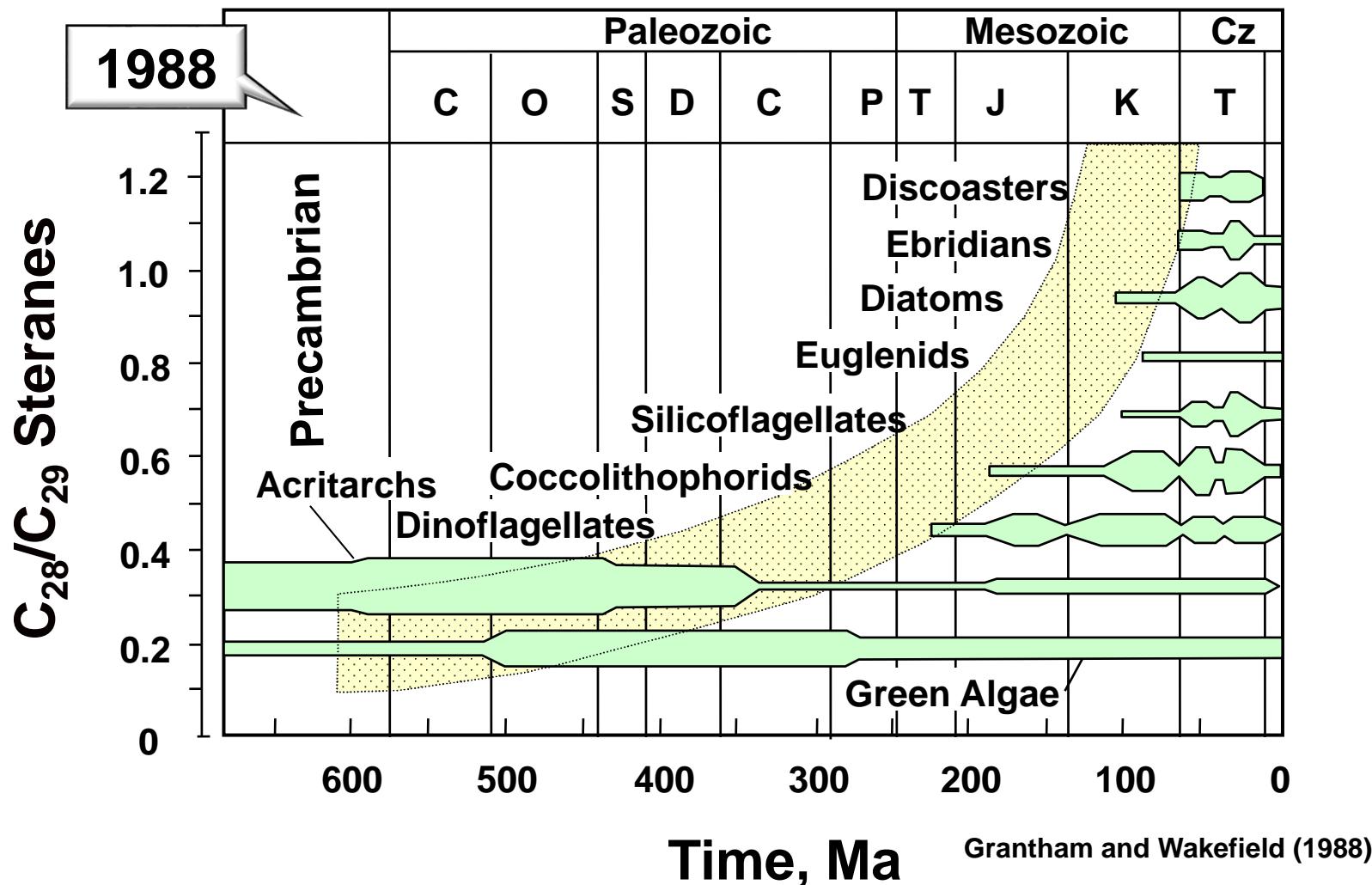


Some Examples of Biomarker Source Indicators

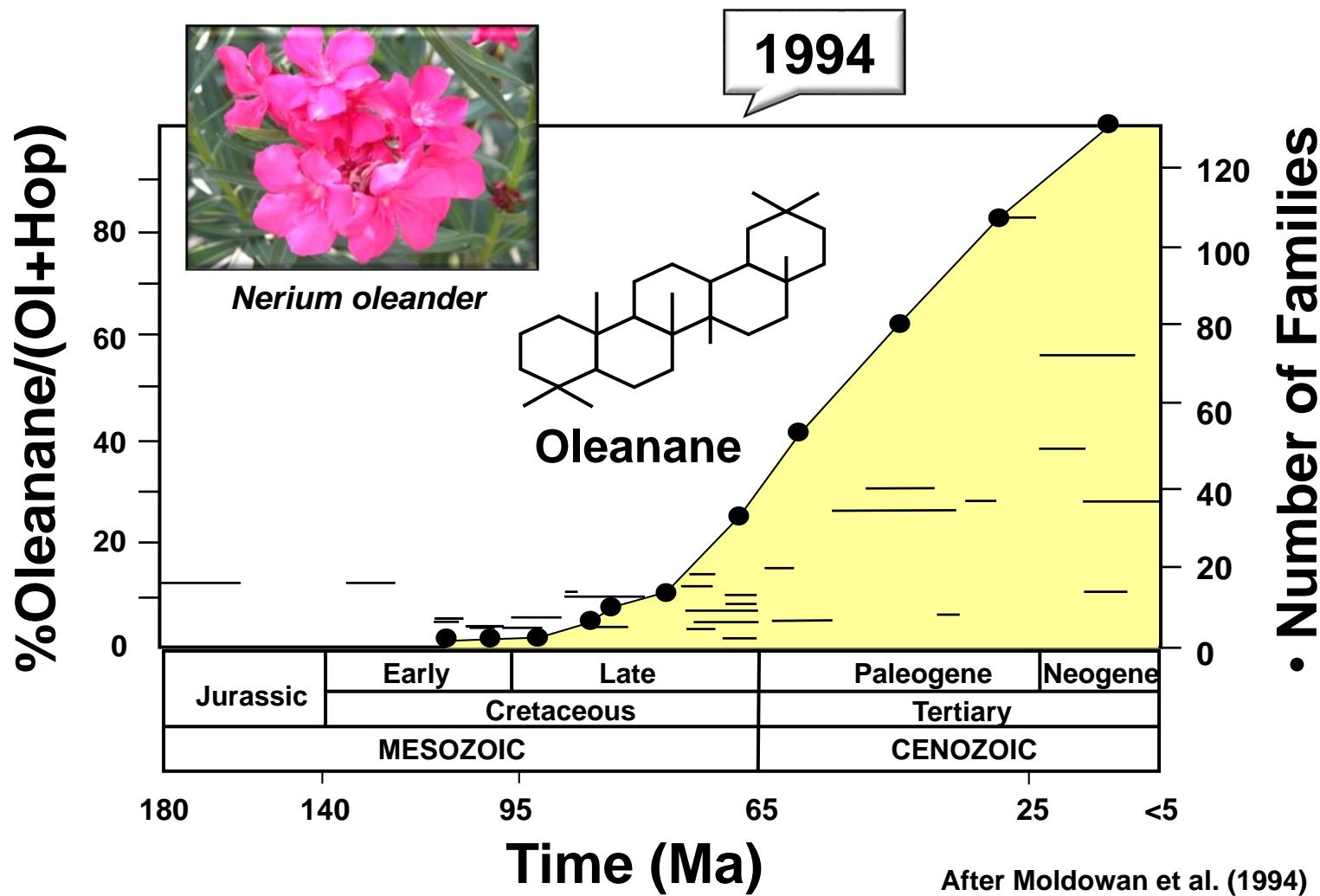
Source Rock Setting	Biomarker Parameter	References
Marine	Odd/even C ₄₂₋₄₆ cyclopentylalkanes	Carlson et al. (1993)
	24-n-propylcholestanes	Moldowan et al. (1990)
Lacustrine	Even/odd C ₄₂₋₄₆ cyclopentylalkanes	Carlson et al. (1993)
	Botryococcane (presence only)	Moldowan et al. (1980), Metzger & Largeau (1999)
	β-Carotane (presence only)	Hall and Douglas (1983), Jiang and Fowler (1986)
	Low steranes/hopanes	Moldowan et al. (1985)
	C ₂₆ /C ₂₅ tricyclic terpanes > 1	Zumberge (1987)
	High tetracyclic polyprenoids	Holba et al. (2000)
	Low C ₃₁ /hopane	Peters et al. (2005)
Coal	Pristane/phytane >3	Hughes et al. (1995)
Higher-plant input	Oleananes, lupanes, taraxeranes	Ekweozor and Udo (1988), Moldowan et al. (1994)
	Bicadinanes (<i>Dipterocarpaceae</i> resin)	Cox et al. (1986)
	Retene, cadalene, tetracyclic ditperanes	Noble et al. (1985)
	C ₂₉ /(C ₂₇ to C ₂₉) steranes	Moldowan et al. (1985)
	Dehydroicetexanes (<i>Cupressaceae</i>)	Nytoft et al. (2019)
Hypersaline	Pristane/phytane <0.5	ten Haven et al. (1987)
	High gammacerane (stratified water)	Sinninghe Damsté et al. (1995)
Anoxic	Pristane/phytane <1	ten Haven et al. (1987)
	C ₃₅ /C ₃₄ homohopanes >1	Peters and Moldowan (1991), Dahl et al. (1994)
	Isorenieratane , trimethylaryl isoprenoids	Summons and Powell (1987), Grice et al. (1998)
	High V/Ni porphyrins	Lewan (1984)
	High 25,28,30- trisnor- & 28,30-bisnorhopane	Moldowan et al. (1984), Schoell et al. (1994)
Carbonate vs. Shale	C ₂₉ /C ₃₀ hopanes >1	Fan Pu et al. (1987), Subroto et al. (1991)
	Low diasteranes/steranes	Hughes (1984)
	Dibenzothiophene/phenanthrene >1	Hughes et al. (1995)
	High 2α-methylhopanes	Summons et al. (1999)

After Peters et al. (2005)

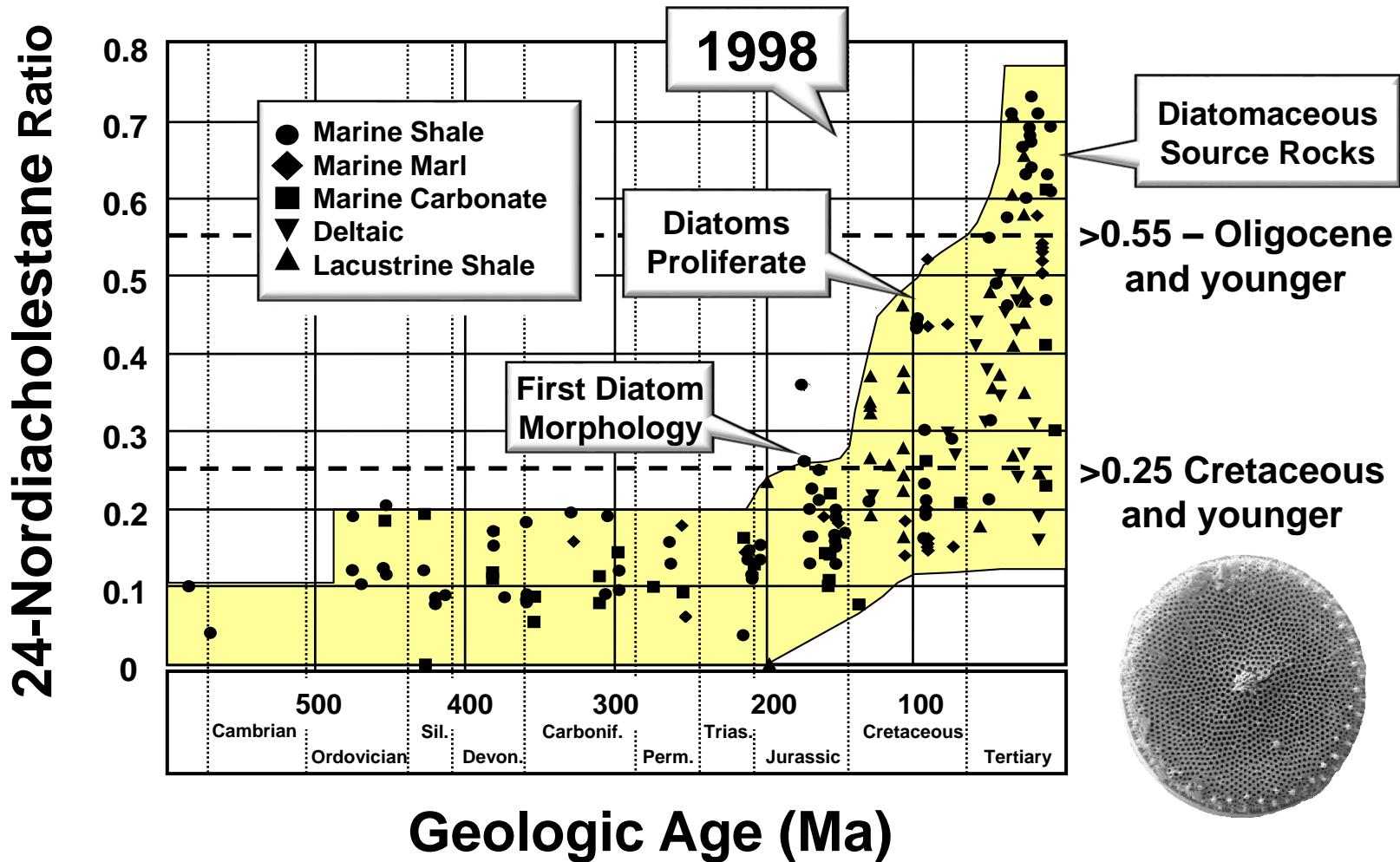
C_{28}/C_{29} Sterane Ratio for Marine Oil Varies Through Time



Oil from Tertiary Source Rock has Oleanane Ratios >20%

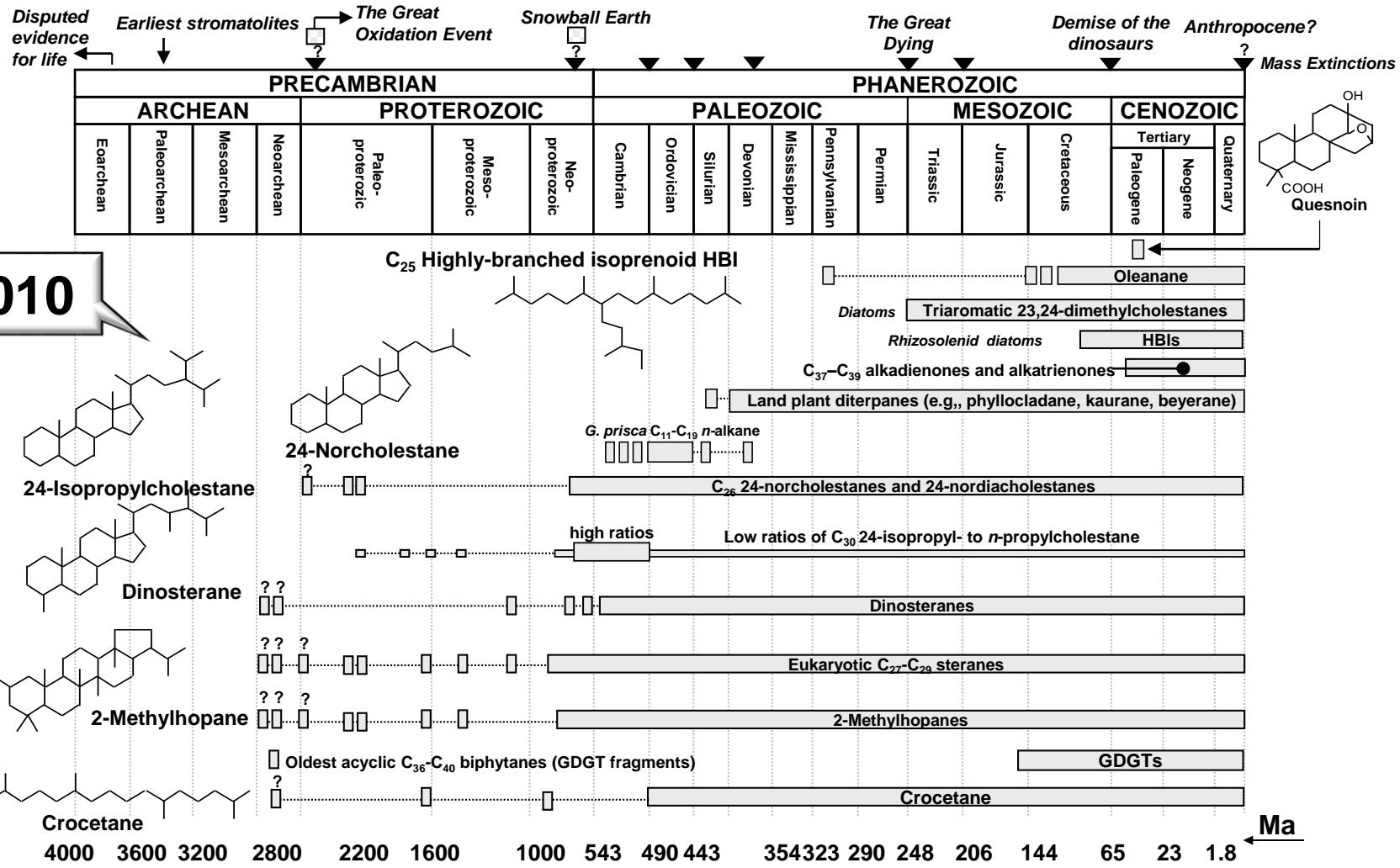


C_{26} Steranes in Oil Help to Assess Source Rock Age



After Holba et al. (1998)

Age Biomarkers Help to Identify Source Rocks for Oils

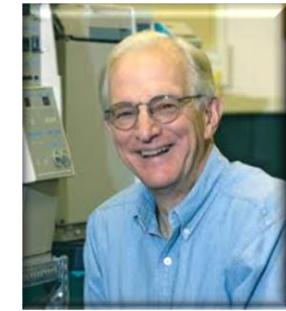


Walters et al. (2010)

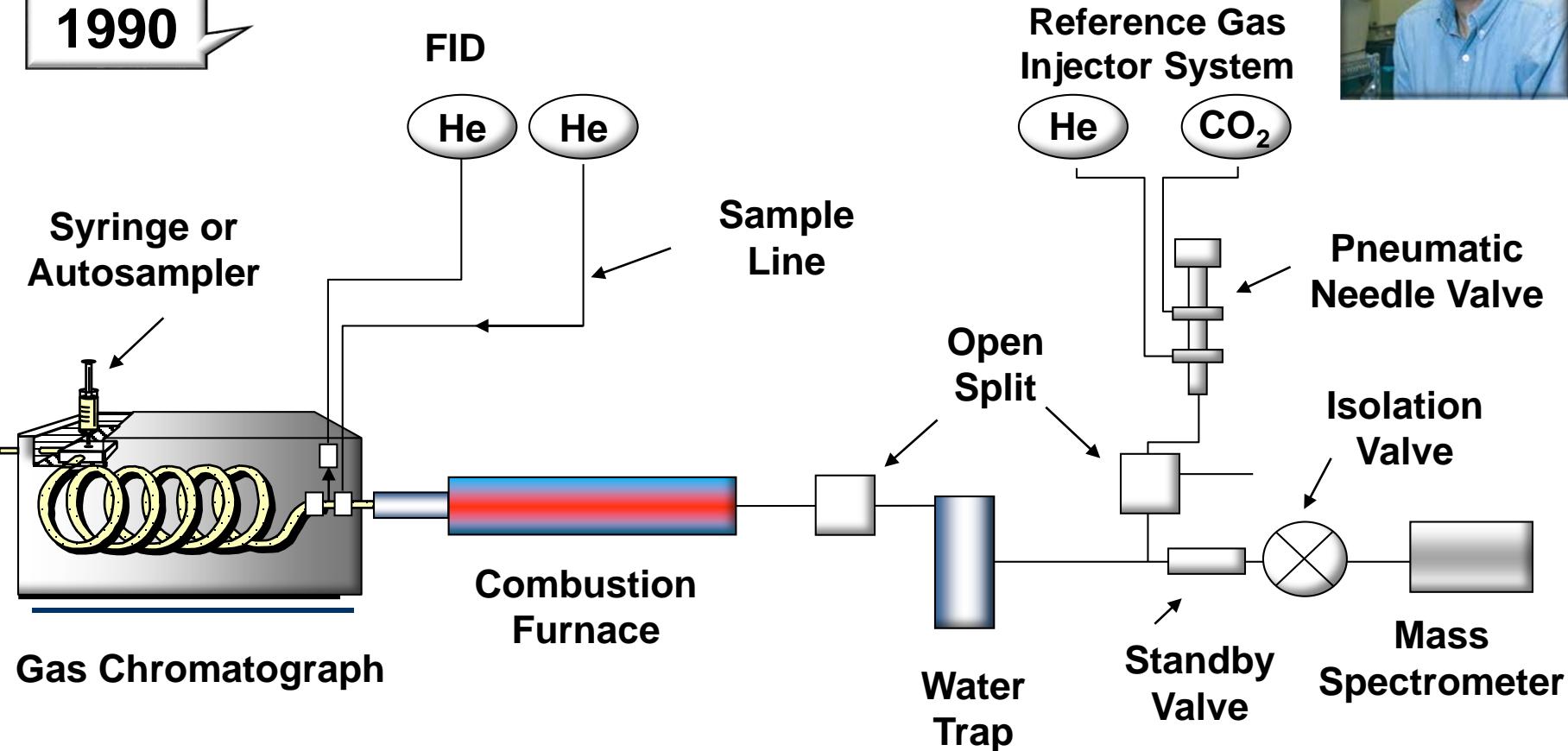
IRM/GCMS: Compound-Specific Isotope Analysis (CSIA)

Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes

J. M. HAYES, KATHERINE H. FREEMAN, BRIAN N. POPP* and CHRISTOPHER H. HOHAM



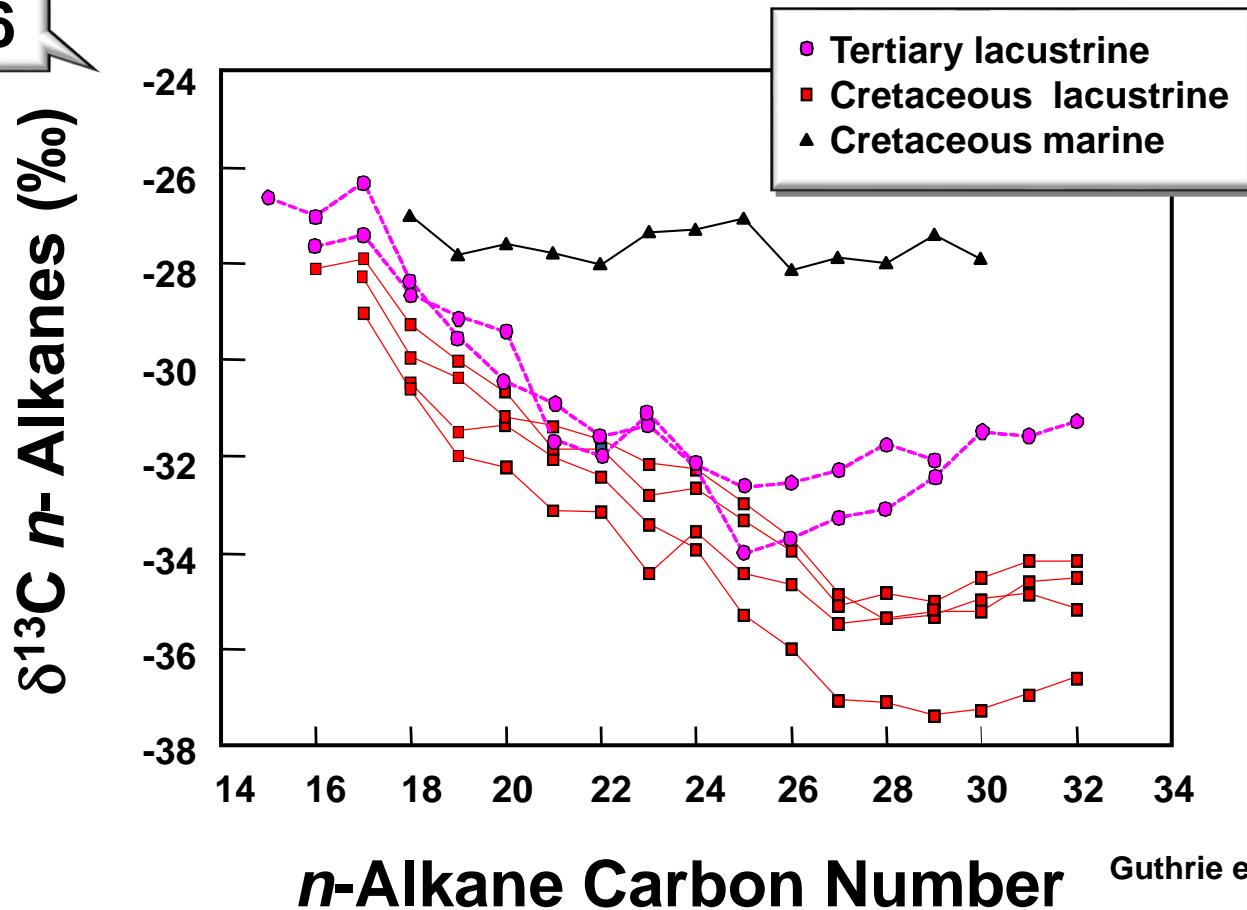
1990



CSIA of *n*-Alkanes Identifies Families of Oils or Extracts

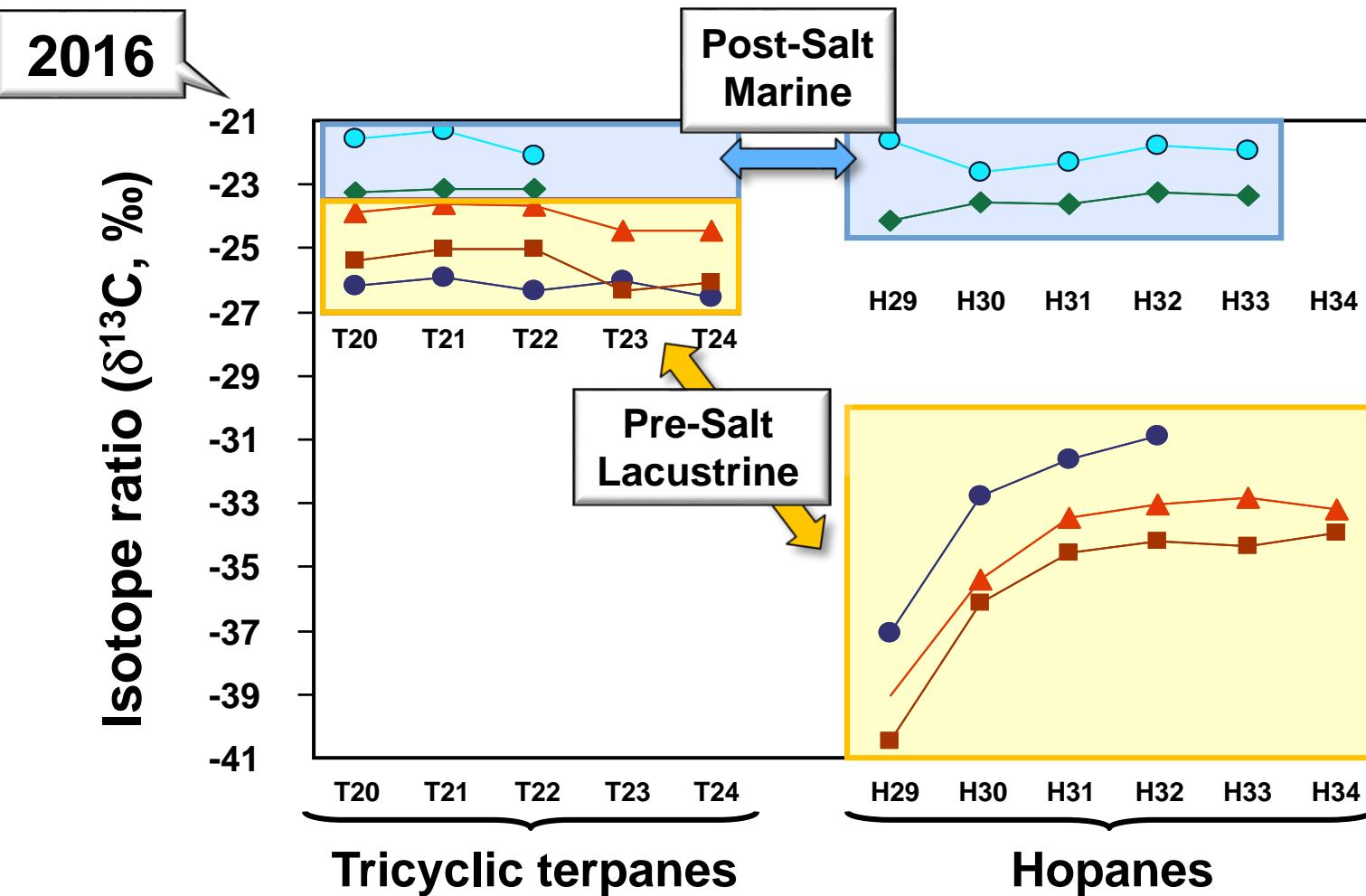
Extracts from Organic-Rich Immature Shales, Brazil

1996



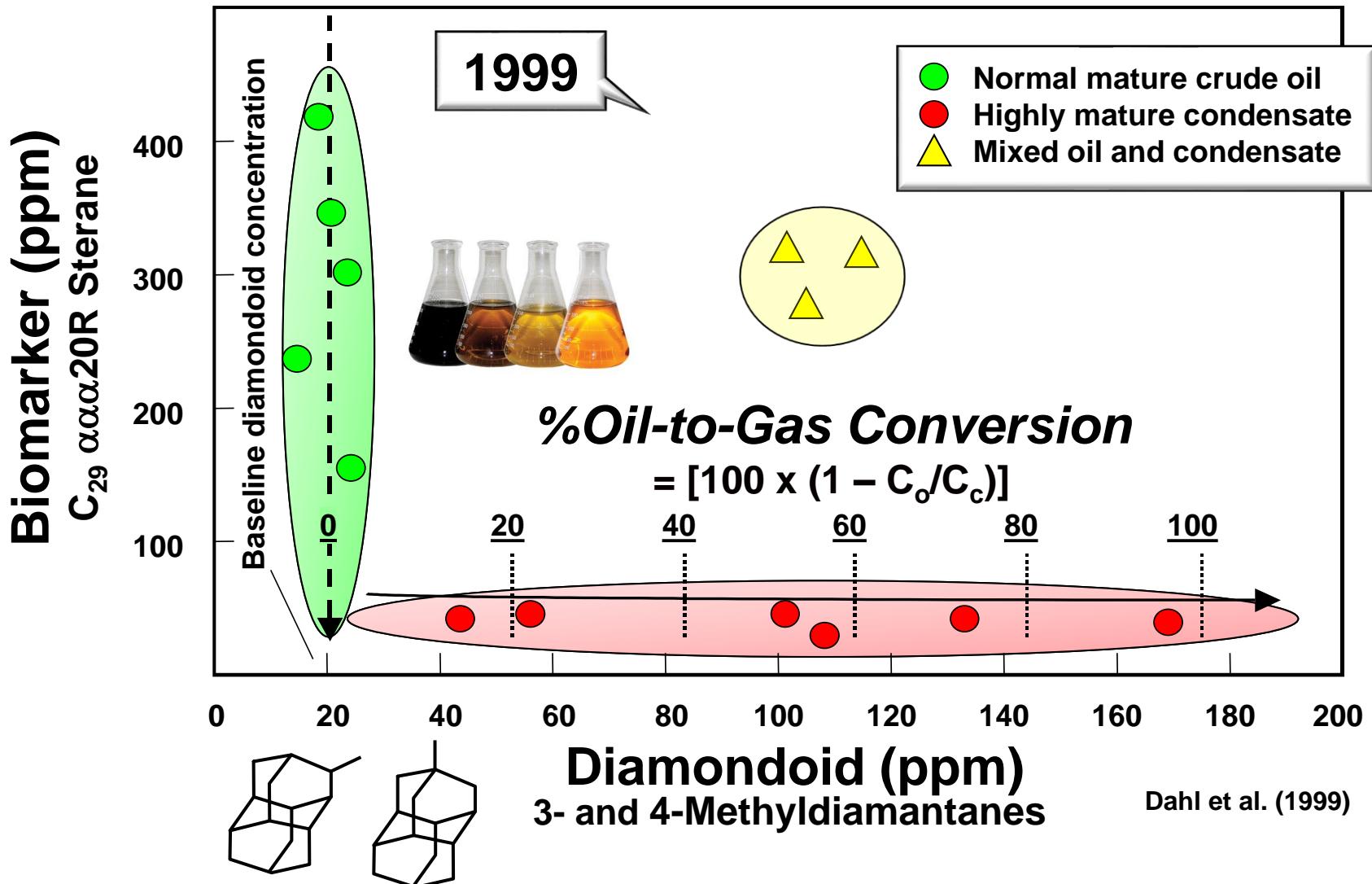
Guthrie et al. (1996)

CSIA of Oil Biomarkers Identifies Pre- and Post-Salt Oils



Courtesy of J.M. Moldowan

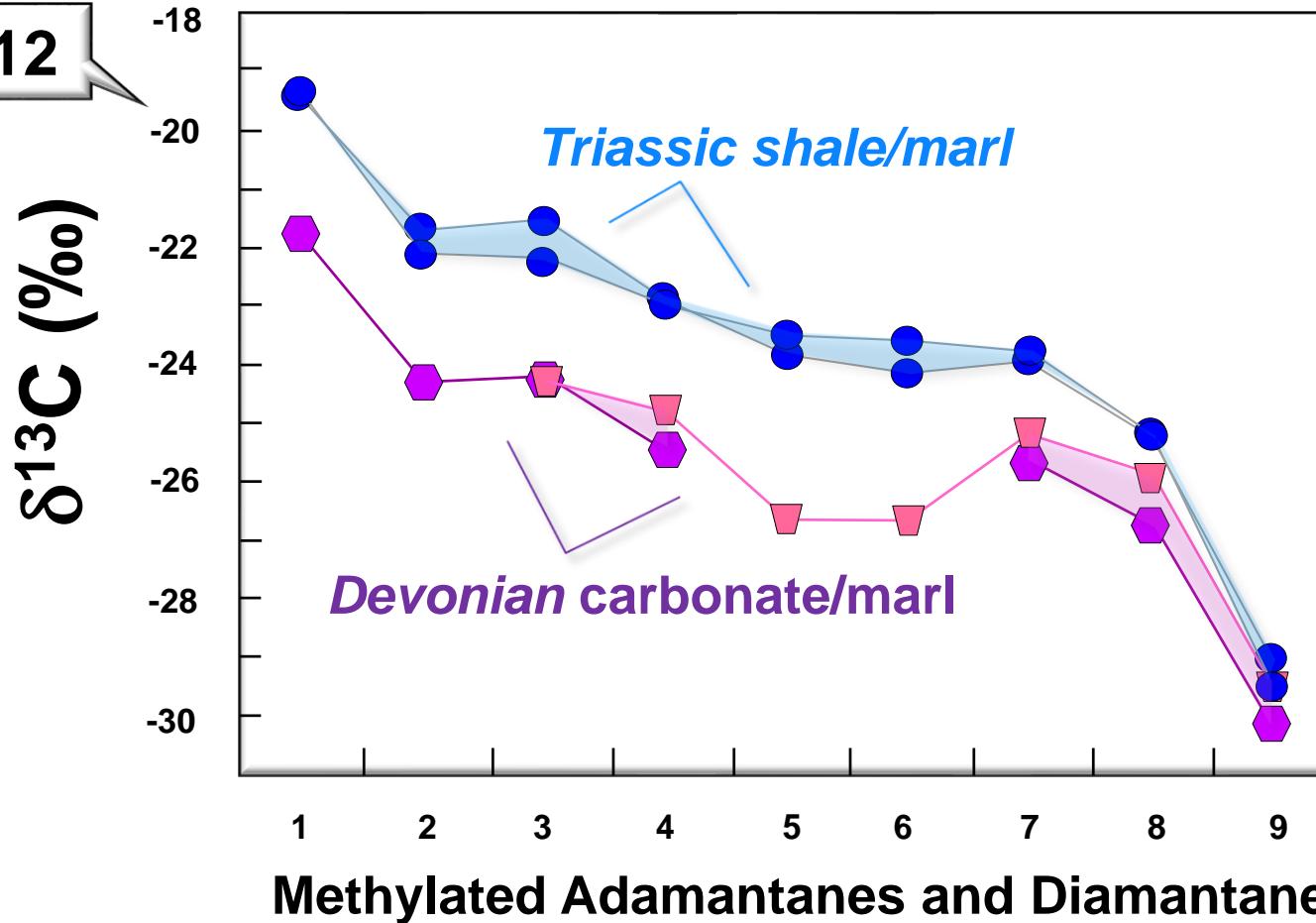
Diamondoids Show Extent of In-Reservoir Oil Cracking



CSIA of Diamondoids Identifies Families and Mixtures

Barents Sea and Northern Timan-Pechora Basin, Russia

2012

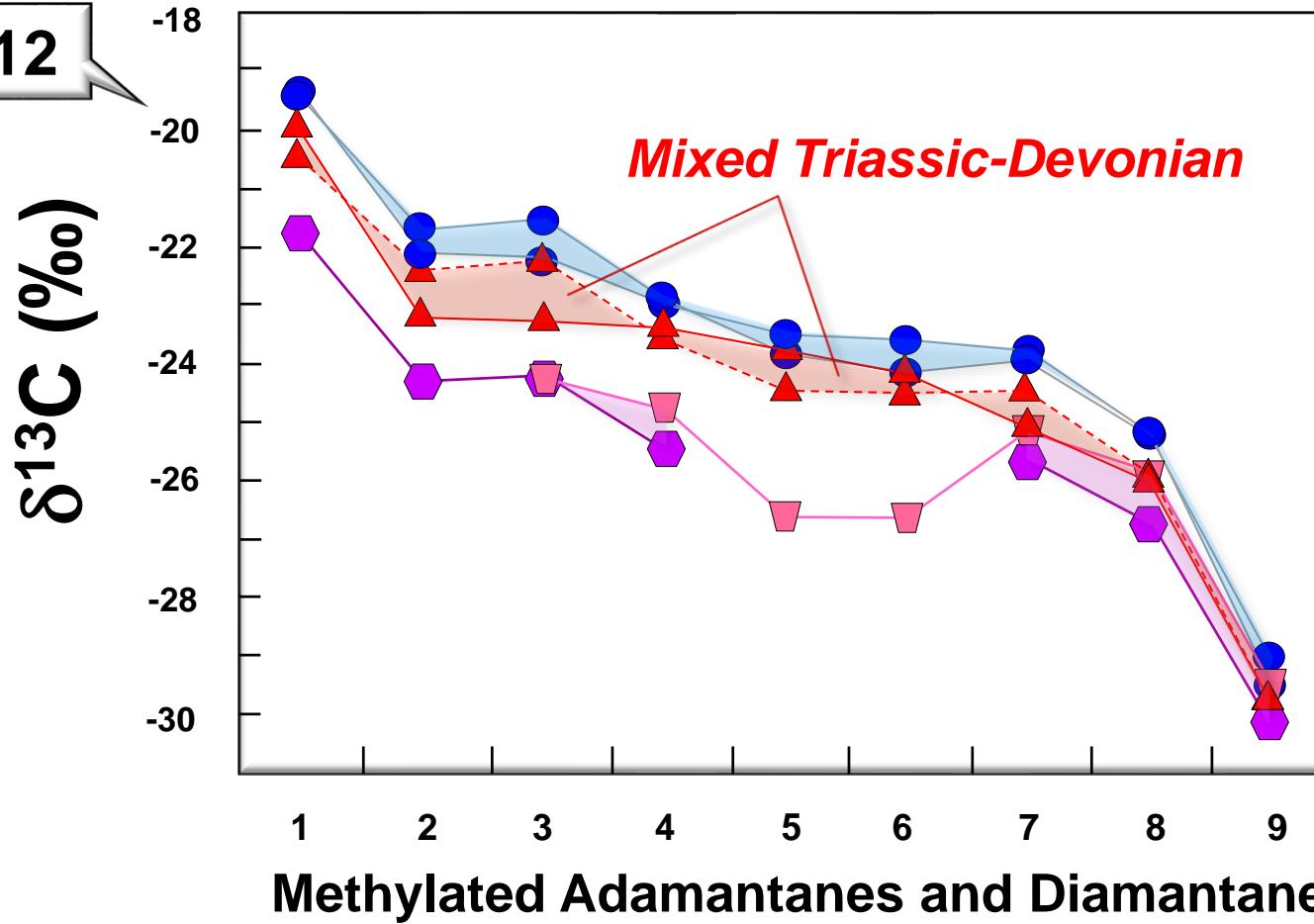


He et al. (2012)

CSIA of Diamondoids Identifies Families and Mixtures

Barents Sea, Northern Timan-Pechora Basin, Russia

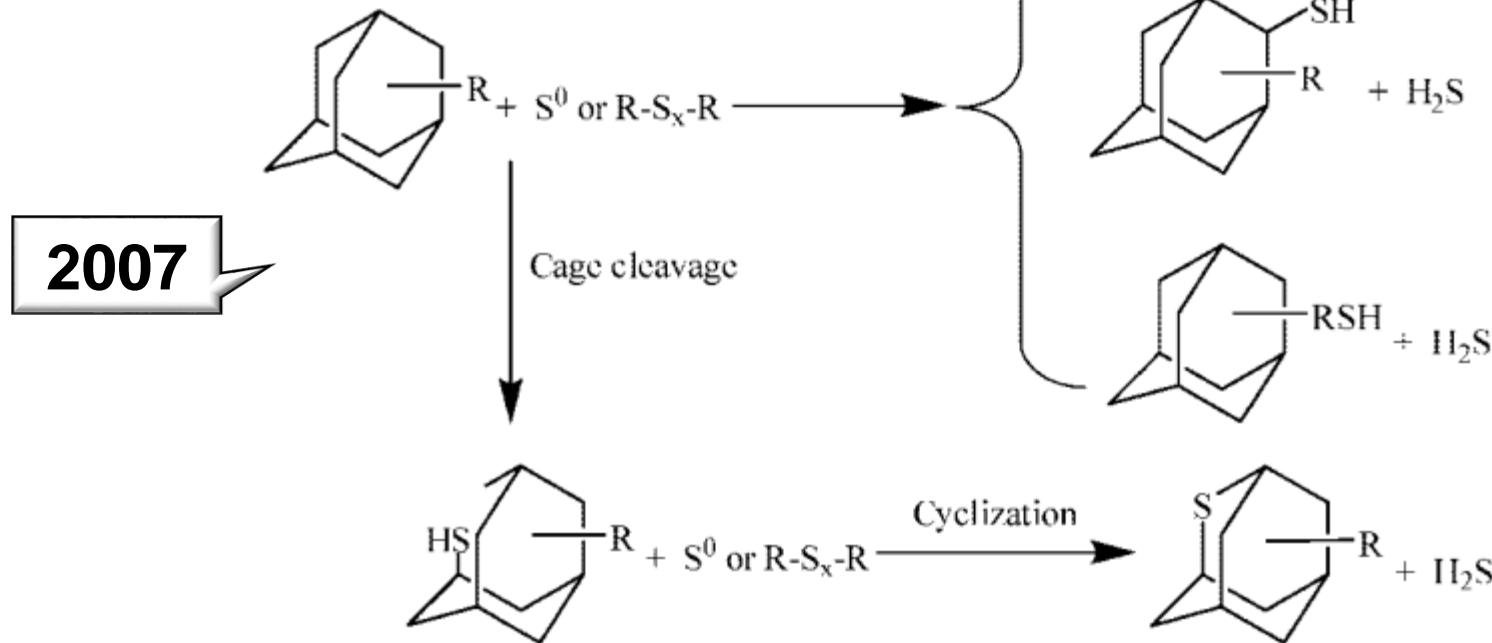
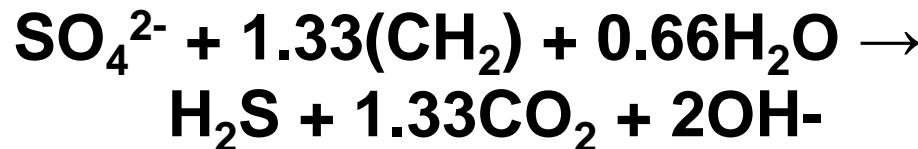
2012



He et al. (2012)

Avoid TSR Using Diamondoidthiols, Thiadiamondoids

Thermochemical Sulfate Reduction

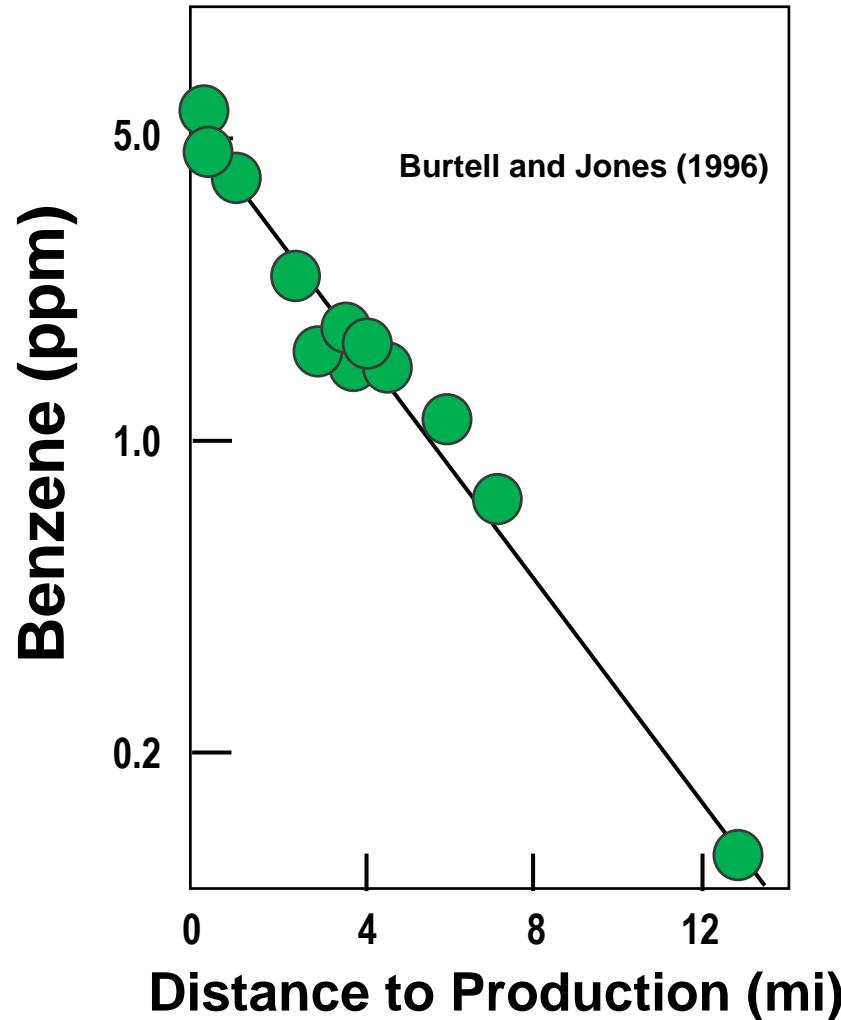


Wei et al. (2007)

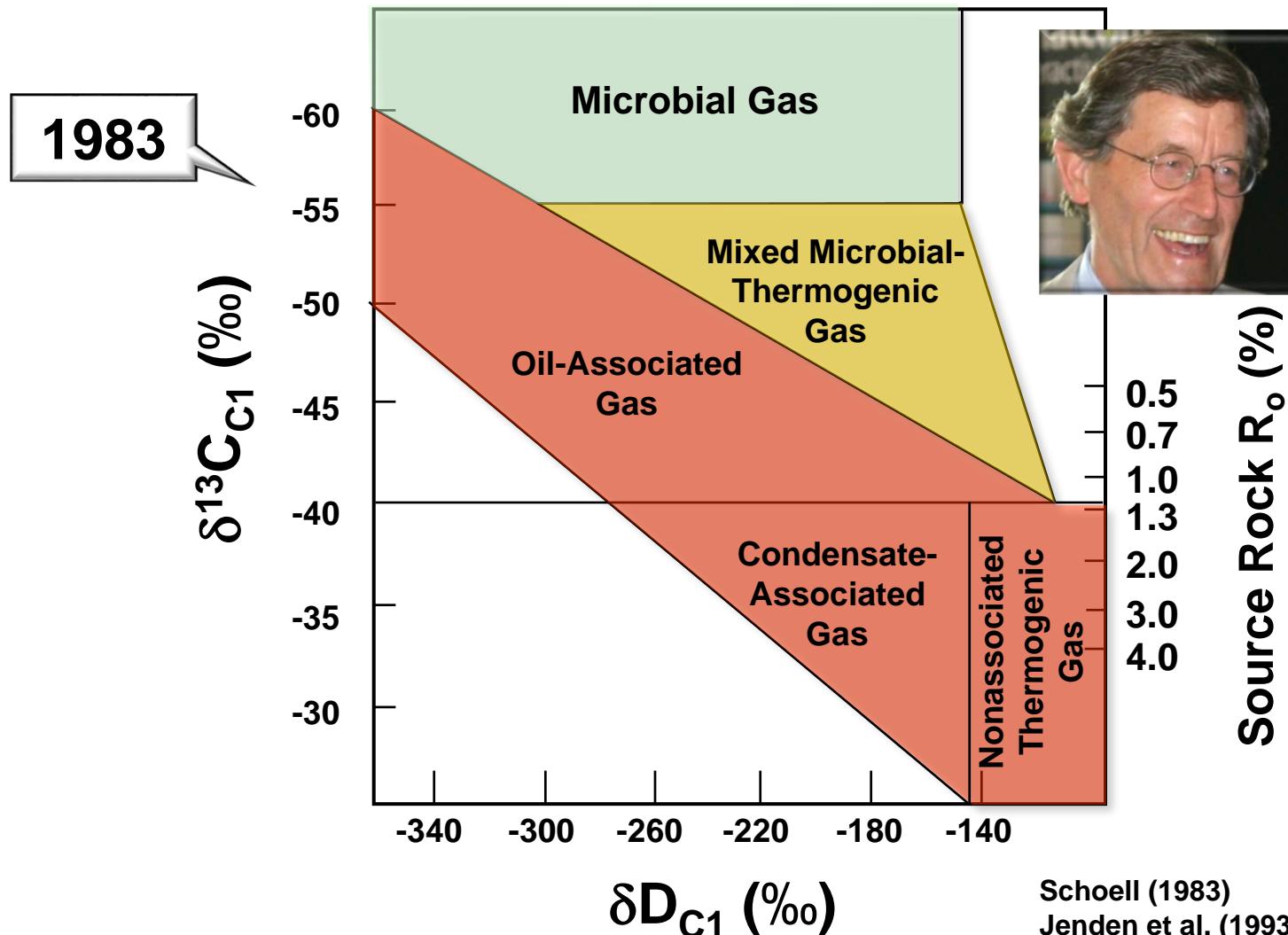
BTEX (Benzene, Toluenes, Xylenes): Proximity to Pay

1996

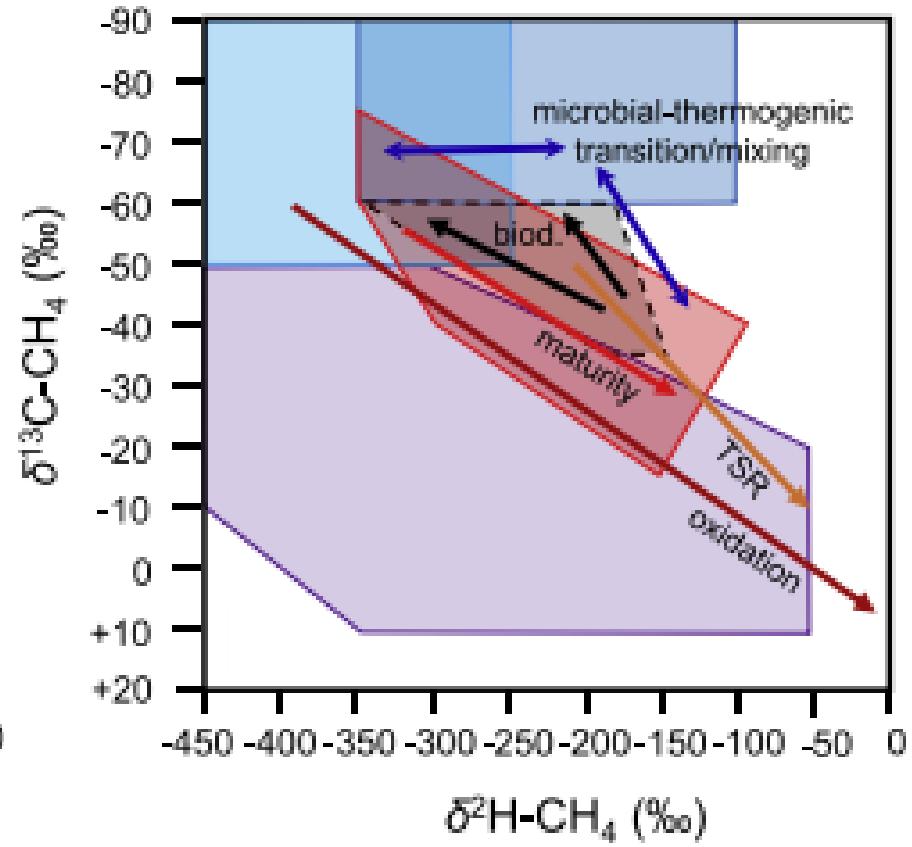
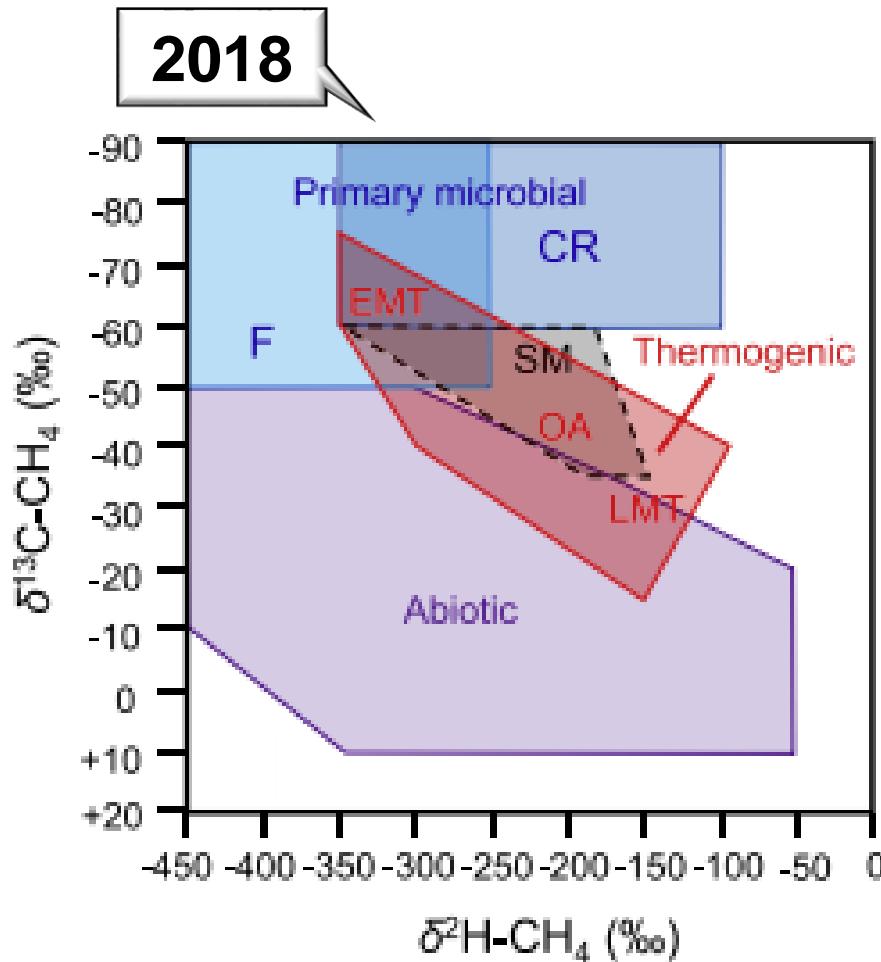
This relationship established distance to source from a dry hole and a discovery was later drilled based on this information.



Empirical Isotope Classification of Hydrocarbon Gases

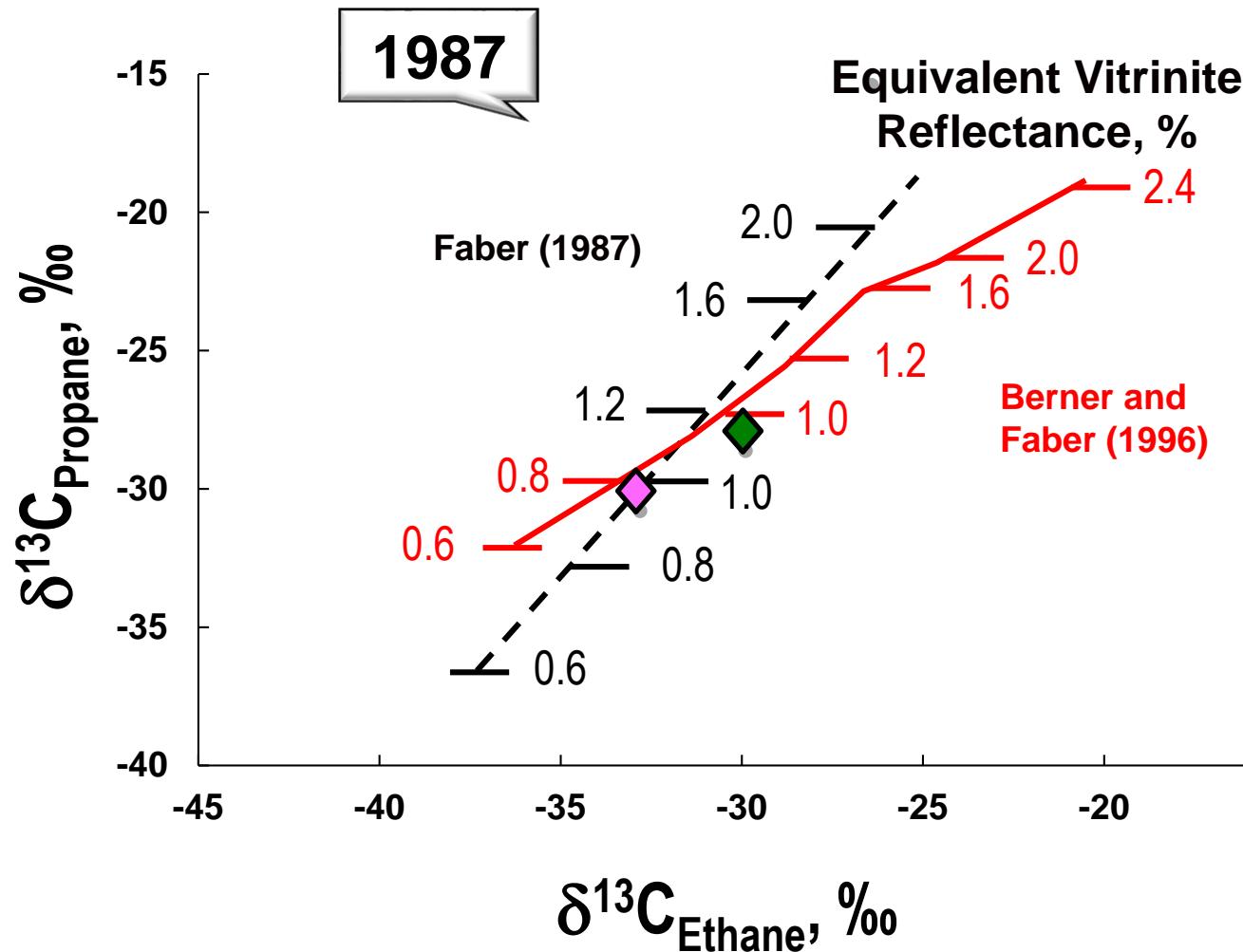


Revised $\delta^{13}\text{C}$ vs. δD Isotope Plots (6,950 Samples)

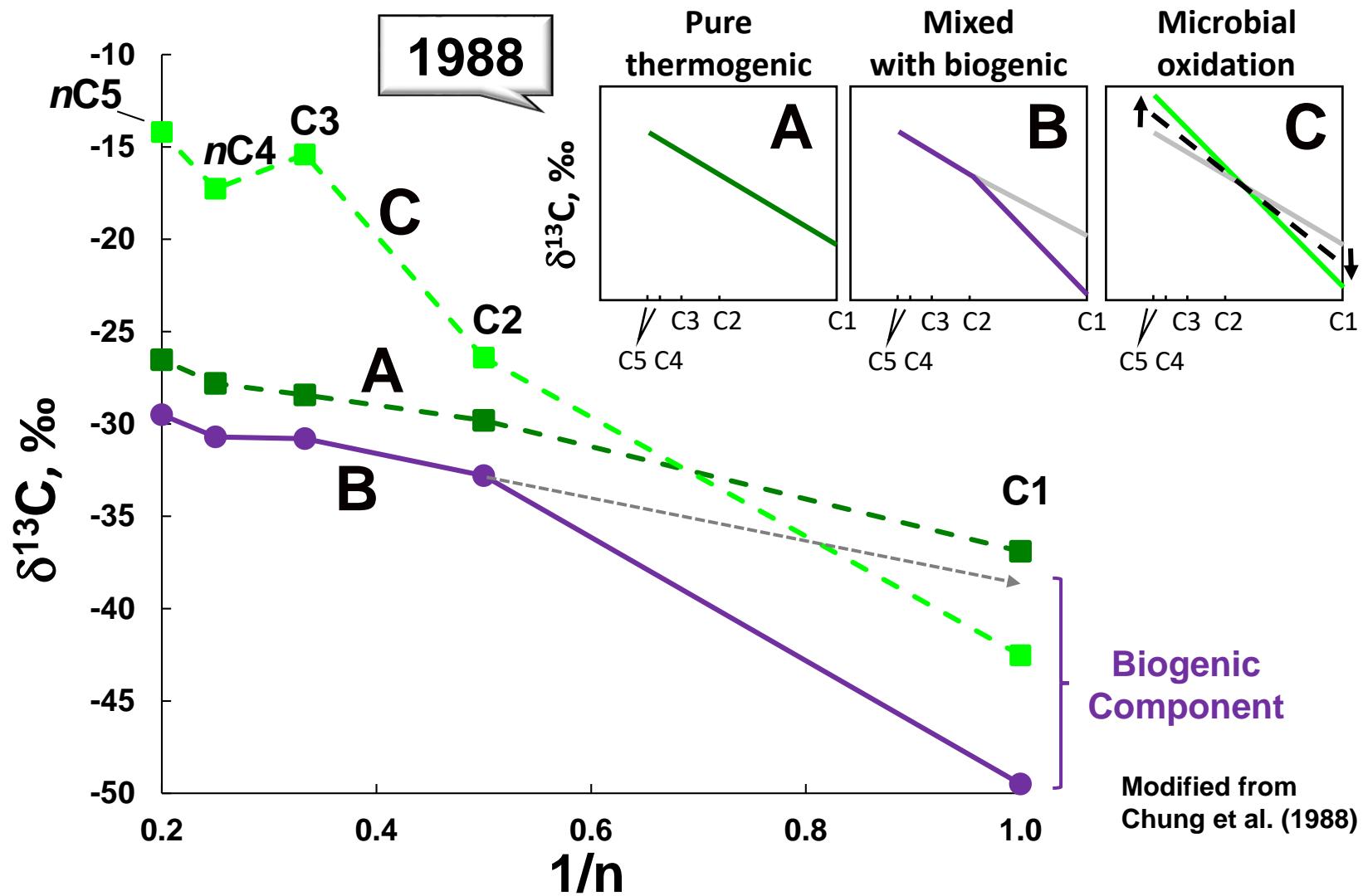


Milkov and Etiope (2018)

Rank Gas Maturity Using Ethane and Propane Isotopes

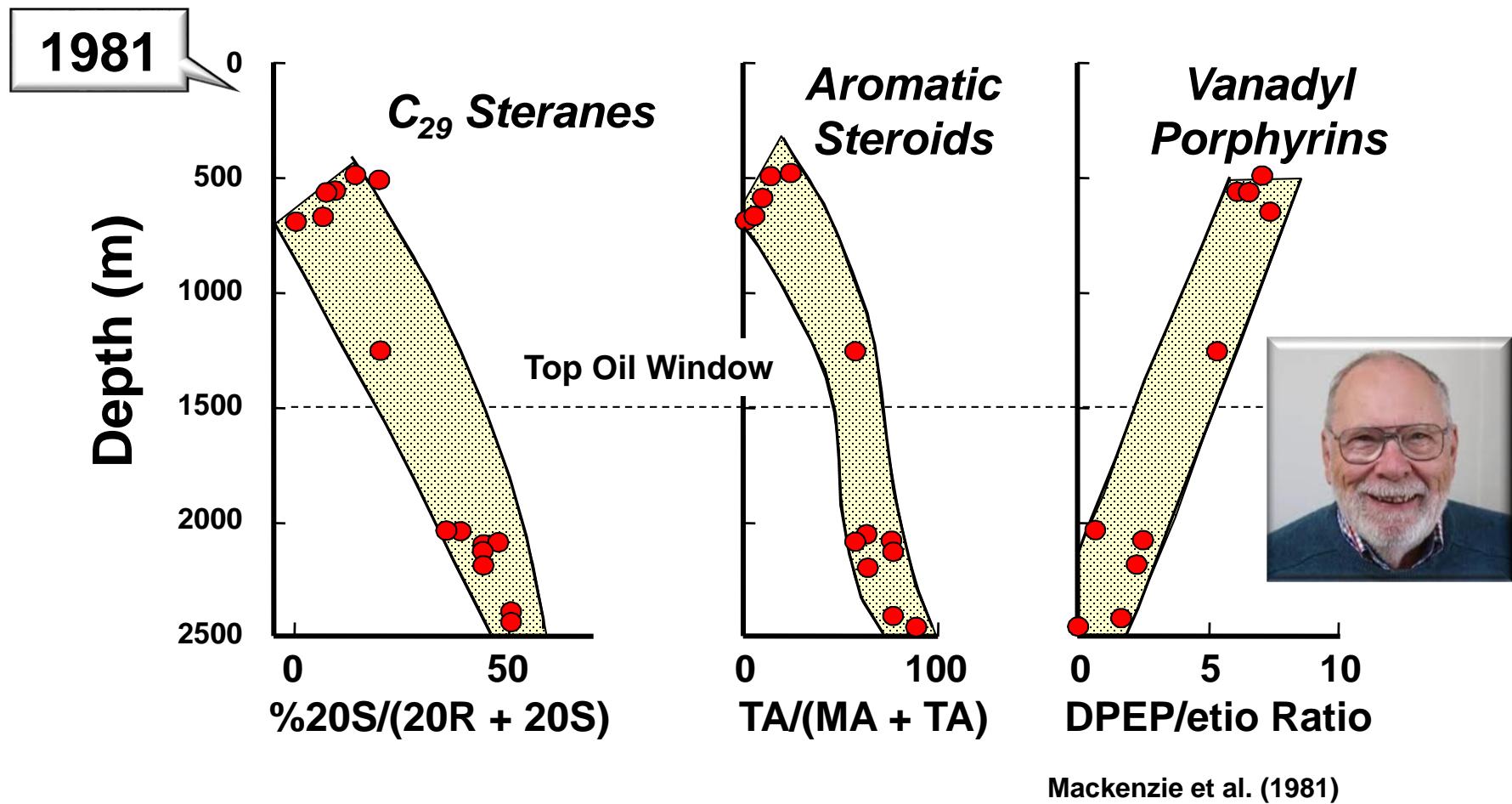


Chung Plots Reveal Secondary Processes Affecting Gas

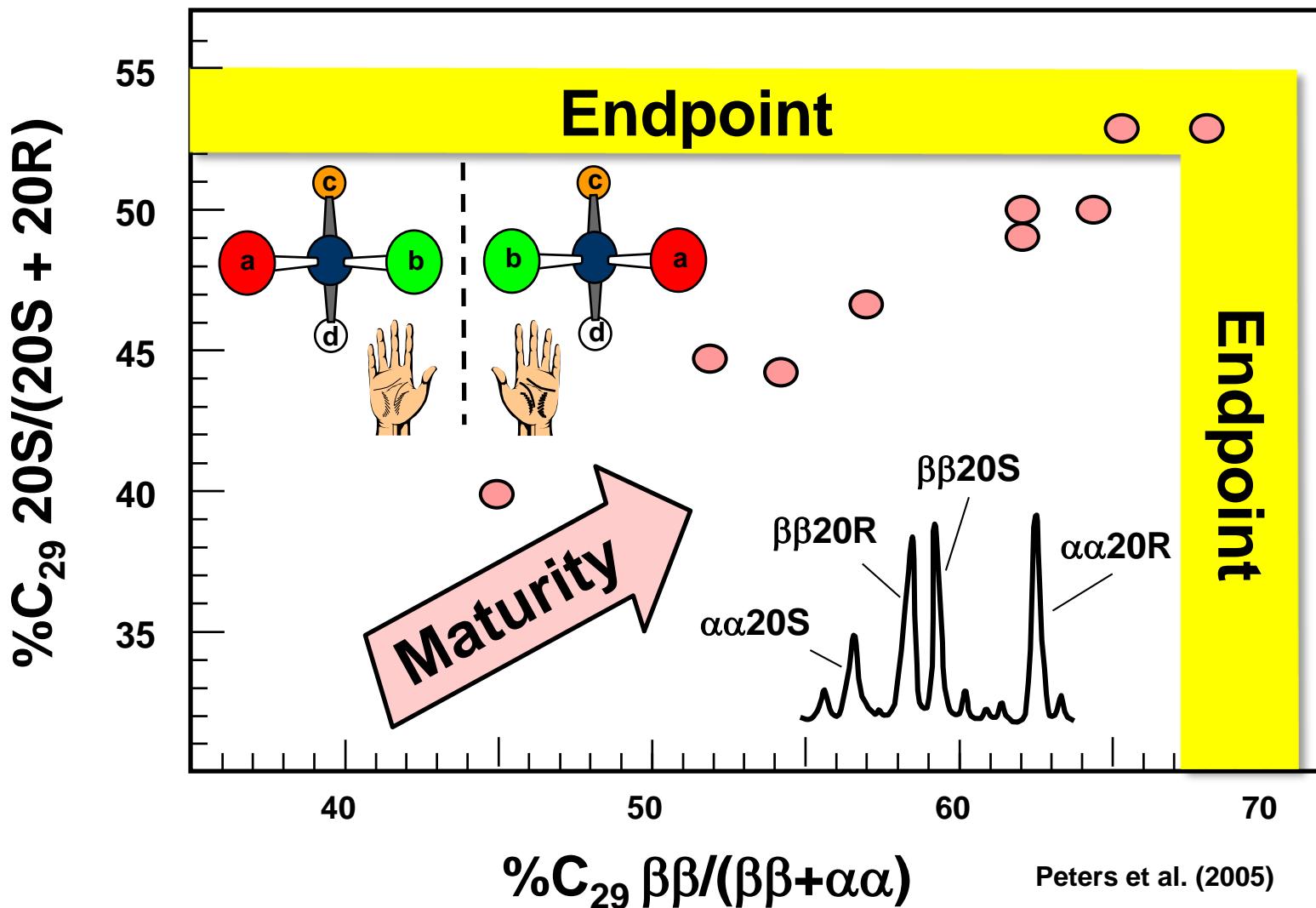


Thermal Maturity Ratios Include Stereoisomerizations

Lower Toarcian Shales, Paris Basin

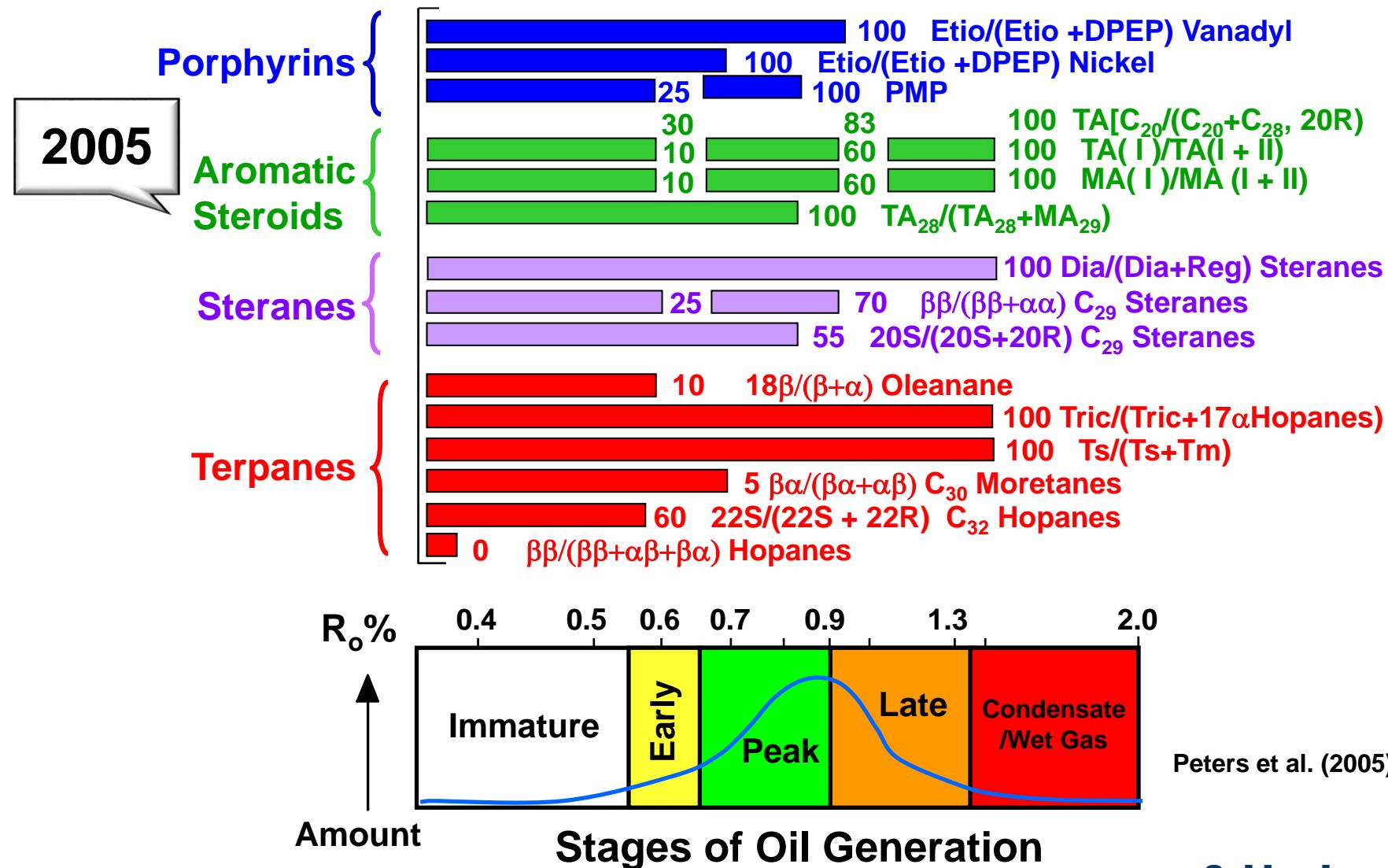


Sterane Isomerization Ratios Help to Rank Maturity



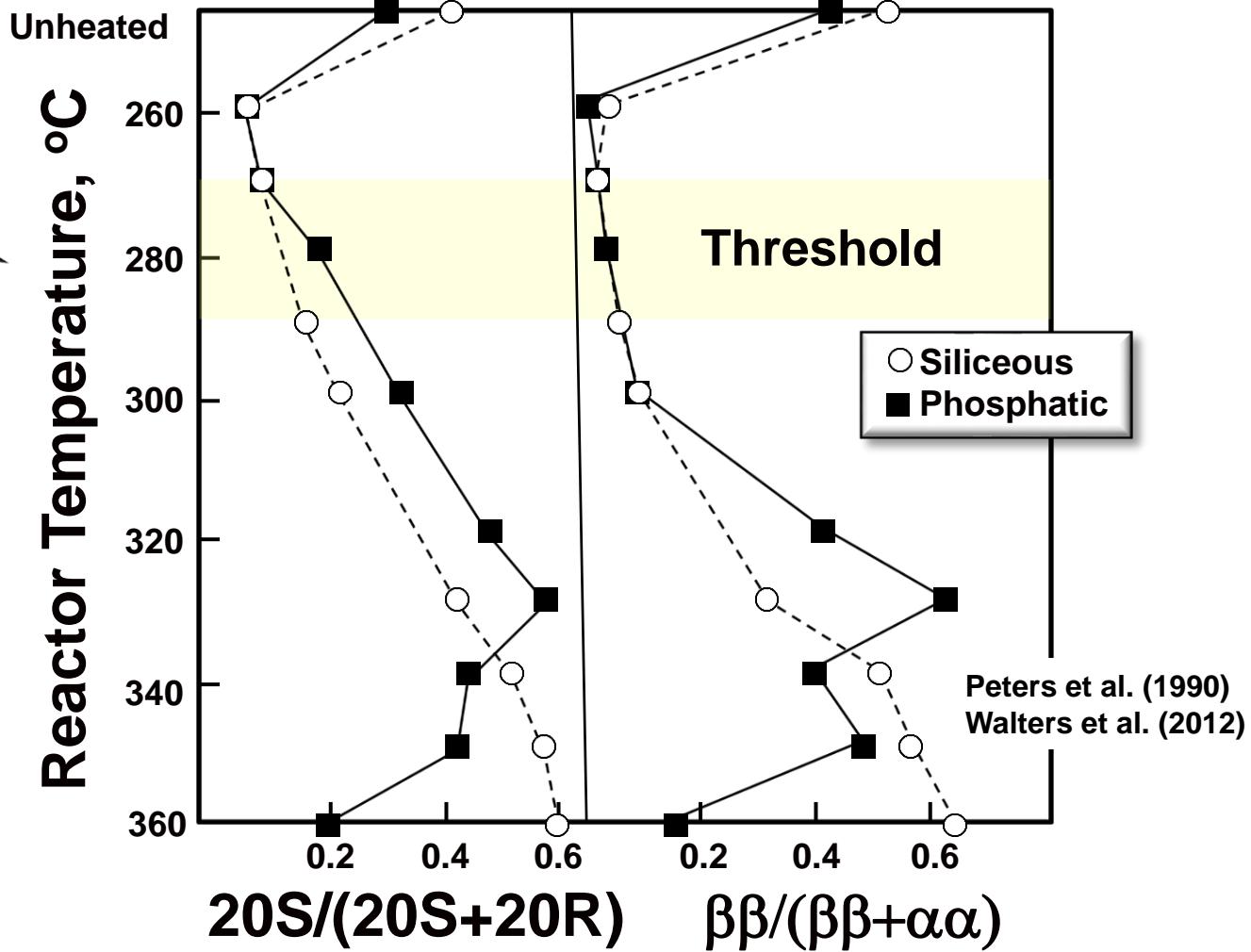
Peters et al. (2005)

Biomarker Ratios Bracket the Level of Thermal Maturity

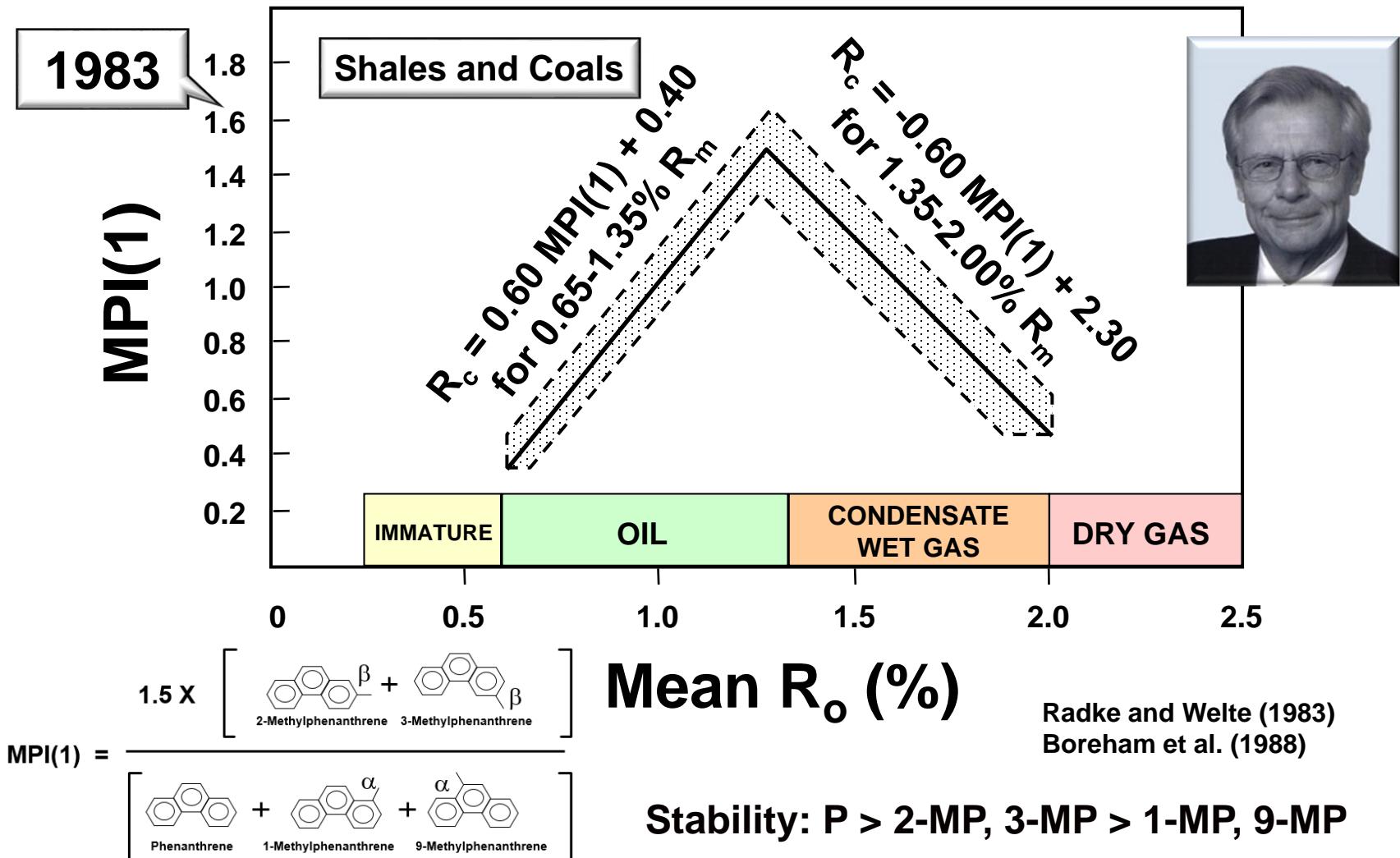


Isomerizations: Limited Use to Calibrate Basin Models

1990



Methylphenanthrene Index: Type III Source Maturity



Rank Oil Biodegradation Using Compound Classes

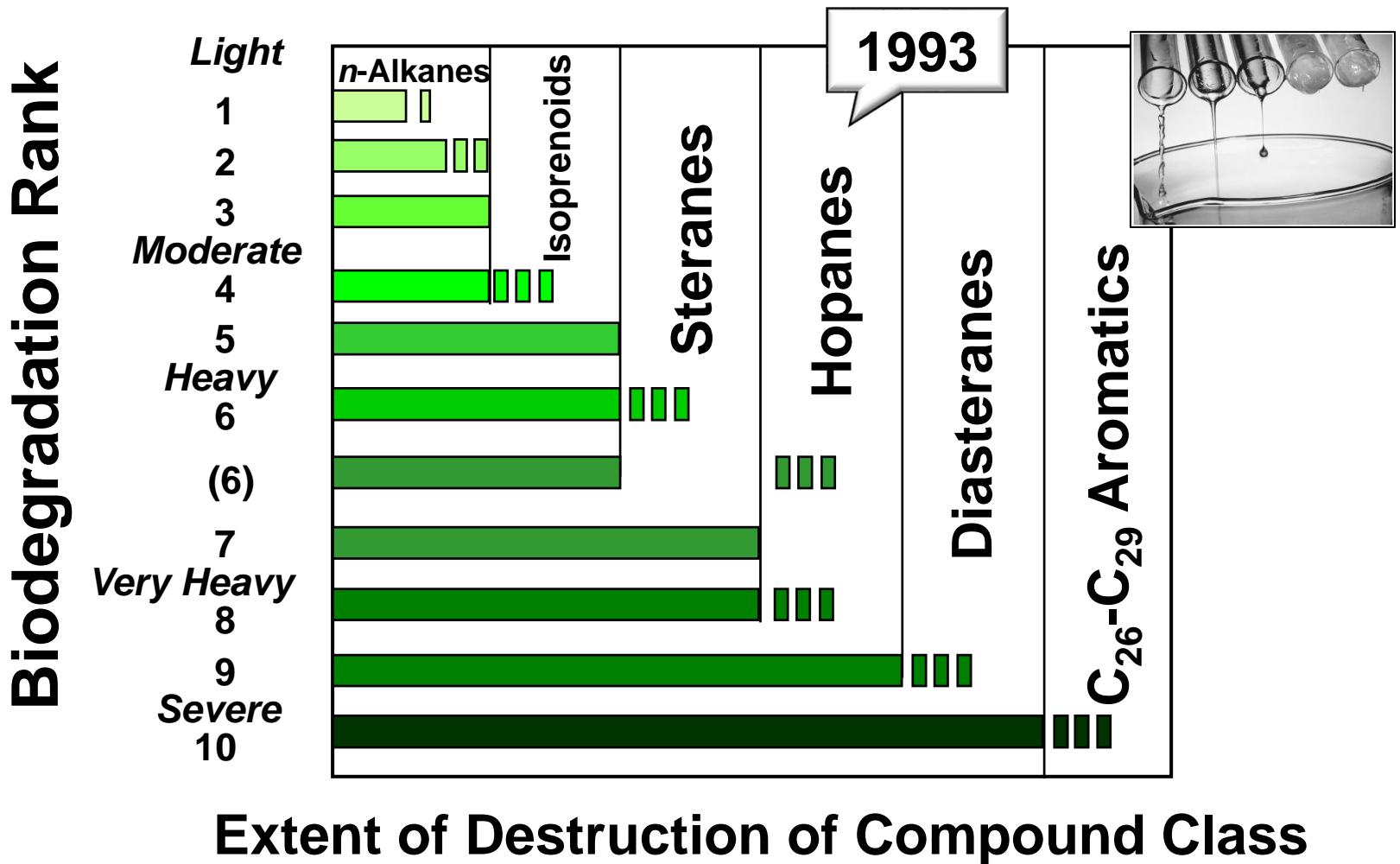
Level	Chemical Composition	Extent of Biodegradation
1	Abundant <i>n</i> -alkanes	Not degraded
2	Light-end <i>n</i> -alkanes removed	Minor
3	>90% <i>n</i> -alkanes removed	
4	Alkylcyclohexanes and alkylbenzenes removed; acyclic isoprenoid alkanes and naphthalene reduced	Moderate
5	Isoprenoid alkanes removed; selective removal of C ₂ -naphthalenes	
6	C ₁₄ -C ₁₆ bicyclic alkanes removed	
7	>50% (20R)-5 α ,14 α ,17 α (H)-steranes removed	Very extensive
8	Distribution of steranes and triaromatic steroids altered; demethylated hopanes abundant	Severe
9	No steranes; demethylated hopanes predominate	Extreme

1984



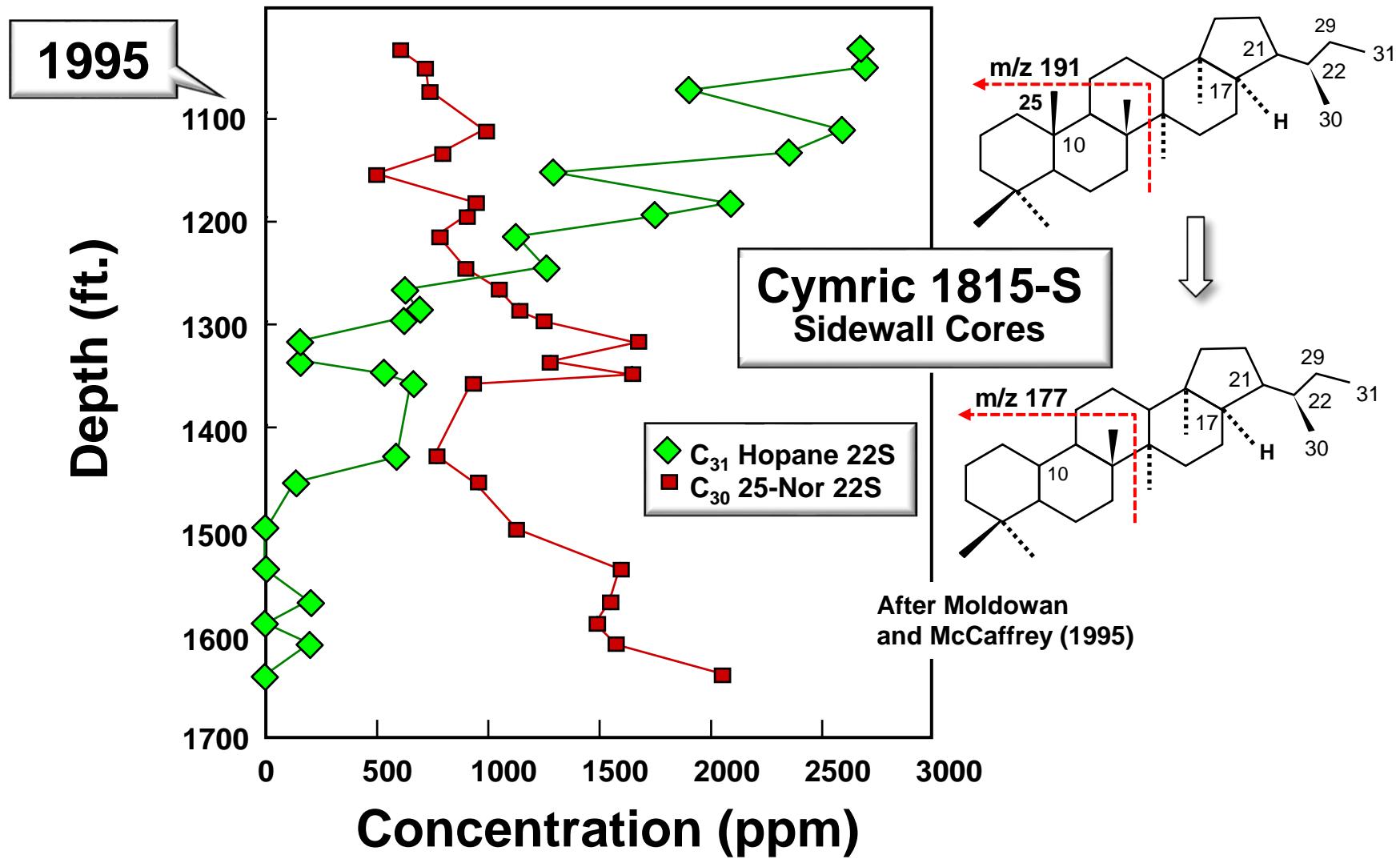
Volkman (1984)

Biodegradation Can Interfere with Oil-Oil Correlation



Peters and Moldowan (1993)

Hopanes Demethylated to 25-Norhopanes in Reservoirs

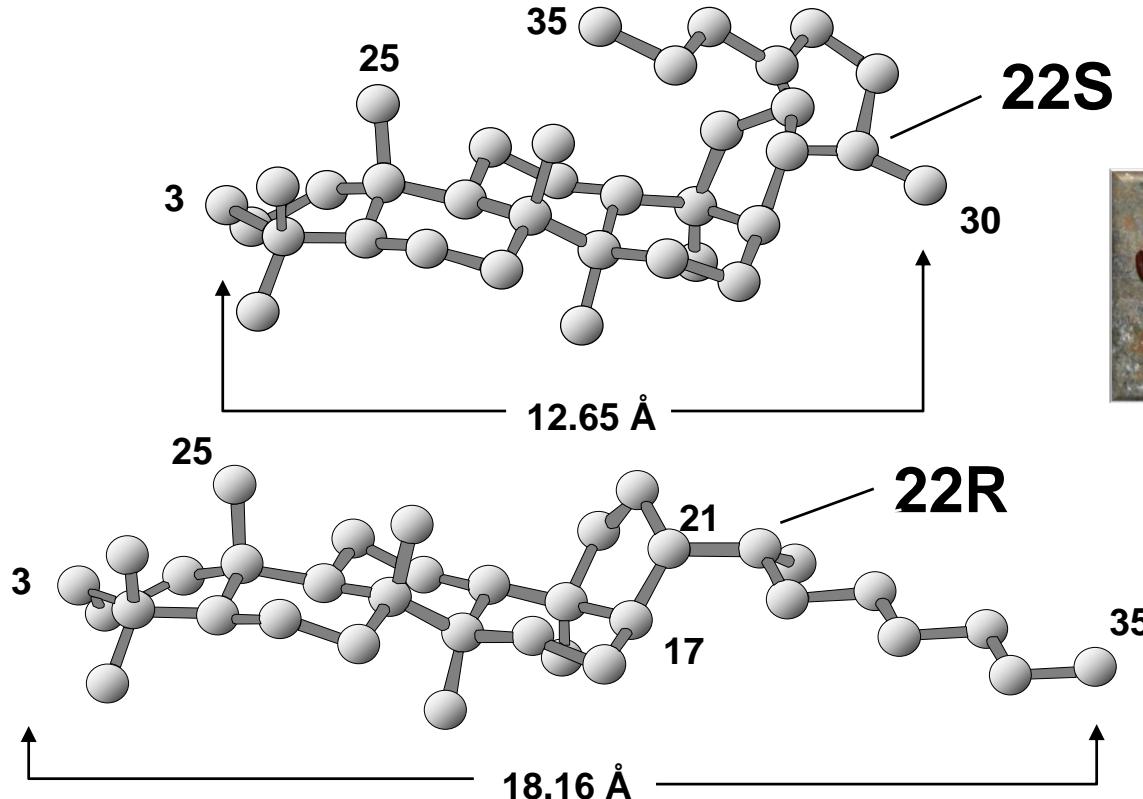


Molecular Mechanics Explains Selective Biodegradation

1996

Selective biodegradation of extended hopanes to 25-norhopanes in petroleum reservoirs. Insights from molecular mechanics*

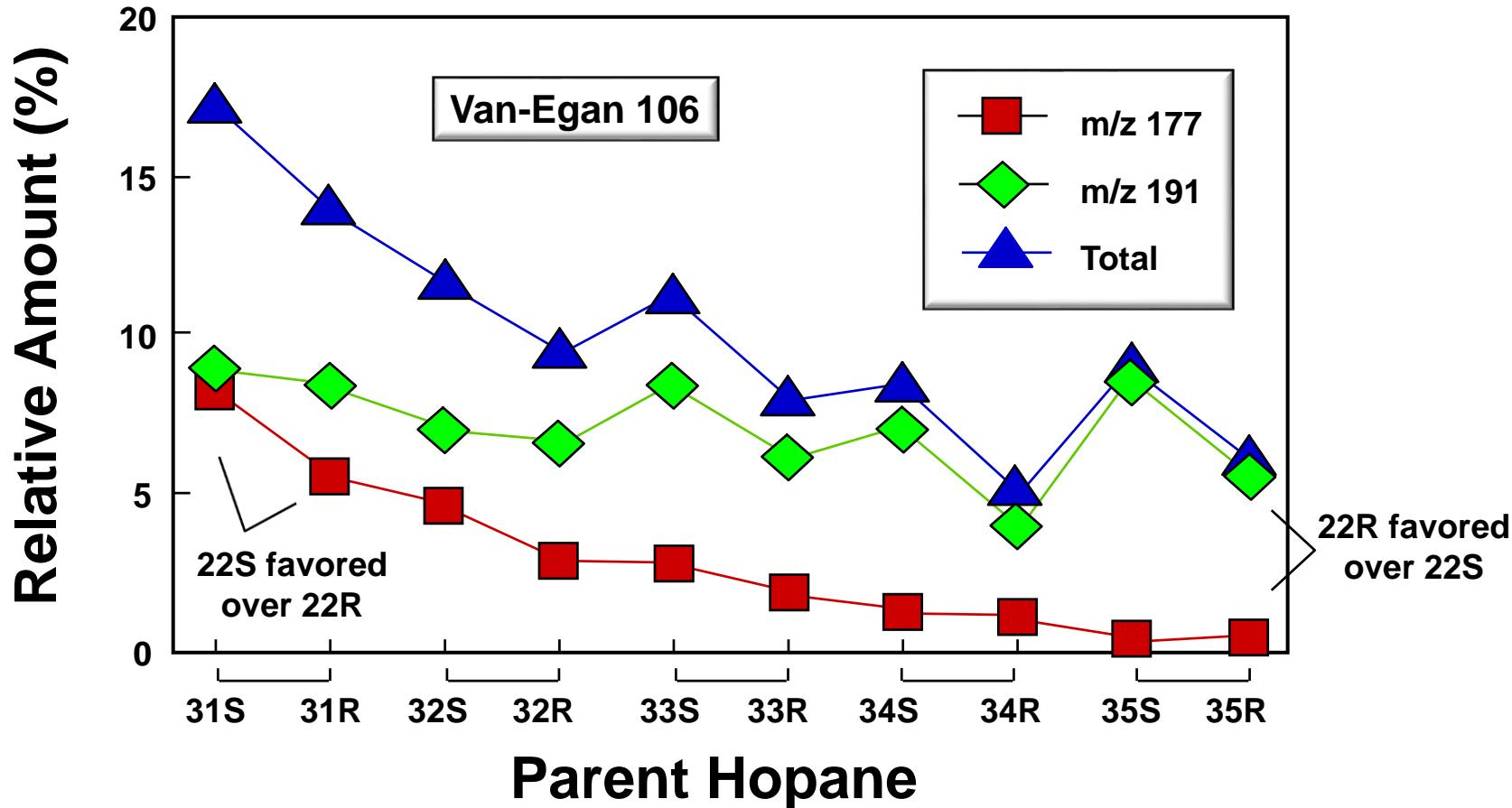
KENNETH E. PETERS¹, J. MICHAEL MOLDOWAN², MARK A. McCAFFREY^{†3}
and FREDERICK J. FAGO²



Peters et al. (1996)

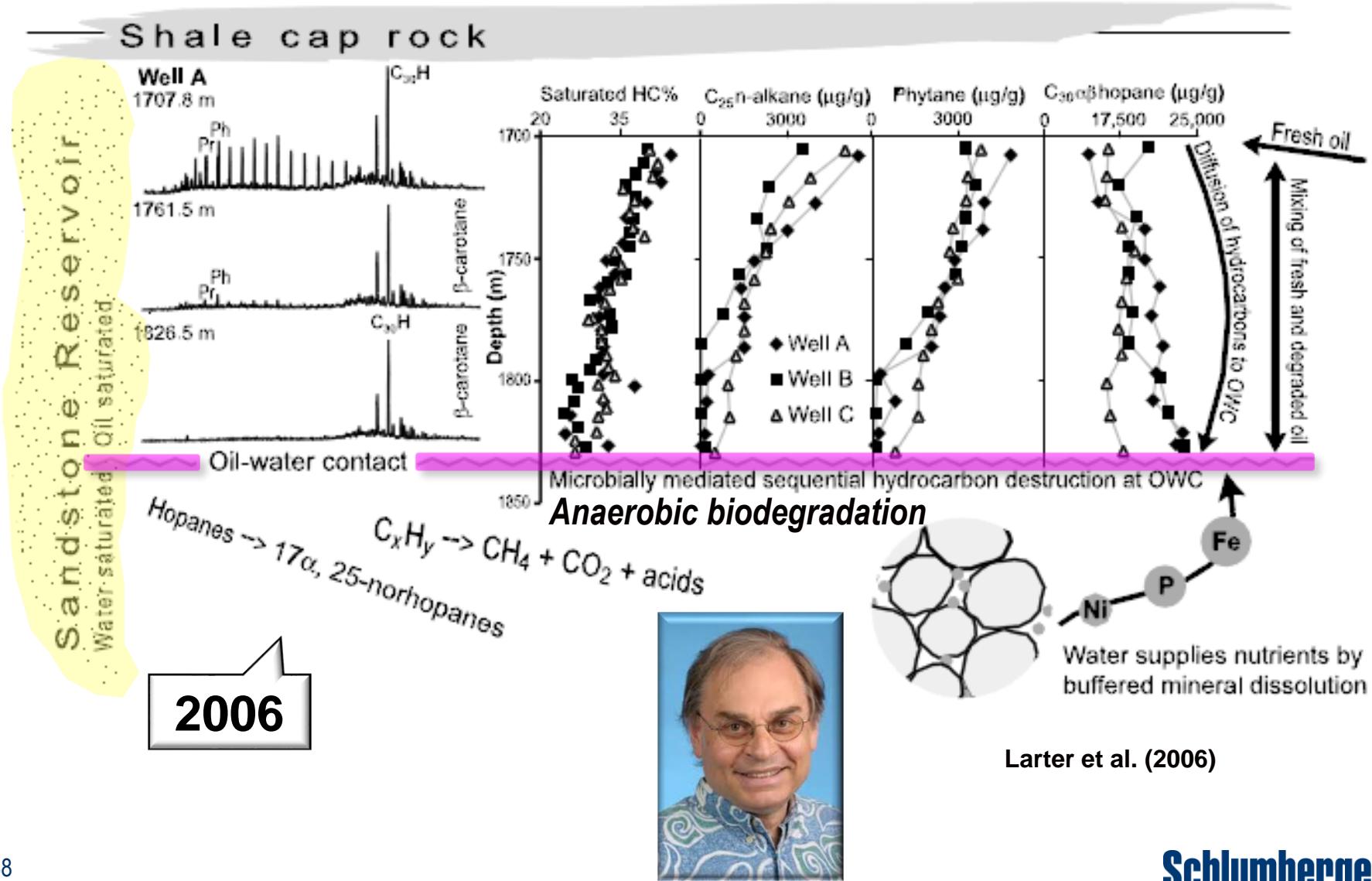
Chain Length and Stereochemistry Affect Demethylation

West Siberia Basin Biodegraded Oil



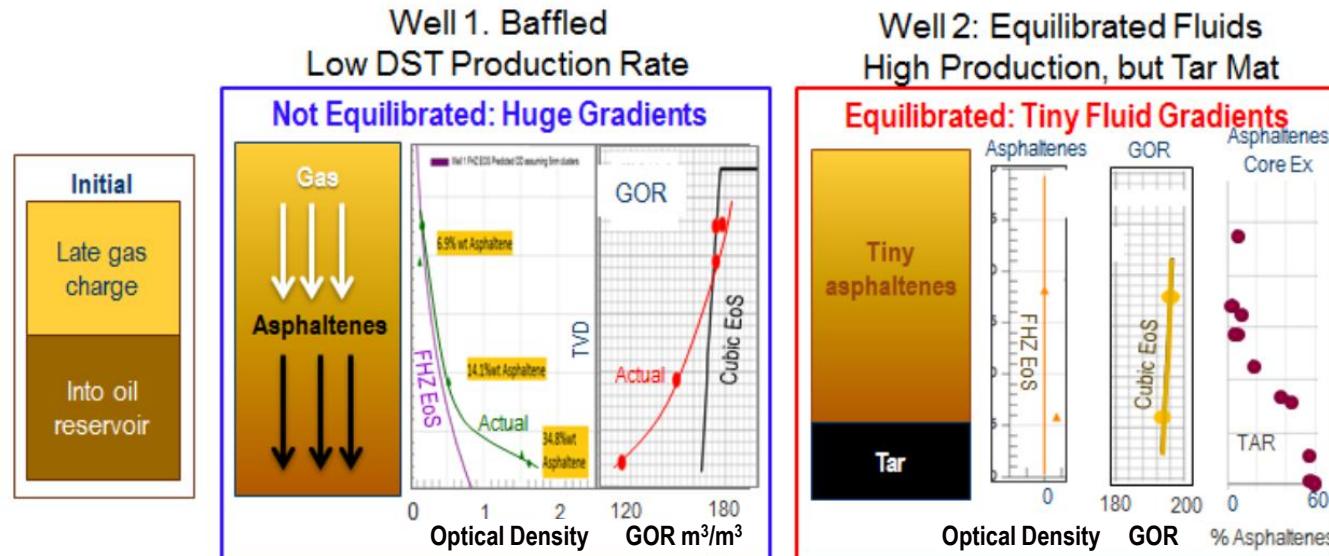
Peters et al. (1996)

Gradients: Shallow Oil Charge, Biodegradation at OWC



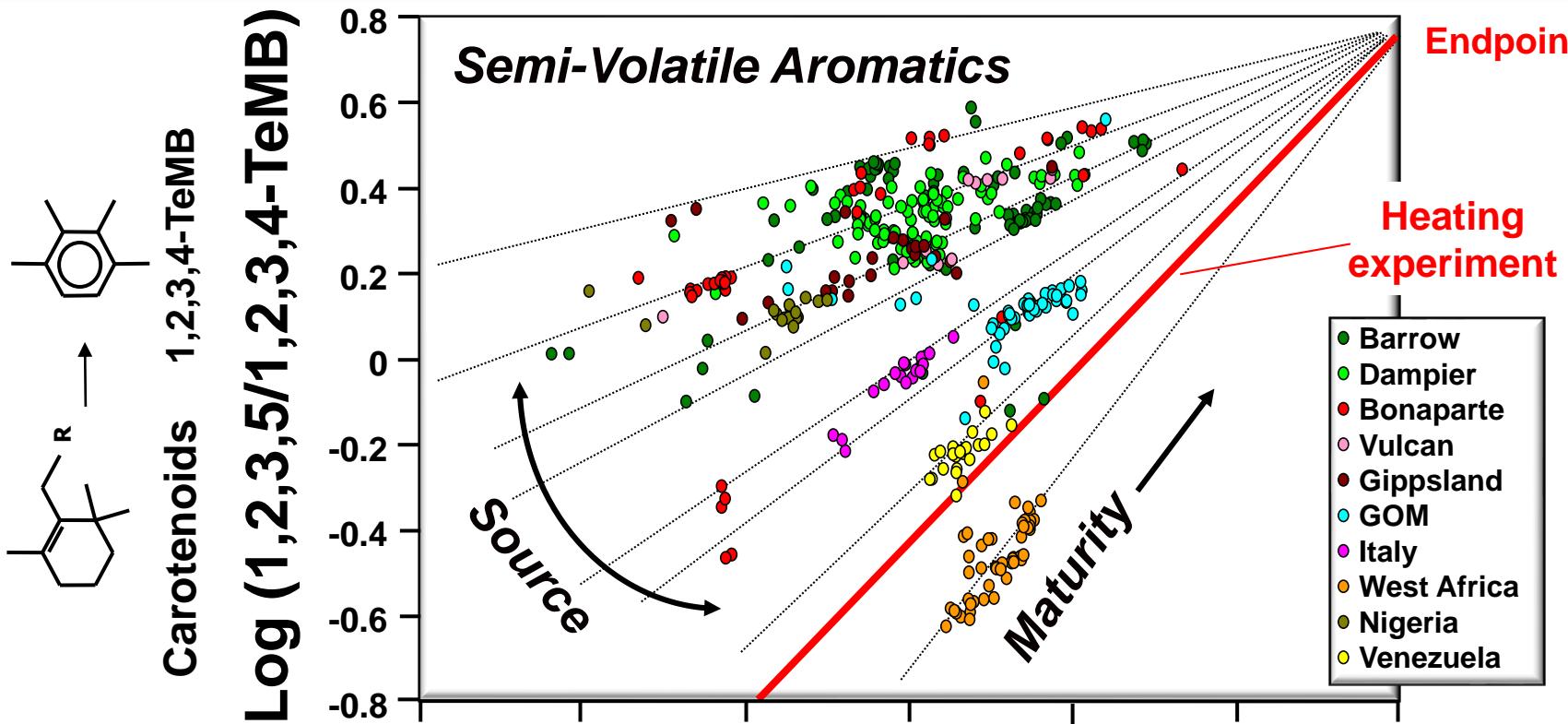
Some Newer Milestones in Molecular Geochemistry

- Fluid inclusion biomarkers (e.g., D. Hall, H. Volk)
- Clumped isotopes for temperature (e.g., D. Stolper)
- Reservoir fluid geodynamics (e.g., O. Mullins)
- Semi-volatile aromatics (e.g., A. Murray)
- Genomics for enhanced production (e.g., C. Turich)



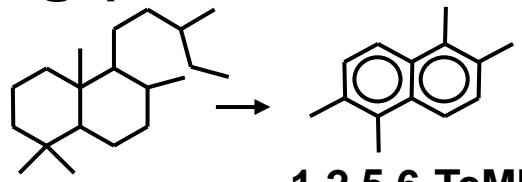
Mullins et al. (2016)

Maturity Increases Isomer Ratios Controlled by Source



Log (1,3,6,7/1,2,5,6-TeMN)

Diterpenoids
(Gymnosperms)



A. Murray pers. comm. based on Van Aarssen et al. (2007). IMOG abstract book P375-TH, p. 906-908.

Some Examples of Valiant Attempts at Milestones

- Carbazoles for migration distance (e.g., S. Larter)
- Dating fluid migration, reservoir filling (e.g., S. Larter)
- Genomics for enhanced production (e.g., C. Turich)



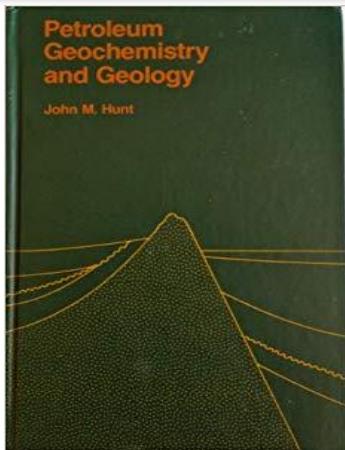
Do Microbes in *Helaeomyia petrolei* Upgrade Heavy Oil?

Brine Fly Larva, La Brea Tar Pits

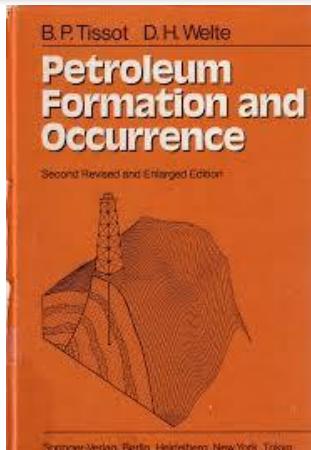


Courtesy of Courtney Turich (2010)

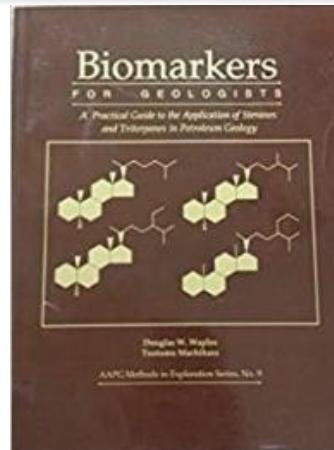
Some Textbooks Highlight Molecular Geochemistry



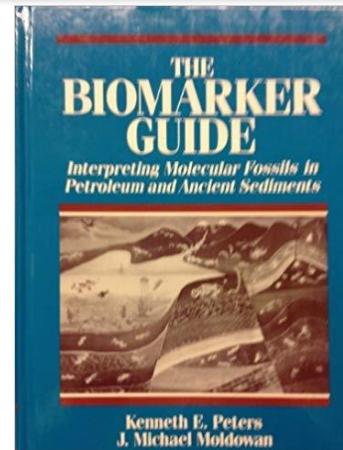
Hunt '79



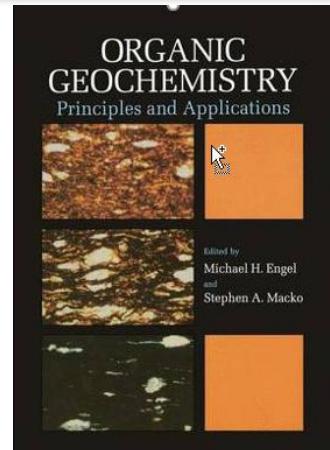
Tissot, Welte '84



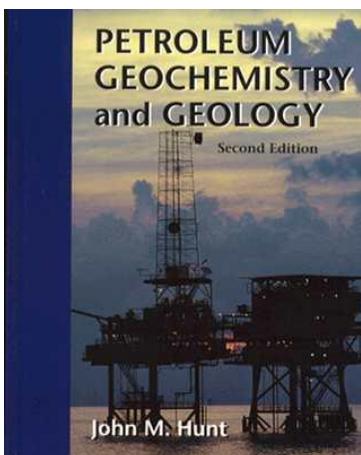
Waples, Machihara, '91



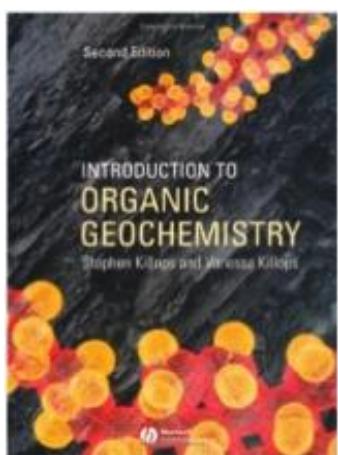
Peters, Moldowan '93



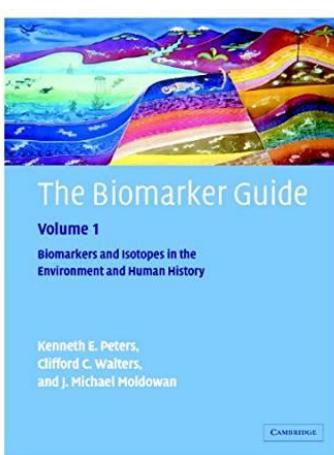
Engel, Macko '93



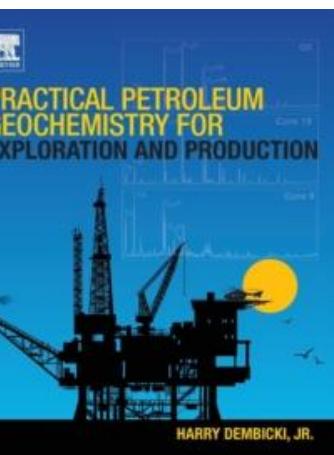
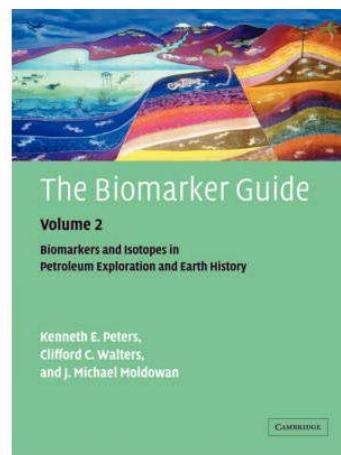
Hunt '96



Killops, Killops '05



Peters, Walters, Moldowan '05



Dembicki '17

Molecular Geochemistry in Exploration & Development

Conceptual Milestones*

Origins

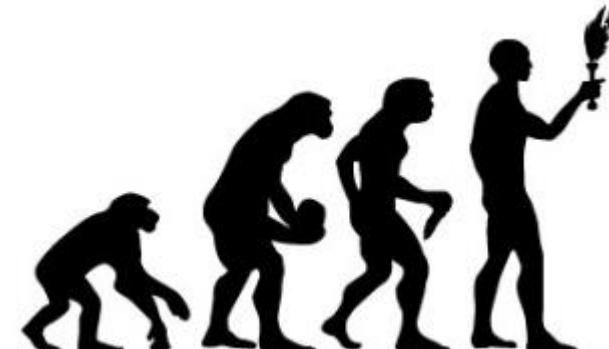
- Source-related biomarker ratios
- Oil-source rock correlation and petroleum system concept
- CSIA for correlation: alkanes, biomarkers, diamondoids
- Age-related biomarker ratios
- Maturity assessment using biomarkers, light aromatics
- Biomarkers to assess biodegradation
- Gas geochemistry for source, maturity, TSR, biodegradation
- Diamondoids: extent of oil cracking, mixed charge
- BTEX to identify directions to accumulations
- Time-lapse reservoir geochemistry

Recent Developments

- Fluid inclusion biomarkers
- Clumped isotopes for temperature assessment
- Reservoir fluid geodynamics

Frontiers

- Carbazoles for migration distance
- Age dating fluid migration, reservoir filling
- Genomics for enhanced production, surfactants





The Evolution of Petroleum Systems Analysis
Houston, TX March 4-6, 2019