12.158 Lecture 10

Molecular Biosignatures:

Real and Potential Biomarkers, Analytical Innovations, Meteorites & Old Rocks

http://marsprogram.jpl.nasa.gov/msl/

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RESEARCH ARTICLE

Search for Past Life on Mars: Possible Relic Biogenic Activity in Martian Meteorite ALH84001

David S. McKay, Everett K. Gibson Jr.,
Kathie L. Thomas-Keprta, Hojatollah Vali,
Christopher S. Romanek, Simon J. Clemett,
Xavier D. F. Chillier, Claude R. Maechling and Richard N. Zare

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PAH proposed to be molecular fossils ?

‘ PAH are abundant as fossil molecules in ancient sedimentary rocks ’

However, PAH are not necessarily biogenic

Topics

- What are useful criteria for biogenicity?
  How can we be sure of measuring the right thing in a sample on Mars or returned from Mars?

- Analytical methods for investigating molecular biosignatures in rocks from Earth & elsewhere

Report of the NASA Biomarker Taskforce 2000

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Molecules, isotopes, microfossils, mineral fabrics

Roger Summons, Pierre Albrecht, Sherwood Chang, Gene McDonald and J. Michael Moldowan

Assumptions

- Extra-terrestrial life will resemble earthly life –
  based on carbon chemistry operating in an aqueous environment
  - carbon is the only element that is sufficiently abundant, ubiquitous and chemically suited for life
- It will process chemicals for carbon and energy, make copies of itself, be autonomous and evolve in concert with its environment
- Biochemical pathways will operate as above
  - comprise energy yielding and replication reactions
  - construct complex molecules from simple, universal precursors
  - evolve

Abiotically produced organic materials

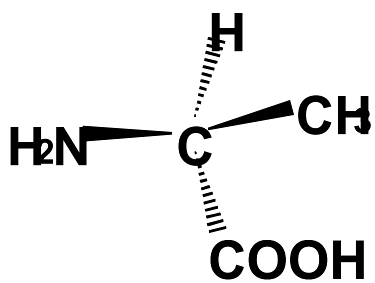
Organic acids and diacids, amino acids, hydroxy acids, alcohols, amines

- n- and branched-hydrocarbons incl. methane
- Aromatic hydrocarbons (PAH)

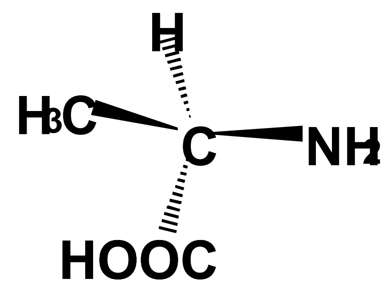
Intrinsic Characteristics (Patterns) of Terrestrial Molecular Biosignatures

- Enantiomeric excess
- Diastereoisomeric preference
- Constitutional isomer preference
- Repeating constitutional sub-units or atomic ratios
- Systematic isotopic ordering at molecular and intramolecular levels
- Systematic distribution patterns or clusters (e.g. C-number, concentration, $d^{13}C$) of structurally related compounds

Enantiomers of Alanine



L-alanine



D-alanine

L-amino acids predominate in biology

L-amino acid XS in Murchison meteorite

(Engel & Macko a-aa's; Cronin & Pizzarello non-protein aa's)

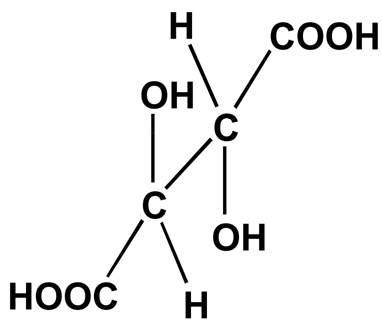
Non-biological processes can yield enantiomeric excess

Asymmetric catalysis and autocatalysis

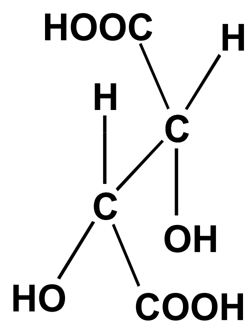
Soai & Sato: slight chiral excess propagated during autocatalytic syntheses

Pizzarello and Weber: AA enantiomeric excess promotes asymmetry in aldol condensations of glycoaldehyde

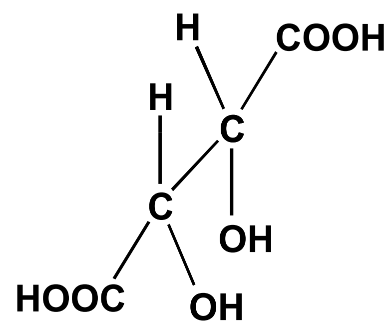
Stereoisomerism in Tartaric Acid



A (meso)



B

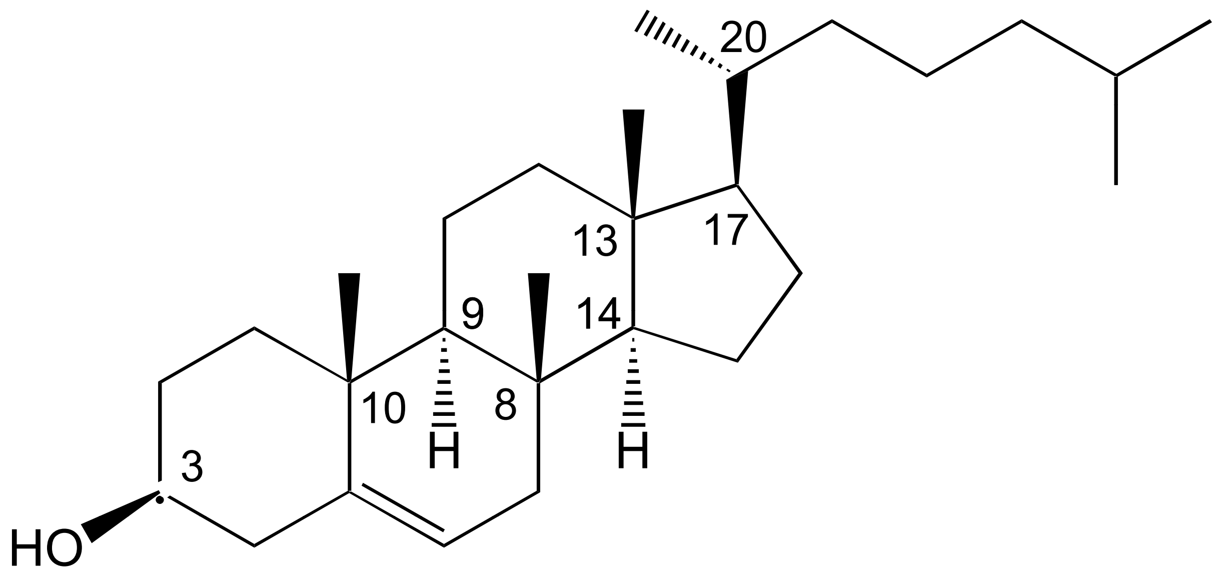


C

B & C enantiomers A & B and A & C are diastereoisomers

Life makes a limited number of all the possible diastereoisomers

Stereoisomerism in Cholesterol



2^8 stereoisomers possible for cholesterol

Biology (ie Eucarya) makes only one

Studies of hydrocarbons as old as 2700 Myr show no deviation of sterane or hopane stereoisomer patterns; the fossils had the same precursors as exist today

Information Preserved in Products of Diagenesis: The Sterol Pathways

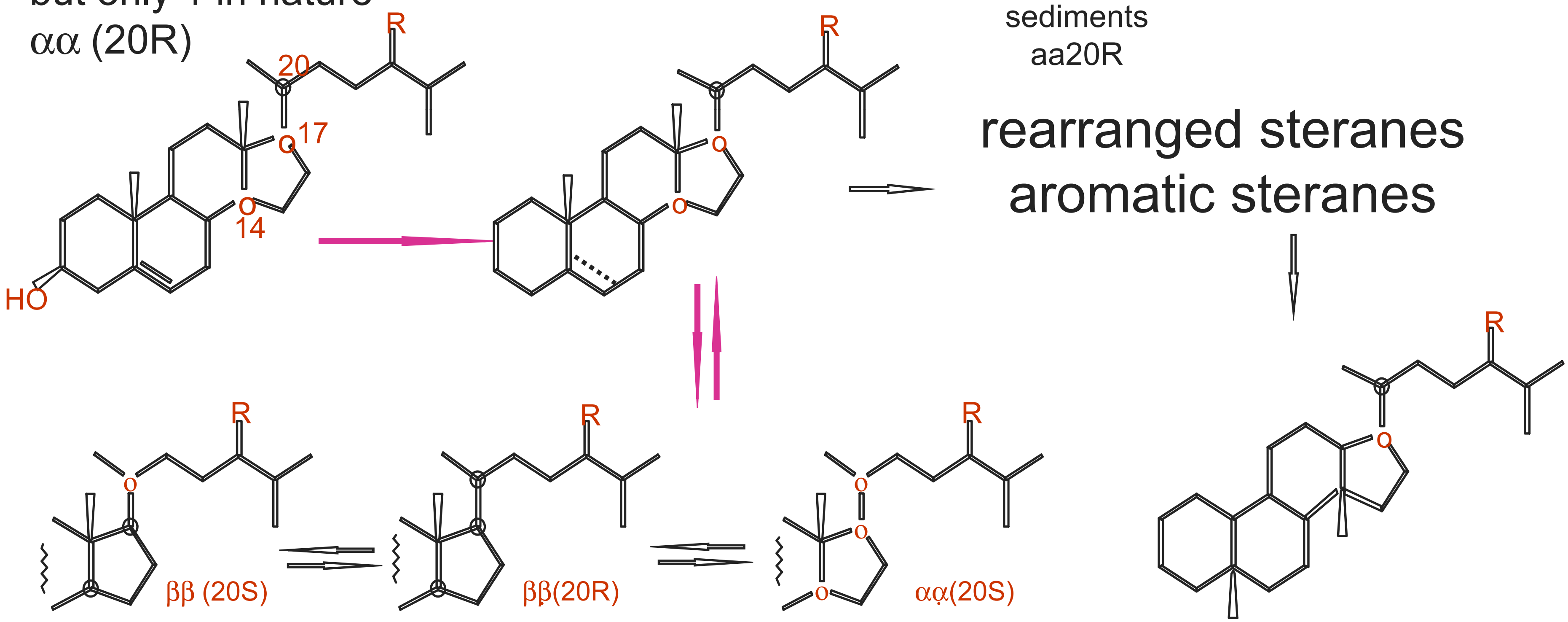
Unique sterol configuration of living organisms

8 sites of asymmetry

$2^8 = 256$ feasible isomers

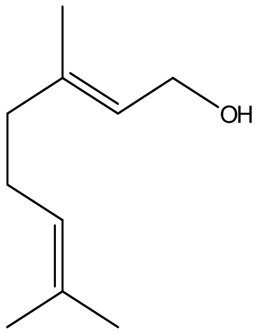
but only 1 in nature

αα (20R)

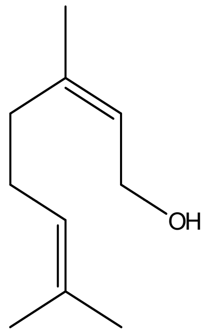


Complex sterane mixture in mature sediments & oil

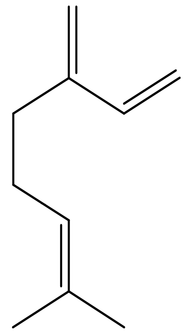
Constitutional Isomers



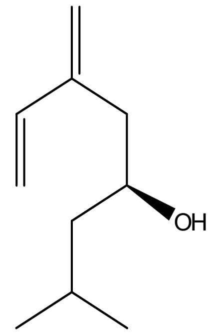
Geraniol



Nerol



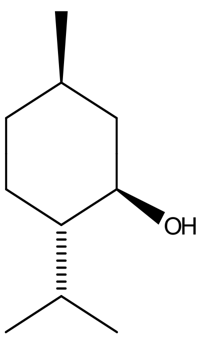
Myrcene



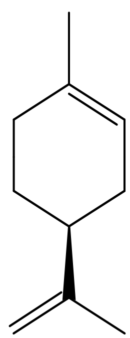
(*S*)-Ipsenol
Pine beetle pheromone

Choleoptera: Scolytidae

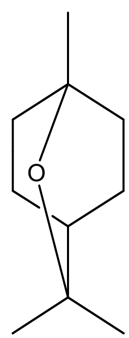
C_{10} compounds (monoterpenes)
- life makes a specific subset of all the possibilities



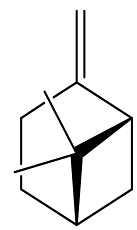
(1*R*,2*S*,5*R*)-(-)-Menthol



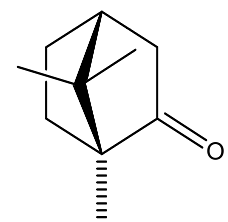
(*S*)-(-)-Limonene

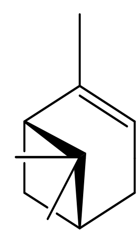


Cineol (eucalyptol)

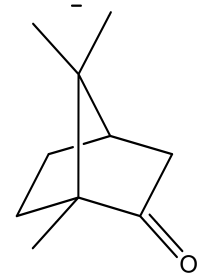


(1*S*)-(-)-β-Pinene





(1*R*)-(+)-α-Pinene



(1*R*)-(+)-Camphor

Constitutional Isomers

α β γ δ ε ζ

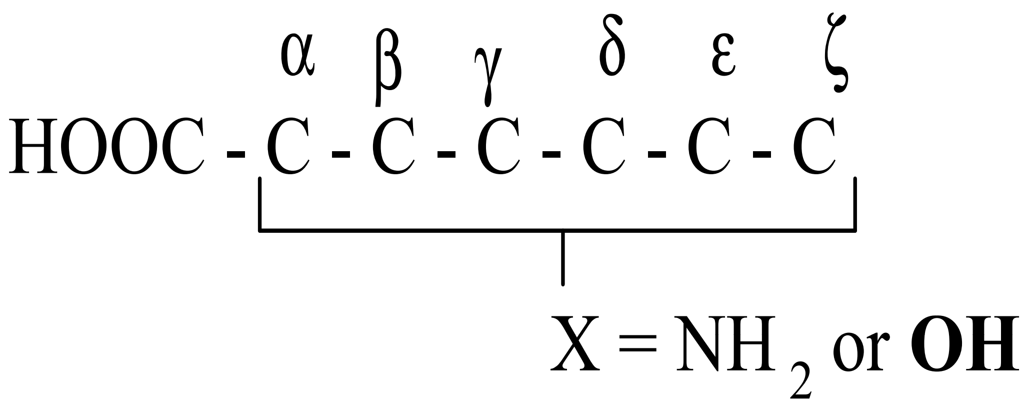
HOOC - C - C - C - C - C - C

$X = NH_2$ or **OH**

Small molecules identified in the Murchison Meteorite tend to occur with the maximum number of possible theoretical isomers

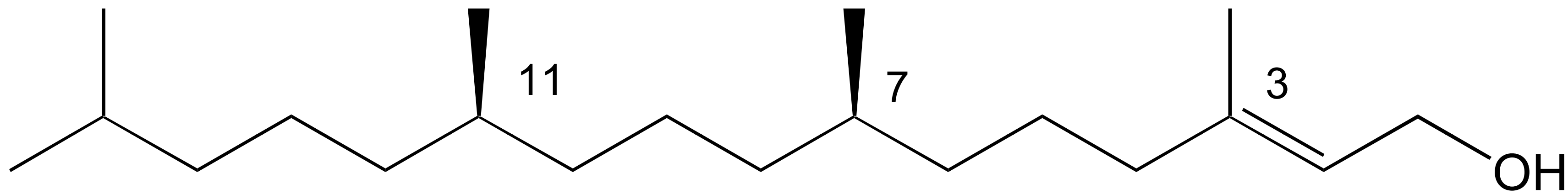
e.g. monoamino monocarboxylic acids and monohydroxy, monocarboxylic acids (Cronin et al. 1993)

Constitutional Isomers



C-atoms	α	β	γ	δ	ε	ζ	unknown
2	***1***, 1, **1**	--	--	--	--	--	--
3	***1***, 1, **1**	***1***, 1, **1**	--	--	--	--	--
4	***2***, 2, **2**	***2***, 2, **2**	***1***, 1, **1**	--	--	--	--
5	***3***, 3, **3**	***6***, 6, **3**	***3***, 3, **3**	***1***, 1, **0**	--	--	**1**
6	***8***, 8, **8**	***12***, 3, **1**	***11***, 4, **0**	***4***, 2 ,**0**	***1***, 1, **0**	--	**2**
7	***18***, 18, **12**	***29***, 0, **0**	***29***, 0, **0**	***20***, 0, **0**	***5***, 0, **0**	***1***, 0, **0**	**2**

Acetogenic Lipids & Polyisoprenoids



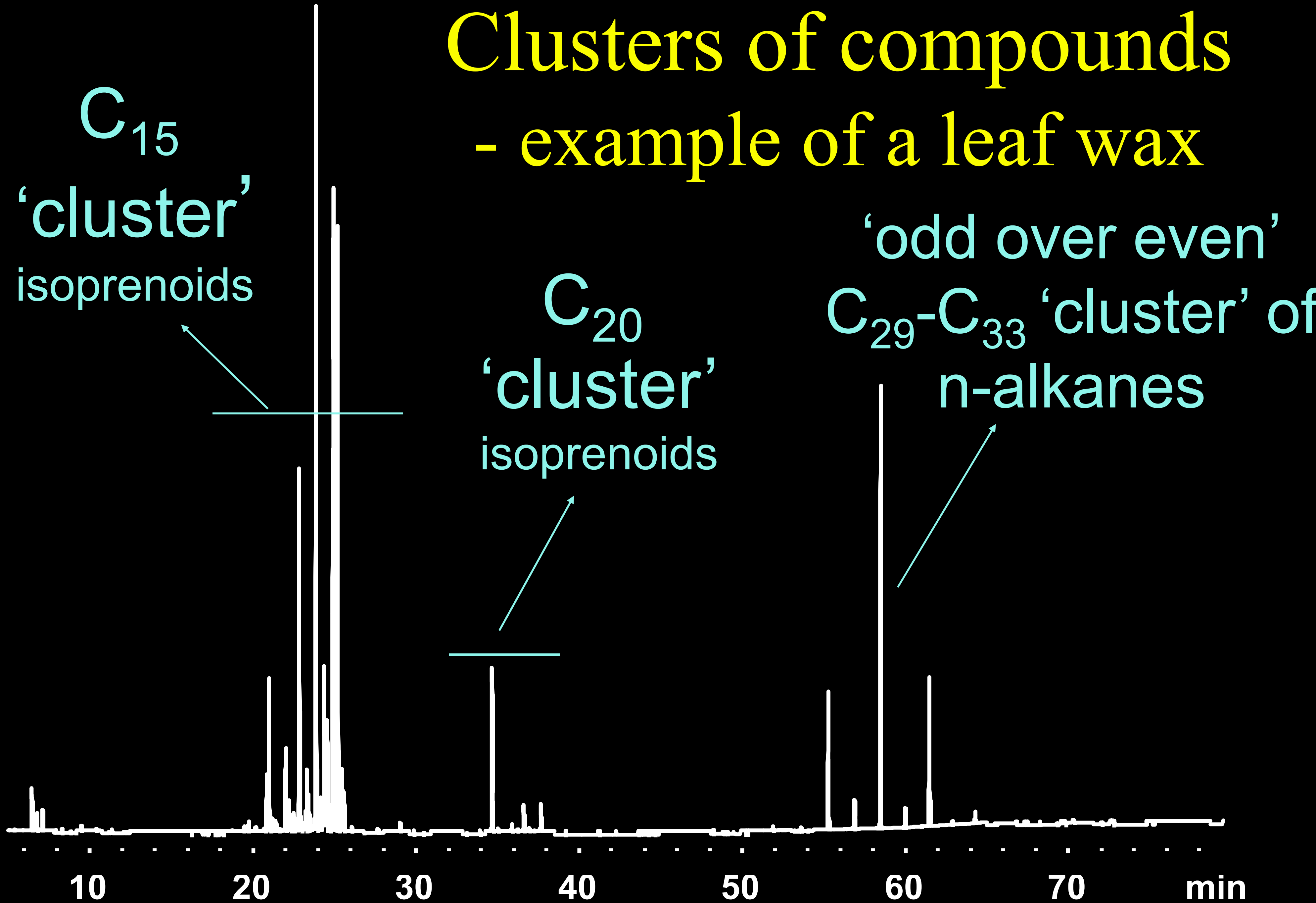
Life makes a limited number of all the possible constitutional isomers because it :

- has evolved 'universal' biochemical pathways
- constructs macromolecules from small, common precursors

(eg 20 amino acids in protein, 4 bases of DNA)

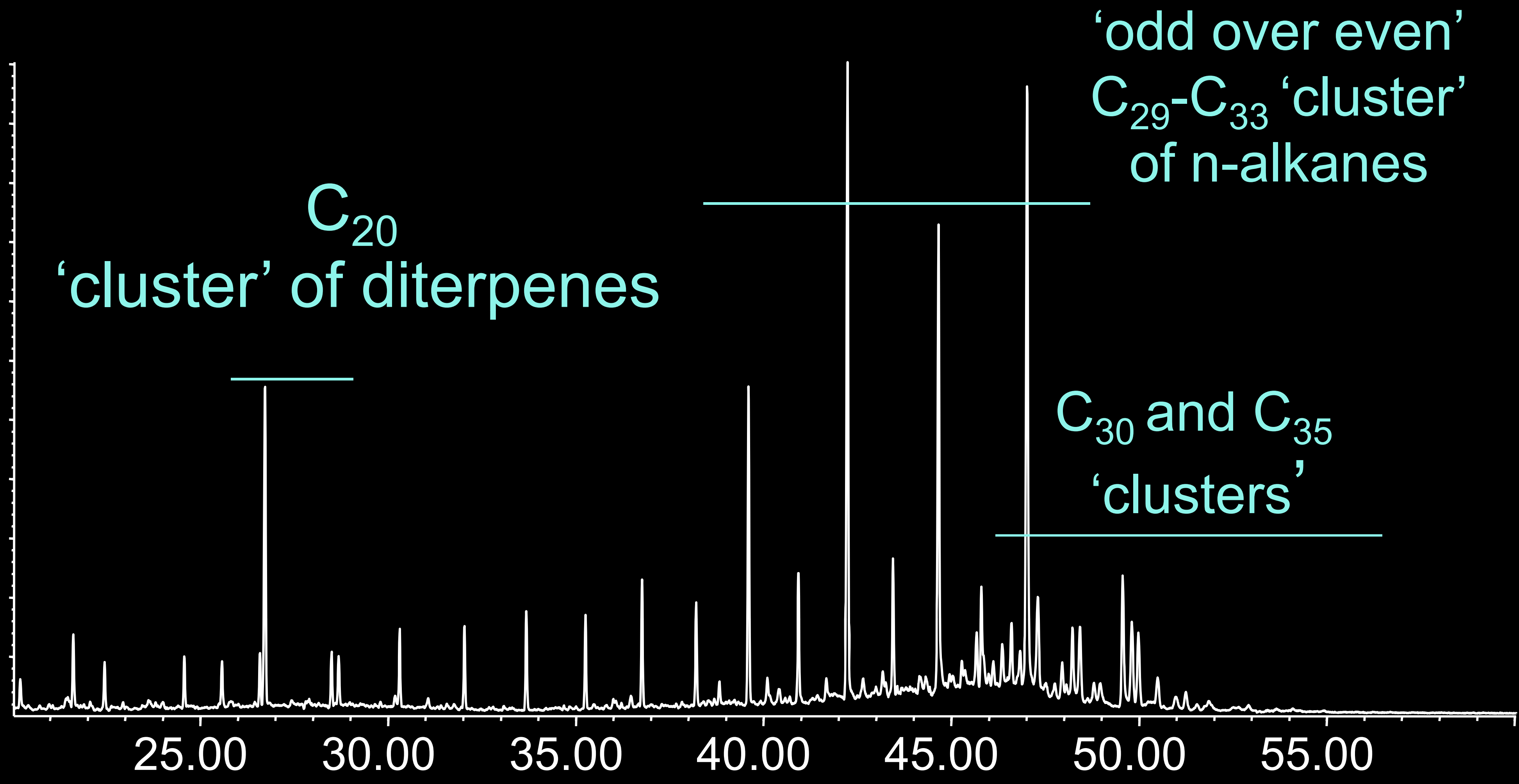
→ → preference for certain carbon numbers (clusters) & systematic isotopic ordering within & between molecules

Clusters of compounds - example of a leaf wax



Clustering is a consequence of universal biochemical pathways

Clusters of Compounds - example of a sediment



NB clustering is 'blurred' by mixed inputs, diagenesis, catagenesis

Isotopic Ordering

Polyisoprenoid lipids

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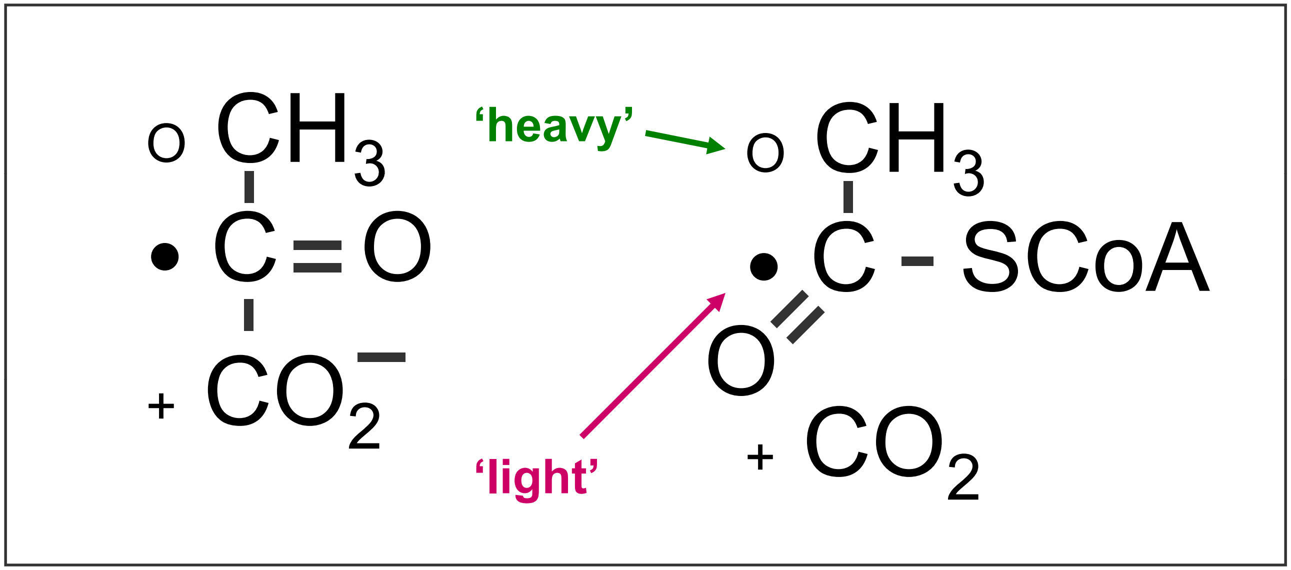
Polymethylenic
= acetogenic lipids

Isotopic ordering is a consequence of the universality of biochemical pathways

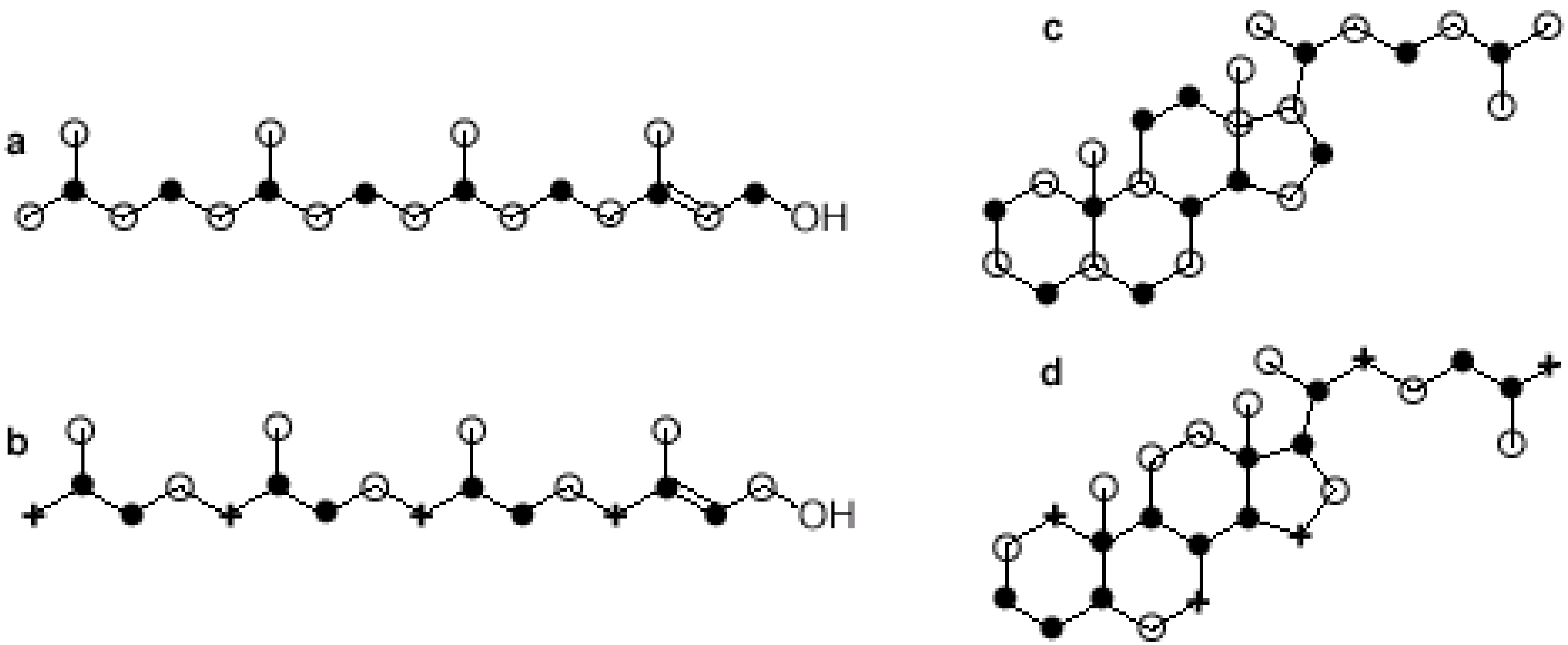
Hayes J. M. (2002) Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. In: *Stable Isotopic Geochemistry*, Valley J. W. and Cole D.R. (eds.) *Reviews in Mineralogy and Geochemistry.*

Acetogenic Lipids



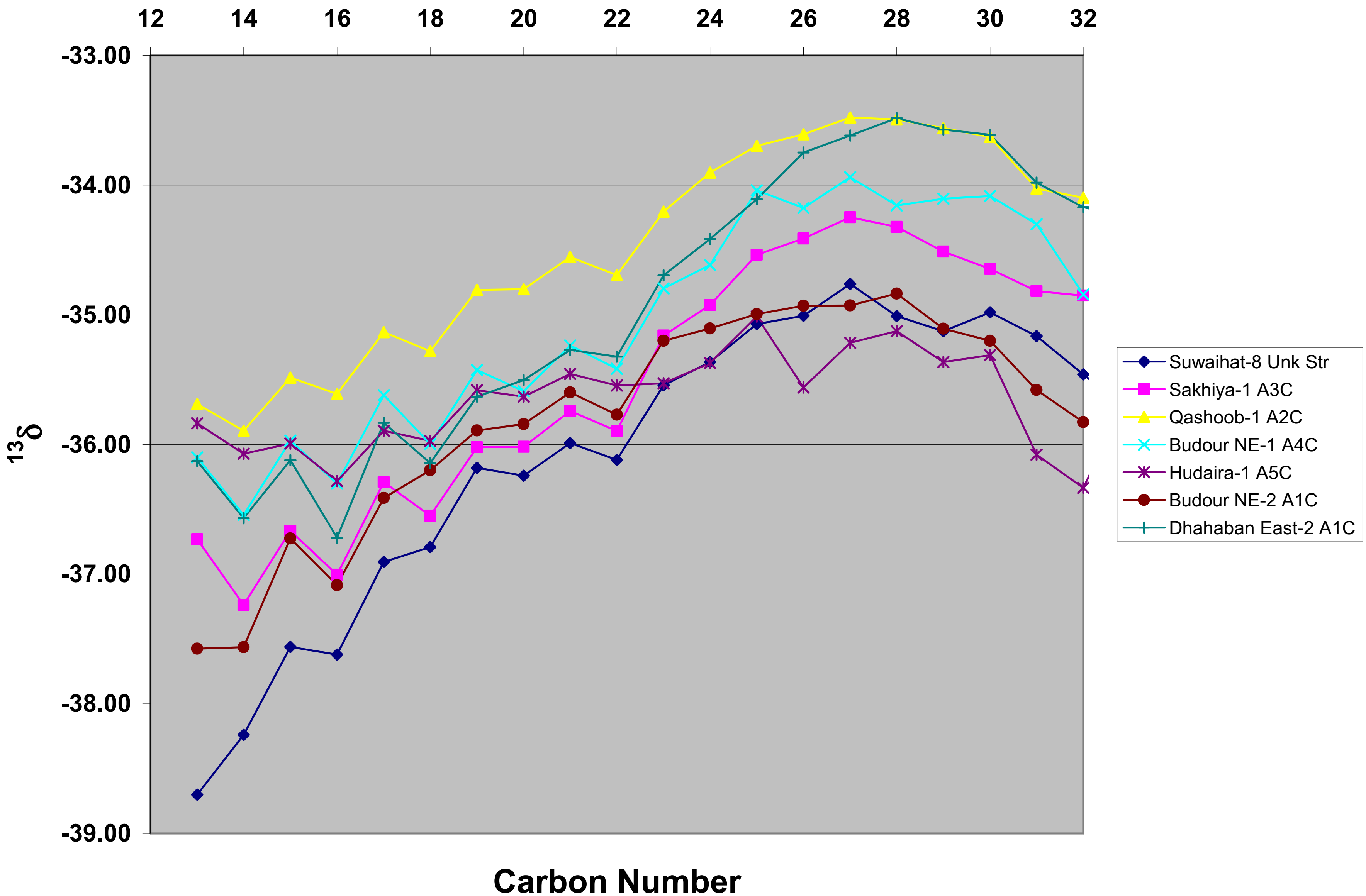
Acetate Methyl-C and Carboxyl-C are isotopically distinct and determined by its metabolic source and the profound isotope effect of pyruvate dehydrogenase

Origin of C-Atoms in Polyisoprenoids & Consequent Isotopic Ordering



Observing this at natural abundance presently a challenge

n-Alkane Carbon Isotopes in Oils



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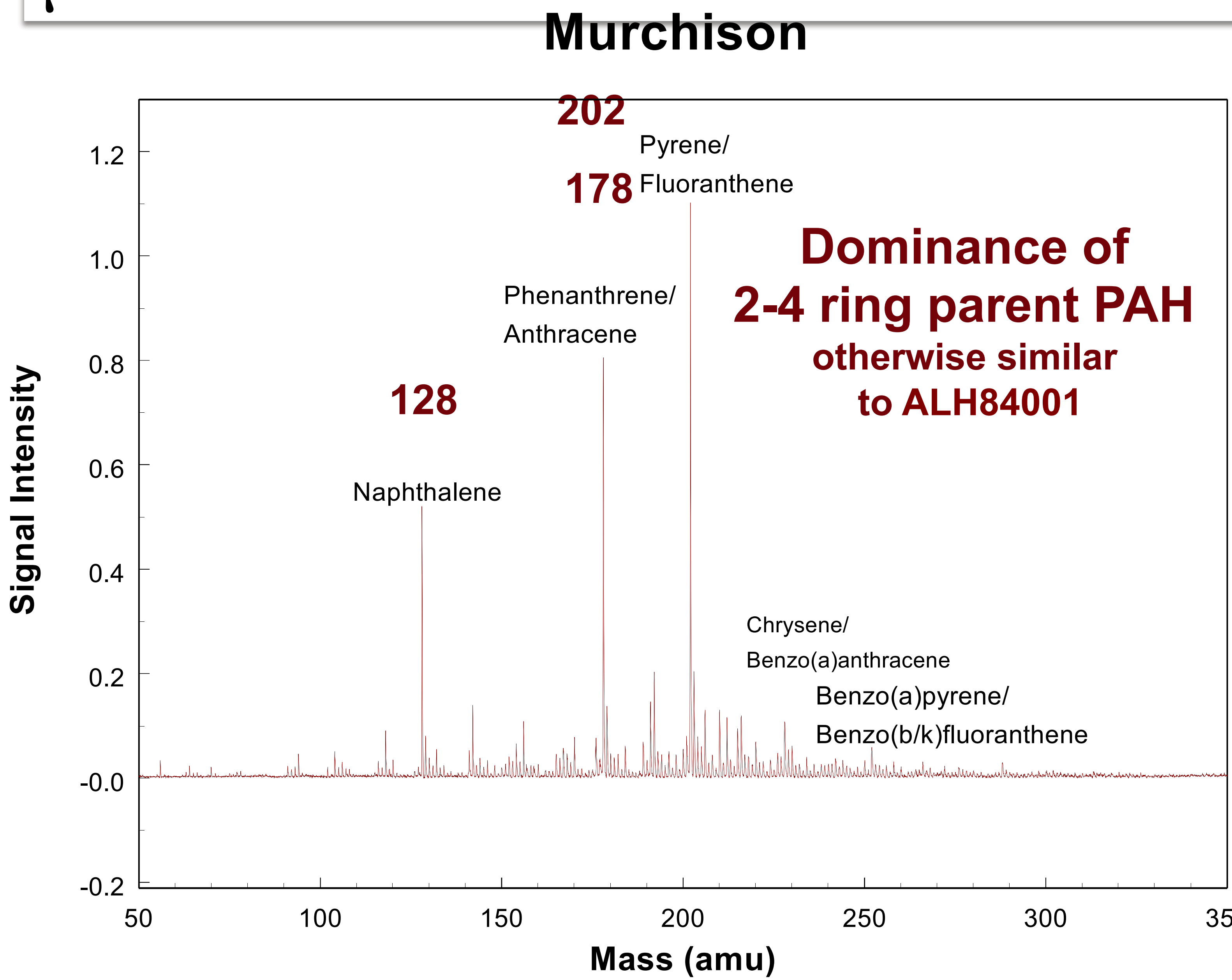
' PAH are abundant as fossil molecules in ancient sedimentary rocks '

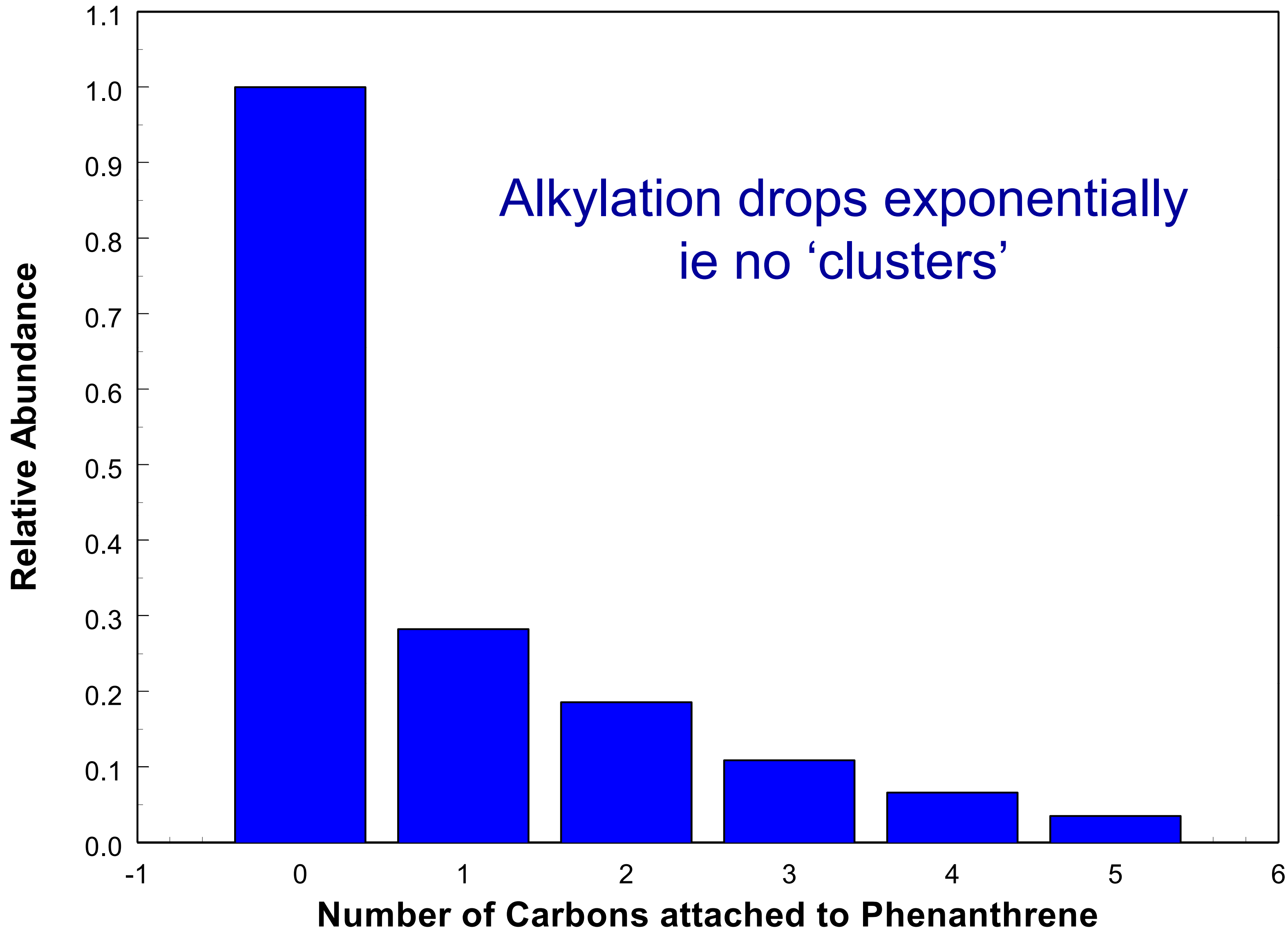
However, PAH are not necessarily biogenic

μL² MS of Murchison Meteorite



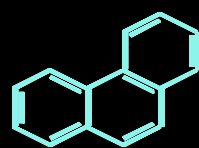
Feb 1, 99

Murchison

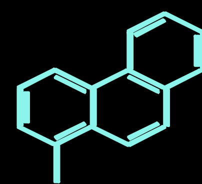


Feb 1, 99

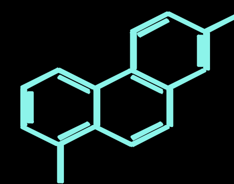
PAH Proposed as molecular fossils ?



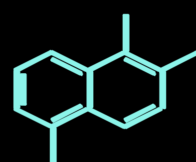
PHENANTHRENE
178



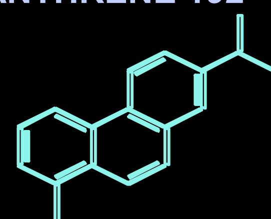
1-METHYL-
PHENANTHRENE 192



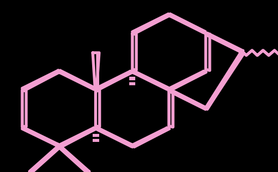
1,7-DIMETHYL-
PHENANTHRENE 206



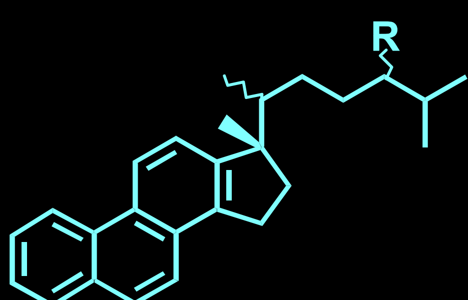
1,2,5-TRIMETHYL-
NAPHTHALENE 156

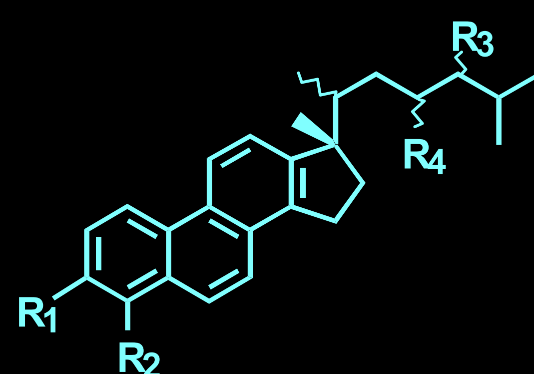


RETENE
234

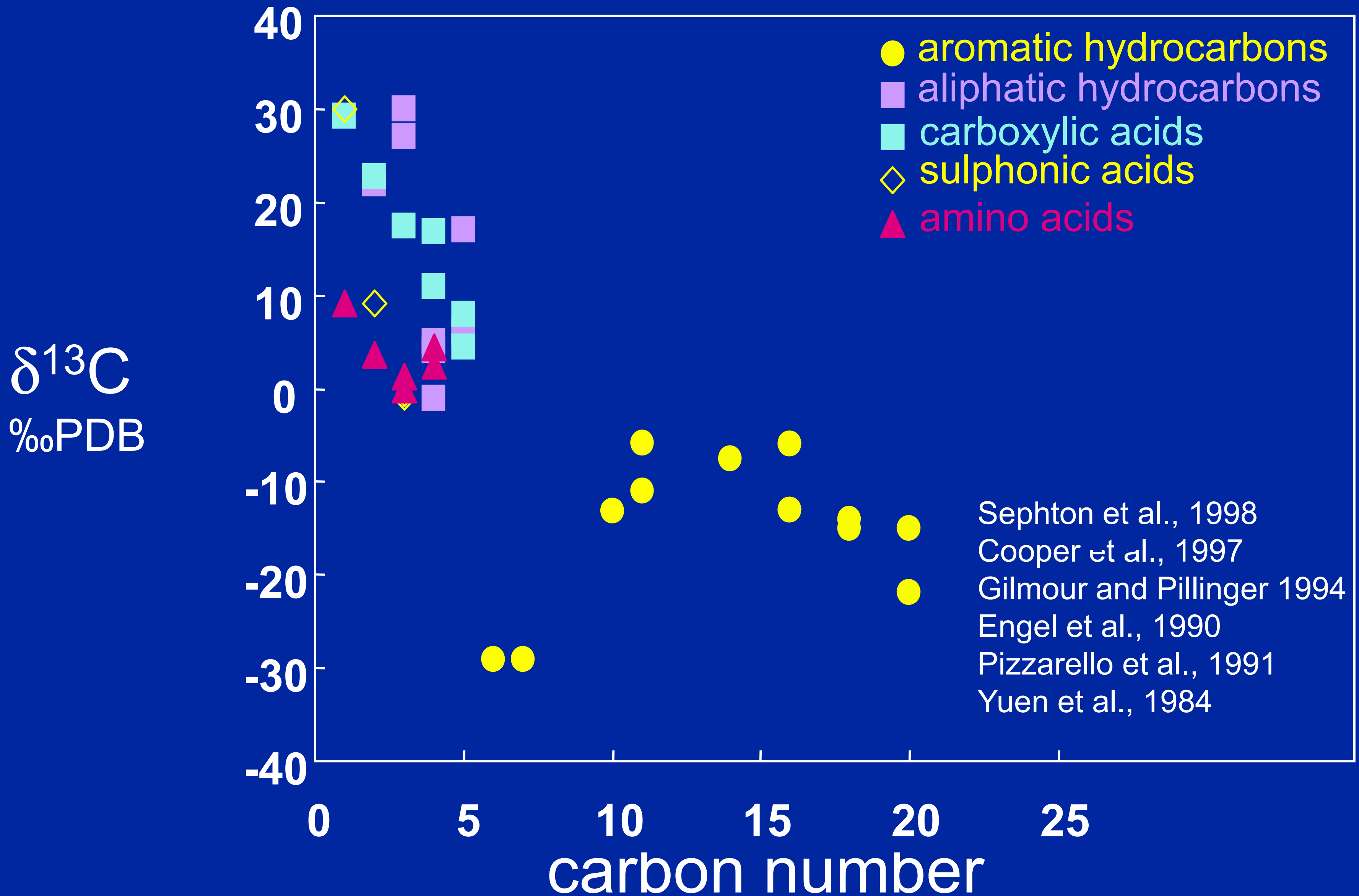


PHYLLOCLADANE





$\delta^{13}C$ Murchison organic compounds

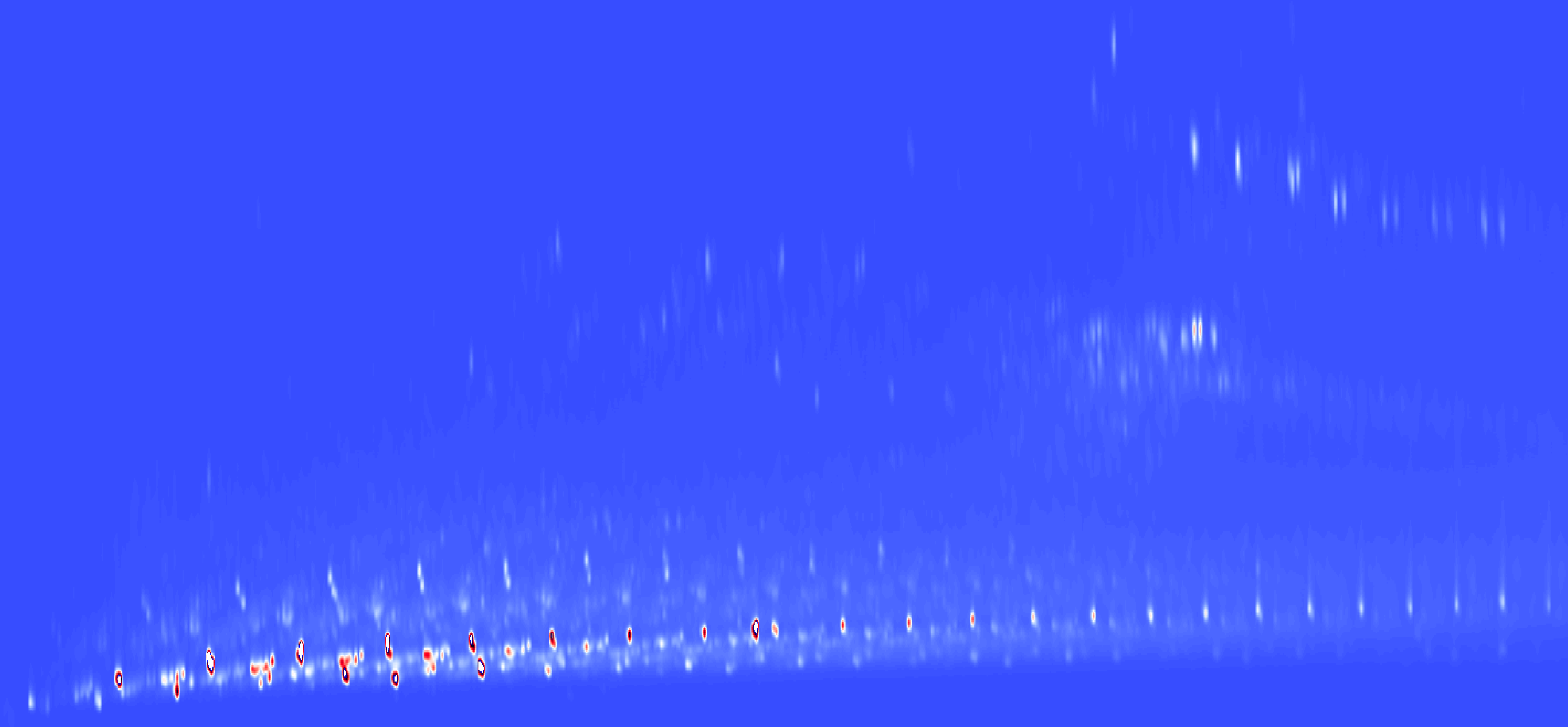


Compilation courtesy of Mark Sephton

Topics

- What are useful criteria for biogenicity?
  How can we be sure of measuring the right thing in a sample on Mars or returned from Mars? Deliberations of the 2000 NASA Biomarker Taskforce – molecular biosignatures
- Analytical methods for investigating molecular biosignatures in rocks from Earth & elsewhere
- New 'technologies' in molecular biosignatures for organisms and ancient environments

OMR017
Buah Fm.



Nelson, Reddy, Freysinger + MIT, unpublished

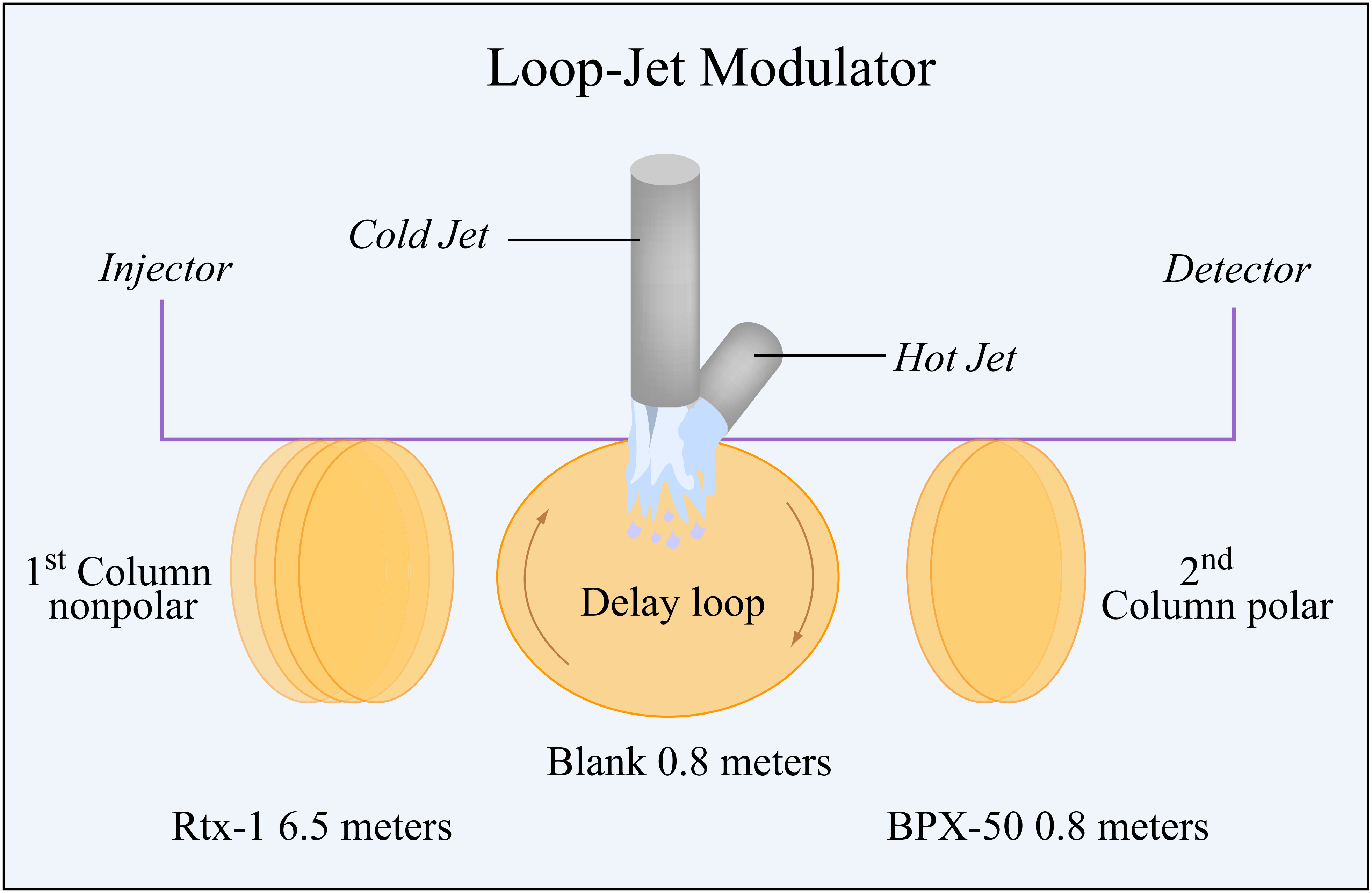
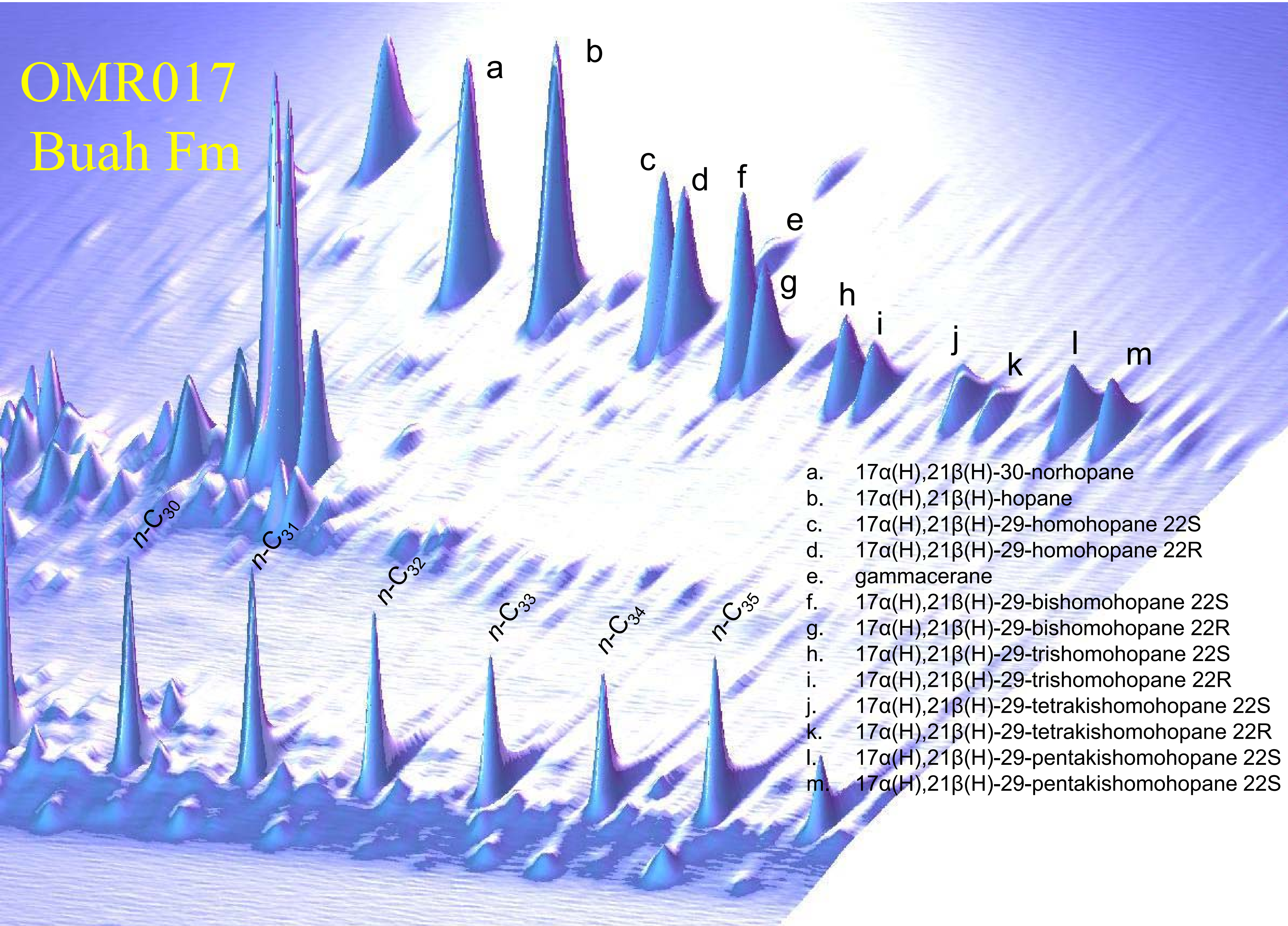
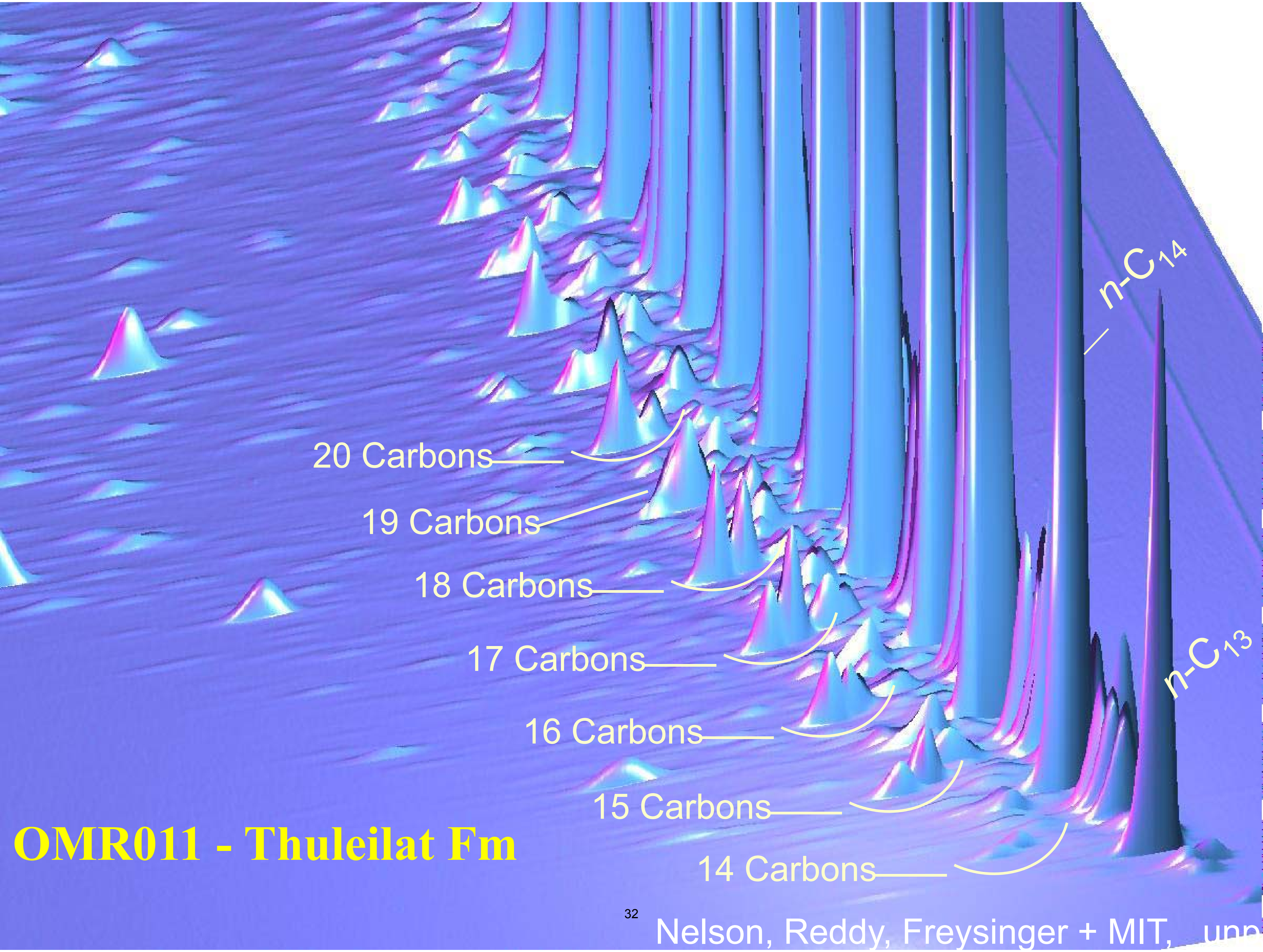


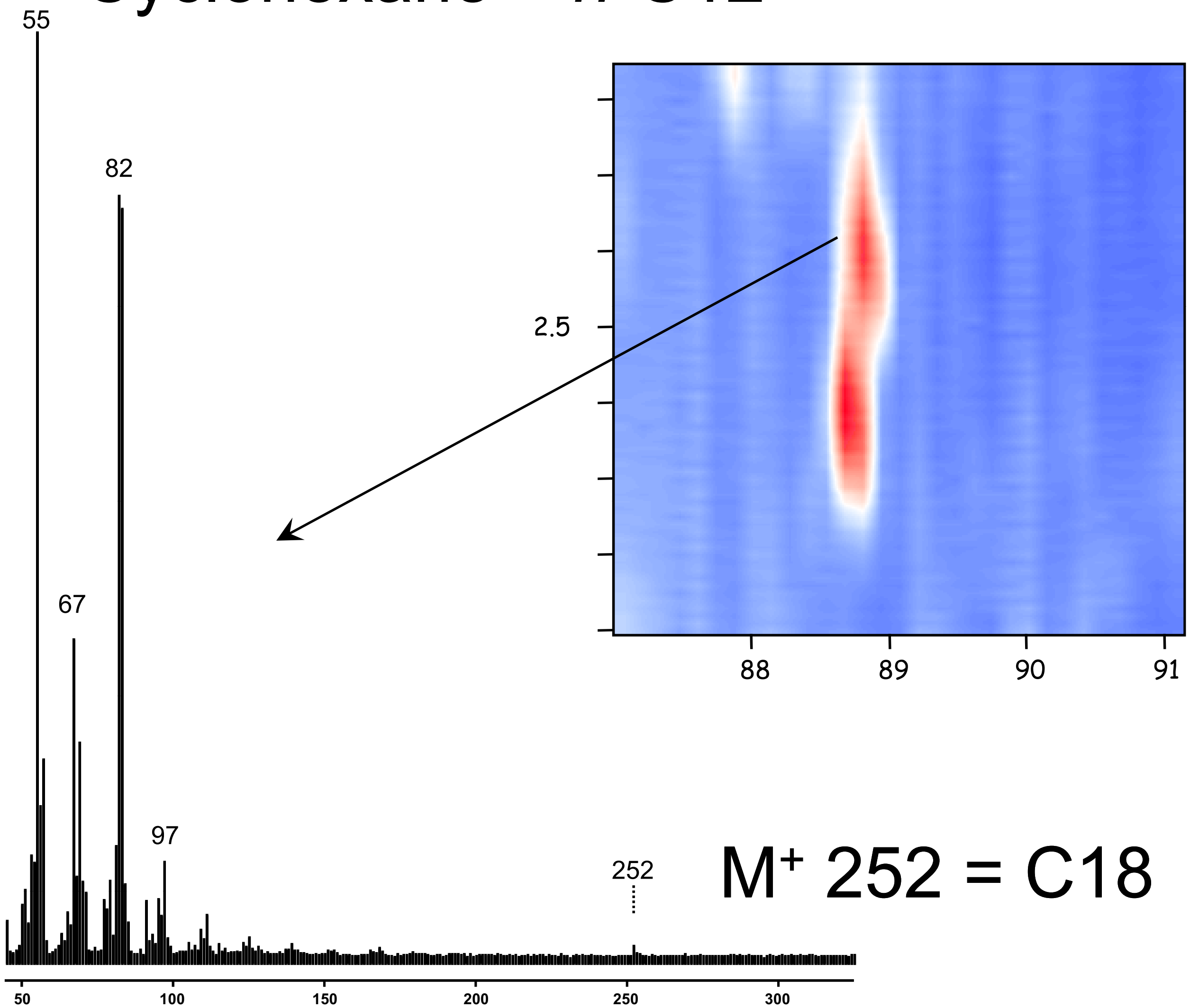
Image by MIT OpenCourseWare.



Nelson, Reddy, Freysinger + MIT, unpu

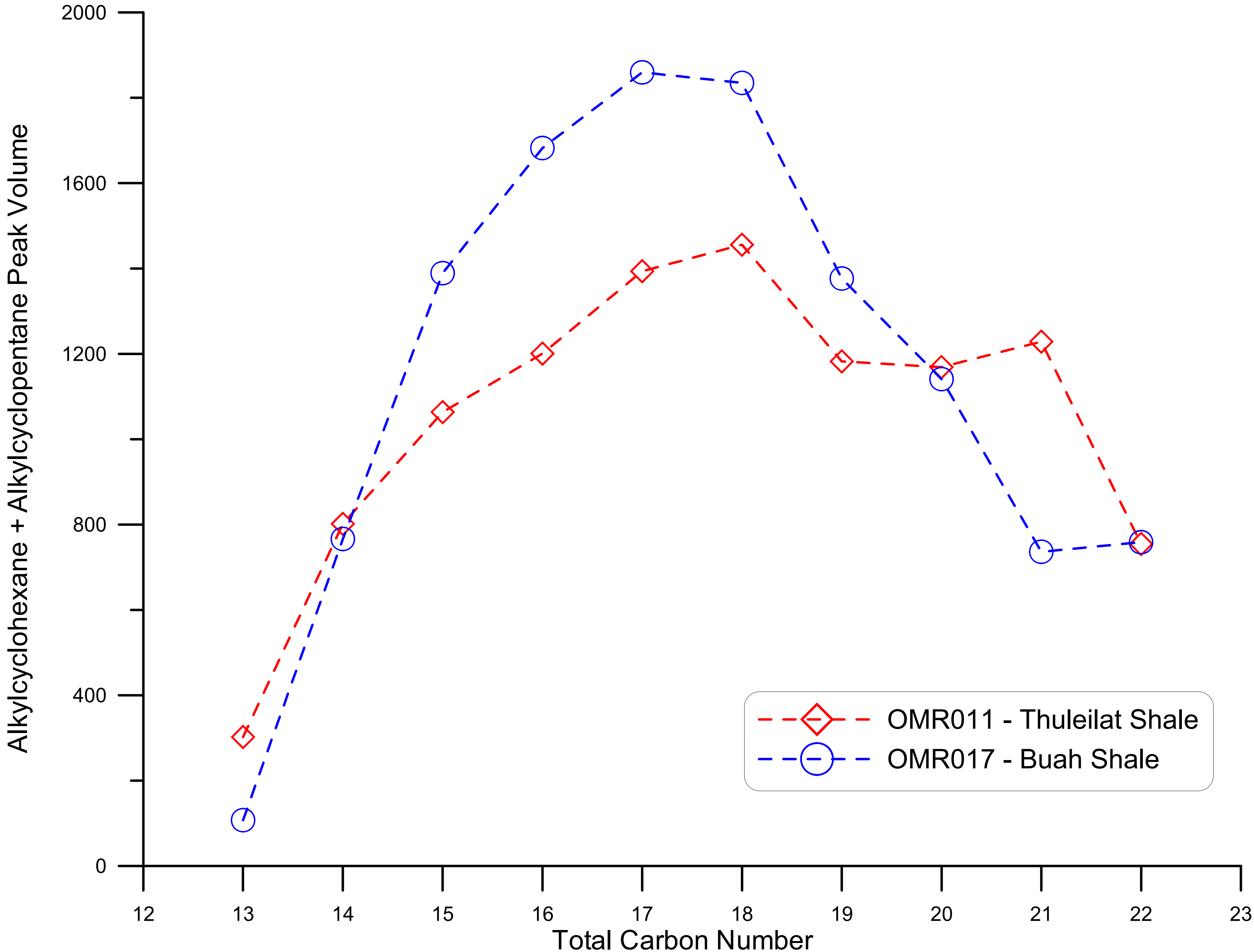

OMR011 - Thuleilat Fm
n-C_{14}
n-C_{13}
20 Carbons
19 Carbons
18 Carbons
17 Carbons
16 Carbons
15 Carbons
14 Carbons
Nelson, Reddy, Freysinger + MIT, unp

Cyclohexane + *n*-C12

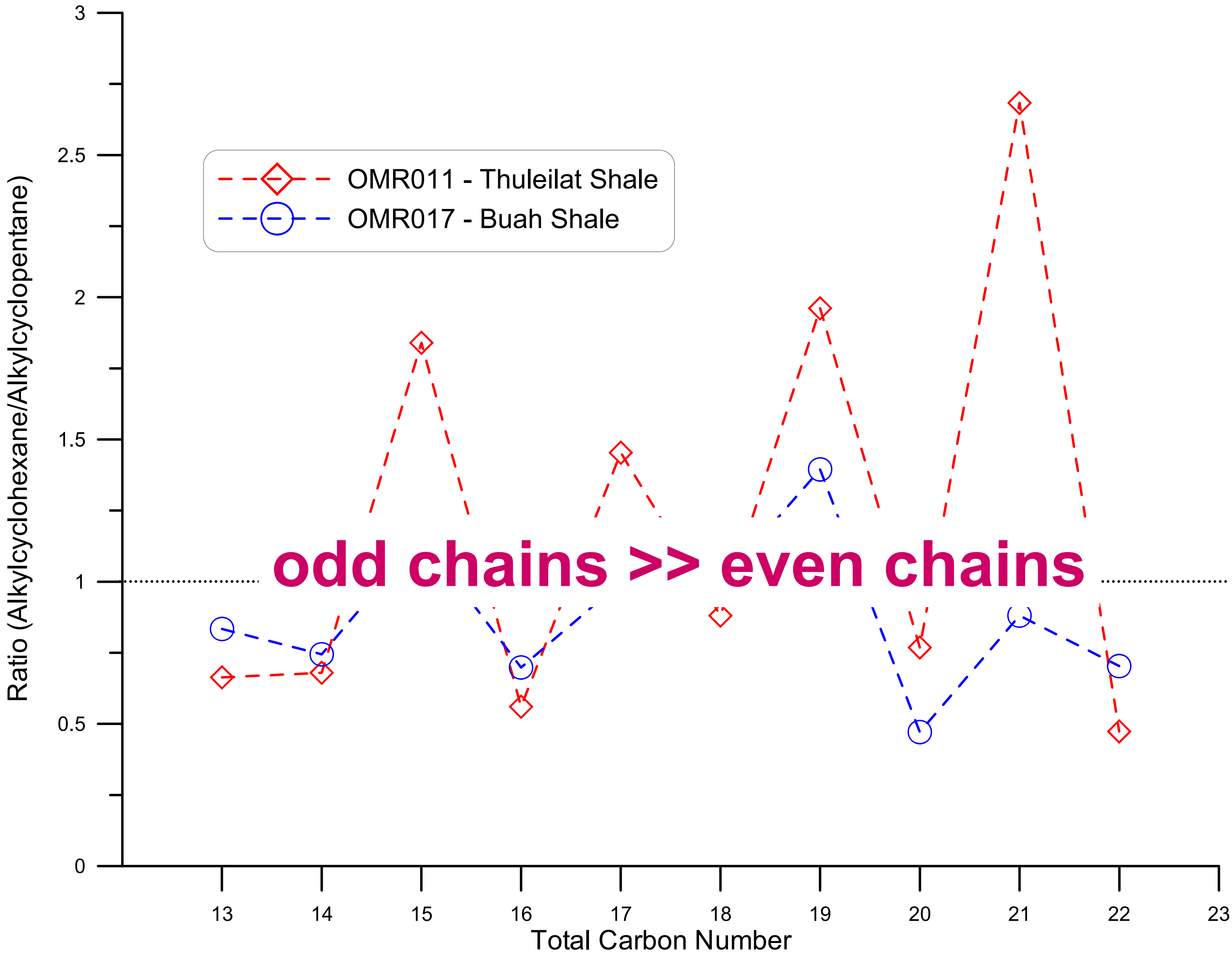


M^+ 252 = C18

Nelson, Reddy, Freysinger + MIT, unpublished



Alkylcyclohexane + Alkylcyclopentane Peak Volume
0
400
800
1200
1600
2000
12
13
14
15
16
17
18
19
20
21
22
23
Total Carbon Number
OMR011 - Thuleilat Shale
OMR017 - Buah Shale



OMR011 - Thuleilat Shale
OMR017 - Buah Shale
odd chains >> even chains
Ratio (Alkylcyclohexane/Alkylcyclopentane)
Total Carbon Number
0
0.5
1
1.5
2
2.5
3
13
14
15
16
17
18
19
20
21
22
23

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  GC^2-TOFMS
  Hydropyrolysis & Strelley Pool C

Biogenic Gases

Mars atmosphere:

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CO_2	95.3%
N_2,	2.7%
Ar	1.6%
CO	0.07%
O_2	0.13%
H_2O	0-300 ppm

CH_4 ppb → seasonally and spatially variable

(Mumma et al., Science 323, 1041, 2009)

Taphonomy - Preservation Windows

Biosignature taphonomic window	Confidence in context	How this informs about potential biosignature preservation
atmospheric gases	exceptional	predictable via chemical modeling
crystalline sedimentary mineral entrainment of organic compounds	very high	can deduce formation mechanism and subsequent history
biofabric lithification	very high	can deduce history from lithology & stratigraphic relationships
body fossil preservation	very high	can deduce history from lithology and stratigraphic relationships
mineral replacement of body fossil	high	can deduce from mineralogy

Taphonomy: The Role of Sediment Lithology

OM preservation by physical protection (Hedges, Keil, Mayer 1990s)

Data for coastal sediments:
C = clay
L= silt
S = sand
B= bulk

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Organic matter concentrations strongly correlate with mineral surface area (or small clay particles). As degradation proceeds an increasingly large fraction of the remaining organic matter is protected by its association with mineral surfaces .

Hedges and Keil, 1995

Biosignature Formation & Preservation

Table 3:

						ID by remote sensing			
Martian context --> Early Mars Environment	**Support Biotic C formation**	**Support for Abiotic C formation**	**Support Carbon Conc**	**Support Preservation**	**Potential for Recent Exhumation**	**geomorphic**	**mineralogic**	**stratigraphic**	**ID by MSL**
Hydrothermal (<100C) subsurface	mod	mod (F/T)	low	mod	low	mod	mod-high	n/a	high
Hydrothermal (<100C) surface	high	low	mod-high	mod	mod	high	mod-high	low	high
Aeolian sediments (sand)	low	low	low	low	low	high	n/a	mod	high
altered aeolinites (dust)	very low	low	low	low	low	low	n/a	n/a	high
Fluvial channel	low	low	low	low	high	high	n/a	high	high
Fluvial floodplain	low-mod	low	mod	mod	possible	high	n/a	high	high
alluvial fan	low	low	low	low	low	high	n/a	high	high
Deltaic	high	low	high	high	low	high	n/a	high	high
Lacustrine (perennial)	high	low	high	high	high	mod	mod	mod	high
Lacustrine (evaporitic) (Cl)	med	low	high	high-very high	high	mod	high	mod	high
Lacustrine (evaporitic) (SO4)	low	low	high	high-very high	high	mod	high	mod	high
Regional Groundwater pore system	low	low	low	low	high	n/a	n/a	n/a	mod
Glacial deposits	low	low	low	low	high	high	n/a	low	high
permafrost	low	low	low	mod	mod	high	n/a	n/a	high
soil (surface fines chemically altered by atmosphere)	low	low	low	low	low	n/a	n/a (albedo and TI)	n/a	high
Pyroclastic Deposits (unaltered)	low	low	low	low	low	mod	low	high	high
Volcanic flows	very low	low	low	low	low	high	high	mod	high
Regolith/Fractured Bedrock (not soil)	low	low	low	low	low	high	n/a	n/a	high

Biosignature Formation Processes

Table 3:

						ID by remote sensing			
Martian context --> Early Mars Environment	**Support Biotic C formation**	**Support for Abiotic C formation**	**Support Carbon Conc**	**Support Preservation**	**Potential for Recent Exhumation**	**geomorphic**	**mineralogic**	**stratigraphic**	**ID by MSL**
Hydrothermal (<100C) subsurface	mod	mod (F/T)	low	mod	low	mod	mod-high	n/a	high
Hydrothermal (<100C) surface	high	low	mod-high	mod	mod	high	mod-high	low	high
Aeolian sediments (sand)	low	low	low	low	low	high	n/a	mod	high
Fluvial channel	low	low	low	low	high	high	n/a	high	high
Fluvial floodplain	low-mod	low	mod	mod	possible	high	n/a	high	high
Deltaic	high	low	high	high	low	high	n/a	high	high
Lacustrine (perennial)	high	low	high	high	high	mod	mod	mod	high

Biosignature Formation Processes

						ID by remote sensing			
Martian context --> Early Mars Environment	**Support Biotic C formation**	**Support for Abiotic C formation**	**Support Carbon Conc**	**Support Preservation**	**Potential for Recent Exhumation**	**geomorphic**	**mineralogic**	**stratigraphic**	**ID by MSL**
Hydrothermal (<100C) subsurface	mod	mod (F/T)	low	mod	low	mod	mod-high	n/a	high
Hydrothermal (<100C) surface	**high**	**low**	**mod-high**	**mod**	**mod**	**high**	**mod-high**	**low**	**high**
Aeolian sediments (sand)	low	low	low	low	low	high	n/a	mod	high
Fluvial channel	low	low	low	low	high	high	n/a	high	high
Fluvial floodplain	low-mod	low	mod	mod	possible	high	n/a	high	high
Deltaic	**high**	**low**	**high**	**high**	**low**	**high**	**n/a**	**high**	**high**
Lacustrine (perennial)	**high**	**low**	**high**	**high**	**high**	**mod**	**mod**	**mod**	**high**

Lost City Hydrothermal Field

Vent Fluids

This image has been removed due to copyright restrictions.

Hydrogen – up to 15 mmol/kg

Methane – up to 2 mmol/kg

Calcium – up to 30 mmol/kg

pH – 9 to 11

Low temp volatile production: Proskurowski et al., Chem. Geology 2006

Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field: Proskurowski et al., Science 2006

Amend, Hoehler, McCollom AbSciCon 2010

$^{13}\delta$ LC methane suggests it is abiogenic

Available online at www.sciencedirect.com

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Extraordinary ^{13}C enrichment of diether lipids at the Lost City Hydrothermal Field indicates a carbon-limited ecosystem

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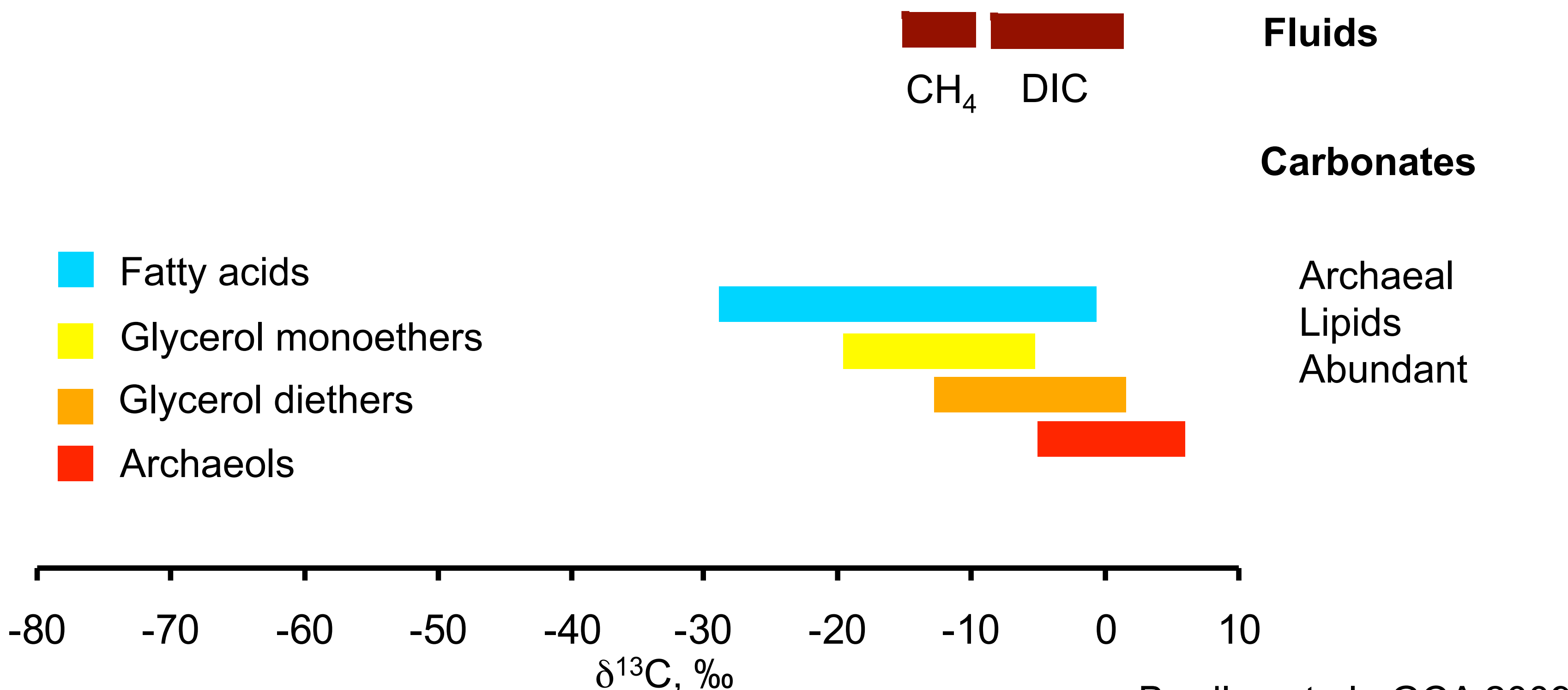
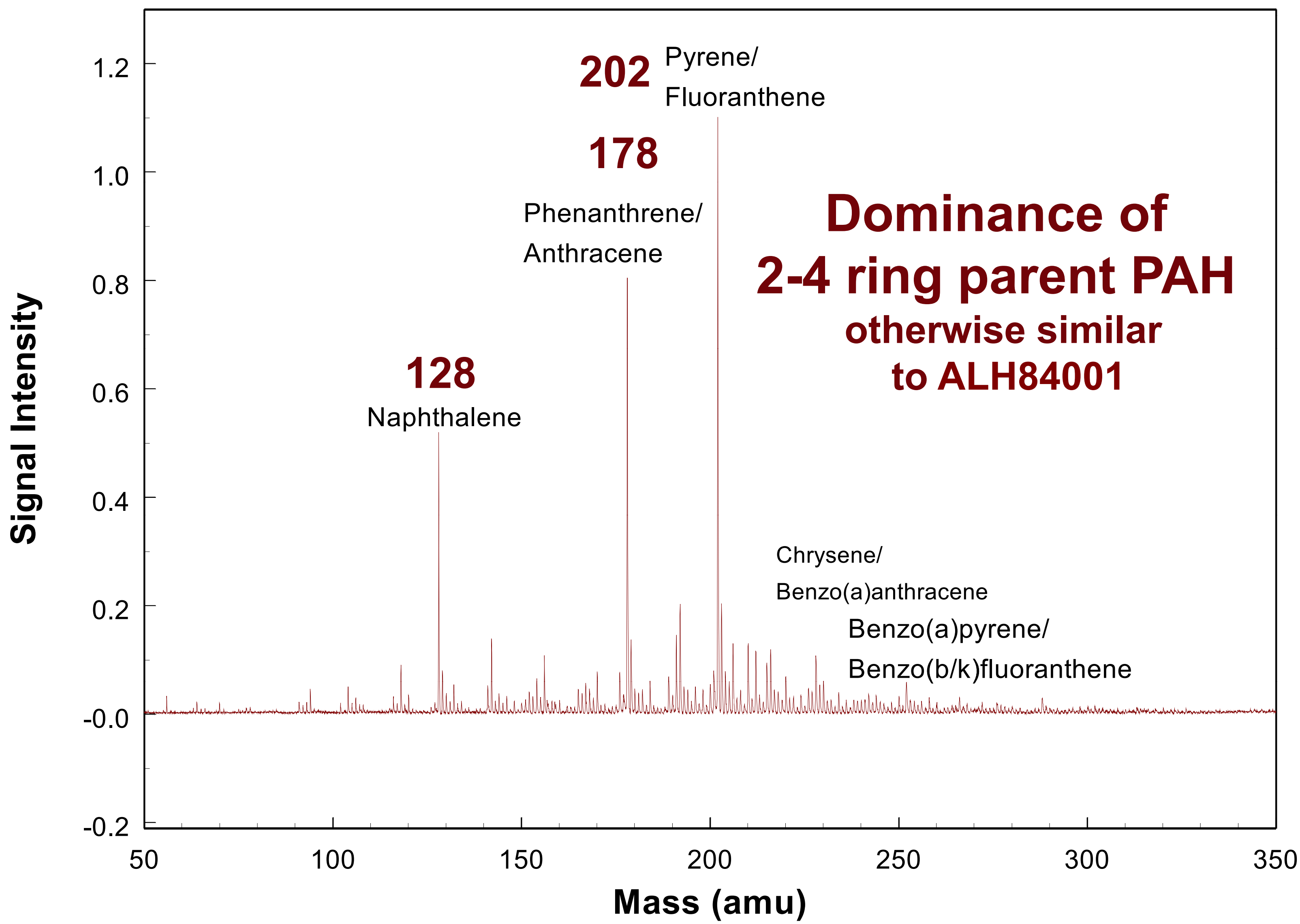
$^{13}\delta$ LC methane suggests it is abiogenic

Structure & $\delta^{13}C$ LC lipids show methane production is also biological



Bradley et al., GCA 2009

Murchison



Feb 1, 99

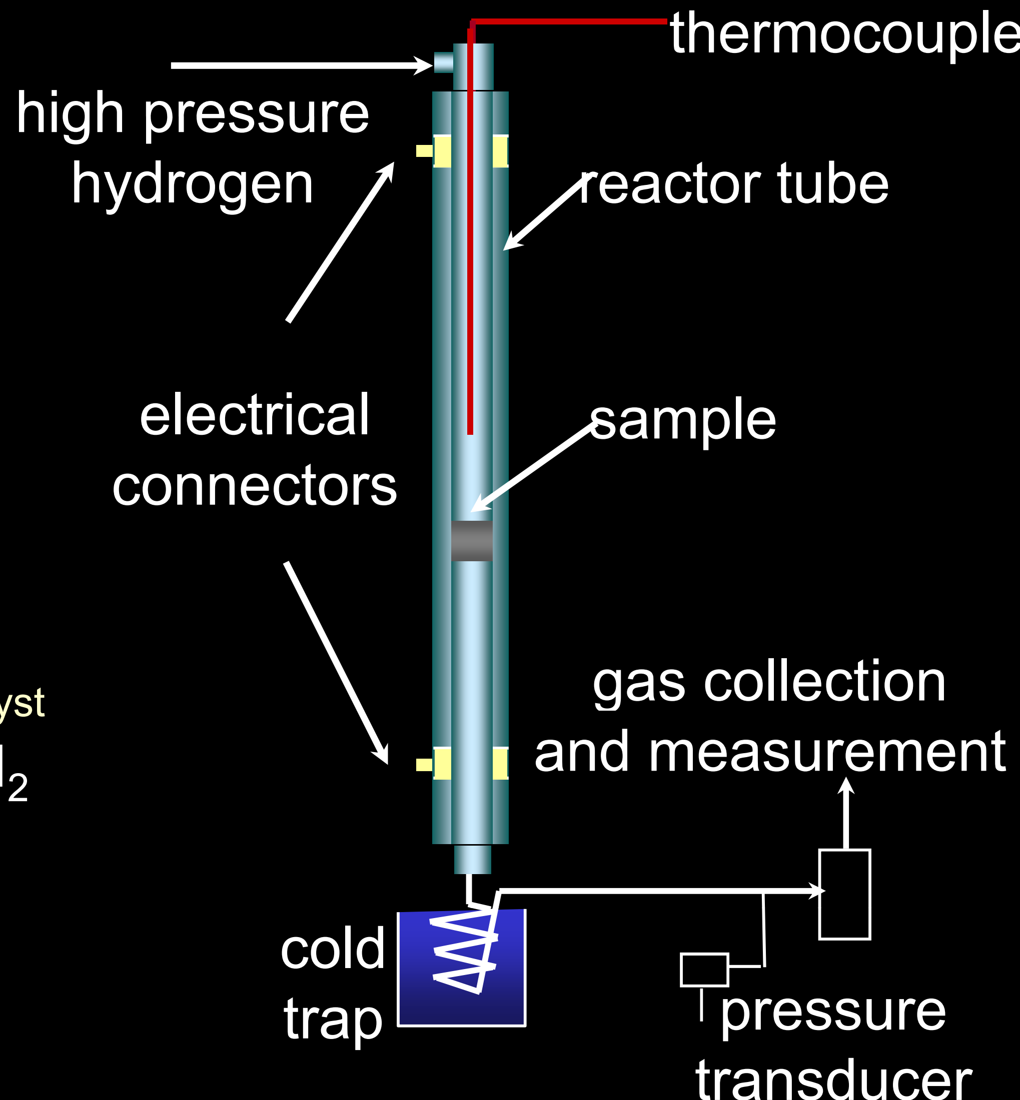
Topics

- What are useful criteria for biogenicity?
  How can we be sure of measuring the right thing in a sample on Mars or returned from Mars? Deliberations of the 2000 NASA Biomarker Taskforce – molecular biosignatures
- Analytical methods for investigating molecular biosignatures in rocks from Earth & elsewhere
  GC^2-TOFMS
- New ‘technologies’ in molecular biosignatures for organisms and ancient environments

Hydropyrolysis (H_2)

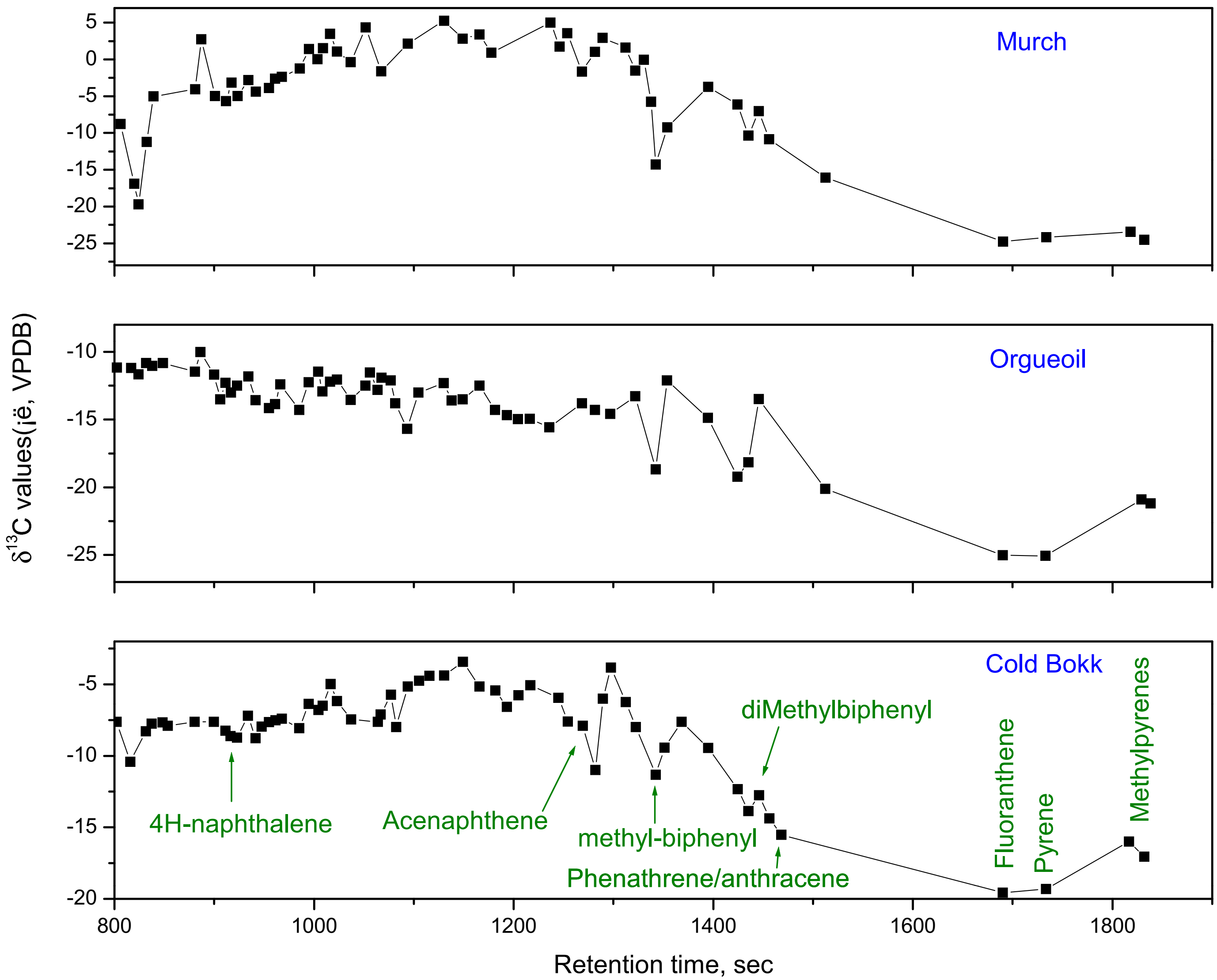
Murchison

- sample impregnated
  - ammonium dioxydithiomolybdate
  - decomposes above 250 °C to catalyst
- continuous high flow of H_2
- heated 220 to 520 ºC
- dry ice trap
- dichloromethane

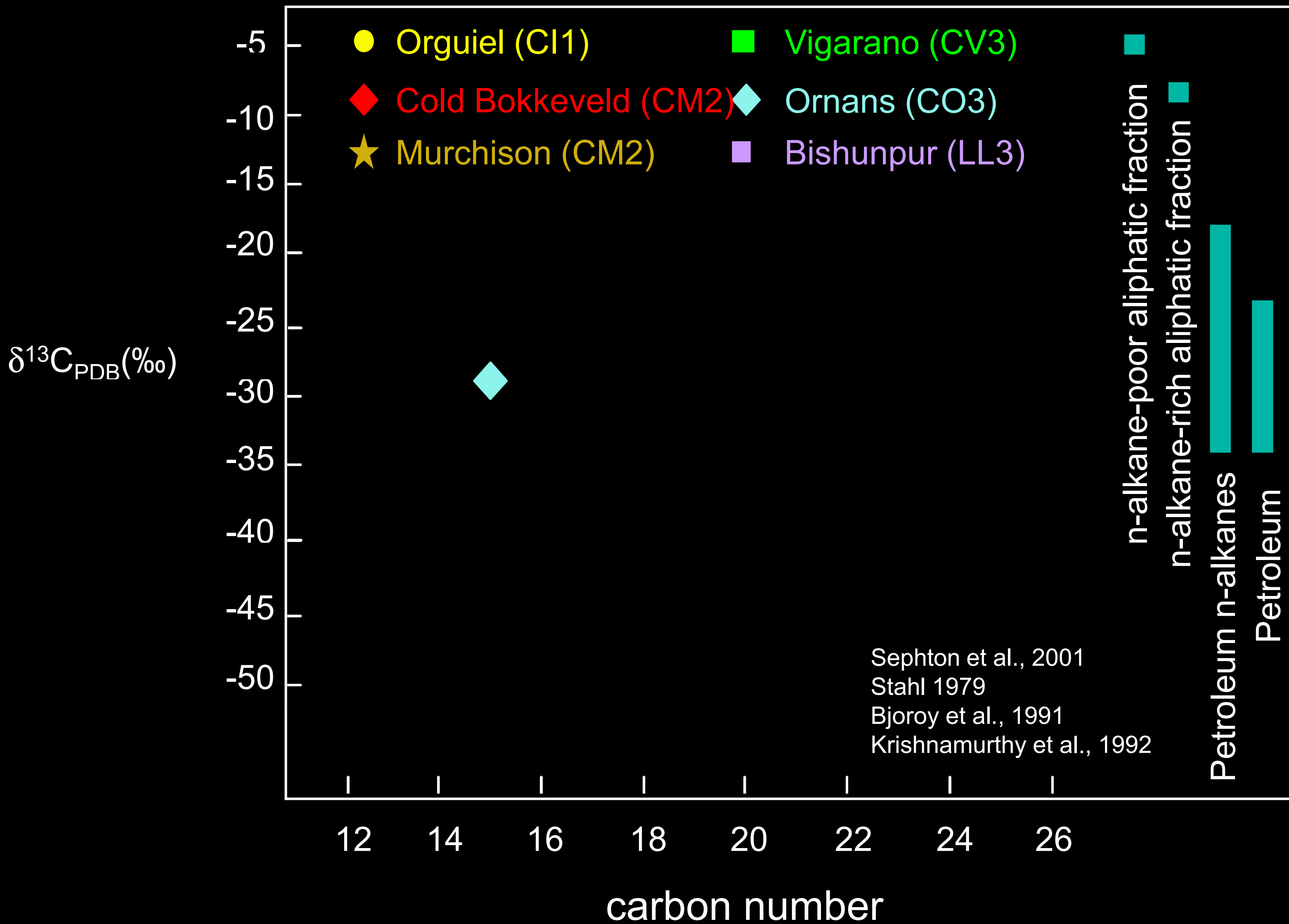


Hydropyrolysis facilitates breakdown of macromolecules & minimises rearrangement

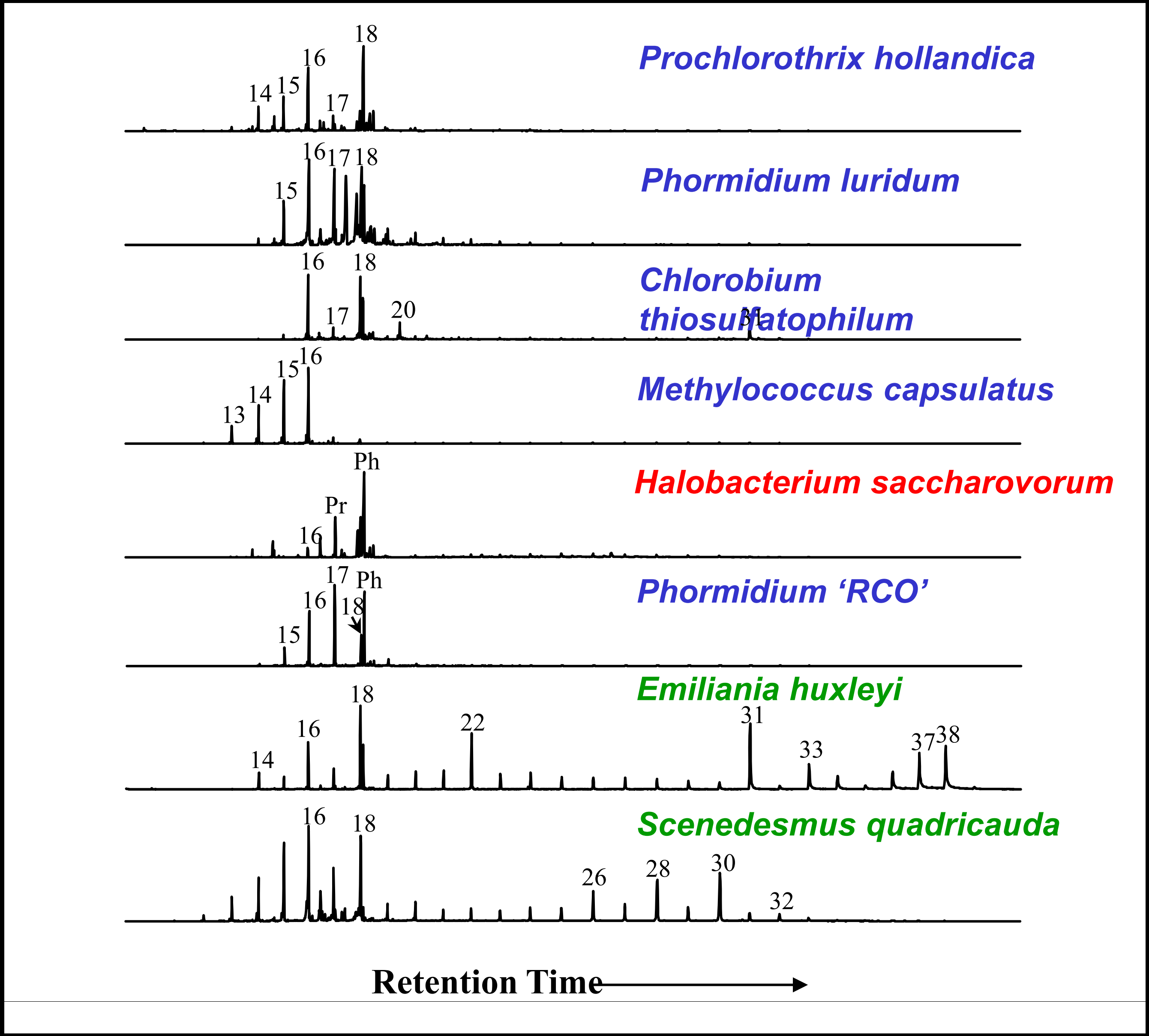
$\delta^{13}C$ profiles for HyPy products of 3 meteorites



$\delta^{13}C$ n-Alkanes in Meteorites



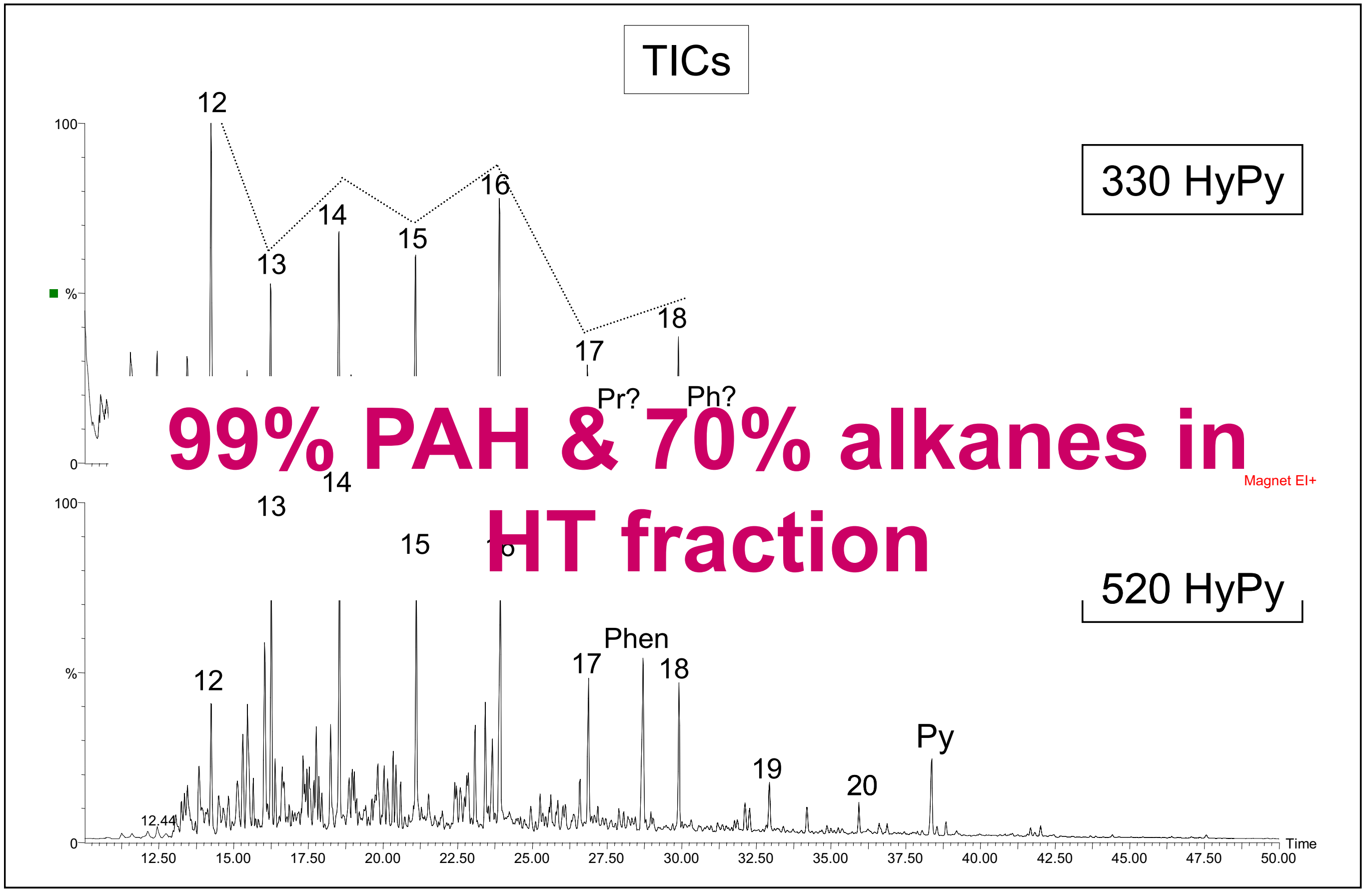
Microbes: Comparison of alkyl chain lengths (*m/z* 85)



- bacteria
- archaea
- algae

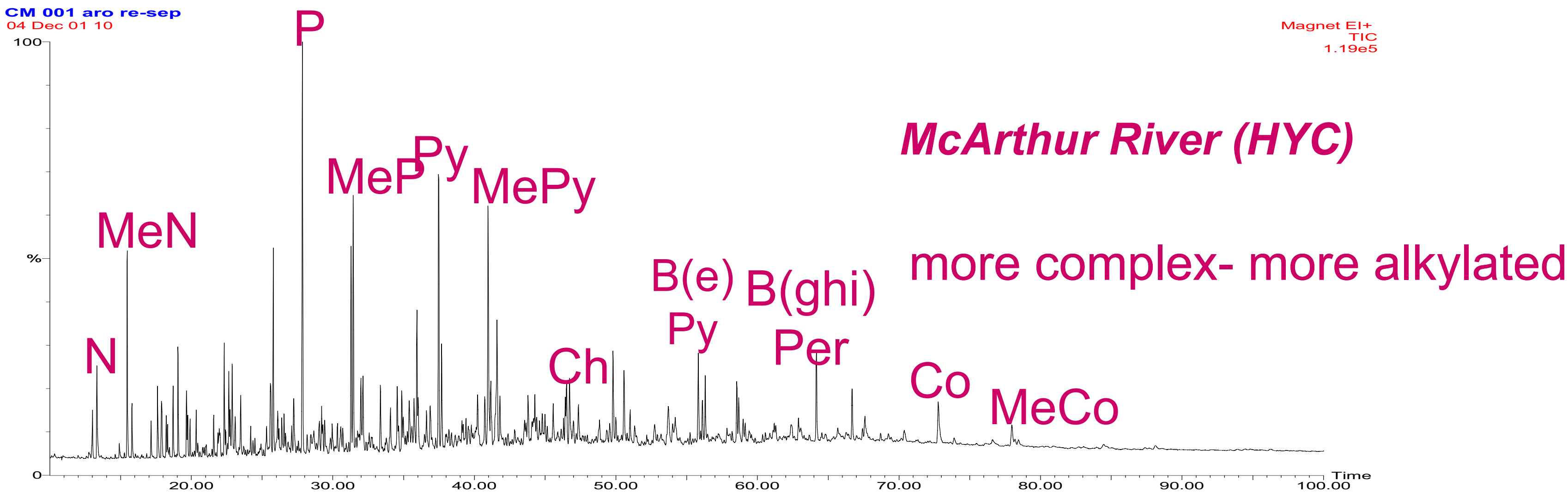

black chert veins and clasts
Complex 'Dyke' Breccia

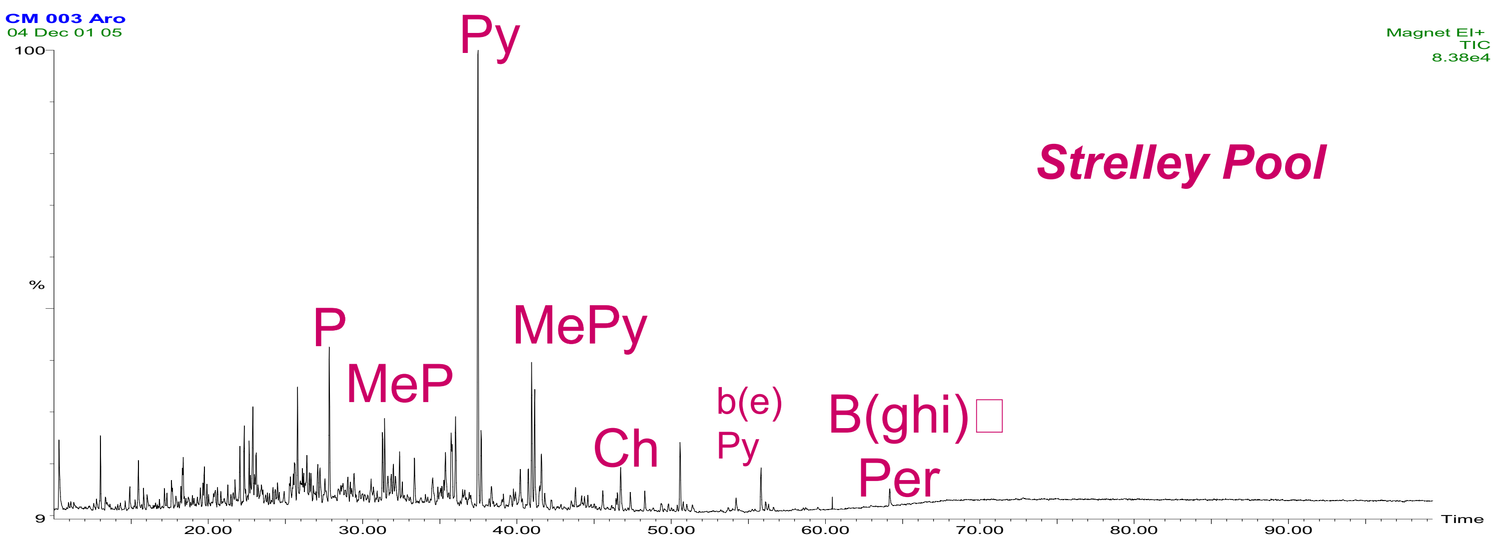
SPC 16 Kerogen sequential HyPy



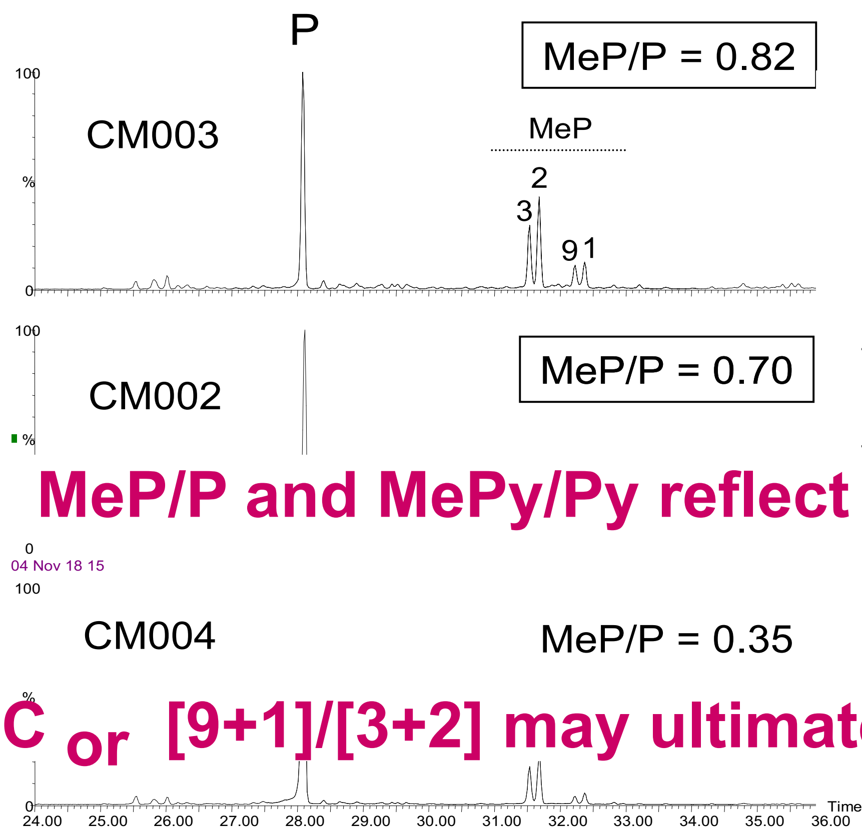
Small EOP of n-alkanes in low T fraction probably indicates some younger contamination e.g. produced from reduction of even C no. fatty acids.

Distribution of aromatic hydrocarbons from HyPy

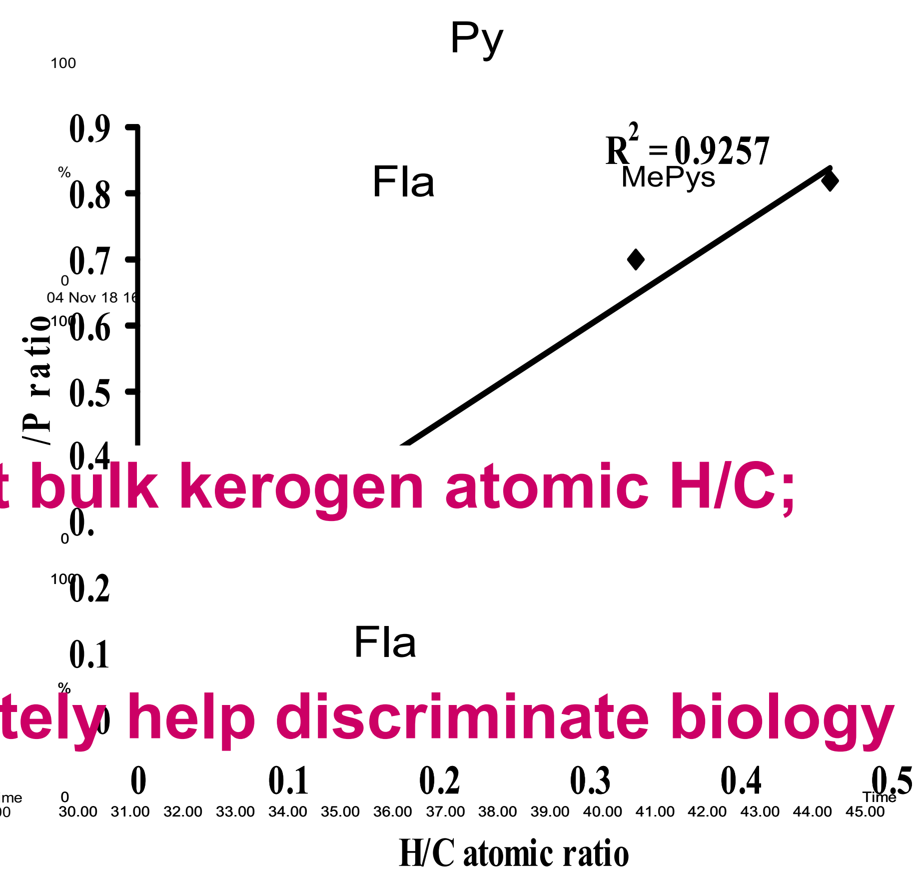




m/z 178+192



m/z 202+216



MeP/P and MePy/Py reflect bulk kerogen atomic H/C;

$\delta^{13}C$ or [9+1]/[3+2] may ultimately help discriminate biology

P = phenanthrene
MeP = methylphenanthrenes

Fla = fluoranthene
Py = pyrene
MePy = methylpyrenes

Concluding Thoughts

1. Organic compounds made by terrestrial organisms have generic structural & isotopic traits. Searching for these features in extraterrestrial OM is a sound approach to life detection.

2. Terrestrial sediments as old as 2700Ma contain an abundance of 'molecular biosignatures'. Lipid biosynthetic pathways are of great antiquity & there is no evidence for there having been alternative pathways or extinct pathways.

3. Hydrocarbons are robust and, of all compound classes, are likely to be preserved under harsh conditions so long as they are sterile. Emerging technologies such as mu ltidimensional GC and GC-TOF are useful analytical tools.

4. Hyropyrolysis assists screening for biosignatures in macromolecular OM and biomass