12.458 Lecture 8

Molecular Fossils from Land Plants

Readings and talks for Monday Nov 8th:

Murray et al., OG 1998
Speelman OG 2009

Topics for presentations Monday Nov 8:
Biomarkers from ferns? Azolla or Anabaena
Biomarkers for lichens
mosses
primitive plants like ginko
structures and origins of fernenes
lupanes and taraxastanes,
Perylene
isotopic composition of leaf wax
isotopic composition of plant terpenes

VIRIDAEPLANTAE

Richard M. McCourt,
R. L. Chapman,
M. A. Buchheim and
Brent D. Mishler

http://tolweb.org/tree?group=Green_plants

VIRIDAEPLANTAE

http://tolweb.org/tree?group=Green_plants

- Green plants as defined here includes a broad assemblage of photosynthetic organisms that all contain chlorophylls a and b, store their photosynthetic products as starch inside the double-membrane-bounded chloroplasts in which it is produced, and have cell walls made of cellulose (Raven et al., 1992). In this group are several thousand species of what are classically considered green algae, plus several hundred thousand land plants.

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VIRIDAEPLANTAE- CHLOROPHYCEAE

http://tolweb.org/tree?group=Green_plants

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Chlorellales, especially *Chlorella* are an important group because of their role as **endosymbionts** inside the tissues of sponges, ciliates and formams.
Green algae produce bioplymers, algeanans, which are recalcitrant, non-hydrolysable biopolymers and feedstock for crude oil.

http://tolweb.org/tree?group=Green_plants

Geobiology (2008), 6, 411–420 DOI: 10.1111/j.1472-4669.2008.00167.x

Sterols in red and green algae: quantification, phylogeny, and relevance for the interpretation of geologic steranes

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[3]*Department of Earth, Atmosphere, and Planetary Sciences, Massachusetts Institute of Technology, 42-44 Carleton St., Cambridge, MA 02139, USA*

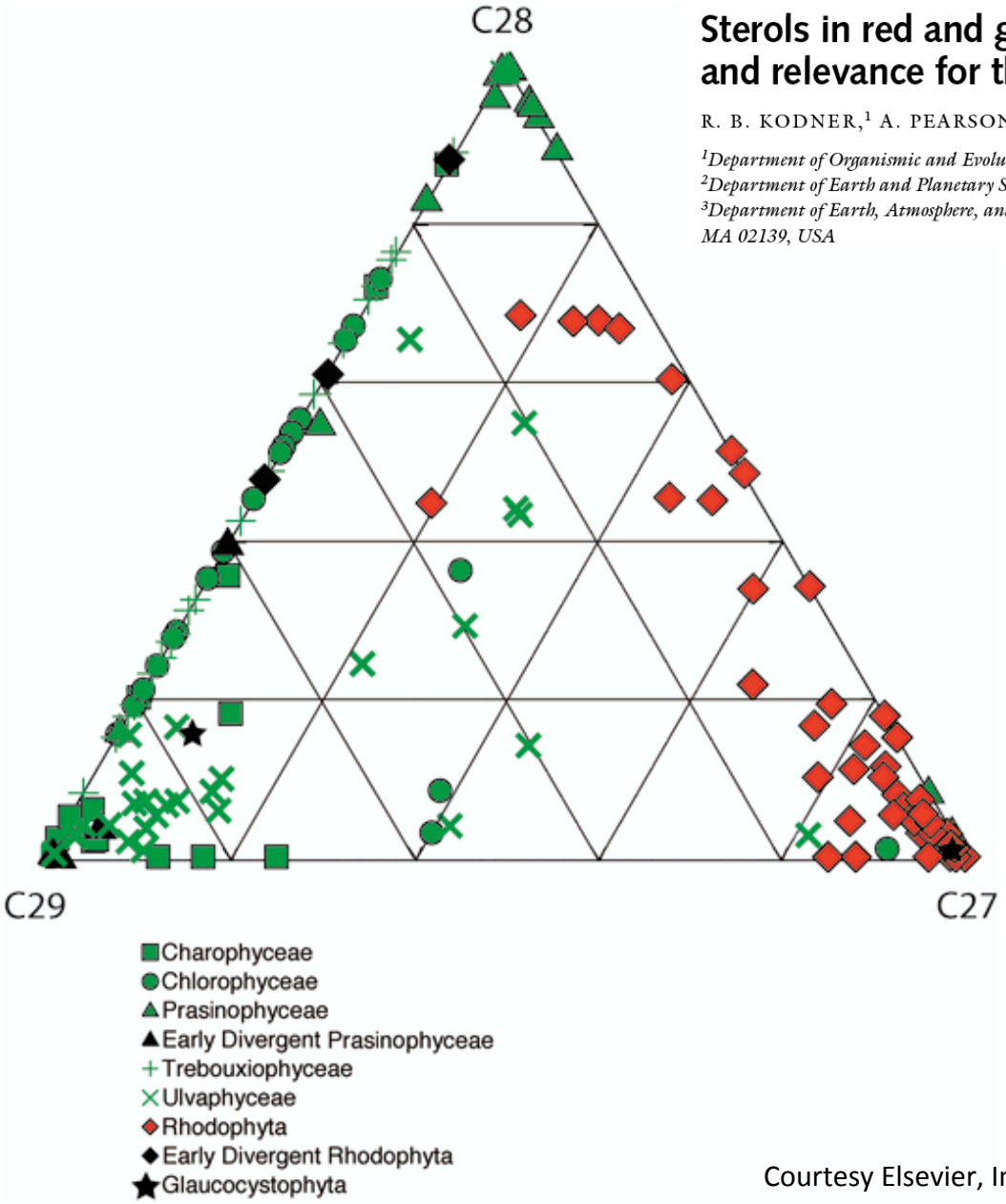

Figure 1. Ternary diagram showing the relative percentages of C_{27}, C_{28}, and C_{29} sterols among modern members of the Plantae, including green algae, red algae, and glaucocystophytes. Early divergent species are shown in black. Individual taxa and associated references are given in Table S1 in Supporting Information.

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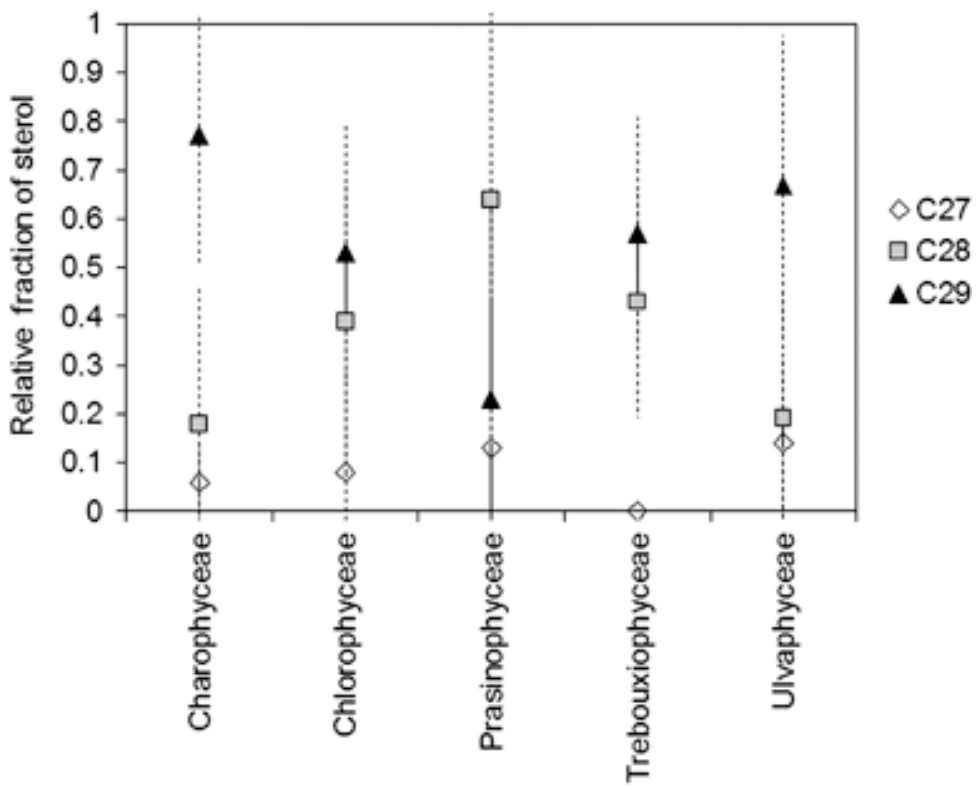

Figure 2. The mean fractional contents of $C_{27–29}$ sterols across green algal classes, with population standard deviations.

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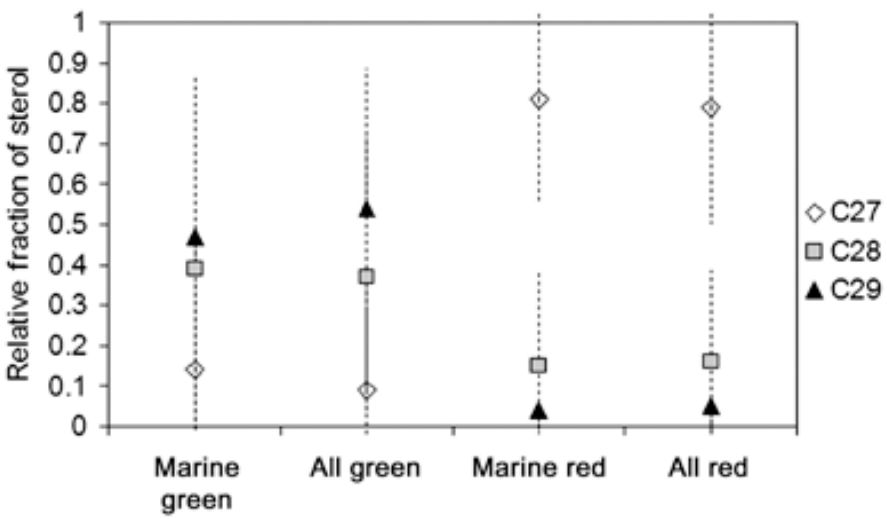

Figure 3. The mean fractional contents of $C_{27–29}$ sterols across marine species of red and green algae, with population standard deviations. For comparison, the mean values from analysis of total (marine plus non-marine) data for each group also are displayed.

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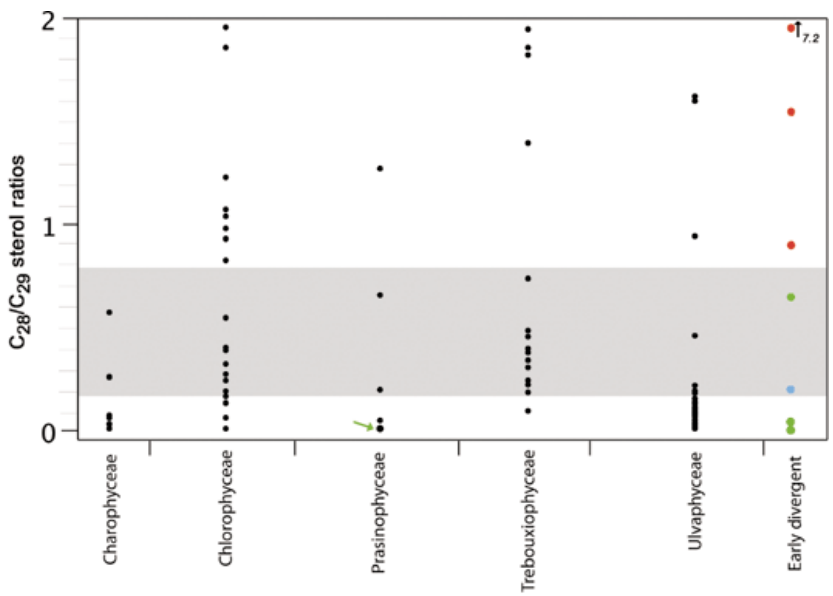
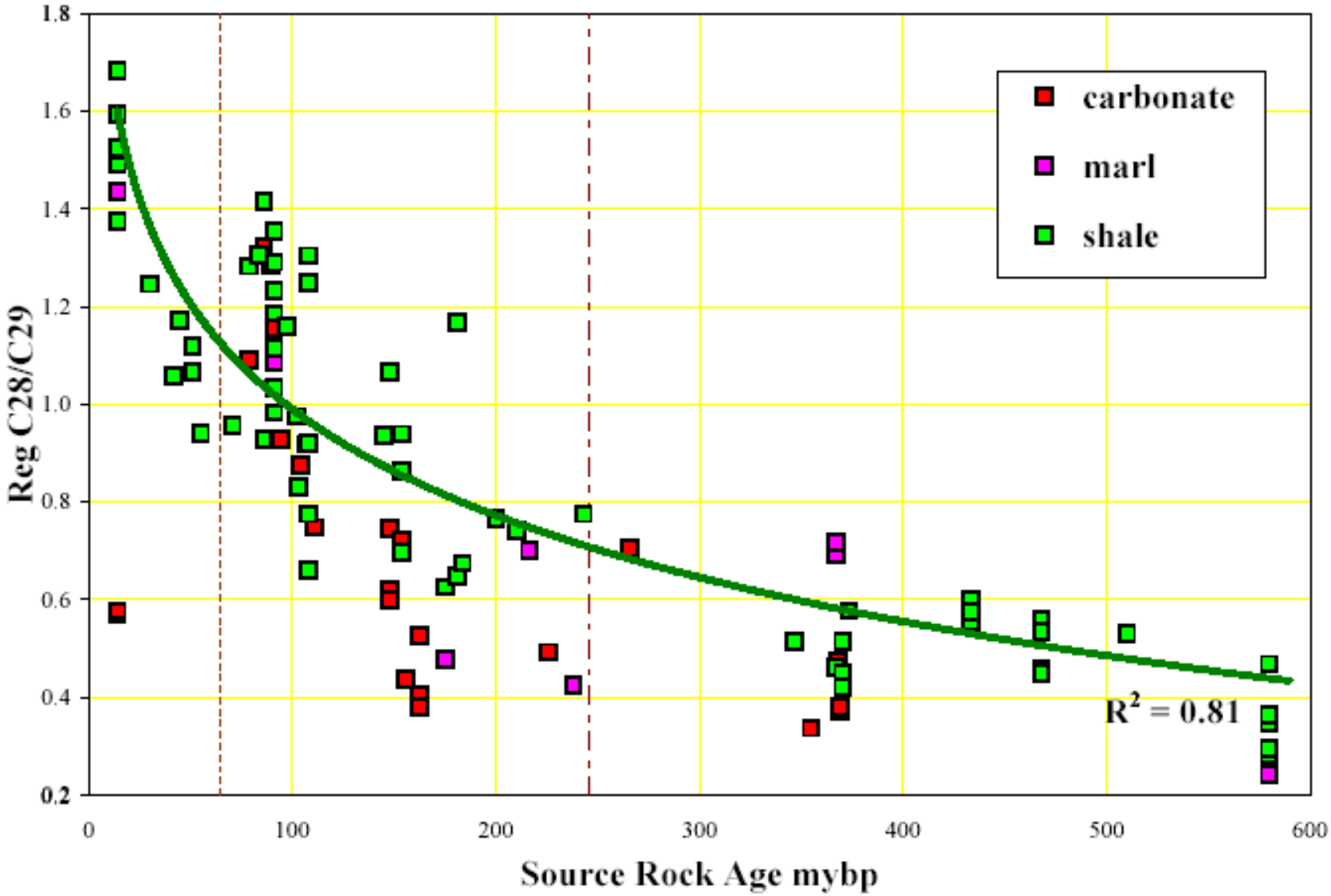


Figure 4. C_{28}/C_{29} sterol ratios for all green algal species in the dataset (black). For comparison, all early divergent taxa are shown in a separate area on the right side and are color-coded according to phylum: green = green algae, red = red algae, blue = glaucocystophytes. One glaucocystophyte highlighted in Fig. 1 does not appear here, because the ratio is undefined; and two green algal species have C_{28}/C_{29} ratios = 0. The red point next to the arrow is off-scale (C_{28}/C_{29} ratio = 7.2). The green arrow in the column of prasinophytes points to *Halosphaera*, the only prasinophyte with a microfossil record. The gray box indicates the range of C_{28}/C_{29} sterane ratios found in bitumens and petroleums from Ediacaran and Paleozoic rocks.

C_{28}/C_{29} Sterane Ratios: The Rise of Modern Plankton



Paul Kenrick and Peter Crane
http://tolweb.org/tree?group=Embryophytes&contgroup=Green_plants

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Oldest evident land plant =
Late Ordovician spore

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Oldest N. Hemisphere vascular plant = Late Silurian Cooksonia

Earliest Land Plants - Lycopsids

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Baragwanathia longifolia
Upper Silurian and Lower Devonian of Australia
To the left a fossil, to the right a reconstruction of a part of the plant.The sporangia are in the axils of the leaves. Drawing J. Hulst

http://www.xs4all.nl/~steurh/eng/ebaragw.html

Ferns

Kathleen M. Pryer and Alan R. Smith

http://tolweb.org/tree?group=Filicopsida&contgroup=Embryophytes#titlefigcaption

FERNS

FERNS date back to at least the Middle Devonian. They include four living groups: **Marattiales**, **Ophioglossales**, **Psilotales** and **leptosporangiate ferns**.
Some early groups that are now extinct, including the **Stauropteridales** and **Zygopteridales**.
The chart below shows the stratigraphic ranges over which each group is known to have existed. The green taxa on the right side of the chart are groups of ferns; the blue taxa to the left are Sphenophytes or Sphenopsids; and the purple Cladoxylopsida in the center are a closely related group.
Of all living ferns, only the Psilotales has no fossil record

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journal homepage: www.elsevier.com/locate/orggeochem

Biomarker lipids of the freshwater fern *Azolla* and its fossil counterpart from the Eocene Arctic Ocean

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[b] *NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands*
[c] *Utrecht University, Faculty of Sciences, Department of Biology, Budapestlaan 4, 3584 CD Utrecht, The Netherlands*

Biomarkers for Azolla or Anabaena????

Conifers

Coniferales

Araucariaceae	Cretaceous to Recent	36 extant species	Southern Hemisphere
Cephalotaxaceae	Jurassic to Recent	5 extant species	Northern Hemisphere
Cupressaceae	Triassic to Recent	157 extant species	both Hemispheres
Pinaceae	Cretaceous to Recent	250 extant species	Northern Hemisphere
Podocarpaceae	Triassic to Recent	131 extant species	Southern Hemisphere
Cheirolepidaceae	Triassic to Cretaceous	extinct	Global
Palissyaceae	Triassic to Jurassic	extinct	Global
Utrechtiaceae	Carboniferous to Permian	extinct	Global

Taxales

Taxaceae	Jurassic to Recent	9 extant species	Northern Hemisphere

Time Chart for Land Plants

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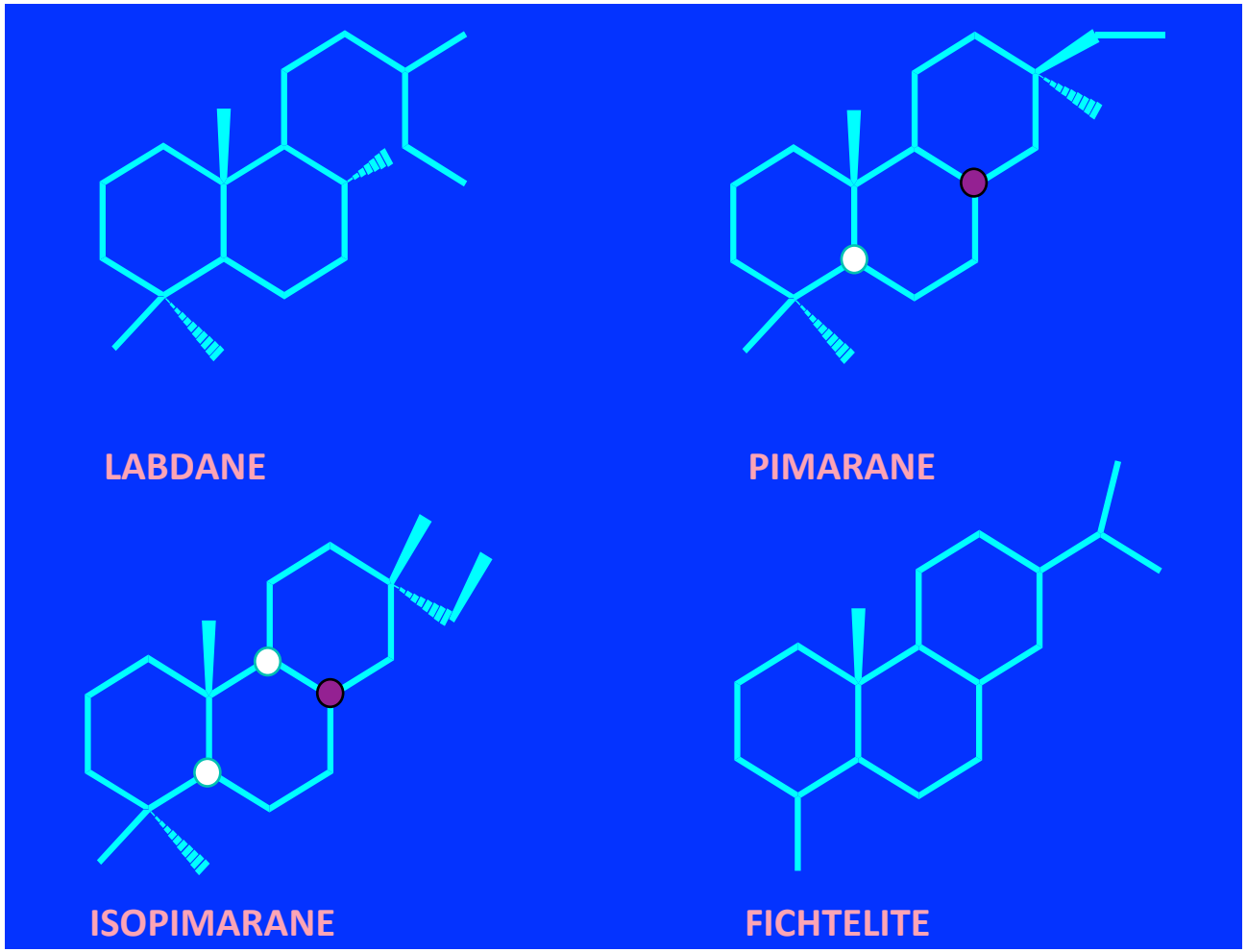
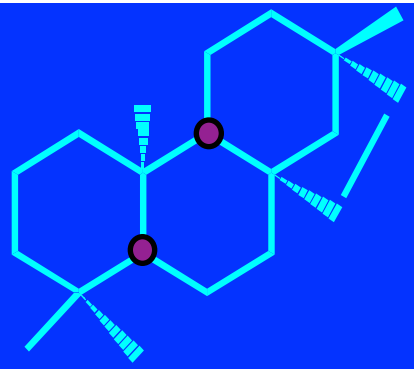
http://www.ucmp.berkeley.edu/plants/plantaefr.gif

Diterpanes from Conifers?

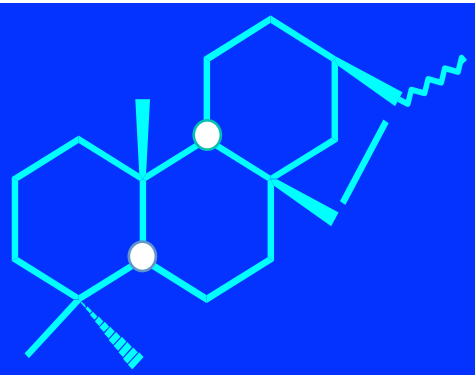
Abundances in rocks and oils track evolution of vascular plants and possibly green algae (David Zinniker PhD Thesis, Stanford, 2003/4)



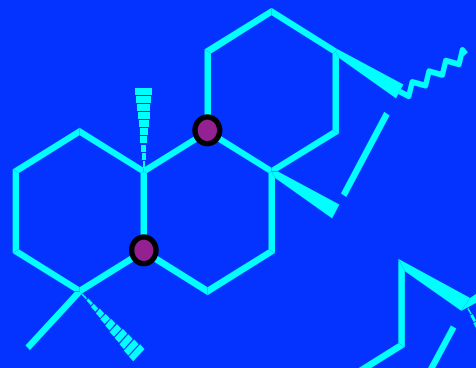
Diterpanes



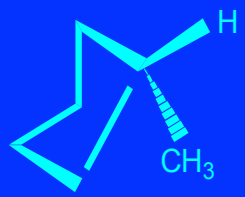
ent-BEYERANE



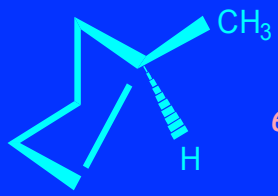
PHYLLOCLADANE



KAURANE



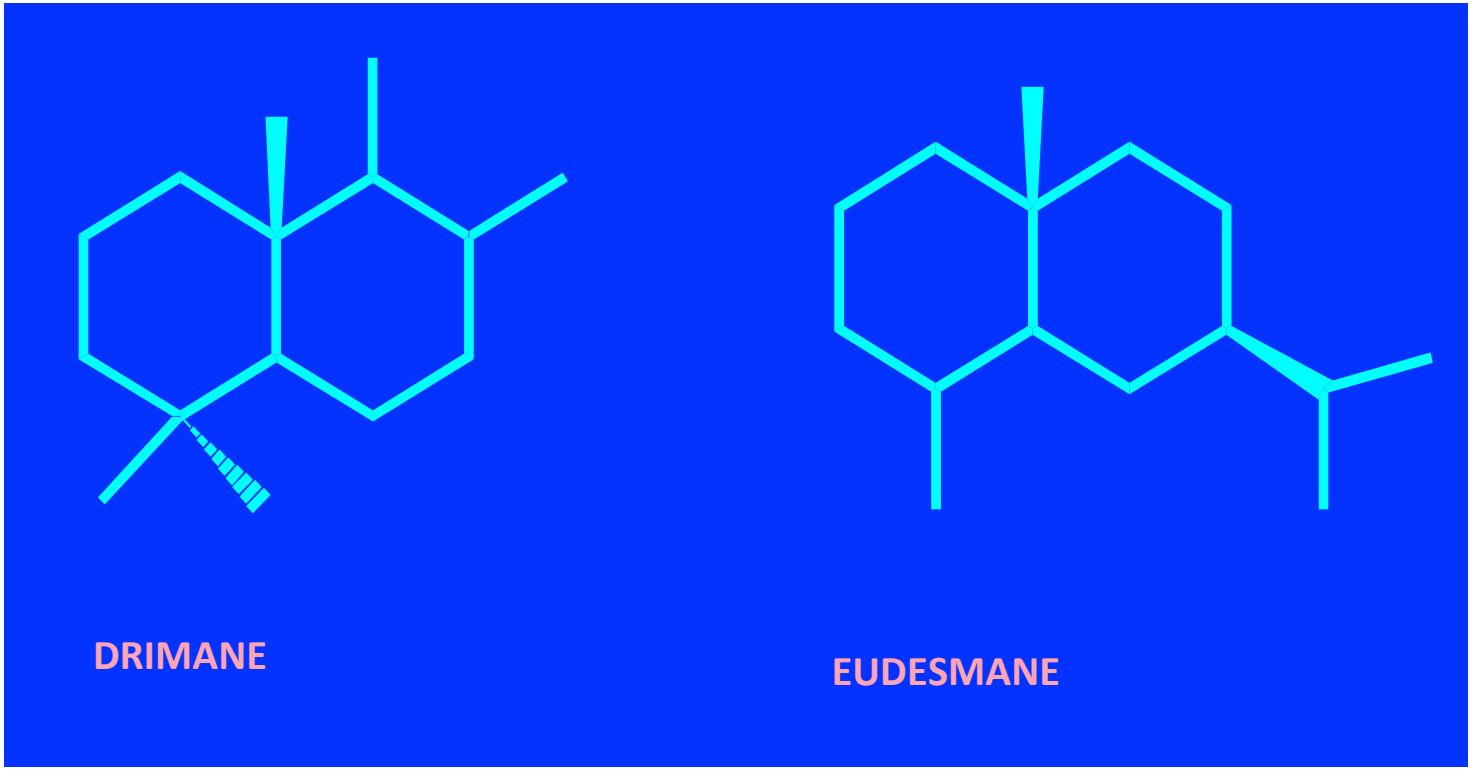
ent-16α(H)



ent-16β(H)

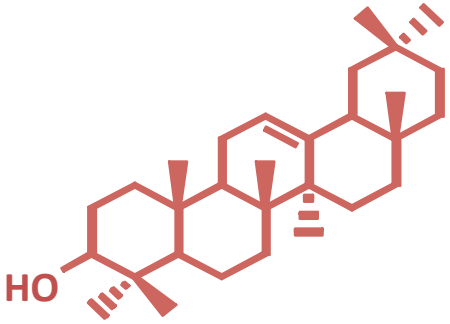
Bicyclic Sesquiterpanes:

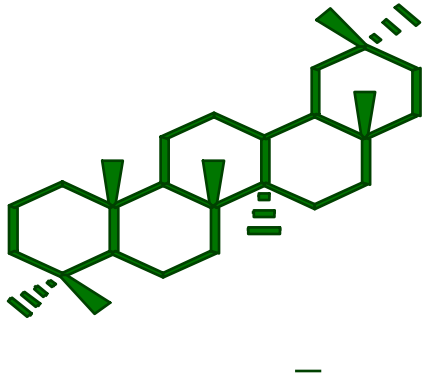
possible bacteriohopane degradation products



Diagnostic Plant Triterpanes

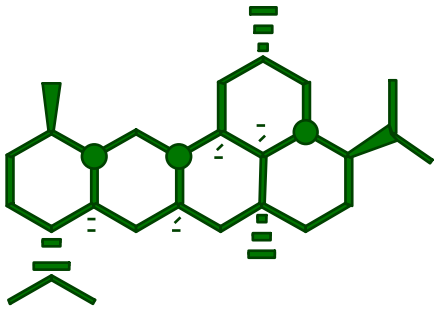
angiosperm β-amyrin





oleanane

polycadinene
resin
angiosperms/dipterocarps?



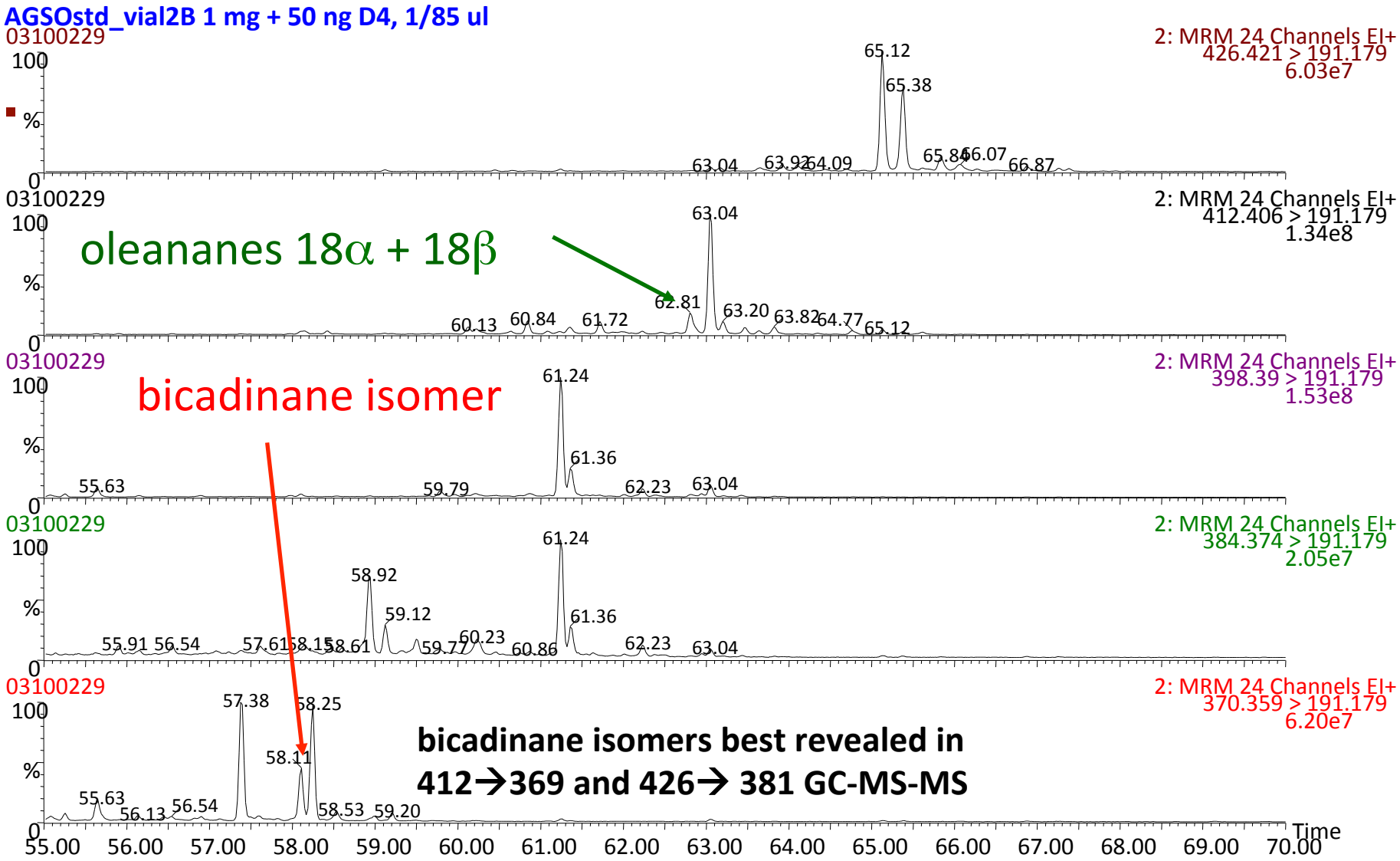
bicadinane

The Molecular Fossil Record of Oleanane and Its Relation to Angiosperms

J. Michael Moldowan, Jeremy Dahl, Bradley J. Huizinga,
Frederick J. Fago, Leo J. Hickey, Torren M. Peakman,
David Winship Taylor

Oleanane has been reported in Upper Cretaceous and Tertiary source rocks and their related oils and has been suggested as a marker for flowering plants. Correspondence of oleanane concentrations relative to the ubiquitous microbial marker 17α-hopane with angiosperm diversification (Neocomian to Miocene) suggests that oleanane concentrations in migrated petroleum can be used to identify the maximum age of unknown or unavailable source rock. Rare occurrences of pre-Cretaceous oleanane suggest either that a separate lineage leads to the angiosperms well before the Early Cretaceous or that other plant groups have the rarely expressed ability to synthesize oleanane precursors.

SCIENCE • VOL. 265 • 5 AUGUST 1994


AGSOstd_vial2B 1 mg + 50 ng D4, 1/85 ul
03100229
2: MRM 24 Channels EI+
426.421 > 191.179
6.03e7
65.12
65.38
63.04
63.92
64.09
65.84
66.07
66.87
03100229
2: MRM 24 Channels EI+
412.406 > 191.179
1.34e8
oleananes 18α + 18β
63.04
62.81
63.20
63.82
64.77
65.12
60.13
60.84
61.72
03100229
2: MRM 24 Channels EI+
398.39 > 191.179
1.53e8
bicadinane isomer
61.24
61.36
55.63
59.79
62.23
63.04
03100229
2: MRM 24 Channels EI+
384.374 > 191.179
2.05e7
61.24
58.92
59.12
61.36
55.91
56.54
57.61
58.15
58.61
59.77
60.23
60.86
62.23
63.04
03100229
2: MRM 24 Channels EI+
370.359 > 191.179
6.20e7
57.38
58.25
58.11
55.63
56.13
56.54
58.53
59.20
bicadinane isomers best revealed in
412→369 and 426→ 381 GC-MS-MS
100
%
0
55.00
56.00
57.00
58.00
59.00
60.00
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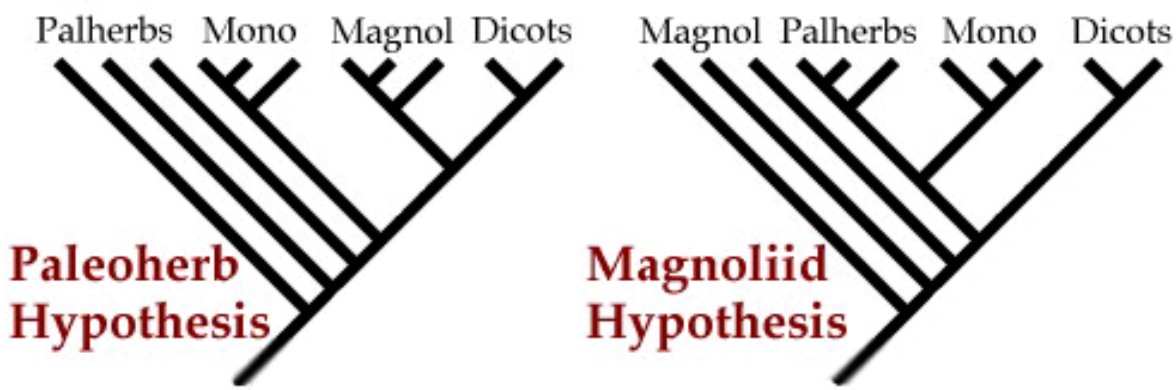
Time



Angiosperm Origins: The two competing hypotheses for angiosperm origins paint very different pictures about the biology of the earliest flowering plants.

The Paleoherb Hypothesis suggests that the basal lineages were herbs with rapid lifecycles.

Magnoliid Hypothesis suggests that the basal lineages were small trees with slower lifecycles. (Dicots=tricolpate dicots; Magnol=magnoliids; Mono=monocots; Palherbs=paleoherbs)

http://www.ucmp.berkeley.edu/anthophyta/anthophytafr.html#origin

- **The Woody Magnoliid Hypothesis** -- Cladistic analyses by Doyle and Donoghue favor an early angiosperm with morphology similar to living members of the Magnoliales and Laurales.

- These groups are small to medium-sized trees with long broad leaves and large flowers with indeterminate numbers perianth parts. The carpels are imperfectly fused, and make a physical intermediate between a folded leaf and fused pistil. This hypothesis is also favored by molecular studies, and so currently is favored by systematic botanists.
- **It suggests that the earliest angiosperms were understory trees and shrubs, and that the flower was NOT the key innovation for the rapid diversification of angiosperms. In fact woody magnoliids are not particularly diverse, even today.**

- **The Paleoherb Hypothesis** -- The alternative view is an herbaceous origin for the angiosperms. This view has been championed in recent years by Taylor and Hickey, paleobotanists whose cladistic analysis of angiosperms suggests a very different scenario from that previously described. In their analysis, the basal angiosperms are tropical paleoherbs, a group of flowering plants with uncomplicated flowers and a mix of monocot and dicot features.

- **The implication here is that the key innovations of flowers and a rapid life cycle were present in the earliest angiosperms. It has been suggested that changes in climate or geography provided opportunities for these early angiosperms to diversify.**

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Accepted species tree for seven plant model species. Names of clades are indicated at internal nodes. See text for discussion of strength of evidence for this phylogeny.
Sanderson and McMahon *BMC Evolutionary Biology* 2007 **7**(Suppl 1):S3 doi: 10.1186/1471-2148-7-S1-S3

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Published online ahead of print July 19, 2010;
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American Journal of Botany

Research Article

The age and diversification of the angiosperms re-revisited[1]

Charles D. Bell[2,5], Douglas E. Soltis[3] and Pamela S. Soltis[4]

Key results: Based on the analysis for which we set fossils to fit lognormal priors, we obtained an estimated age of the angiosperms of 167–199 Ma (Early Jurassic) and the following age estimates for major angiosperm clades: Mesangiospermae (139–156 Ma); Gunneridae (109–139 Ma); Rosidae (108–121 Ma); Asteridae (101–119 Ma).

• *Conclusions*: With the exception of the age of the angiosperms themselves, these age estimates are generally younger than other recent molecular estimates and very close to dates inferred from the fossil record.

Pergamon

Org. Geochem. Vol. 29, No. 5–7, pp. 1199–1214, 1998

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PII: S0146-6380(98)00126-0

Carbon isotope biogeochemistry of plant resins and derived hydrocarbons

ANDREW P. MURRAY*[1], DIANNE EDWARDS[1], JANET M. HOPE[1], CHRISTOPHER J. BOREHAM[1], WEBBER E. BOOTH[2], ROBERT A. ALEXANDER[3] and ROGER E. SUMMONS[1]†

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Anderson's Resin Classification Scheme

Class I	polymeric labdanoid diterpenes; + occluded sesqui-, di and triterpenoids Agathis/Araucaria - Baltic amber Hymenaea - Dominican, Mexican amber
II	polymeric sesquiterpenes;polycadinene + occluded sesqui- and triterpenoids Dammar/Dipterocarpaceae - SE Asia
III	polystyrene
IV	non-polymeric cedrane sesquiterpenoids
V	non-polymeric abietane/pimarane diterps

Semantics

- resins - solid, discrete organic materials derived from higher plant resins - modern samples

- amber = resinite - fossil samples

- balsam, elemi, incense, dammar, sandaracs, mastics and copals-common resins from specific taxa

Resin Characterisation Tools

- 1960's IR, C, H, O, plus volatiles & extracts

- recently- bulk ^{13}C, D and ^{18}O data
  GC-MS of extractables
  pyrolysis-GC-MS of polymers

- this study- ditto plus Compound Specific
  Isotope Analysis plus data on other

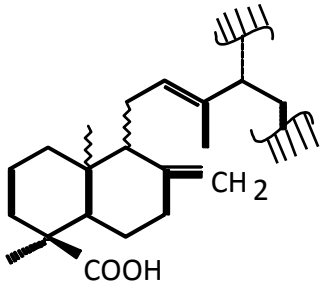
recalcitrant products leaf wax, leaf biopolymer

Australian Coastal Resinites

Resin	Pedigree	$\delta^{13}C$
Bales Bay, Kangaroo Is	DE AGSO # 6183	-27.3
No Two Rocks SA	DE AGSO # 6184	-28.0
Three Mile Rocks SA	DE AGSO # 6187	nd
Lake Bonney SA	DE AGSO # 6186	nd
Brunei resinite	Belait Fm # 6182	-26.2
Gippsland resinite	Yallourn #1982	-22.3
Kauri resin	SA museum #6281	-24.9
Recent dammar	Fluka lab grade	-28.0

Class I "Conifer" Resins and Associated Diterpenoids

labdatriene polymer



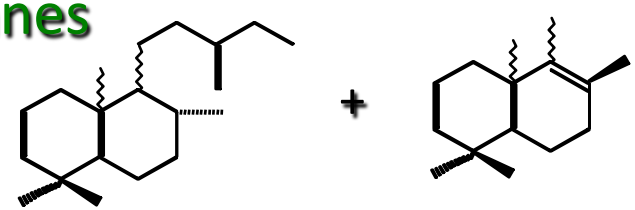
+

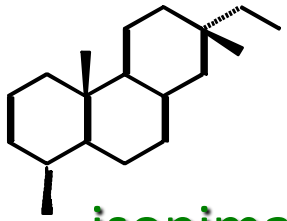
"leaf resins"
e.g.
phyllocladenes,
pimaradienes
+
"resin acids",
e.g. abietic acid

Thermal dissociation

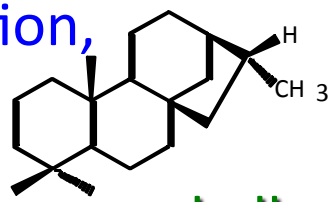
Reduction, defunctionalisation,
intra-molecular cyclisation

labdanes

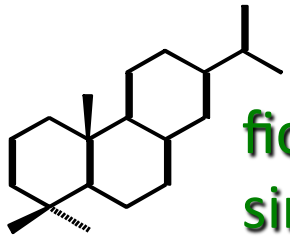




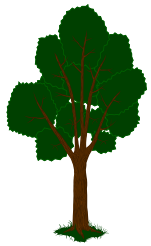
isopimaranes



phyllocladanes

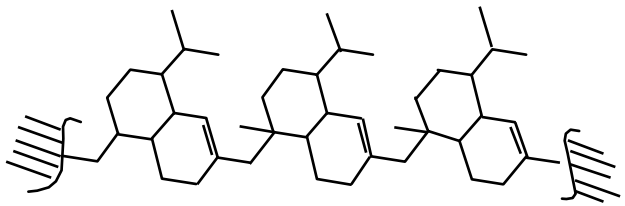


fichtelites,
simonellite

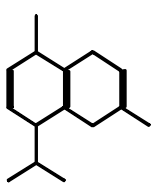


Class II "Angiosperm" Resins

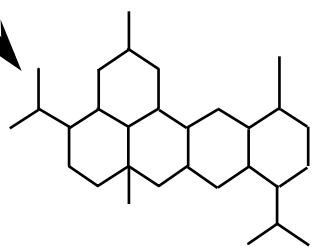
polycadinene



Thermal dissociation
reduction, intra-molecular
cyclisation



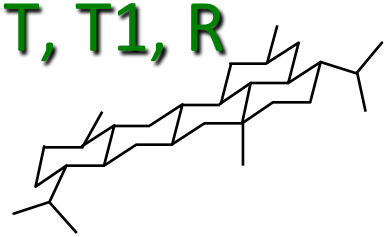
cadinanes

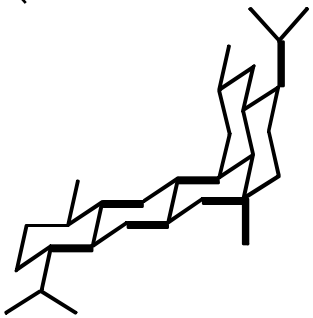


bicadinanes

bicadinan
e isomers

trans-trans-trans
T, T1, R

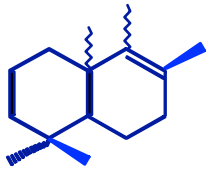


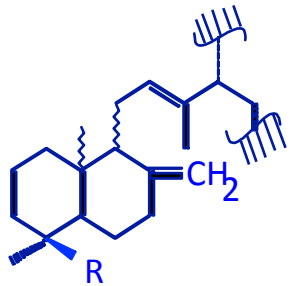


cis-cis-trans
W

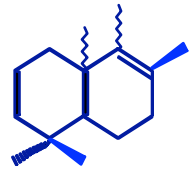
Kauri Resinite (Class I) - Pyrolysate

bulk resinite
- 24.9 ‰

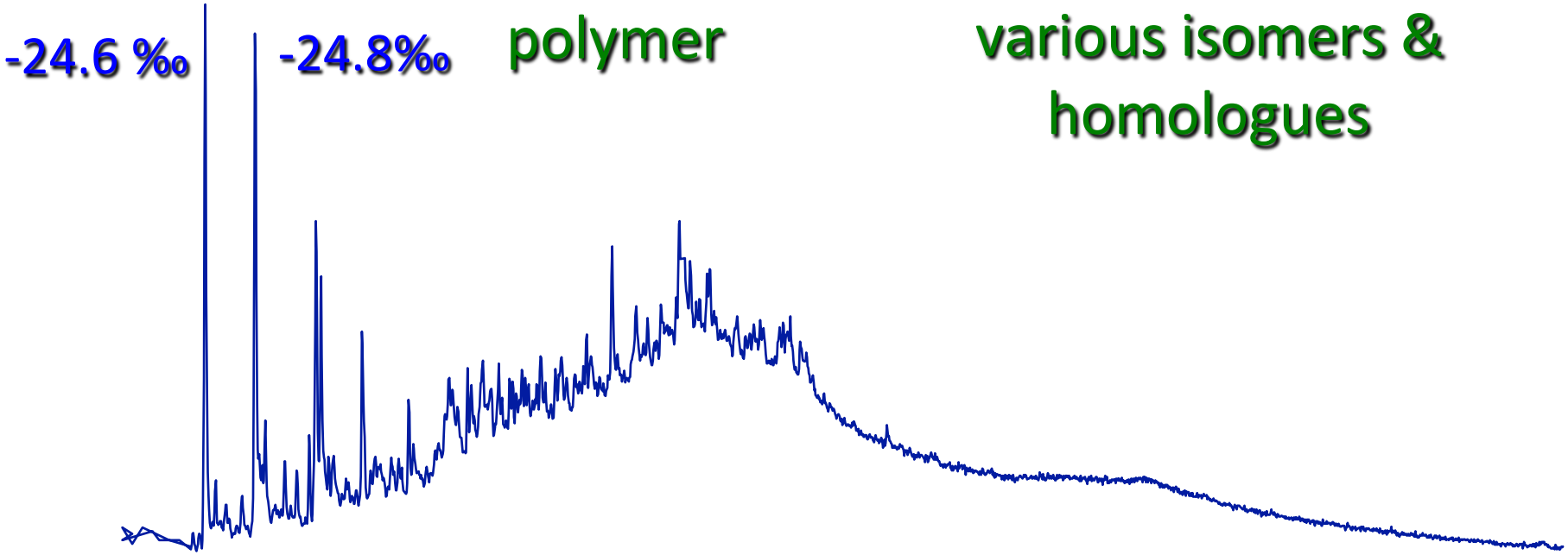




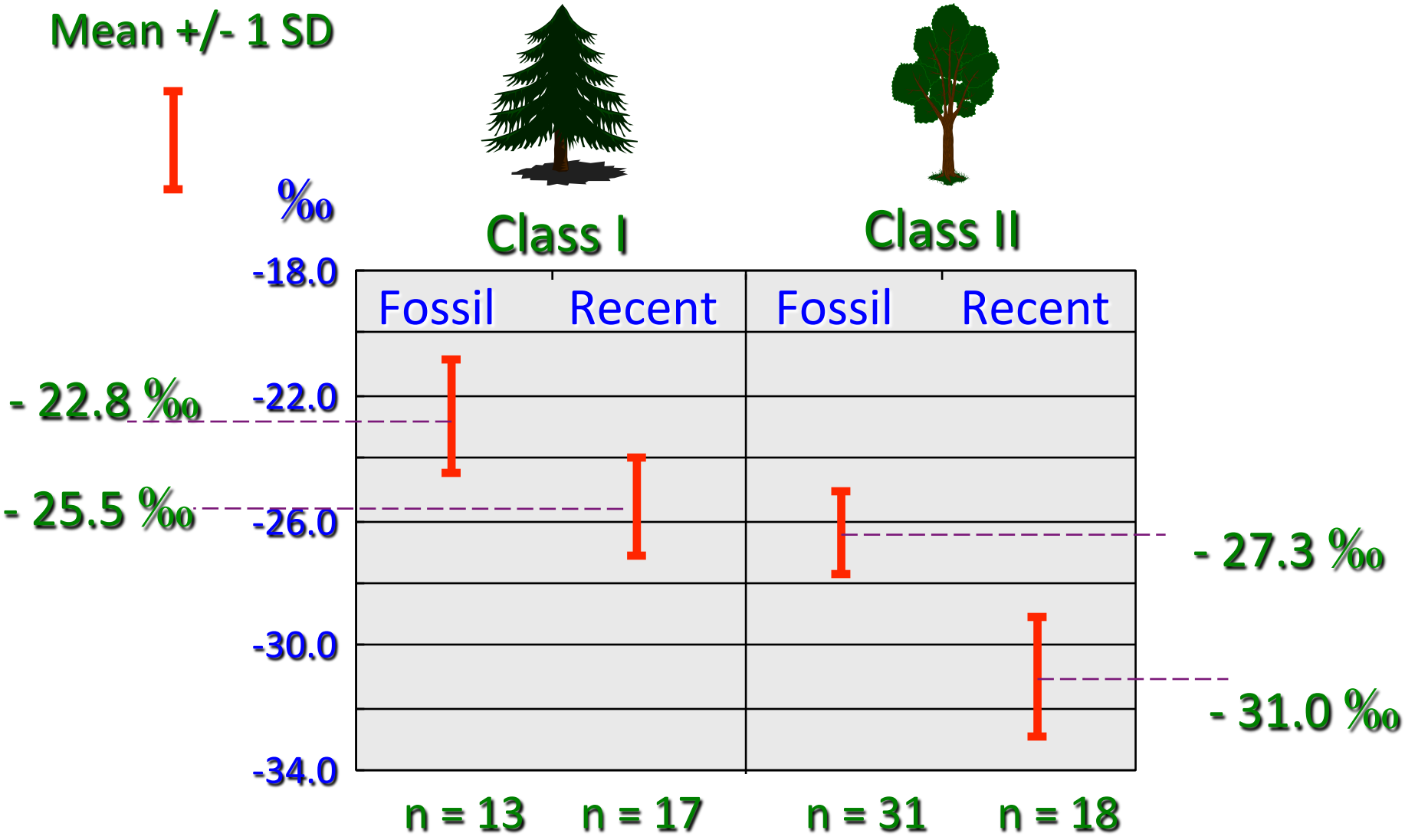
labdatriene polymer



bicyclic hydrocarbons, various isomers & homologues



Bulk Carbon Isotope Composition of Modern & Fossil Resins

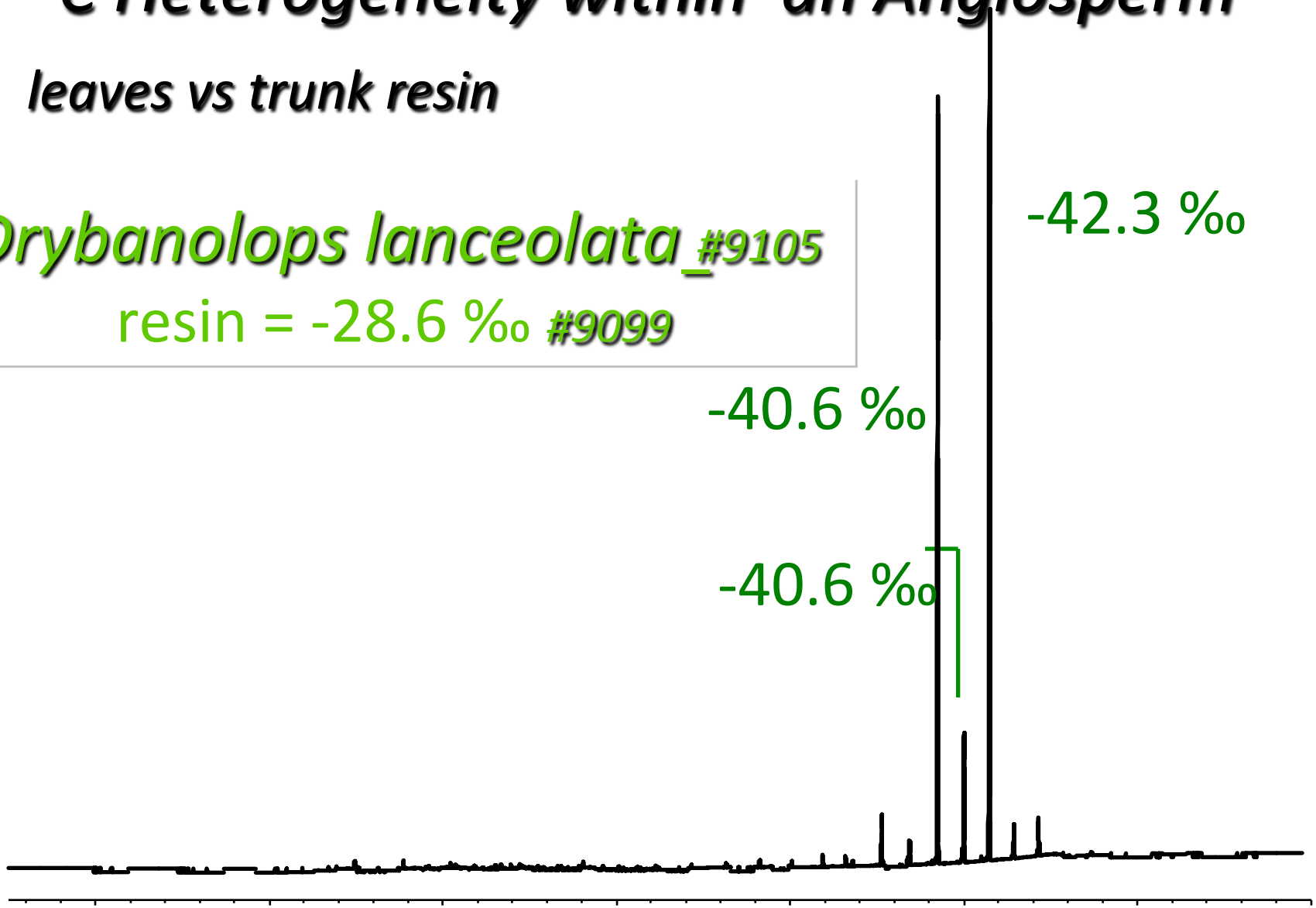


^{13}C Heterogeneity within an Angiosperm

leaves vs trunk resin

Drybanolops lanceolata #9105

resin = -28.6 ‰ #9099



^{13}C Heterogeneity within an Angiosperm

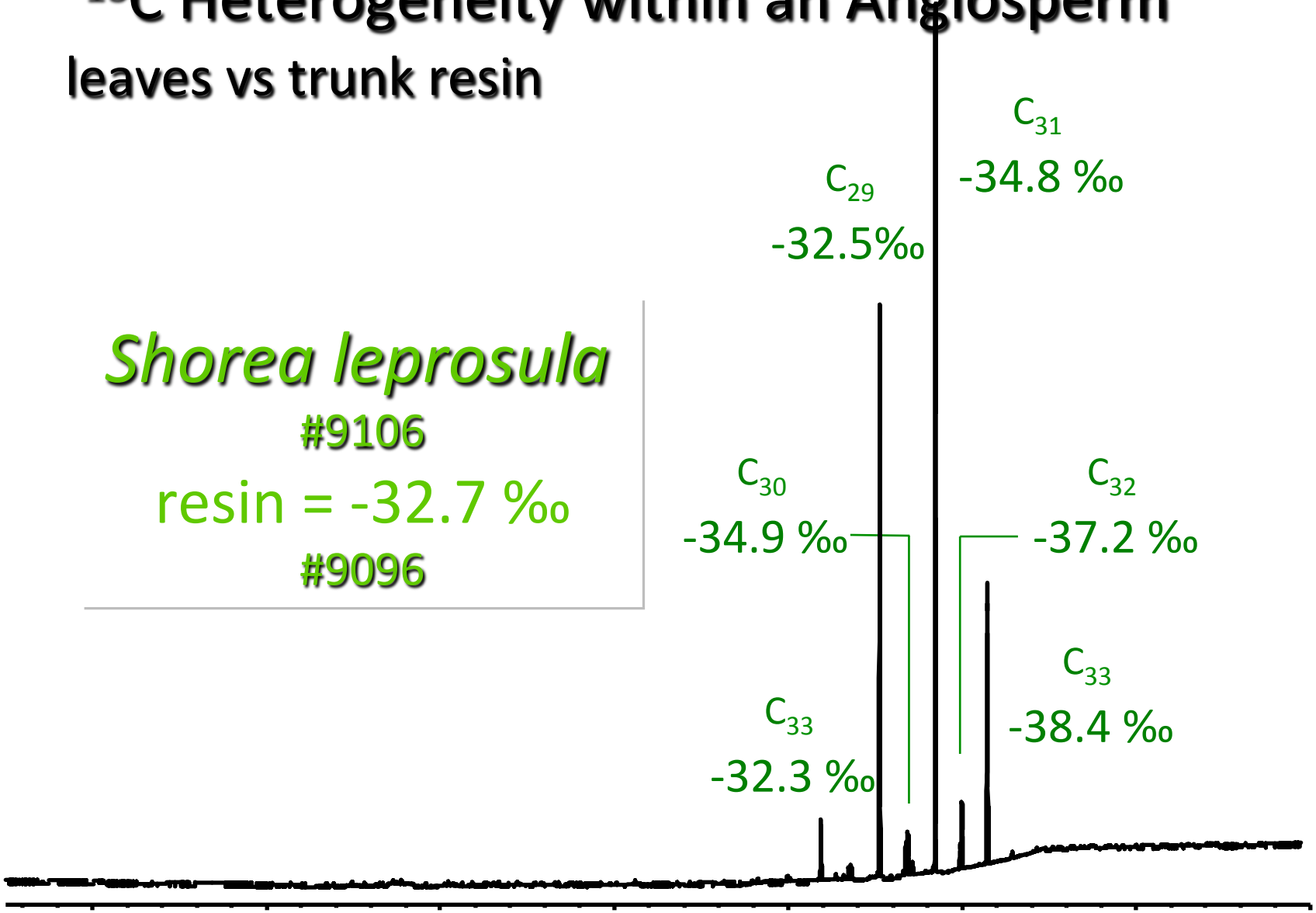
leaves vs trunk resin

Shorea leprosula

#9106

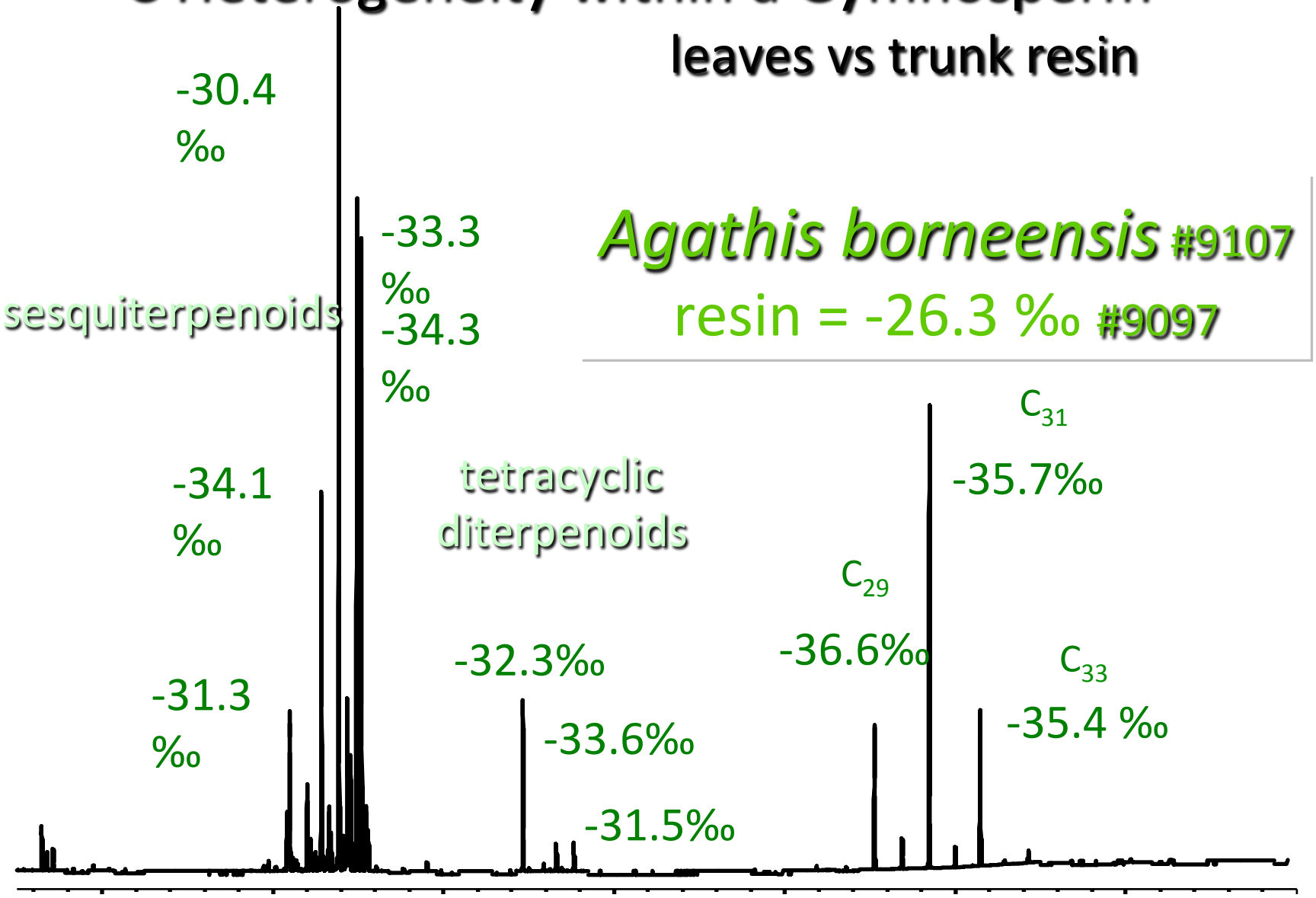
resin = -32.7 ‰

#9096



^{13}C Heterogeneity within a Gymnosperm

leaves vs trunk resin



Agathis borneensis #9107

resin = -26.3 ‰ #9097

^{13}C Heterogeneity within a Gymnosperm

Araucaria heterophylla

#9128

resin = -27.2 ‰

#9127

leaves vs trunk resin

-30.2 ‰

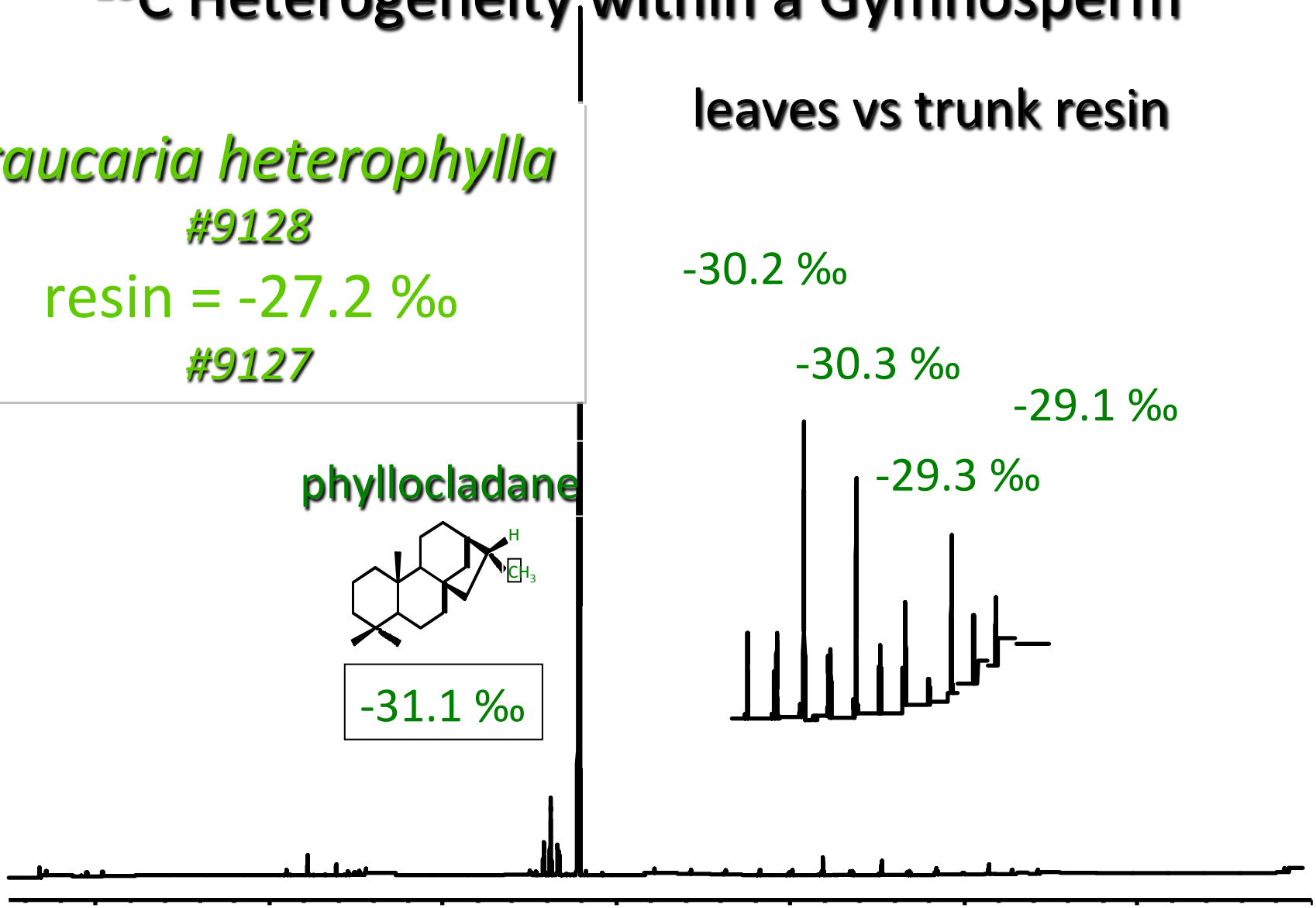
-30.3 ‰

-29.1 ‰

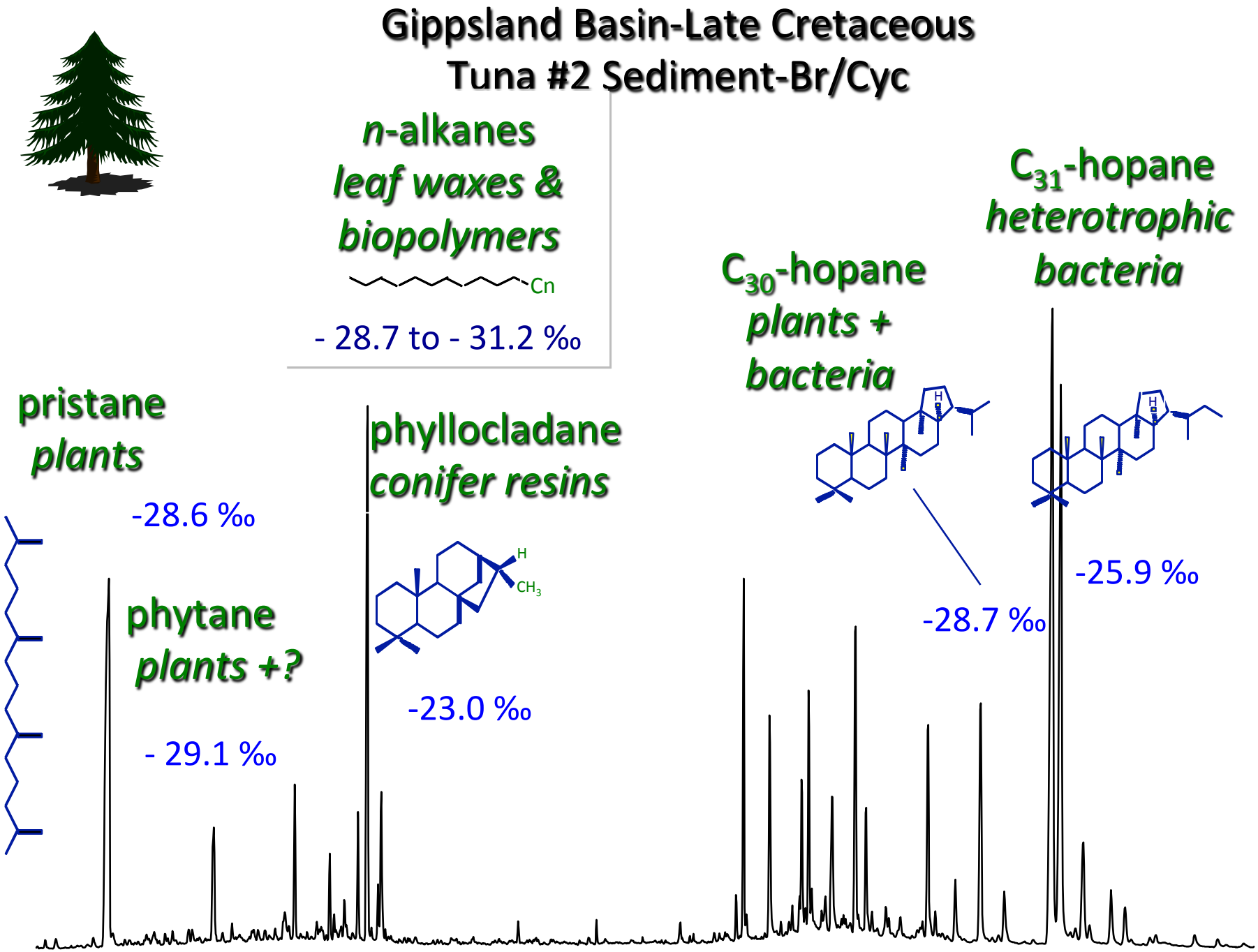
-29.3 ‰

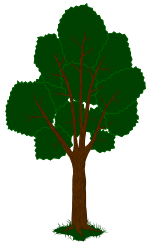
phyllocladane

-31.1 ‰



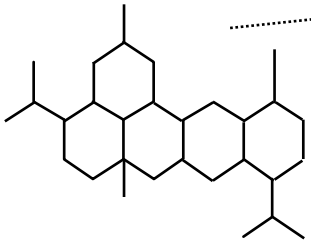
Gippsland Basin-Late Cretaceous
Tuna #2 Sediment-Br/Cyc

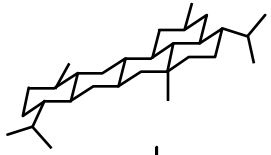




Brunei Resinite (Class II) Pyrolysate

bulk resinite
- 26.2 ‰

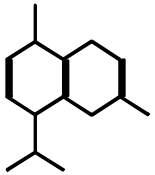




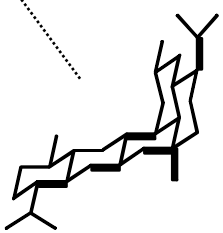
ttt
- 26.4 ‰

bicadinanes

cadinanes

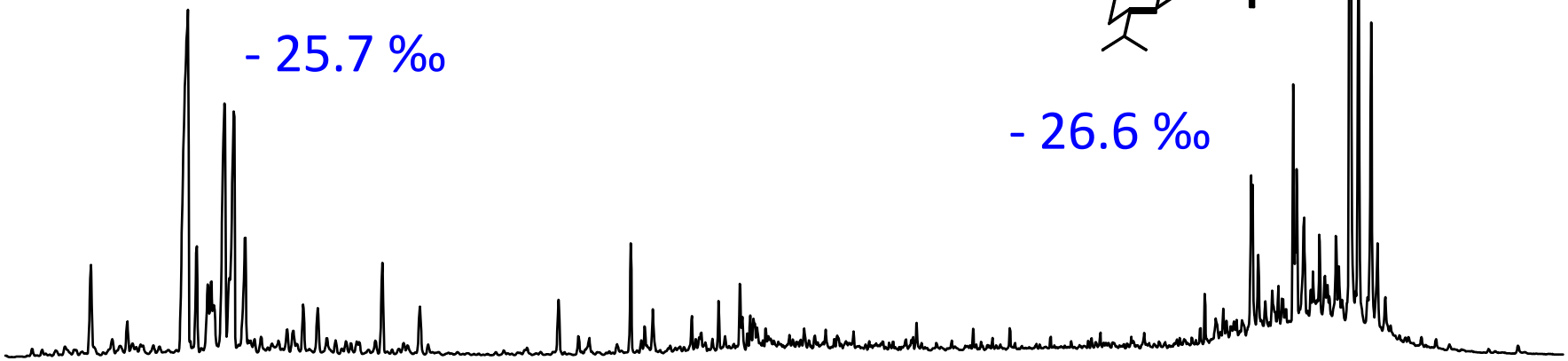


cct

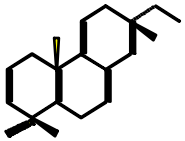


- 25.7 ‰

- 26.6 ‰



NZ Taranaki Basin-Maui Oil-Br/Cyc



pristane
plants

-28.7‰

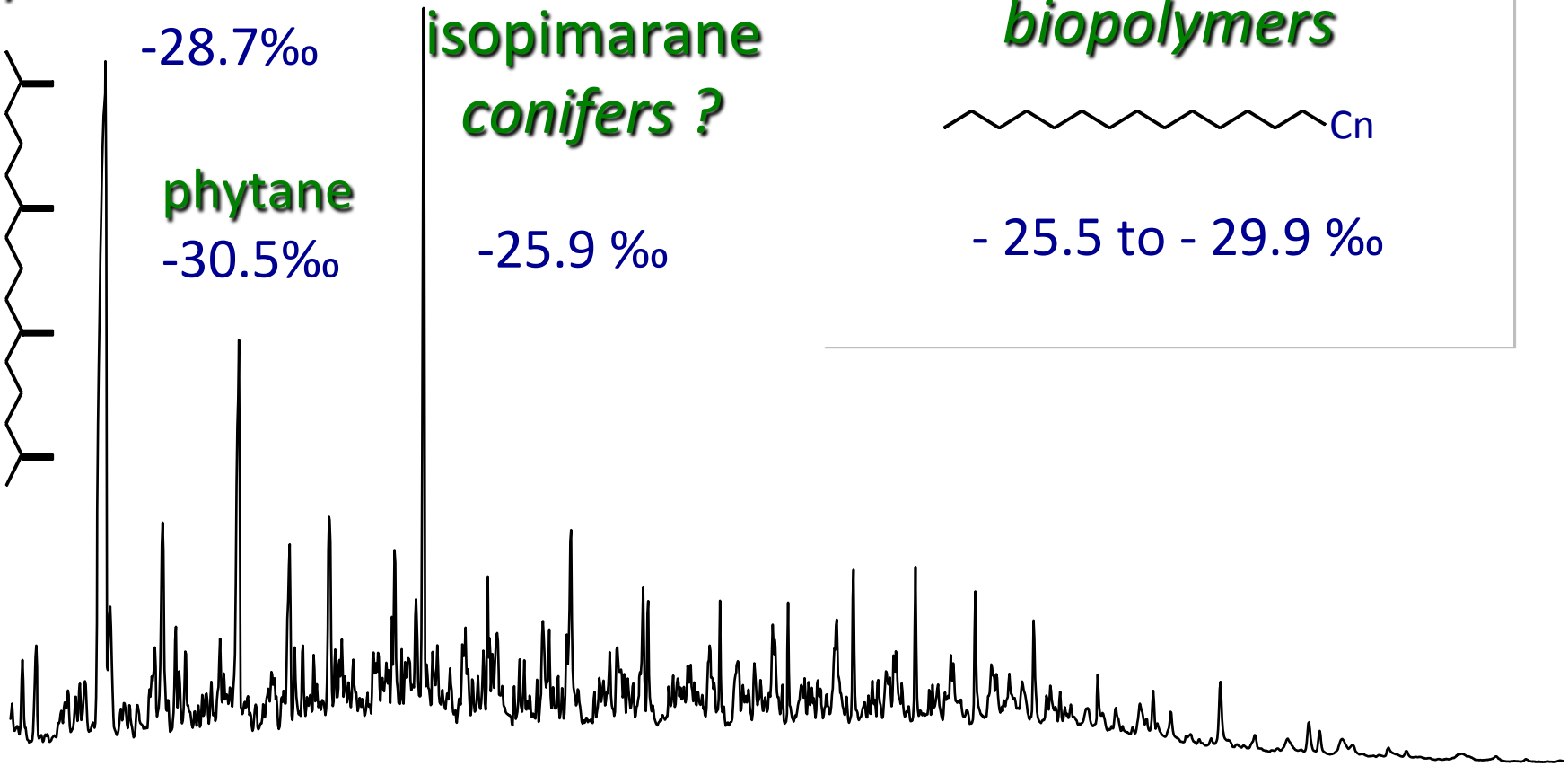
isopimarane
conifers ?

phytane
-30.5‰

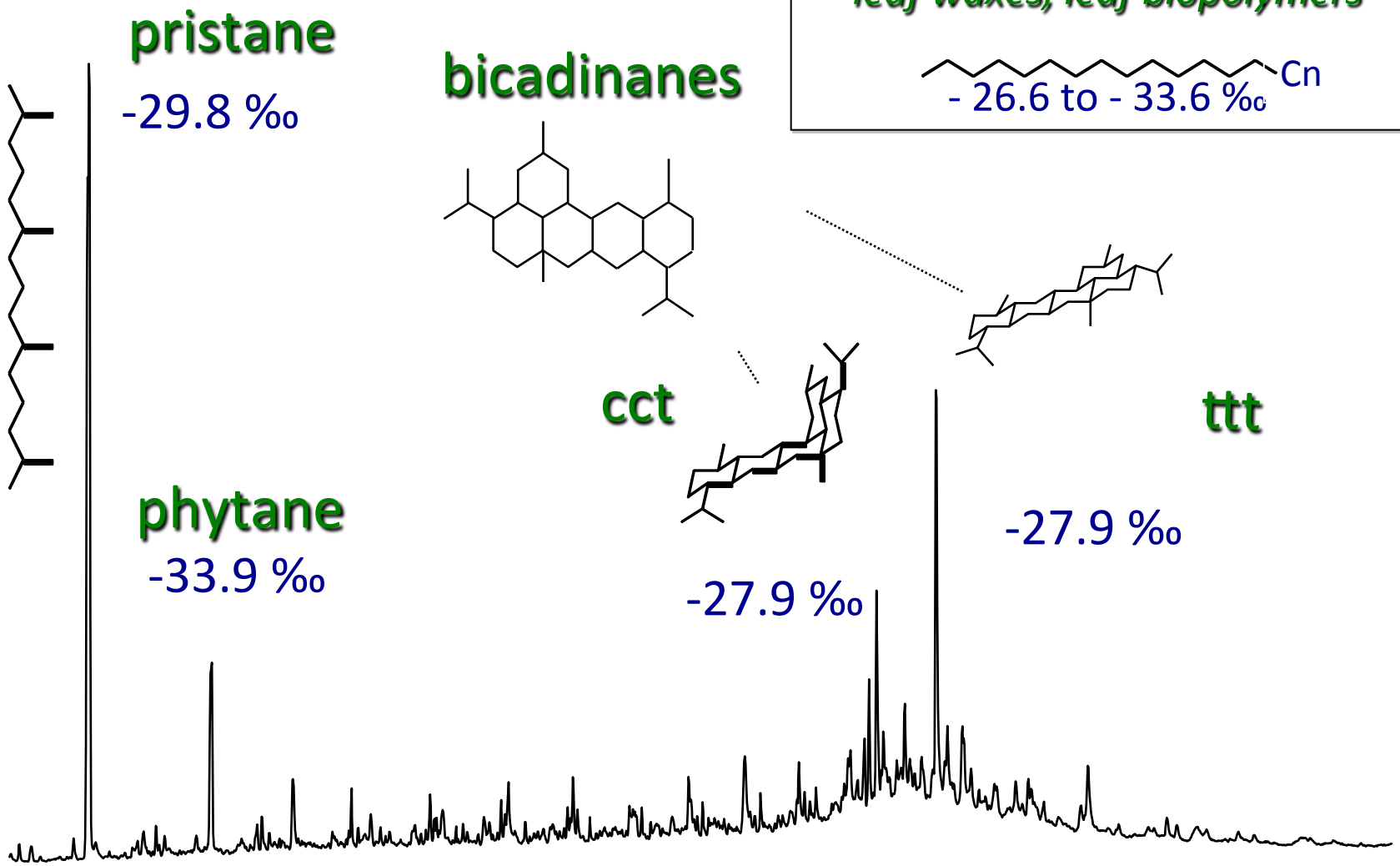
-25.9 ‰

n-alkanes
leaf waxes, leaf biopolymers

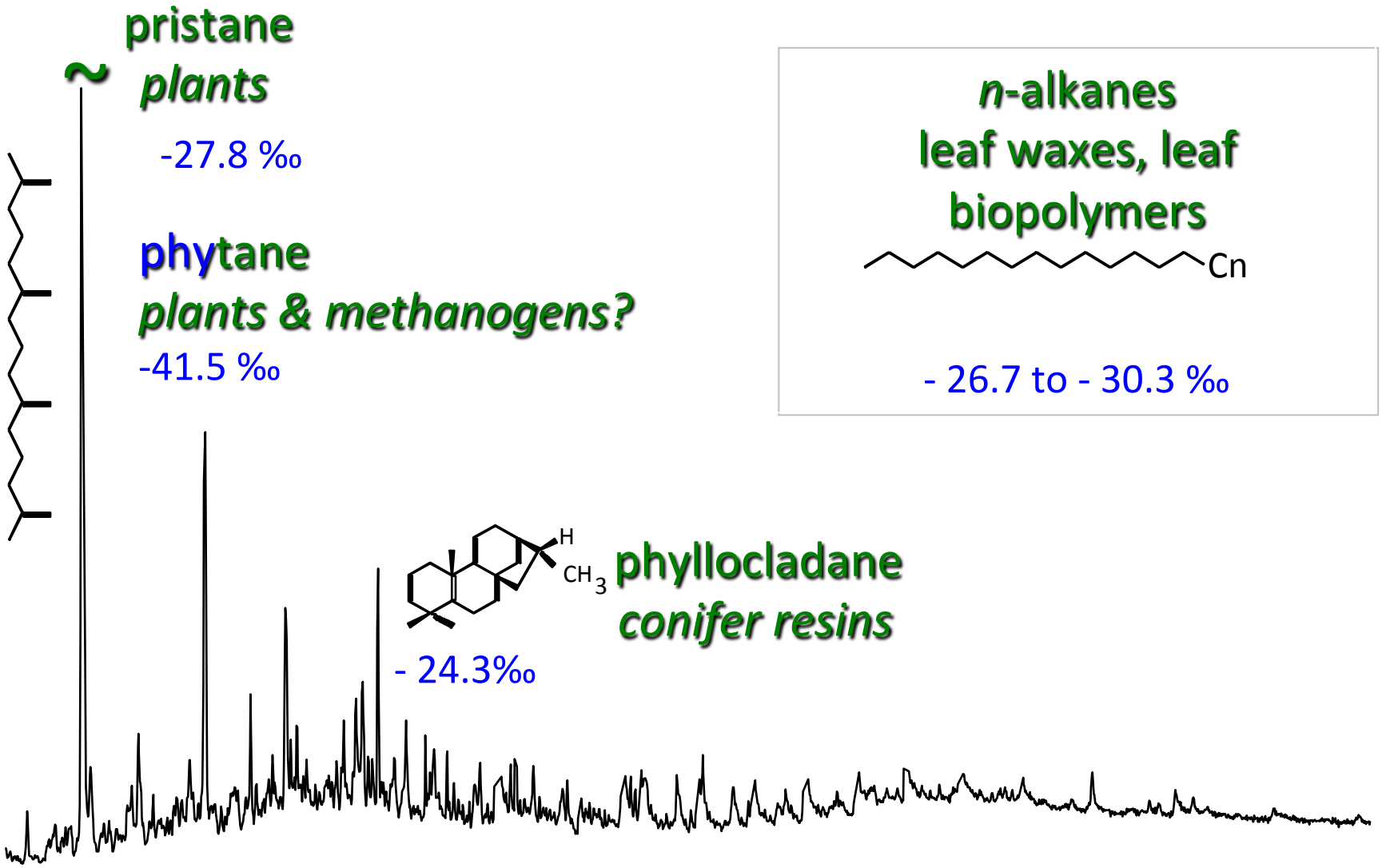
- 25.5 to - 29.9 ‰



S. Sumatra Basin Oil - Br/Cyc



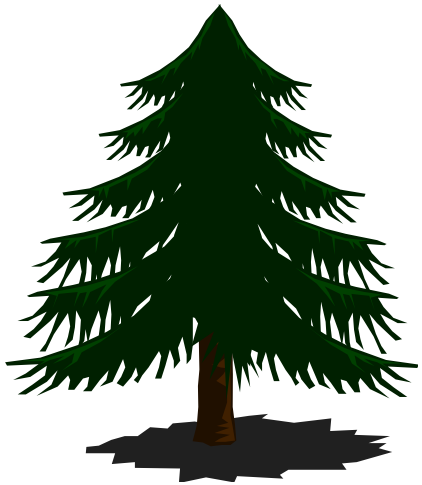
Gippsland Basin-Dolphin oil-B/C



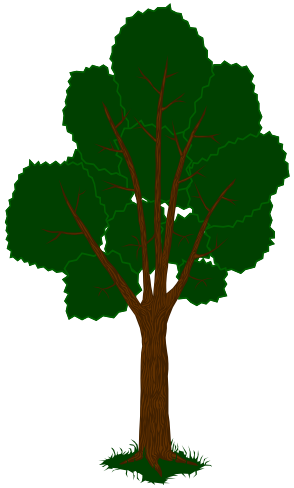
n-alkanes
leaf waxes, leaf biopolymers

- 26.7 to - 30.3 ‰

Plants optimise stomatal conductance to maximise access to CO_2 & minimise loss of water ∴ water conservative plants have isotopically 'heavier' carbon



Average 3 ‰ difference in $\delta^{13}C$



Conifer

Needle leaf morphology
Water conservative
Restricted access to CO_2
Discriminates less against ^{13}C
$\delta^{13}C$ values for wood typically:

~ - 21 ‰

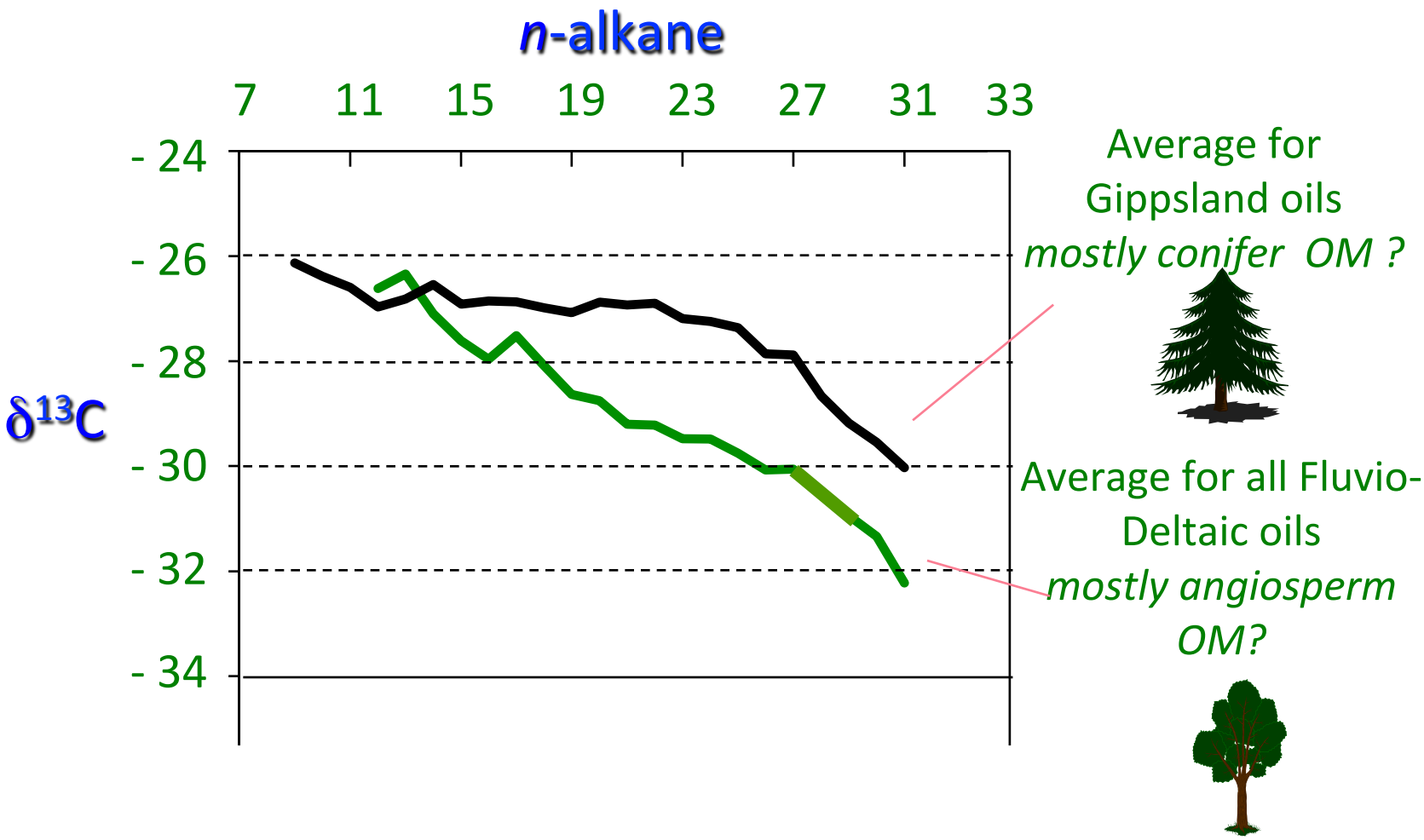
Angiosperm

Broad leaf morphology
Less water conservative
Less restricted access to CO_2
Discriminates more against ^{13}C
$\delta^{13}C$ values for wood typically:

~ - 24 ‰

*Data from Stuiver and Braziunas, 1987 for 40° latitude, modern plants

Fluvio-Deltaic oils - n-alkane isotope profiles



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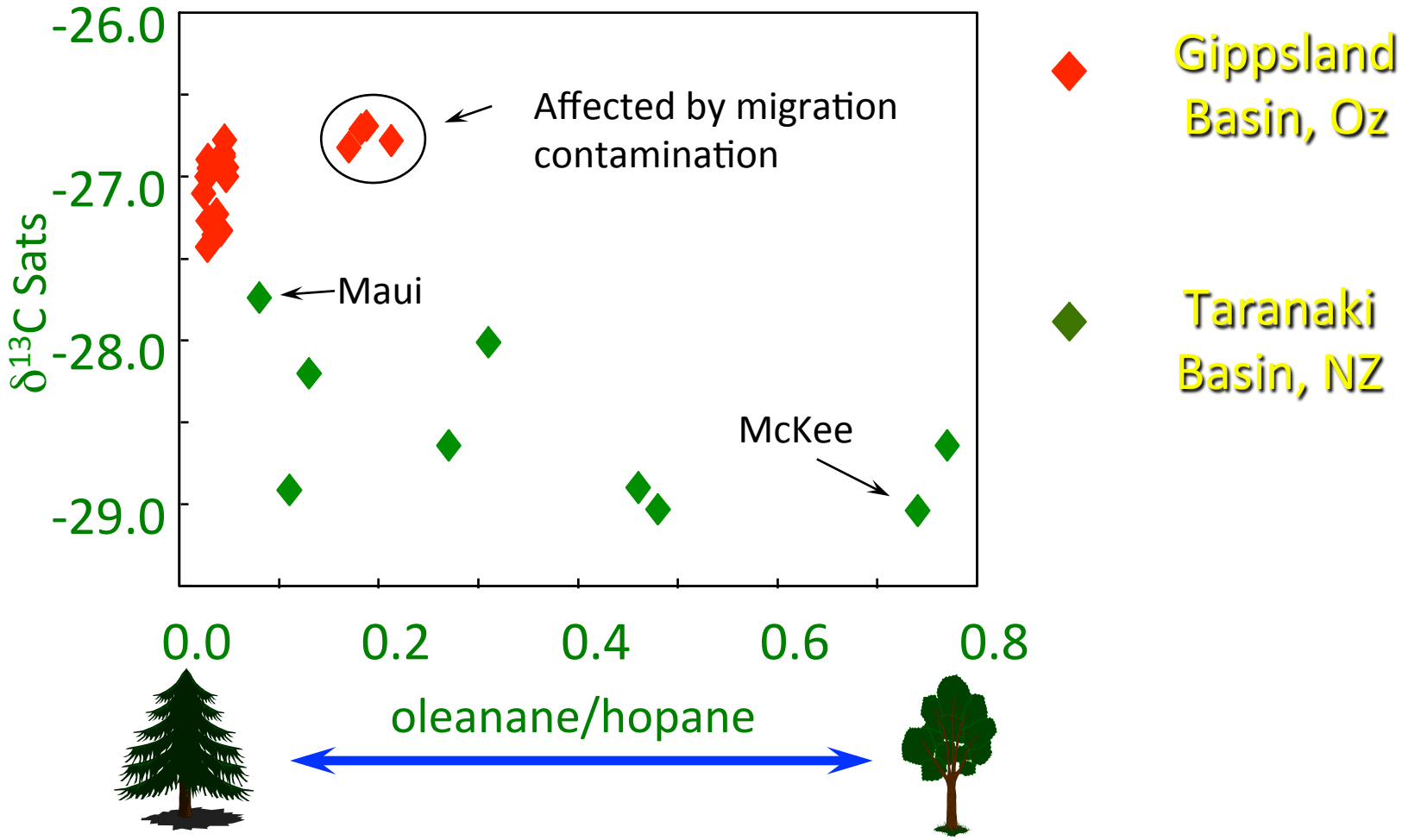
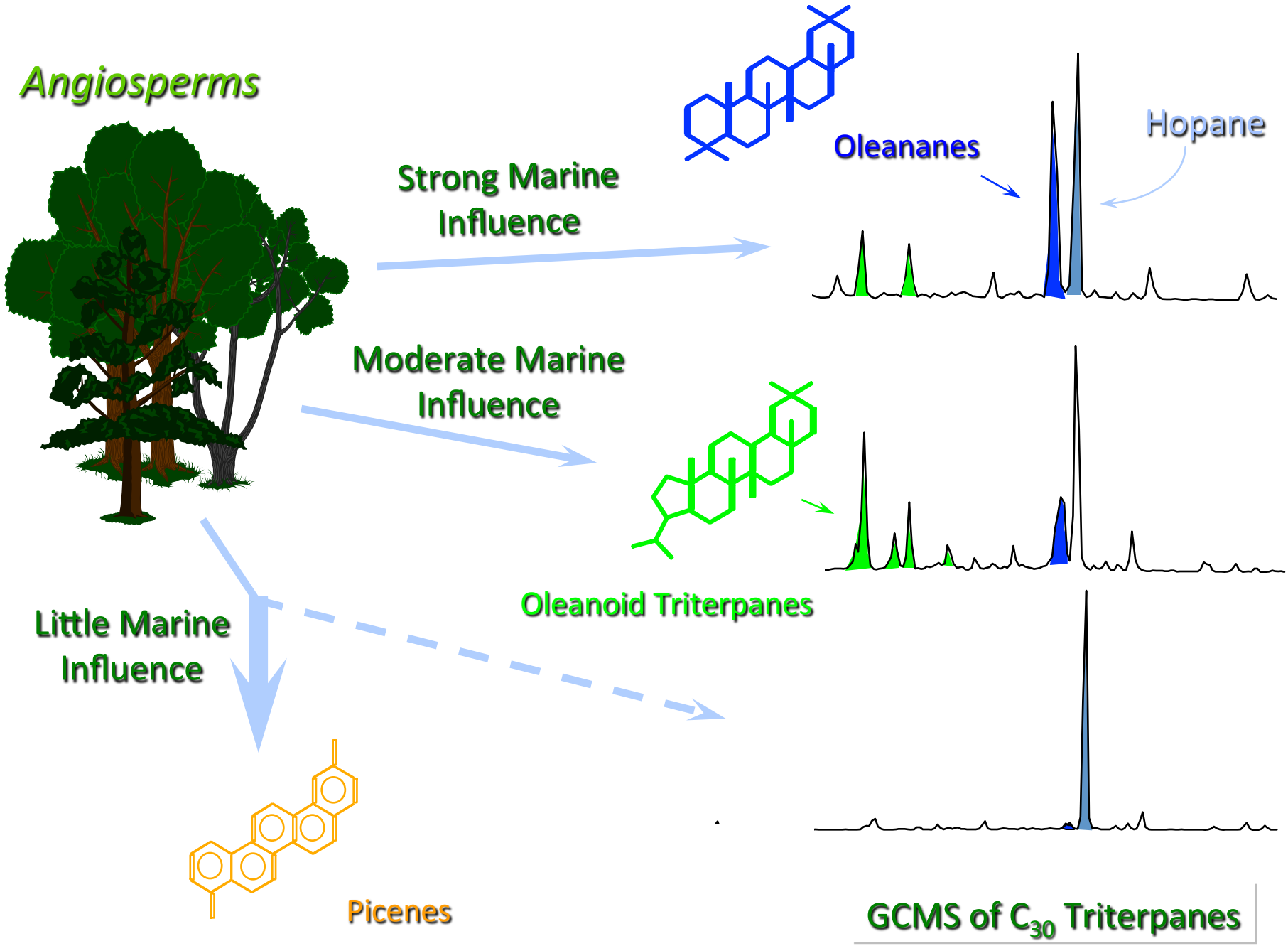
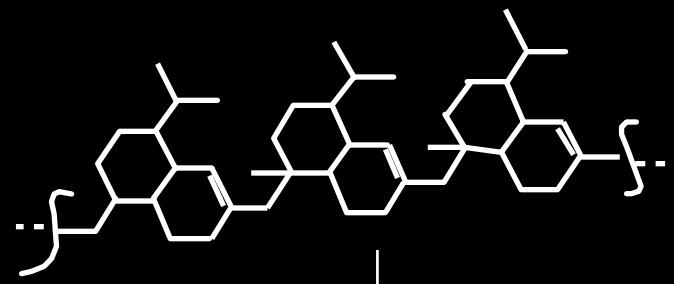
Oils with Conifer vs Angiosperm OM

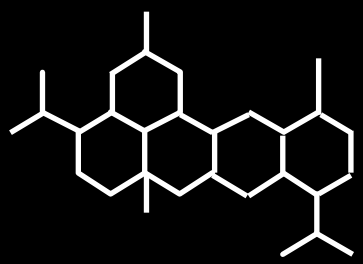
Carbon Isotopes vs Oleanane/Hopane




Angiosperms
Strong Marine Influence
Moderate Marine Influence
Little Marine Influence
Oleananes
Hopane
Oleanoid Triterpanes
Picenes
GCMS of C_{30} Triterpanes

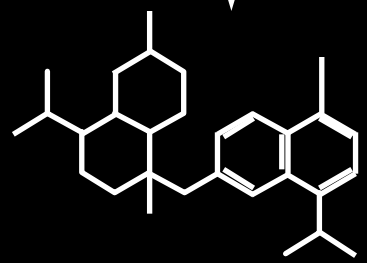
Catagenesis of POLYCADINENE from *Dipterocarps* and other higher plants produces many compounds found in oils, e.g.....



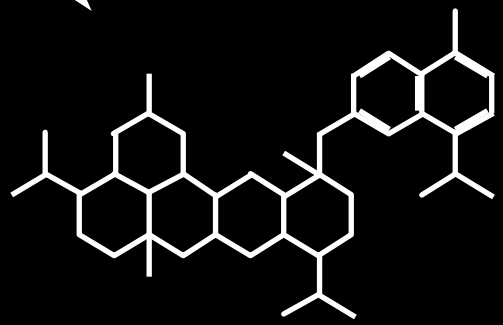


Bicadinanes

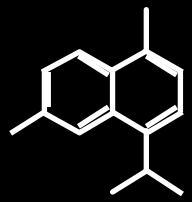
Compounds
"W", "T", "R"



Diaromatic
Secobicadinanes

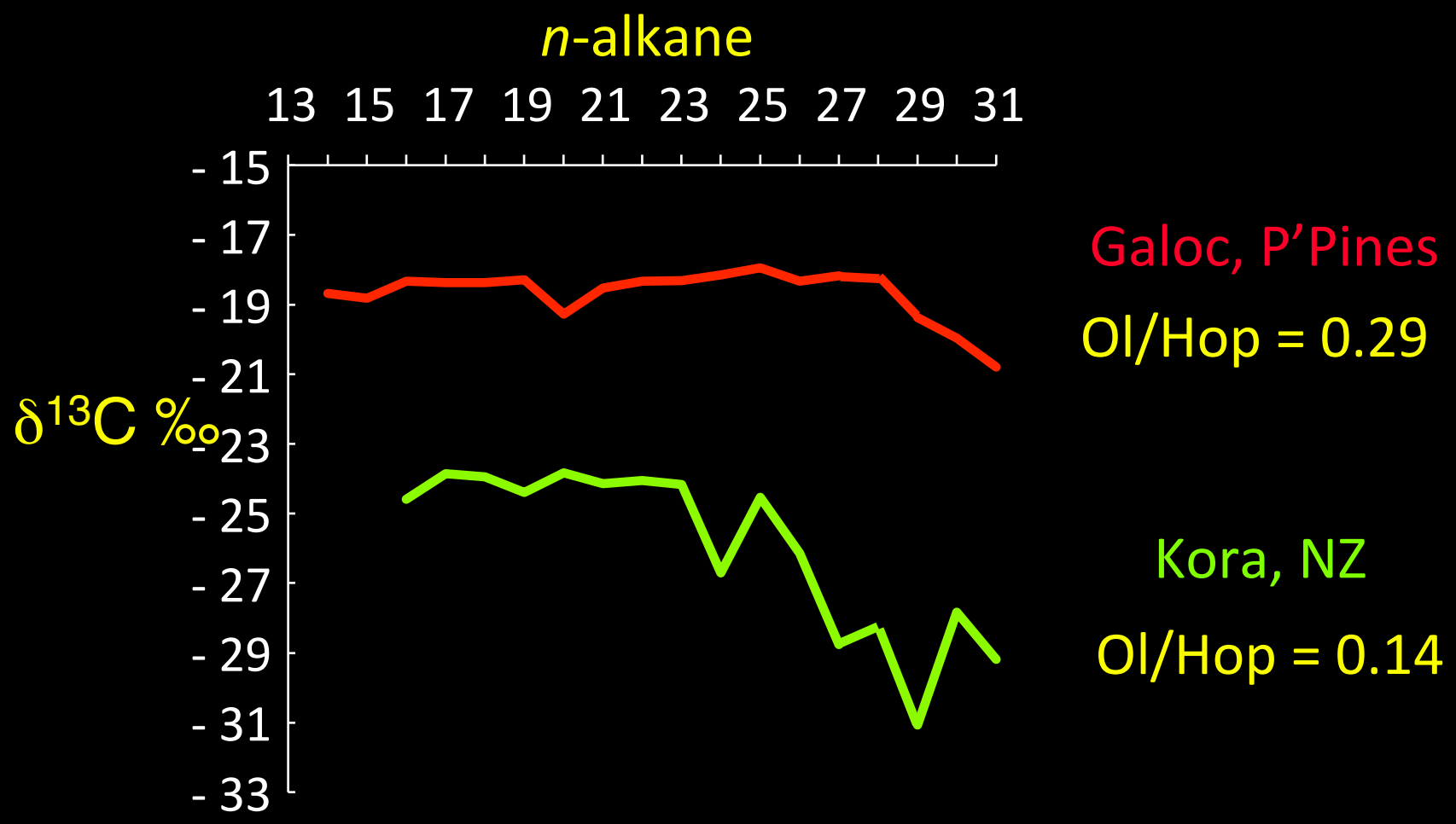


Diaromatic
Secotricadinanes

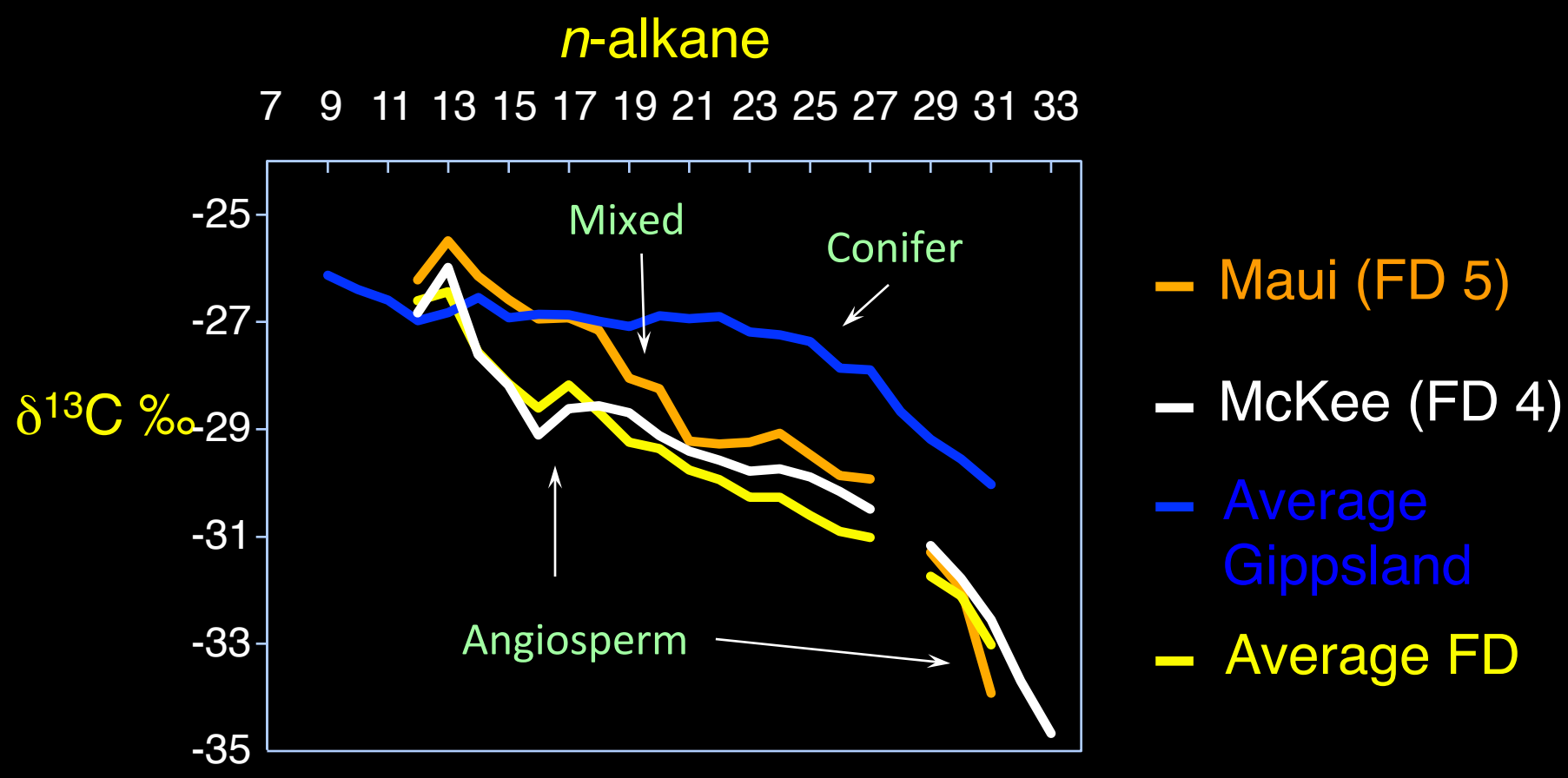


Cadalenes

Land plant input to marine oils: biomarkers vs. *isotopes*

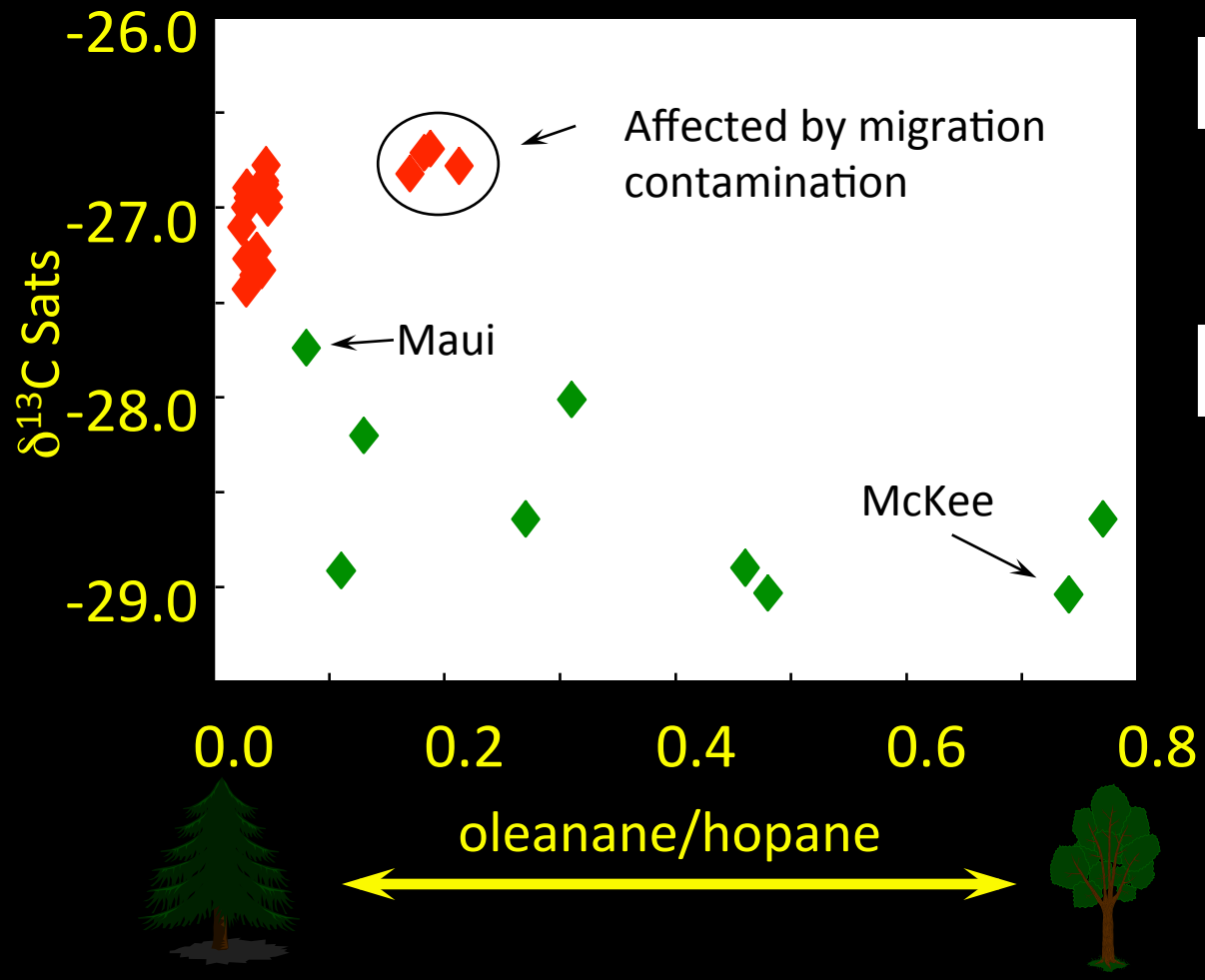


N-alkane isotope profiles for fluvio-deltaic (FD) oils



Oils with Conifer vs Angiosperm OM

Carbon Isotopes vs Oleanane/Hopane



Gippsland Basin, Oz

Taranaki Basin, NZ

Data from AGSO/Geomark
Biodegraded oils excluded

Summary

- Conifer resins have more ^{13}C than angiosperm resins
- Ditto for derived biomarkers
- Significant variability within single plants and within resin types

Summary

- Gymnosperm-Angiosperm balance likely an important control on $\delta^{13}C$ of terrestrial-C

- Secular change in terrestrial-C best studied using taxon-specific biomarkers; rigorous age control will be required

- Resin studies useful for understanding oil composition & hydrocarbon origins

Applying carbon isotope ratios ($\delta\ ^{13}C$) in deltaic petroleum systems

- Carbon isotope ratios of whole oils or oil fractions (saturates, aromatics etc) are not very useful for deltaic oils/sediments because:

- The $\delta^{13}C$ values are more affected by secondary processes than those of marine or lacustrine samples

- There is still an inadequate understanding of the fundamental factors controlling the carbon isotope composition of land-plant derived oils

12.158 Molecular Biogeochemistry

Fall 2010