

12.158 Lecture 10

Molecular Biosignatures:

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

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



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

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

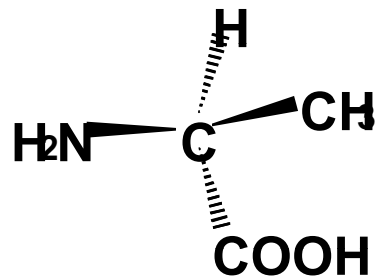
Organic acids and diacids, amino acids, hydroxy acids, alcohols, amines

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

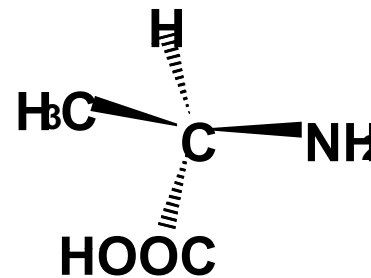
Intrinsic Characteristics (Patterns) of Terrestrial Molecular Biosignatures

- 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, $\delta^{13}\text{C}$) 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)

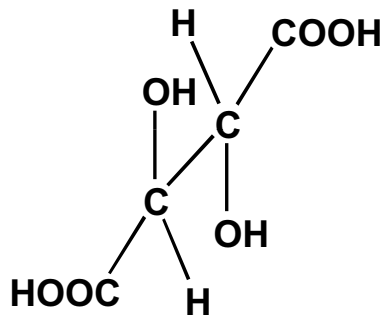
Non-biological processes can yield enantiomeric excess

Asymmetric catalysis and autocatalysis

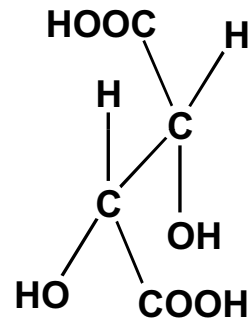
Soai & Sato: slight chiral excess propagated during autocatalytic syntheses

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

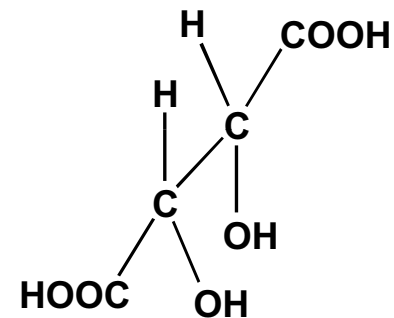
Stereoisomerism in Tartaric Acid



A (meso)



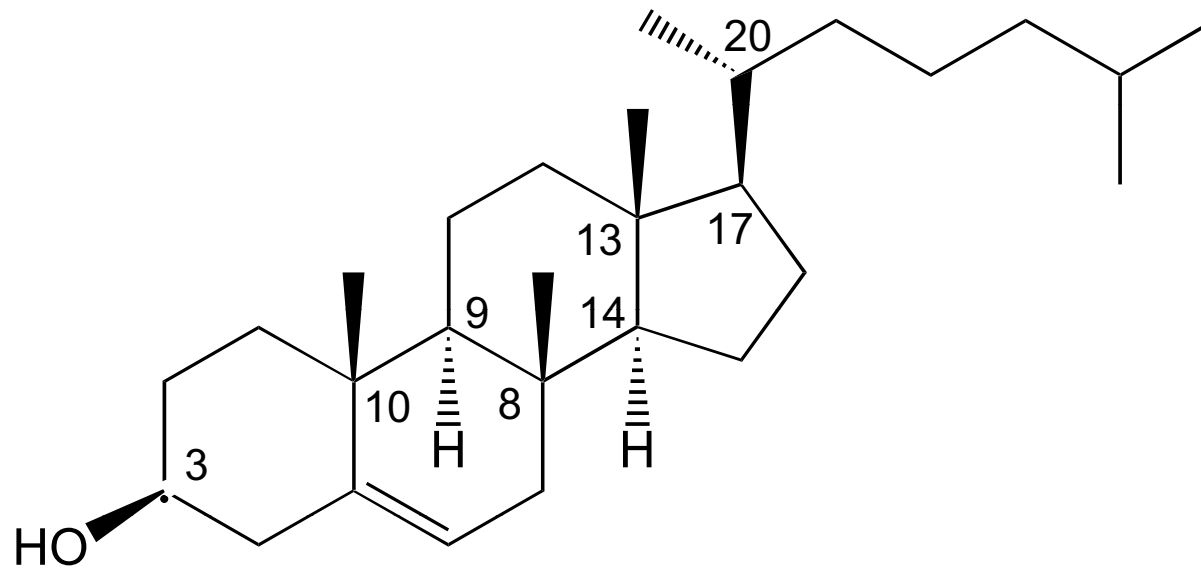
B



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

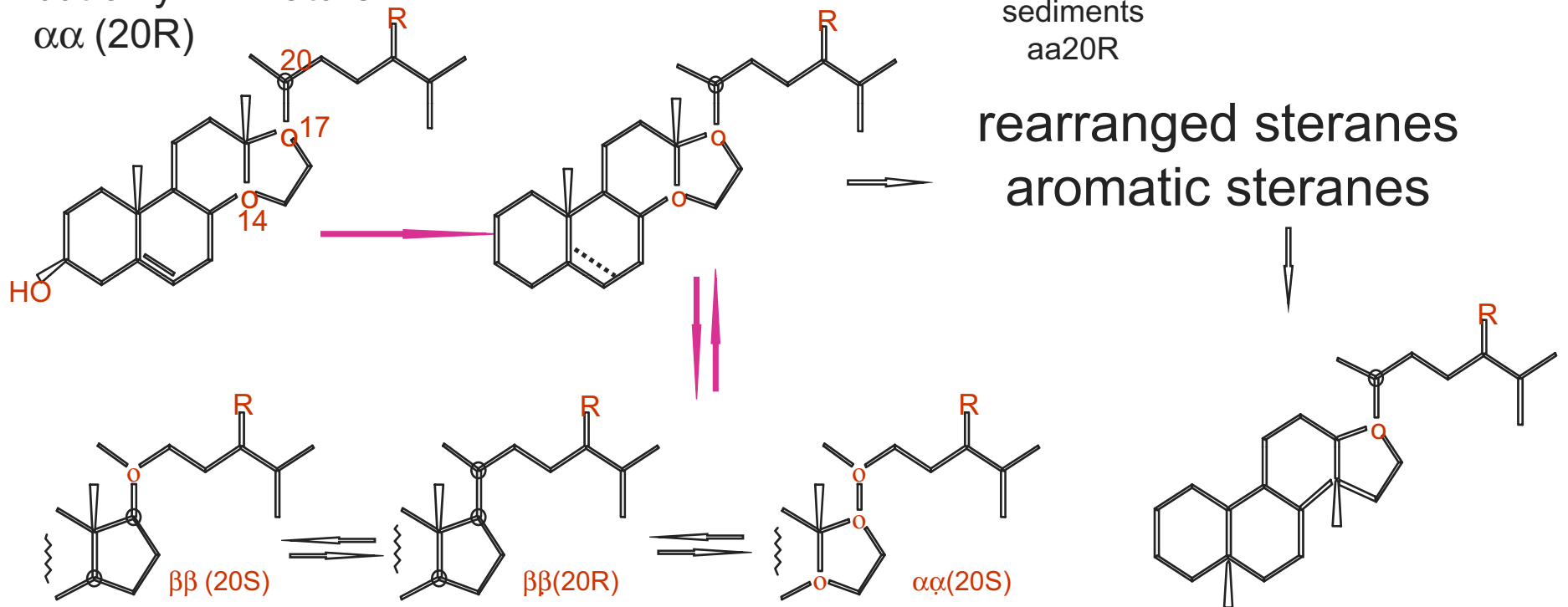
Unique sterol configuration of living organisms

8 sites of asymmetry

$2^8 = 256$ feasible isomers

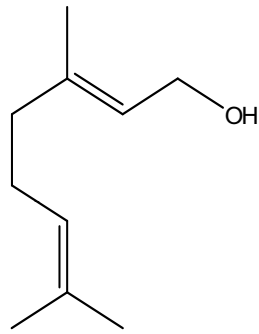
but only 1 in nature

$\alpha\alpha$ (20R)

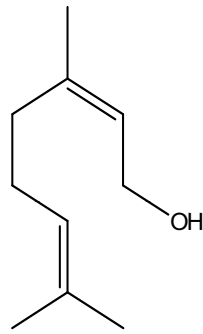


Complex sterane mixture in mature sediments & oil

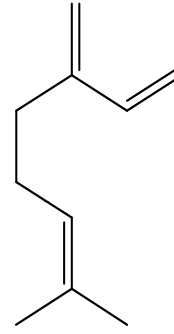
Constitutional Isomers



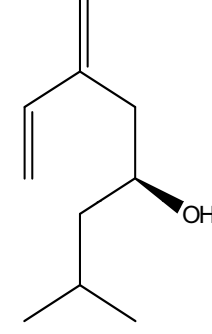
Geraniol



Nerol



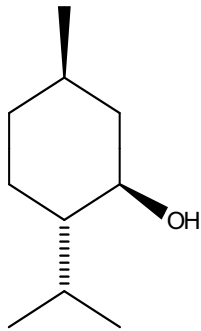
Myrcene



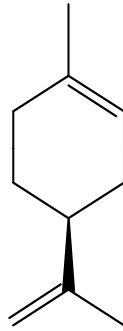
(S)-lpsenol
Pine beetle pheromone

Choleoptera: Scolytidae

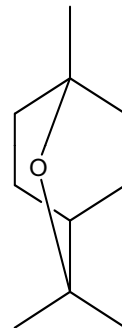
C_{10} compounds (monoterpenes)
- life makes a specific subset of all the possibilities



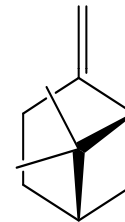
(1R,2S,5R)-(-)-Menthol



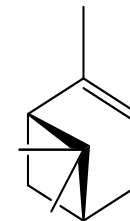
(S)-(-)-Limonene



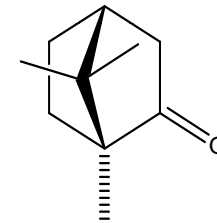
Cineol (eucalyptol)



(1S)-(-)-β-Pinene

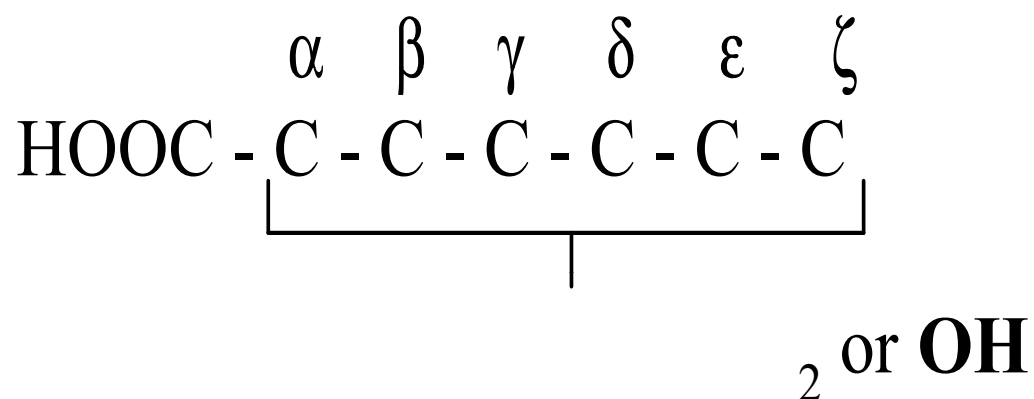


(1R)-(+)-α-Pinene



(1R)-(+)-Camphor

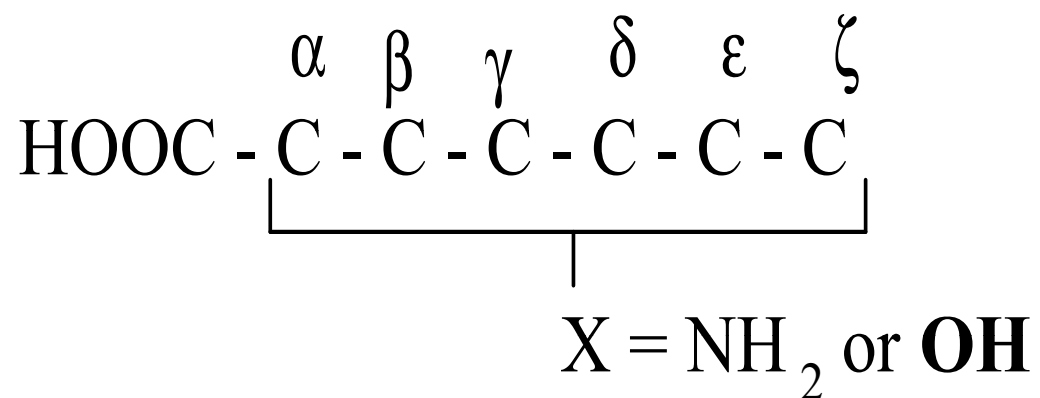
Constitutional Isomers



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

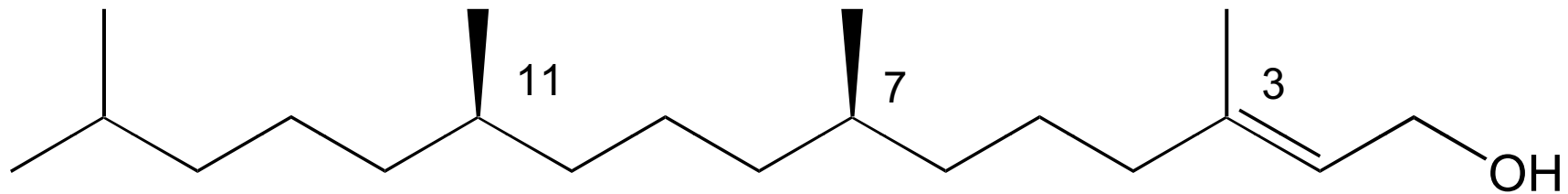
e.g. monoamino monocarboxylic acids and monohydroxy, monocarboxylic acids (Cronin et al. 1993)

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

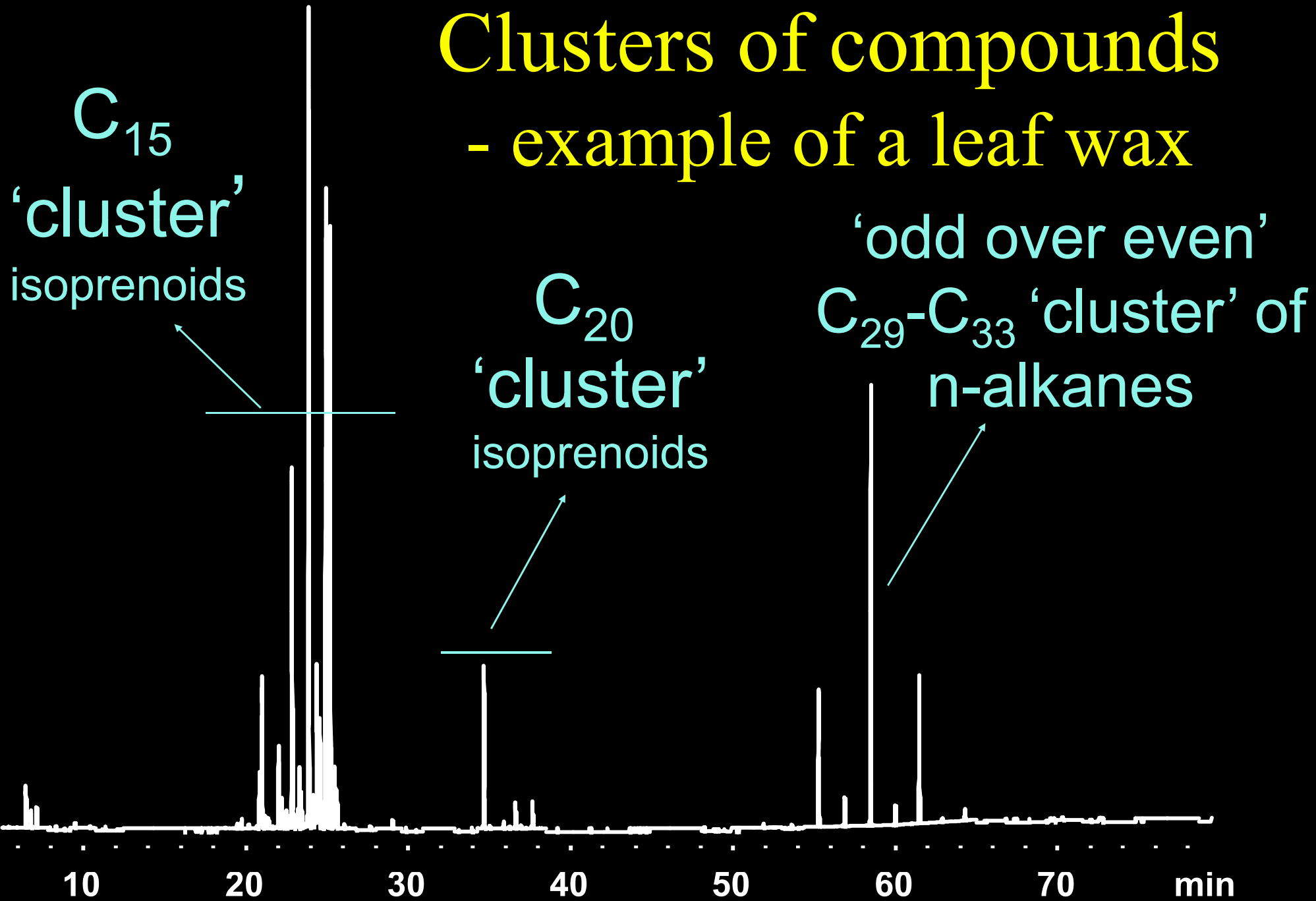


Life makes a limited number of all the possible constitutional isomers because it :

- has evolved 'universal' biochemical pathways
- constructs macromolecules from small, common precursors
(eg 20 amino acids in protein, 4 bases of DNA)

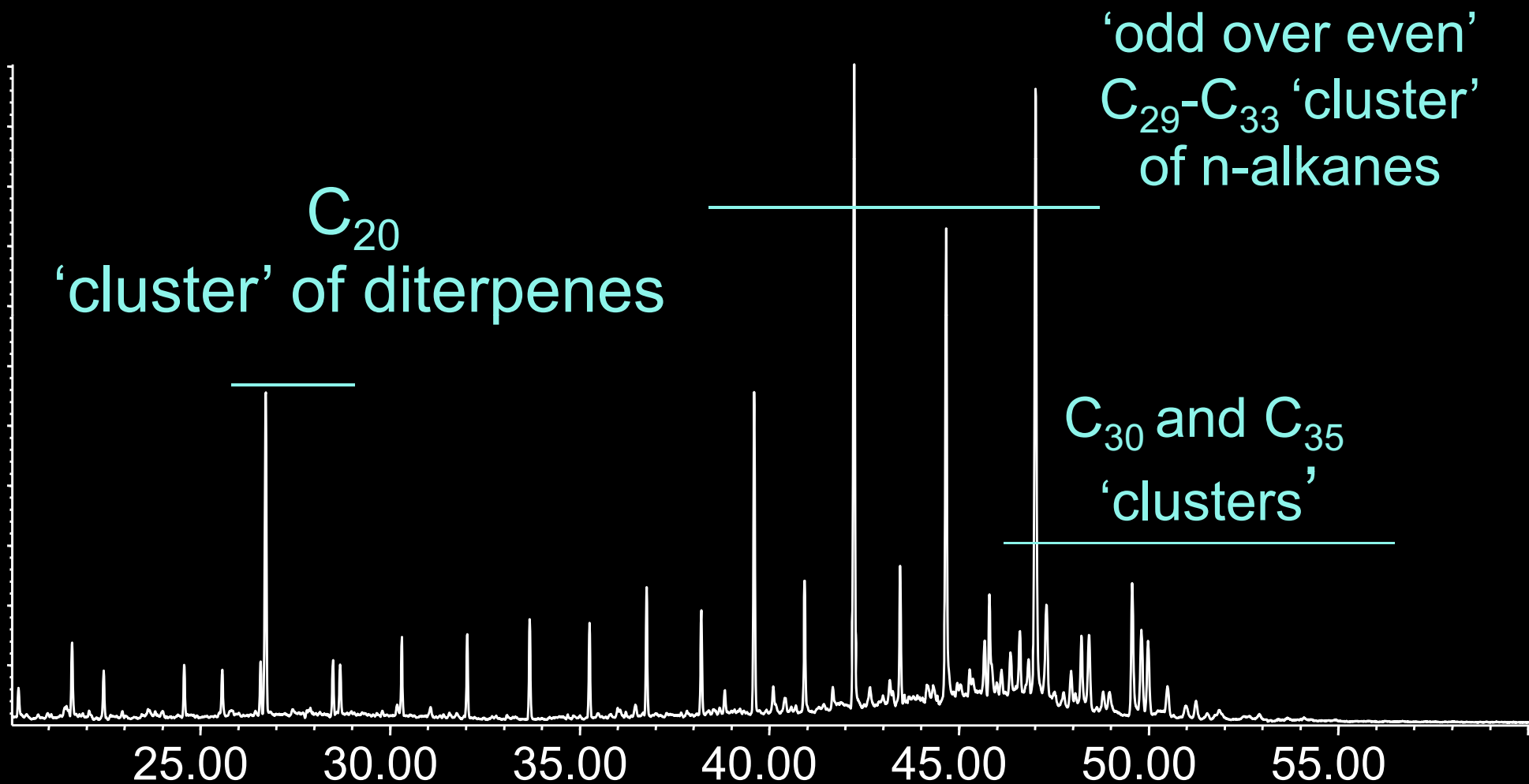
→ → preference for certain carbon numbers (clusters) & systematic isotopic ordering within & between molecules

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

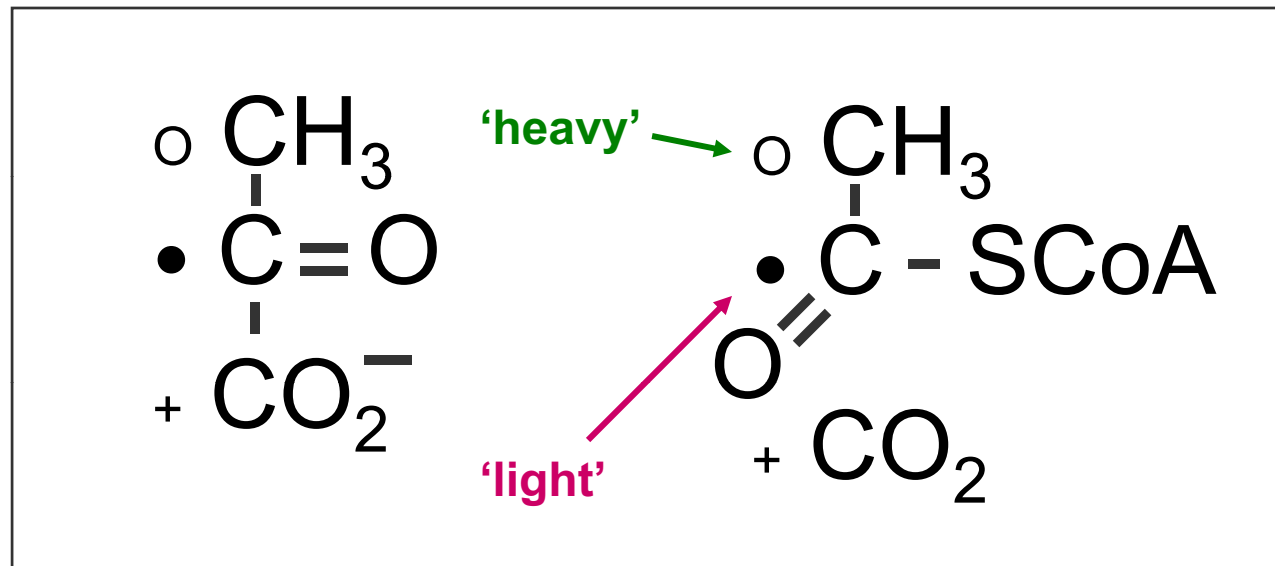
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Polymethylenic
= acetogenic lipids

Isotopic ordering is a
consequence of the
universality of biochemical
pathways

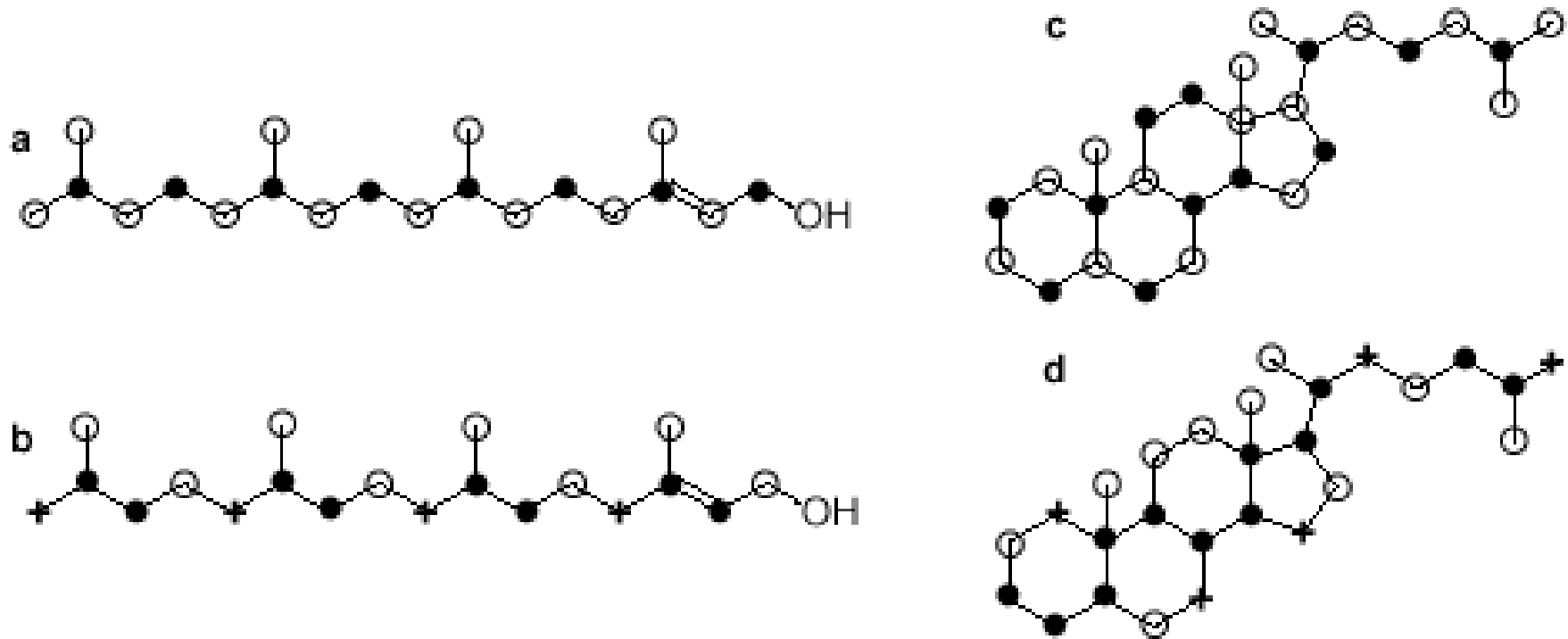
Hayes J. M. (2002) Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. In: *Stable Isotopic Geochemistry*, Valley J. W. and Cole D.R. (eds.) *Reviews in Mineralogy and Geochemistry*.

Acetogenic Lipids



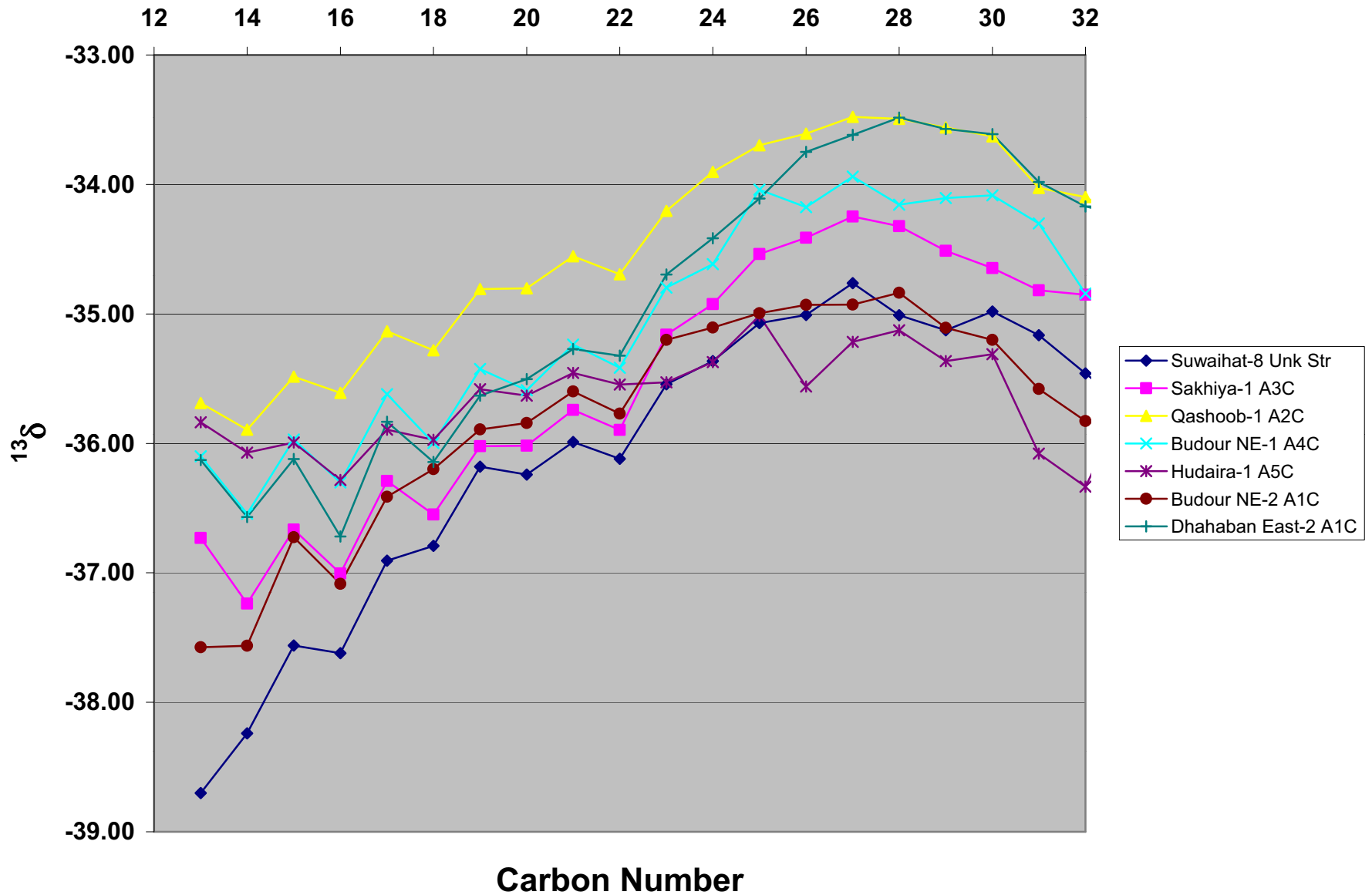
Acetate Methyl-C and Carboxyl-C are isotopically distinct and determined by its metabolic source and the profound isotope effect of pyruvate dehydrogenase

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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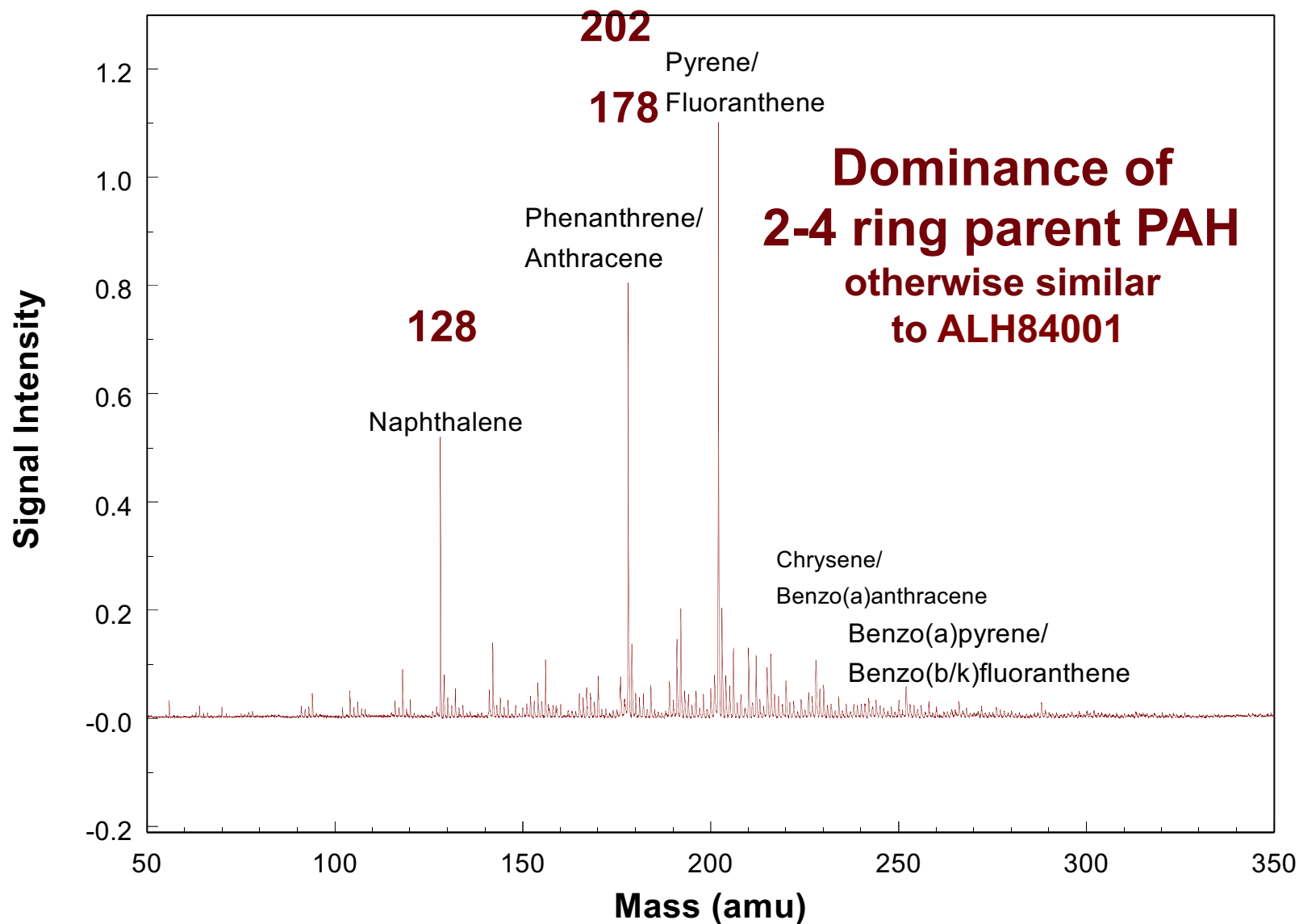
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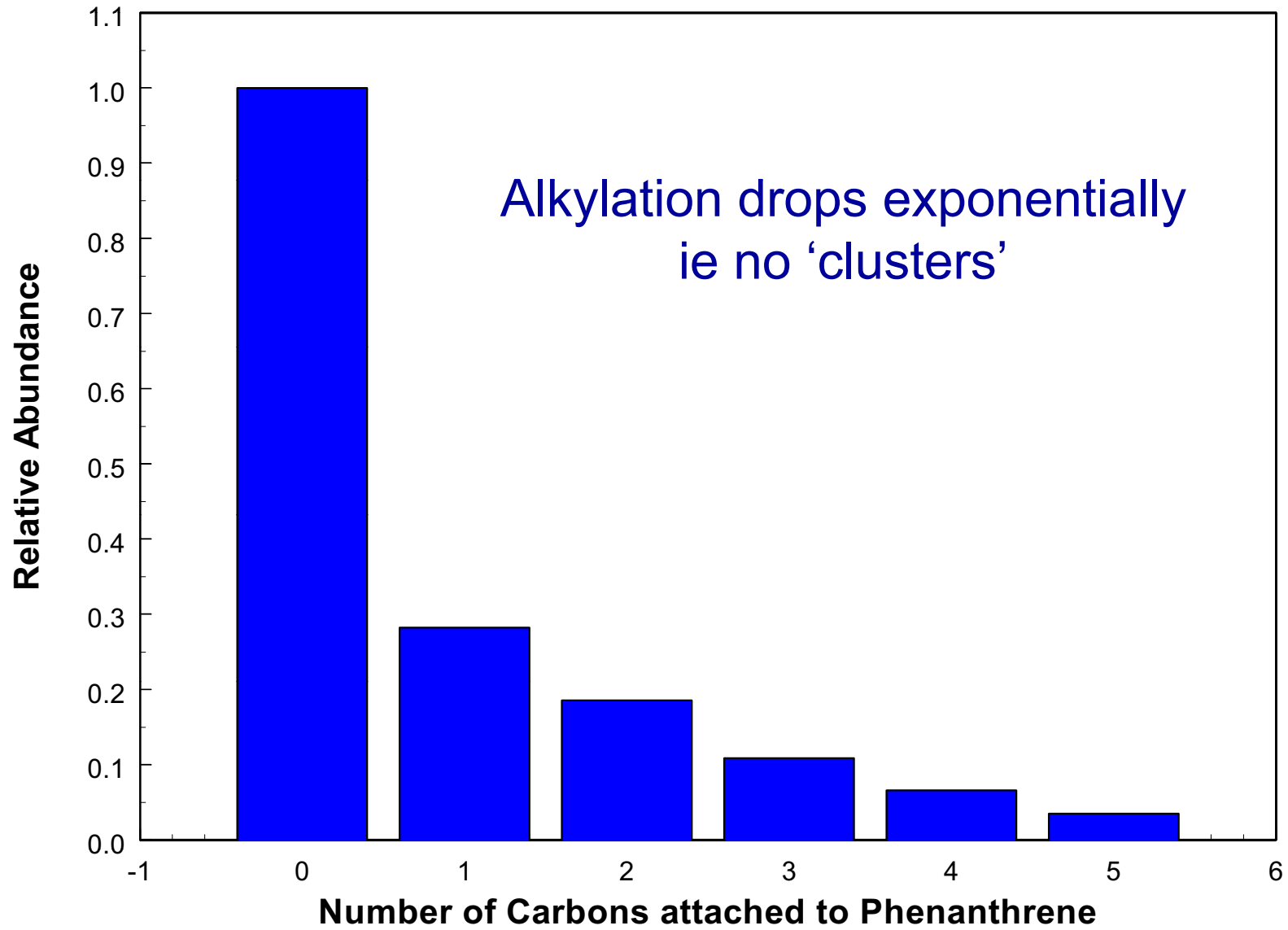
However, PAH are not necessarily
biogenic

μL^2 MS of Murchison Meteorite

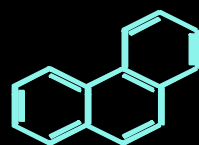
Murchison



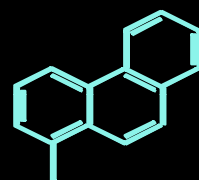
Murchison



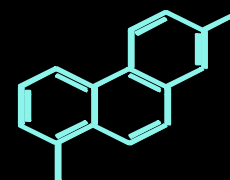
PAH Proposed as molecular fossils ?



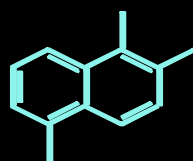
PHENANTHRENE
178



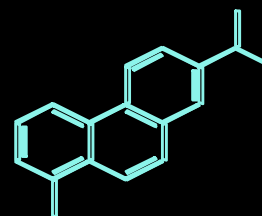
1-METHYL-
PHENANTHRENE 192



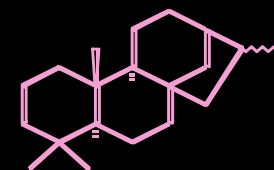
1,7-DIMETHYL-
PHENANTHRENE 206



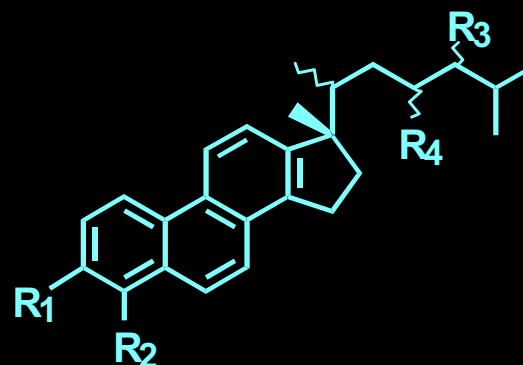
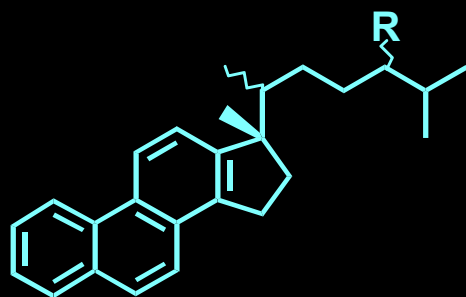
1,2,5-TRIMETHYL-
NAPHTHALENE 156



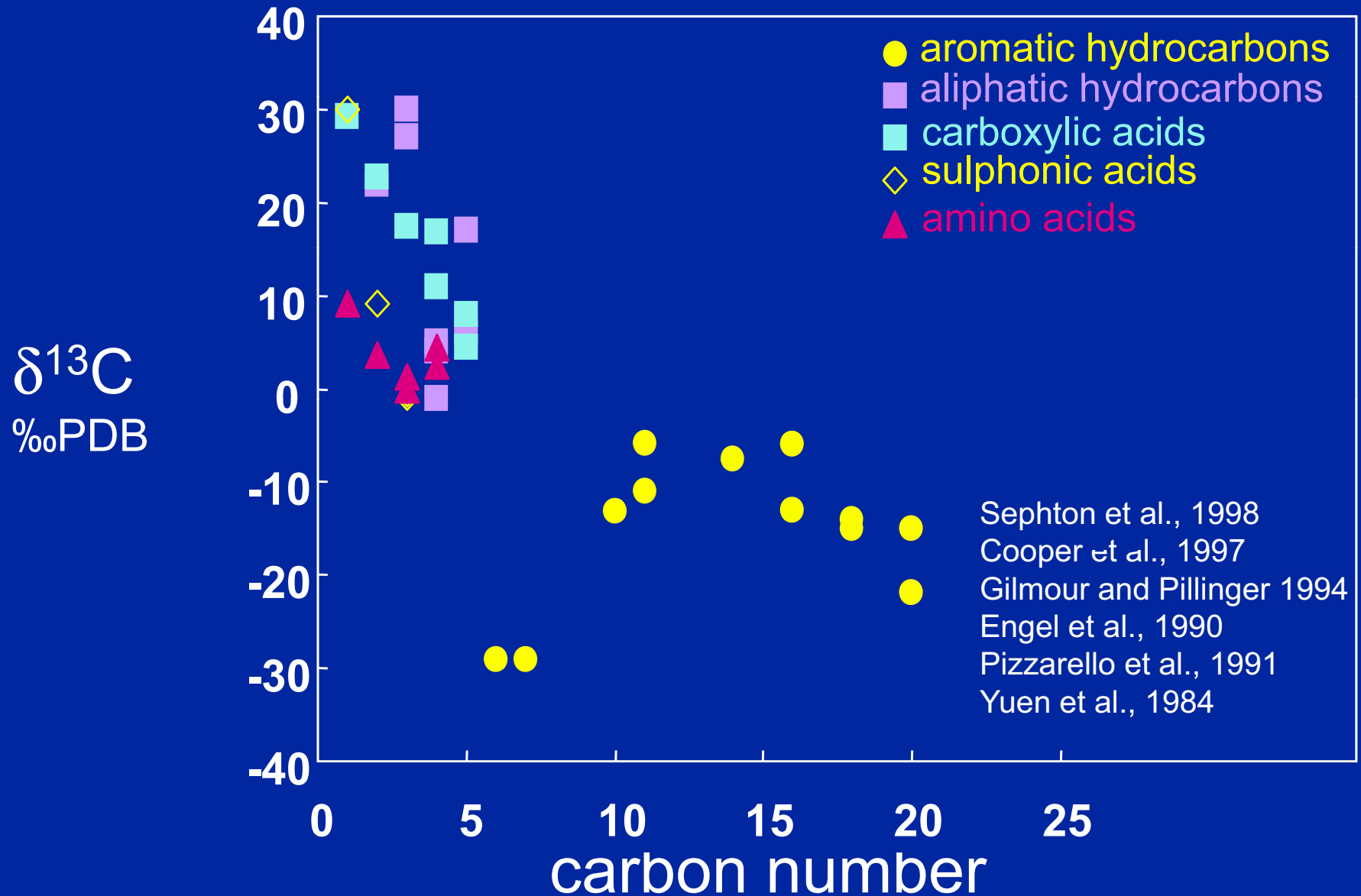
RETENE
234



PHYLLOCLADANE



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



Compilation courtesy of Mark Sephton

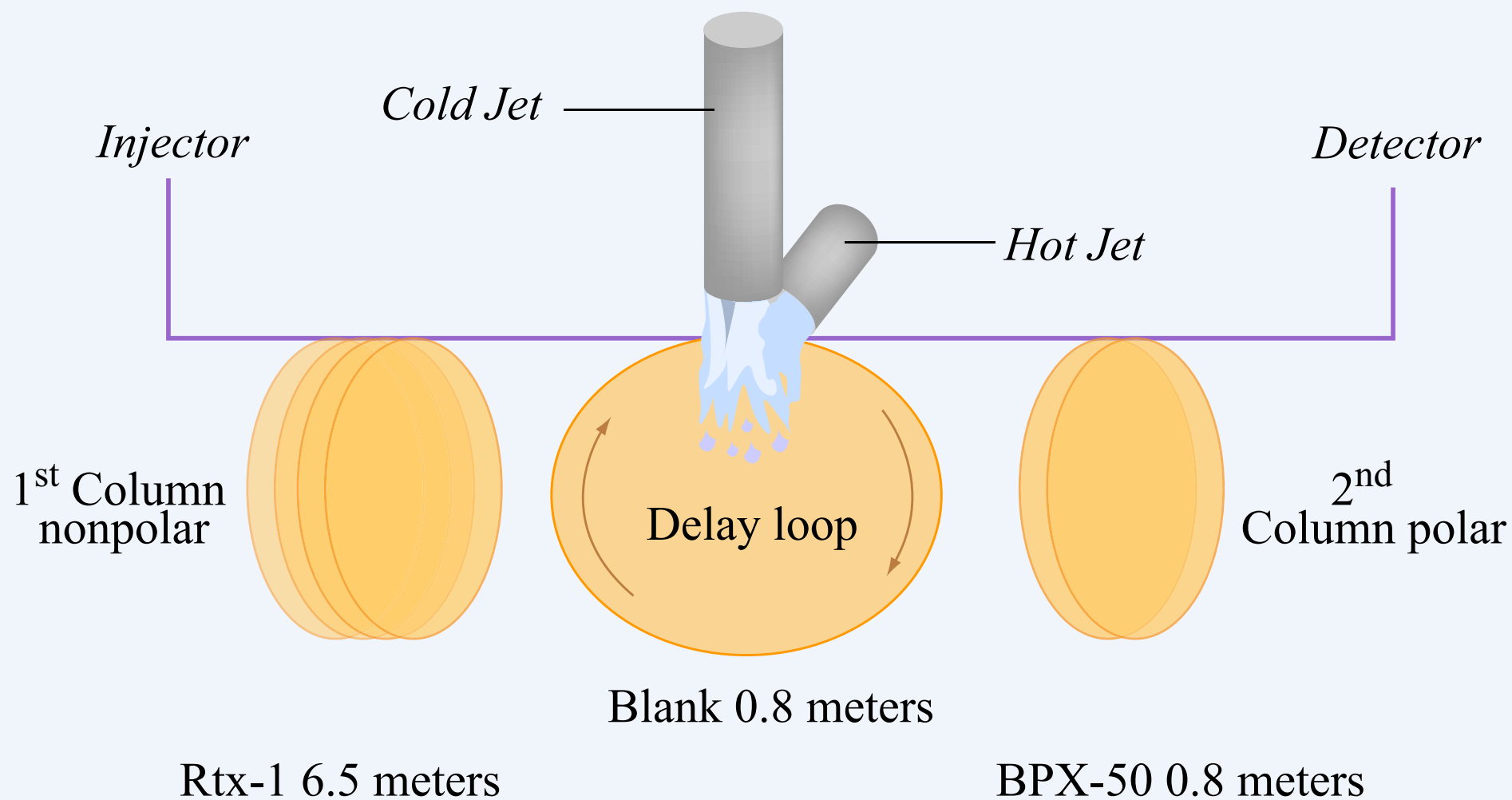
Topics

- 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

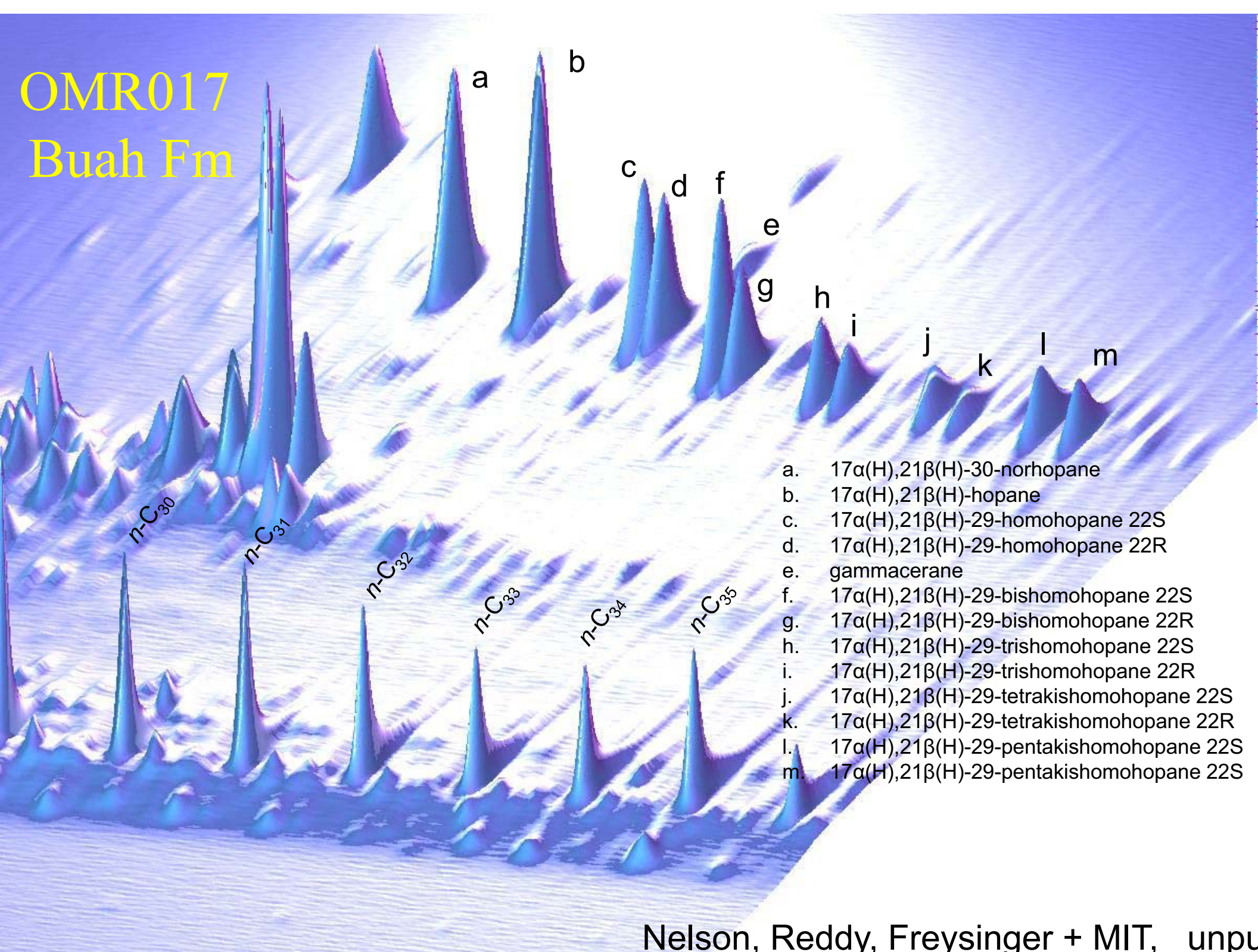
OMR017

Buah Fm.

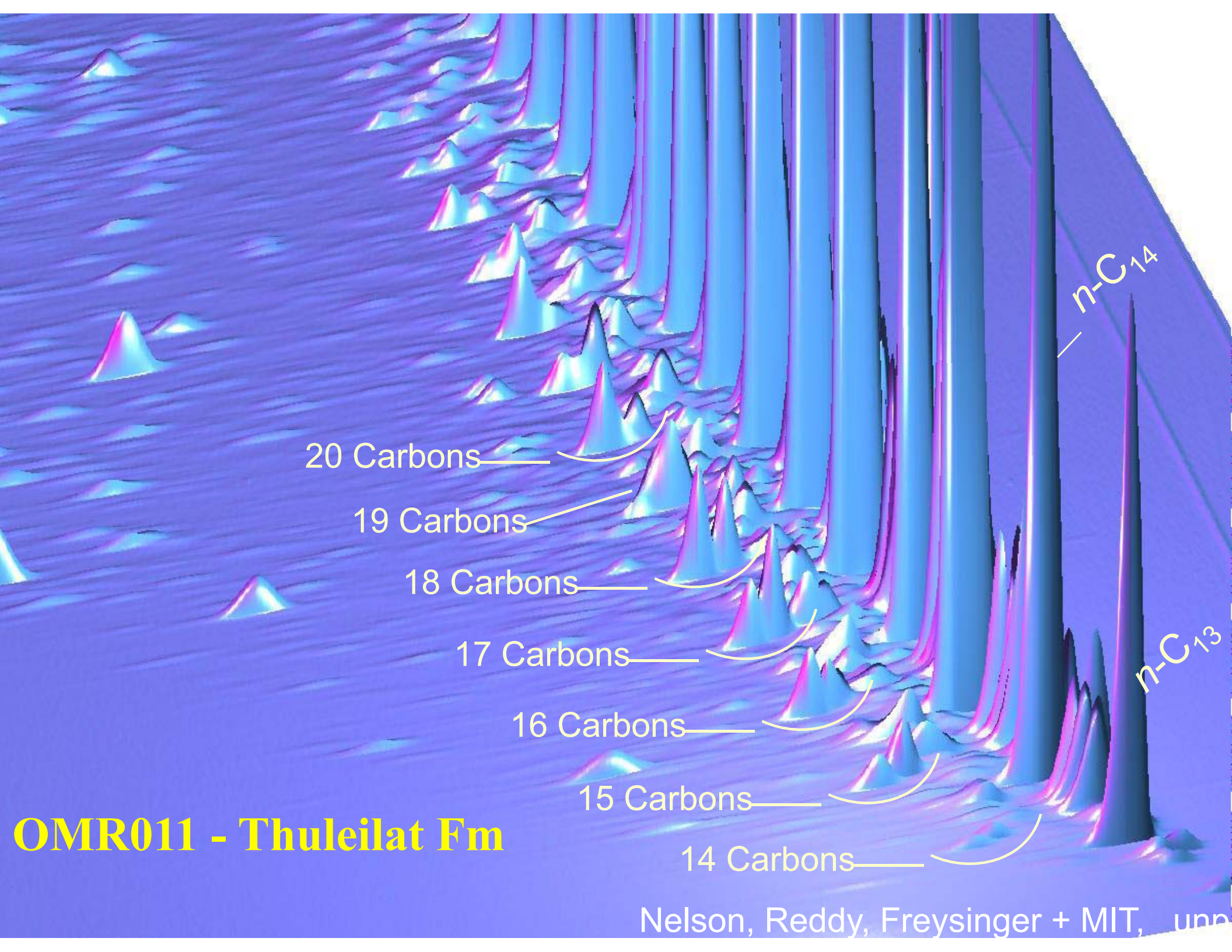
Loop-Jet Modulator



OMR017
Buah Fm



- a. 17 α (H),21 β (H)-30-norhopane
- b. 17 α (H),21 β (H)-hopane
- c. 17 α (H),21 β (H)-29-homohopane 22S
- d. 17 α (H),21 β (H)-29-homohopane 22R
- e. gammacerane
- f. 17 α (H),21 β (H)-29-bishomohopane 22S
- g. 17 α (H),21 β (H)-29-bishomohopane 22R
- h. 17 α (H),21 β (H)-29-trishomohopane 22S
- i. 17 α (H),21 β (H)-29-trishomohopane 22R
- j. 17 α (H),21 β (H)-29-tetrakishomohopane 22S
- k. 17 α (H),21 β (H)-29-tetrakishomohopane 22R
- l. 17 α (H),21 β (H)-29-pentakishomohopane 22S
- m. 17 α (H),21 β (H)-29-pentakishomohopane 22S



20 Carbons

19 Carbons

18 Carbons

17 Carbons

16 Carbons

15 Carbons

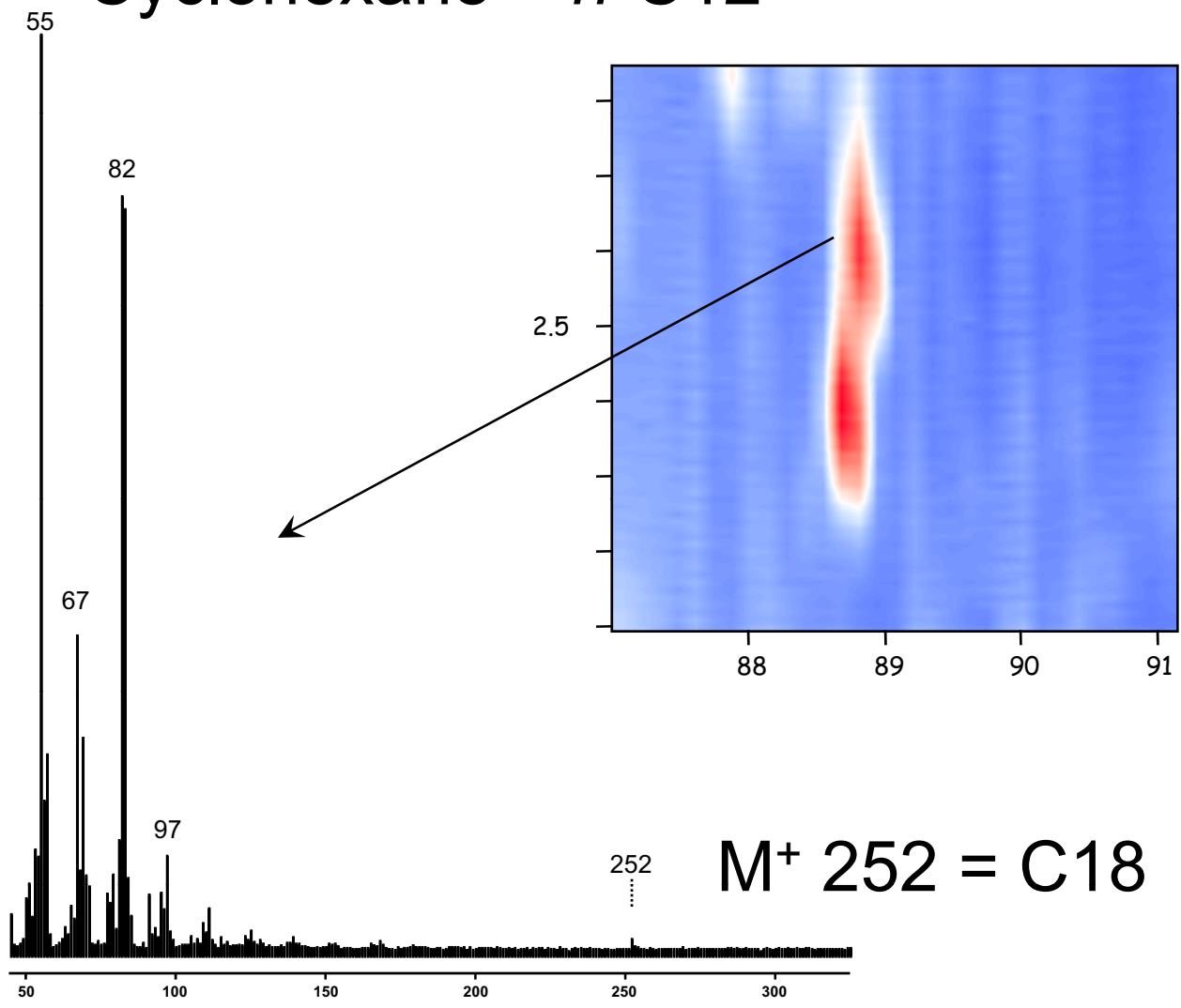
14 Carbons

n-C₁₄

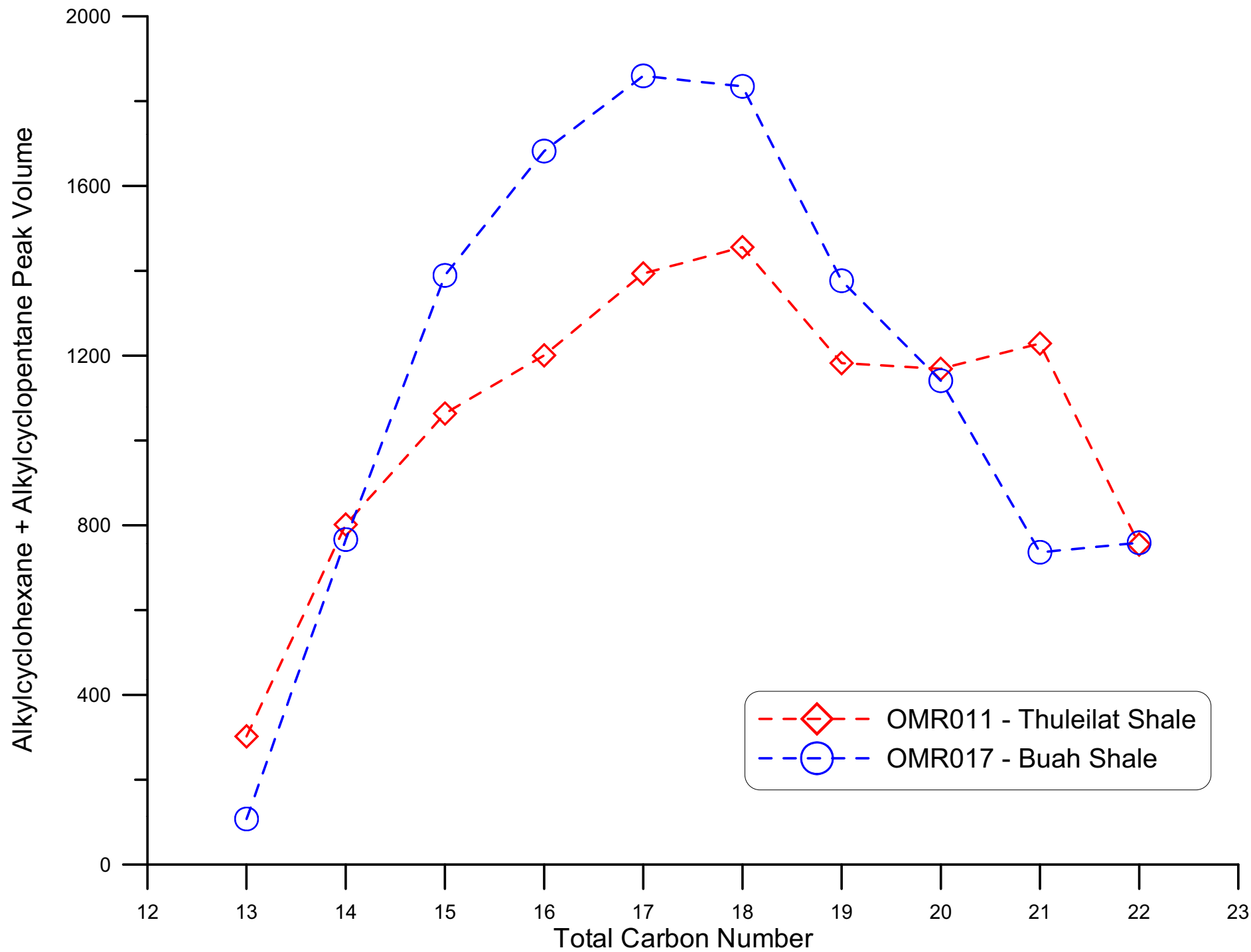
n-C₁₃

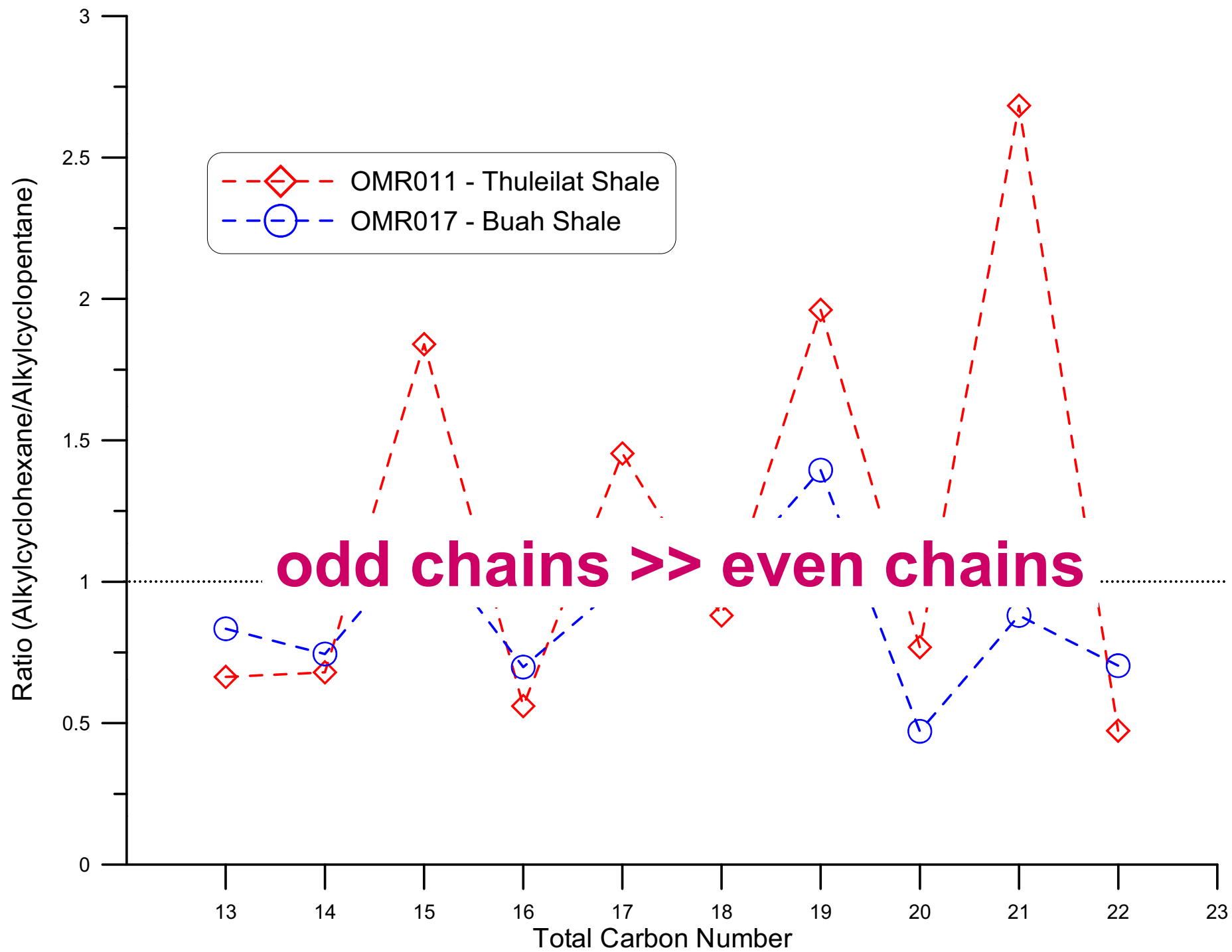
OMR011 - Thuleilat Fm

Cyclohexane + *n*-C12



Nelson, Reddy, Freysinger + MIT, unpublished





Topics

- What are useful criteria for biogenicity?
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- Analytical methods for investigating molecular biosignatures in rocks from Earth & elsewhere
 - GC²-TOFMS
 - Hydropyrolysis & Strelley Pool C

Biogenic Gases

Mars atmosphere:

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CO₂ 95.3%

N₂, 2.7%

Ar 1.6%

CO 0.07%

O₂ 0.13%

H₂O 0-300 ppm

CH₄ 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 entrapment 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:

Martian context --> Early Mars Environment	Support Biotic C formation	Support for Abiotic C formation	Support Carbon Conc	Support Preservation	Potential for Recent Exhumation	ID by remote sensing			ID by MSL
						geomor phic	minera logic	stratigr aphic	
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

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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

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**

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



Available online at www.sciencedirect.com



Geochimica et Cosmochimica Acta 73 (2009) 102–118

**Geochimica et
Cosmochimica
Acta**

www.elsevier.com/locate/gca

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

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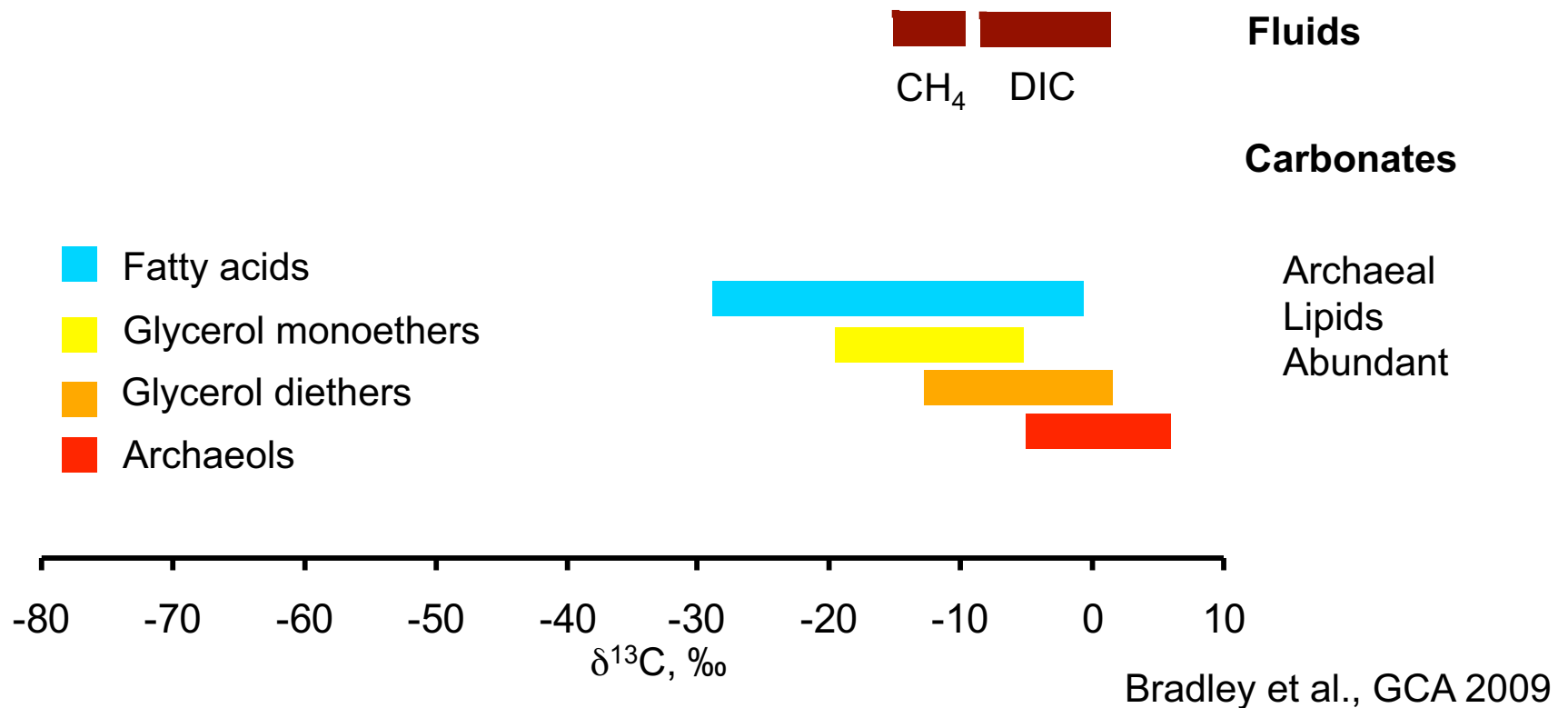
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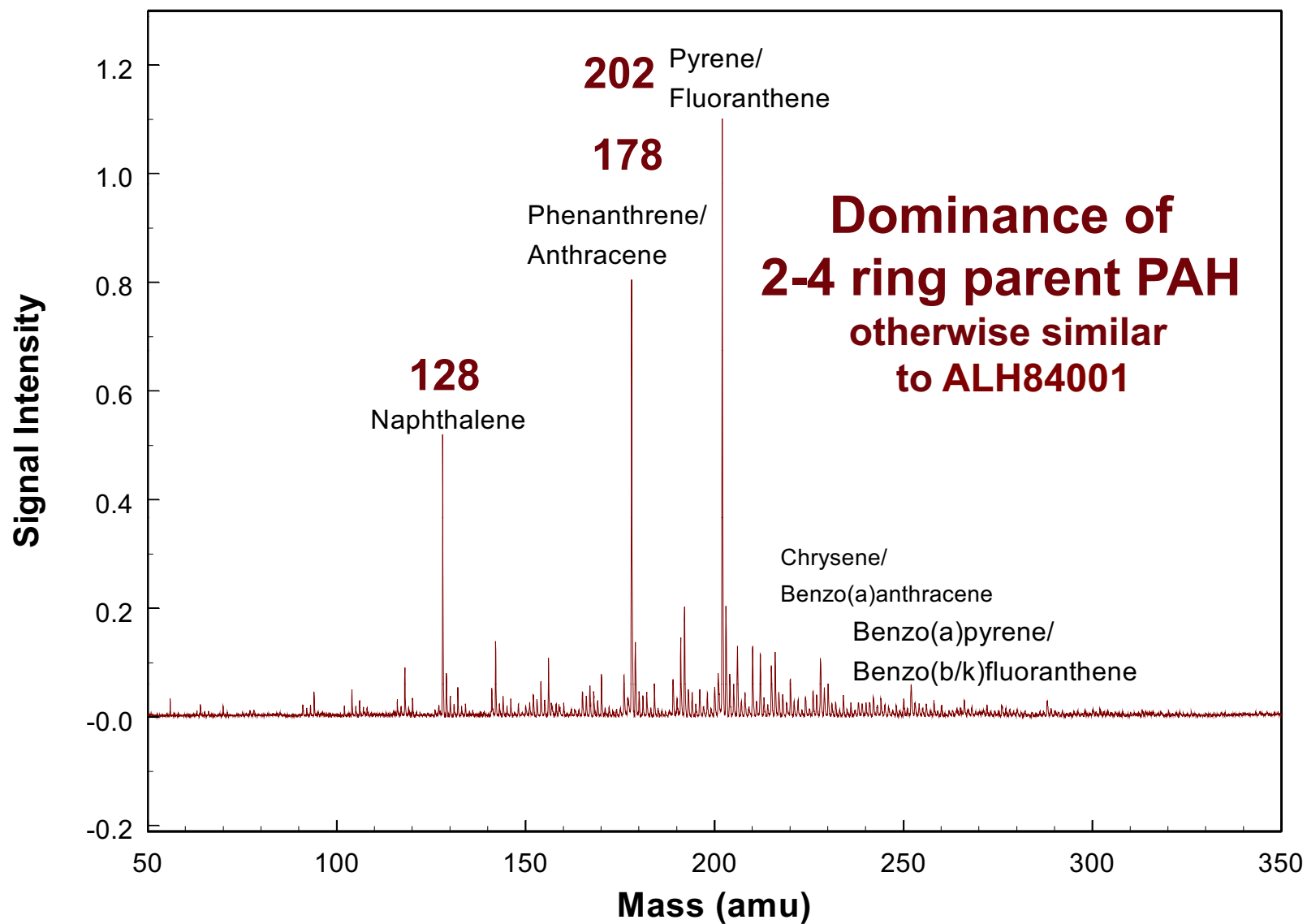
$^{13}\delta$ LC methane suggests it is abiogenic

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



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Murchison



Topics

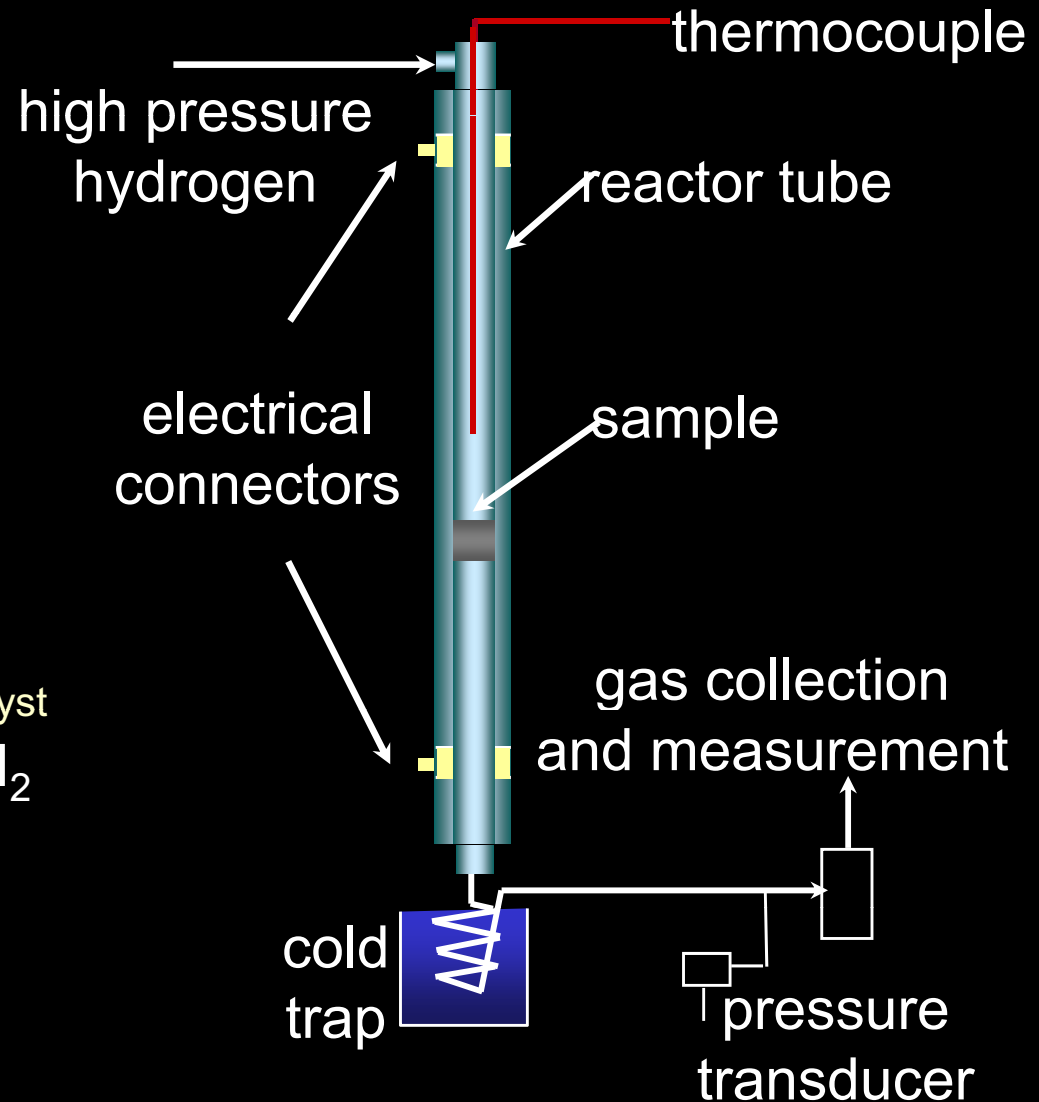
- What are useful criteria for biogenicity?
How can we be sure of measuring the right thing in a sample on Mars or returned from Mars? Deliberations of the 2000 NASA Biomarker Taskforce – molecular biosignatures
- Analytical methods for investigating molecular biosignatures in rocks from Earth & elsewhere
GC²-TOFMS
- New ‘technologies’ in molecular biosignatures for organisms and ancient environments

Hydropyrolysis (H₂)

Murchison

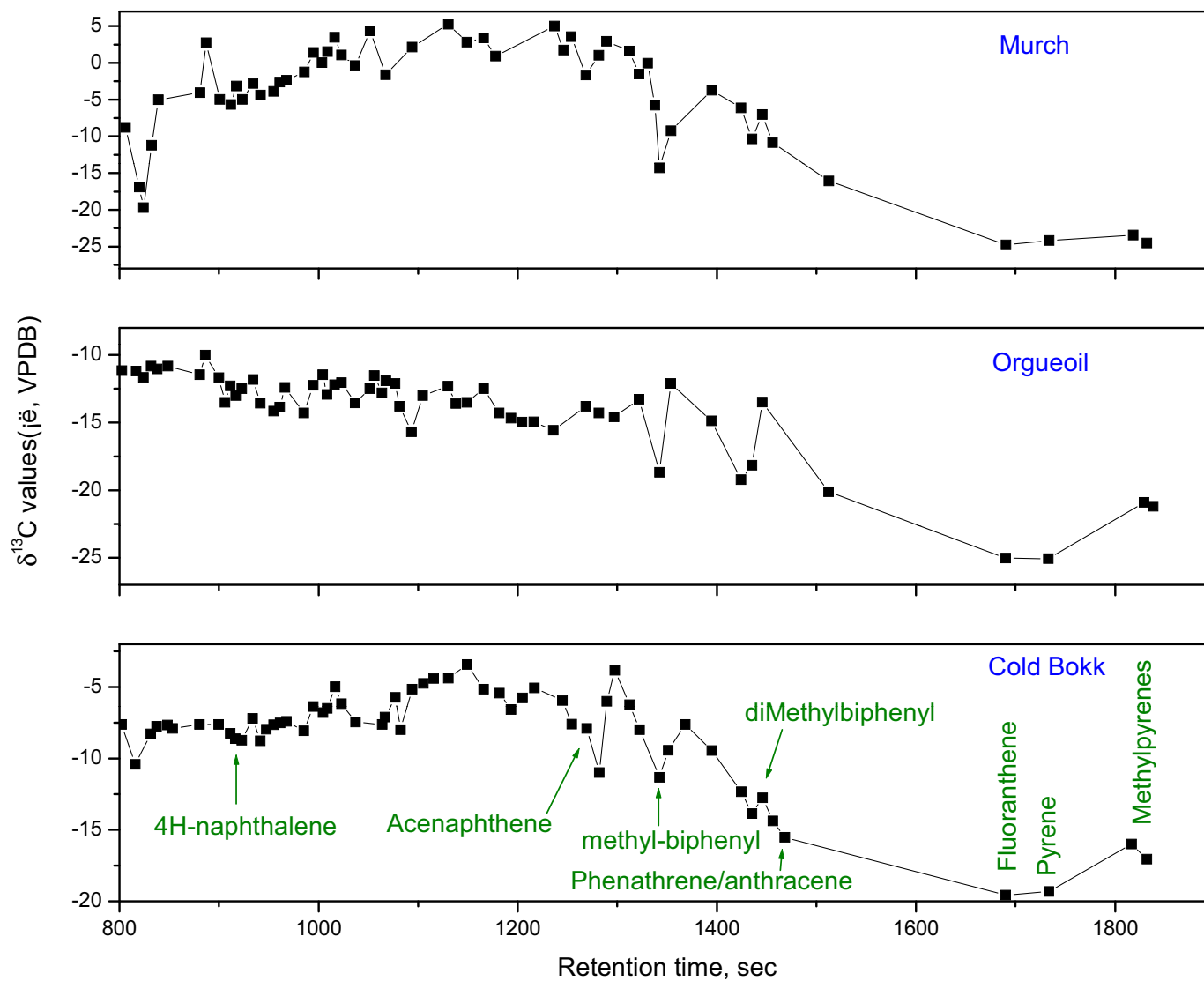


- sample impregnated
 - ammonium dioxydithiomolybdate
 - decomposes above 250 °C to catalyst
- continuous high flow of H₂
- heated 220 to 520 °C
- dry ice trap
- dichloromethane

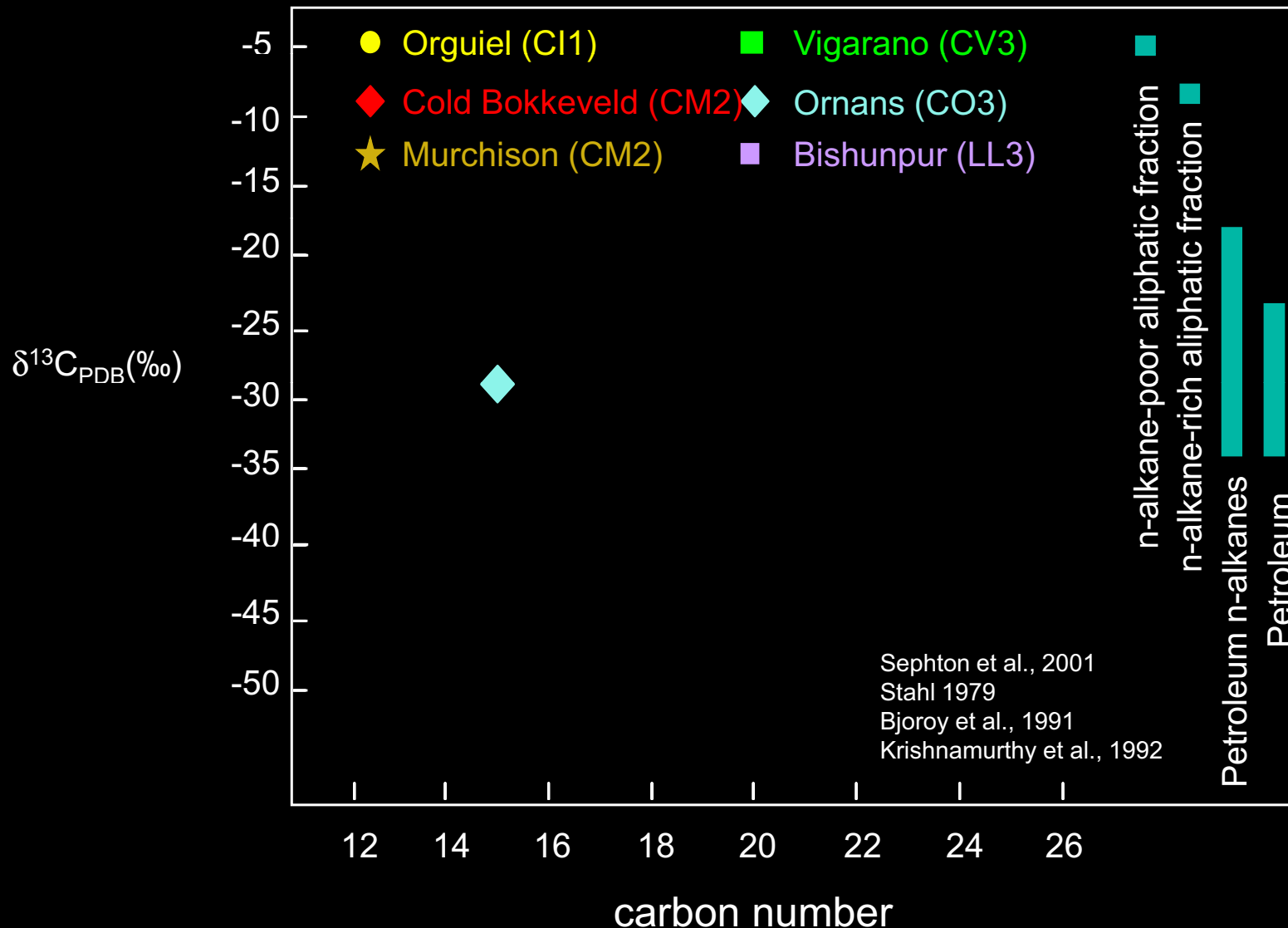


Hydropyrolysis facilitates breakdown of macromolecules & minimises rearrangement

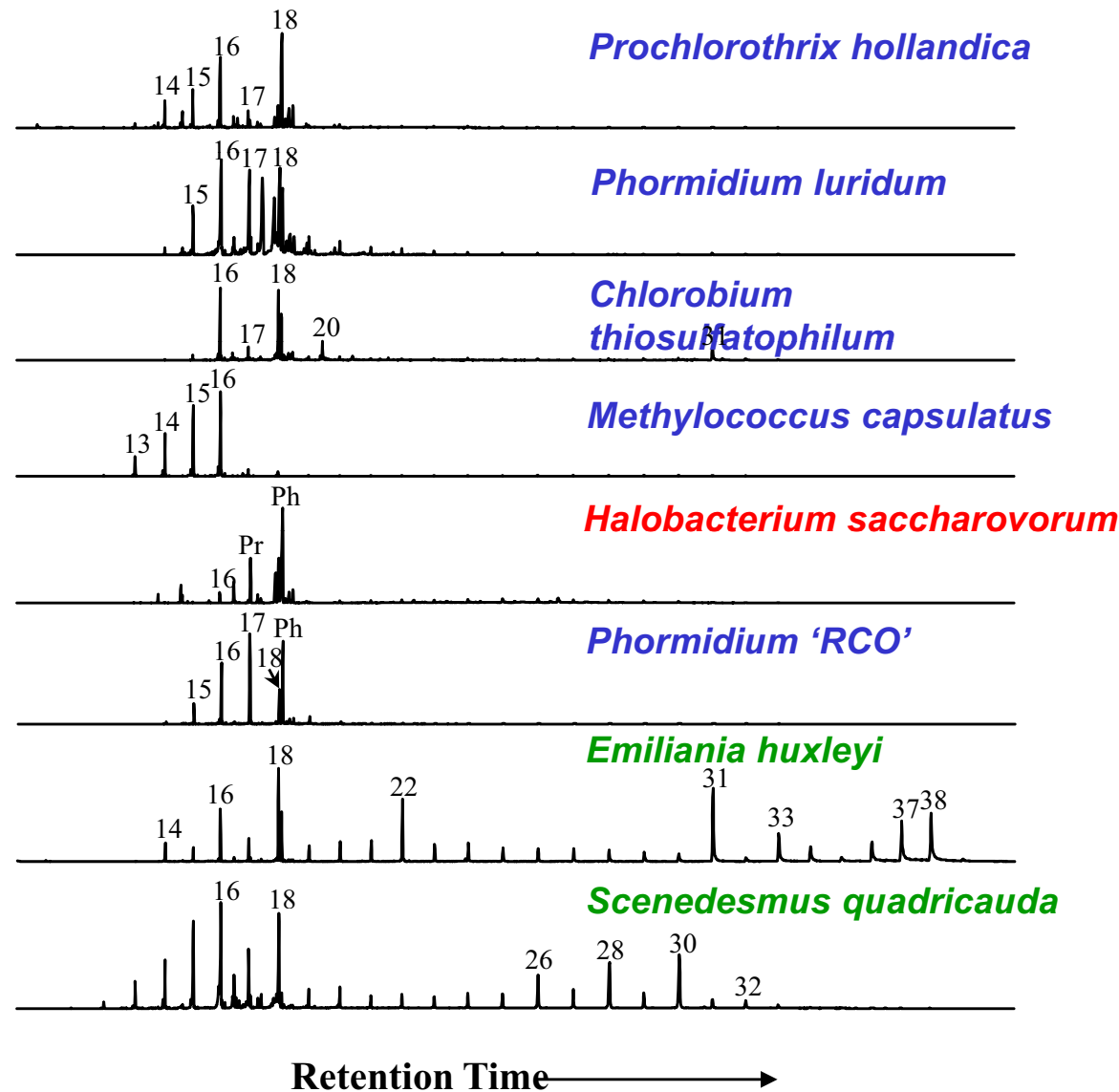
$\delta^{13}\text{C}$ profiles for HyPy products of 3 meteorites



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



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



- bacteria
- archaea
- algae

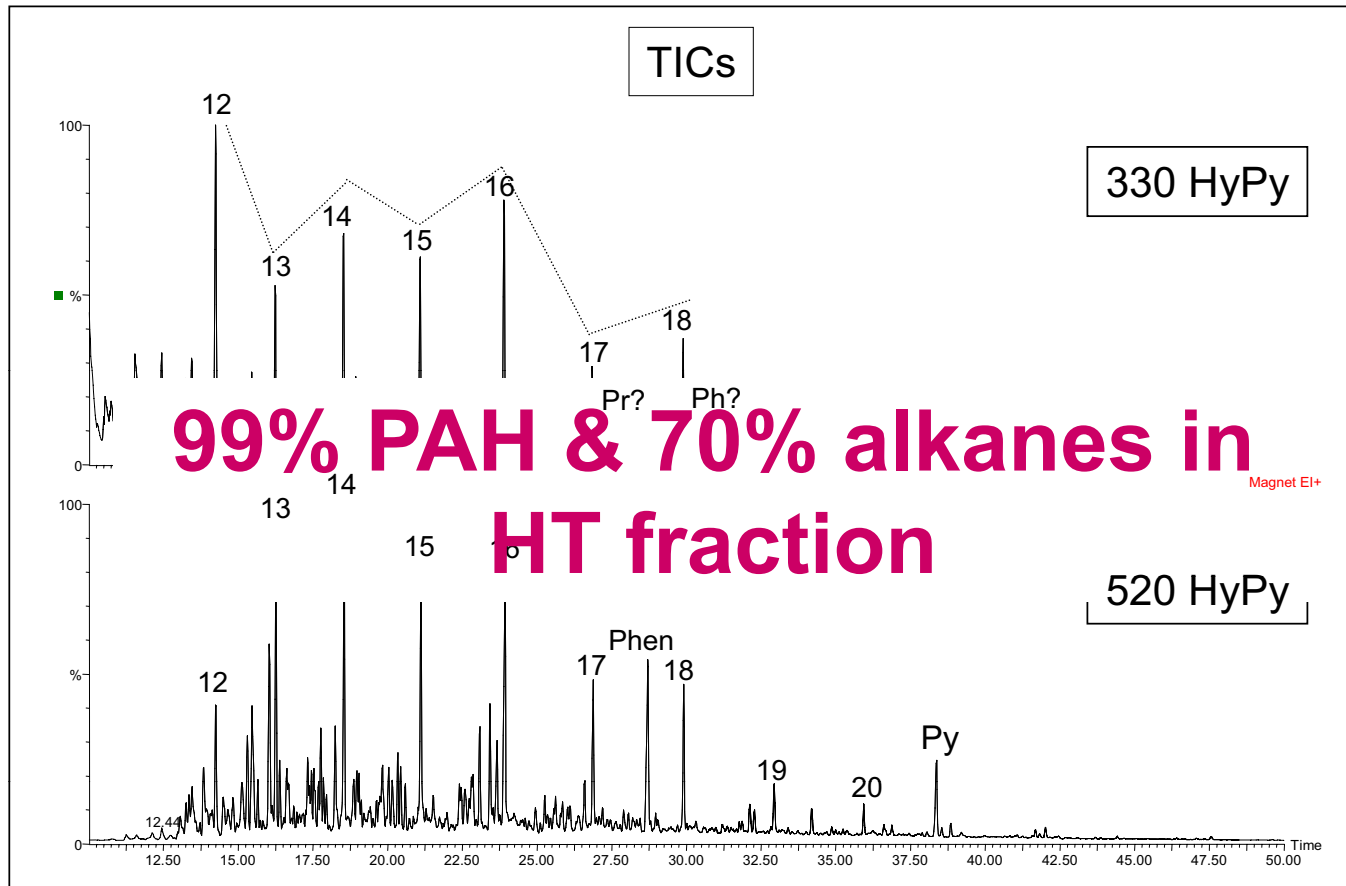


black chert veins and clasts

Complex 'Dyke' Breccia

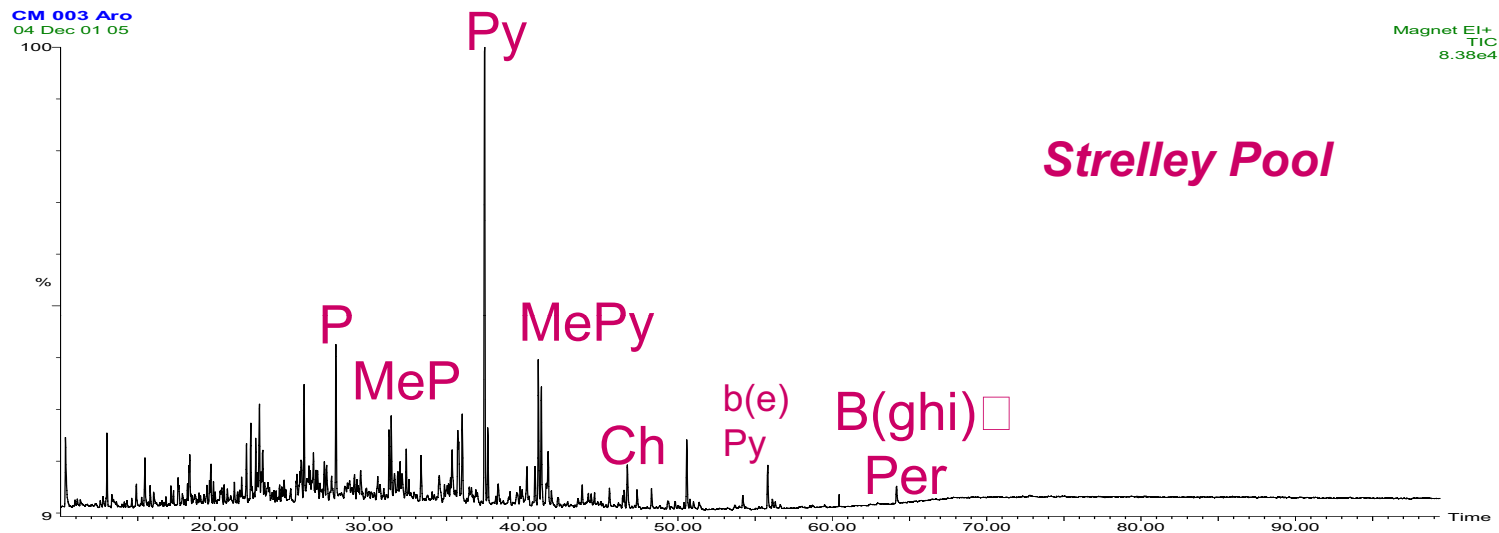
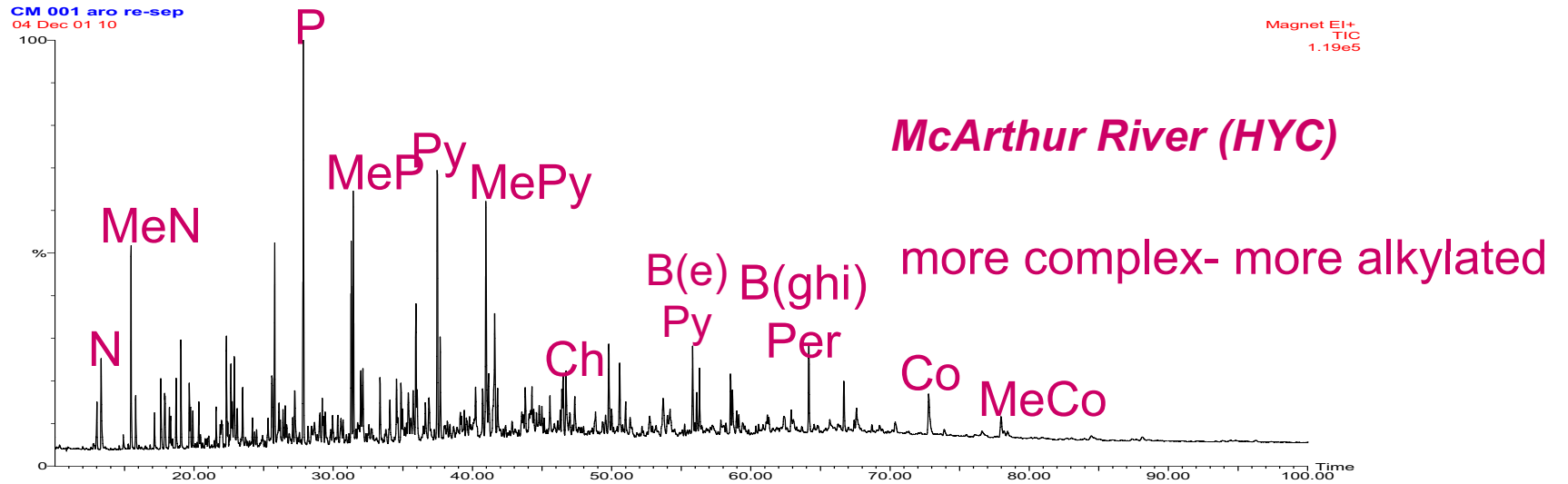


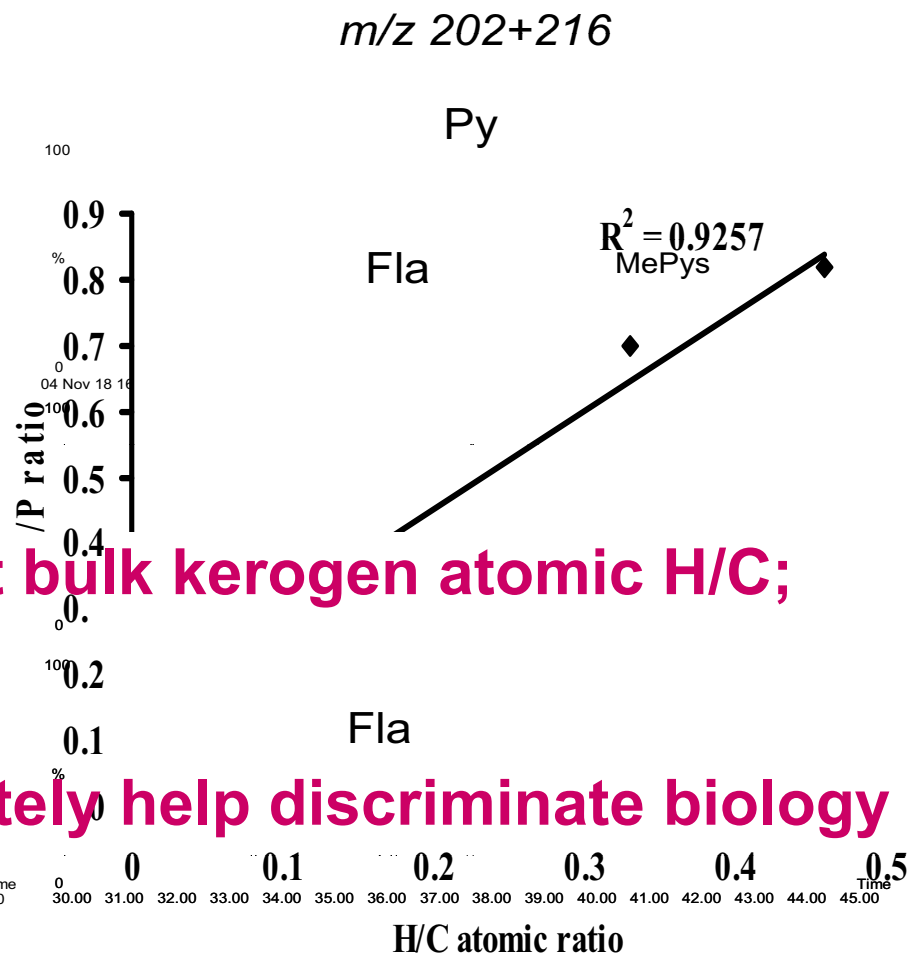
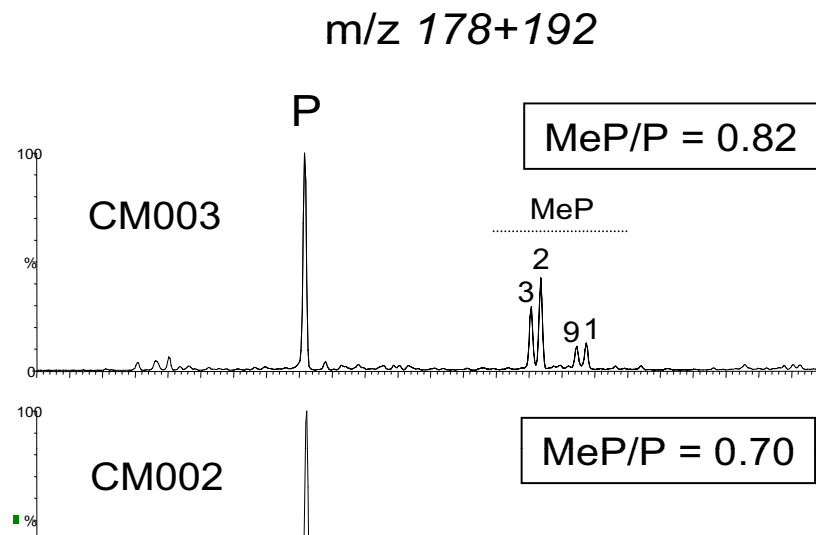
SPC 16 Kerogen sequential HyPy



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.

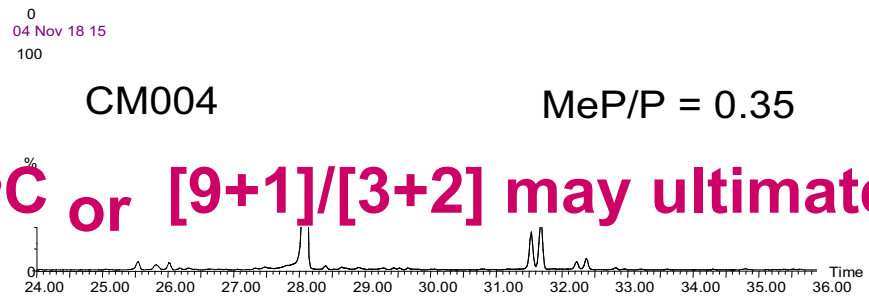
Distribution of aromatic hydrocarbons from HyPy





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 multidimensional GC and GC-TOF are useful analytical tools.
4. Hyropyrolysis assists screening for biosignatures in macromolecular OM and biomass

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