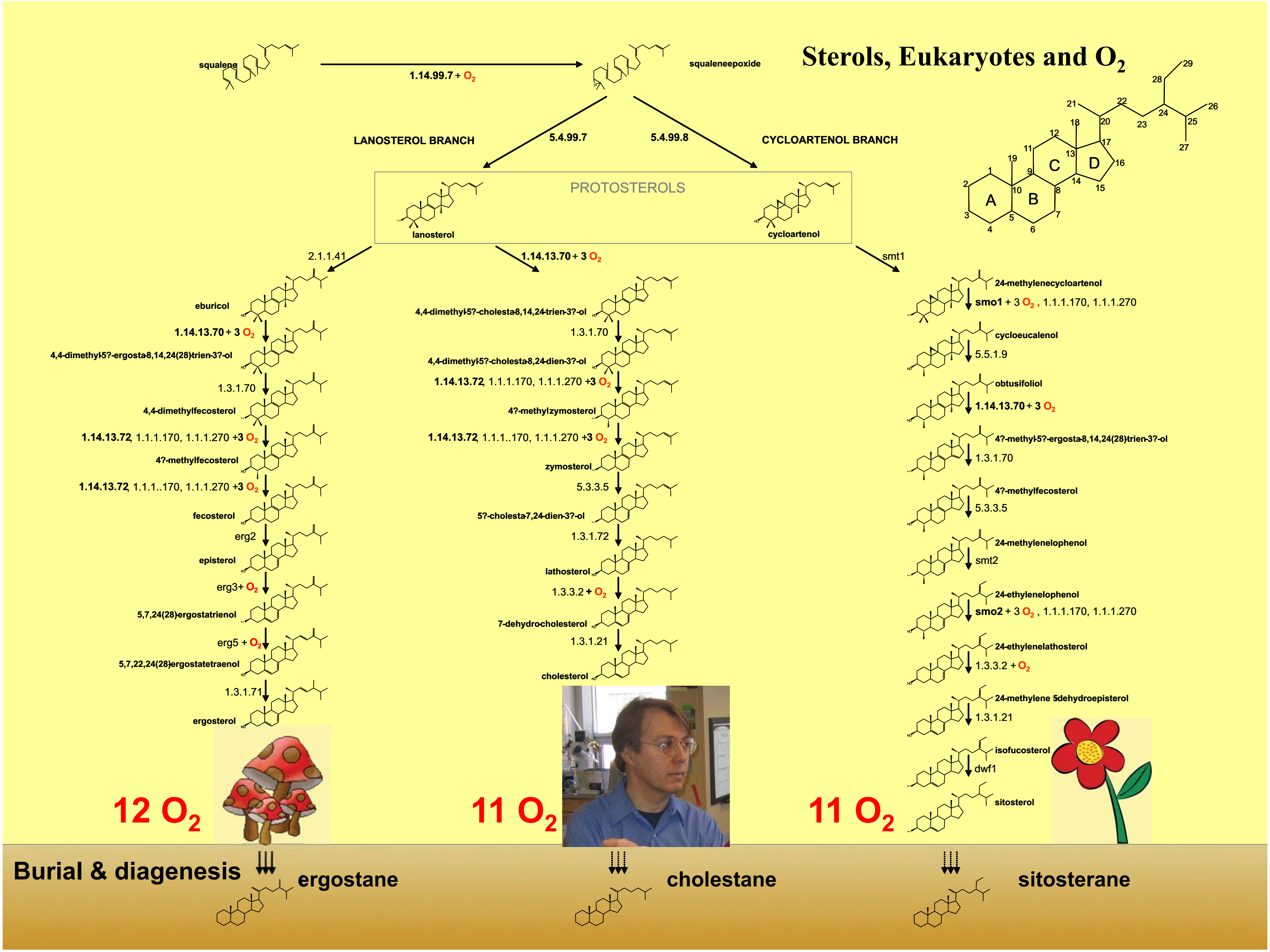
12.158 Lecture 7

- Sterols part 2
  - Sterol biosynthesis review and revision
  - Steroids as age and environment indicators
  - Enigmatic steroids 2- and 3-alkyl and carboxysteroids



Sterols, Eukaryotes and O_2
squalene
1.14.99.7 + O_2
squaleneepoxide
LANOSTEROL BRANCH
5.4.99.7
5.4.99.8
CYCLOARTENOL BRANCH
PROTOSTEROLS
lanosterol
cycloartenol
A
B
C
D
2.1.1.41
1.14.13.70 + 3 O_2
smt1
eburicol
1.14.13.70 + 3 O_2
4,4-dimethyl-5?-ergosta-8,14,24(28)-trien-3?-ol
1.3.1.70
4,4-dimethylfecosterol
1.14.13.72, 1.1.1.170, 1.1.1.270 +3 O_2
4?-methylfecosterol
1.14.13.72, 1.1.1..170, 1.1.1.270 +3 O_2
fecosterol
erg2
episterol
erg3+ O_2
5,7,24(28)-ergostatrienol
erg5 + O_2
5,7,22,24(28)-ergostatetraenol
1.3.1.71
ergosterol
4,4-dimethyl-5?-cholesta-8,14,24-trien-3?-ol
1.3.1.70
4,4-dimethyl-5?-cholesta-8,24-dien-3?-ol
1.14.13.72, 1.1.1.170, 1.1.1.270 +3 O_2
4?-methylzymosterol
1.14.13.72, 1.1.1..170, 1.1.1.270 +3 O_2
zymosterol
5.3.3.5
5?-cholesta-7,24-dien-3?-ol
1.3.1.72
lathosterol
1.3.3.2 + O_2
7-dehydrocholesterol
1.3.1.21
cholesterol
24-methylenecycloartenol
smo1 + 3 O_2 , 1.1.1.170, 1.1.1.270
cycloeucalenol
5.5.1.9
obtusifoliol
1.14.13.70 + 3 O_2
4?-methyl-5?-ergosta-8,14,24(28)-trien-3?-ol
1.3.1.70
4?-methylfecosterol
5.3.3.5
24-methylenelophenol
smt2
24-ethylenelophenol
smo2 + 3 O_2 , 1.1.1.170, 1.1.1.270
24-ethylenelathosterol
1.3.3.2 + O_2
24-methylene 5-dehydroepisterol
1.3.1.21
isofucosterol
dwf1
sitosterol
12 O_2
11 O_2
11 O_2
Burial & diagenesis
ergostane
cholestane
sitosterane

The effect of oxygen on biochemical networks and the evolution of complex life.

Jason Raymond and Daniel Segre' Science 311, 1764-1767 (2006)

Cholesterol

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squalene
hopene,
tetrahymanol

http://prelude.bu.edu/O2/networks.html

Oxidosqualene Cyclase

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Symbiogenesis: the phylogenetic tapestry of eukaryotes

http://www.life.umd.edu/labs/delwiche/

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Eukaryote Diversity & Chloroplast Endosymbiosis

Anaerobes
stem of tree?

Algae

Forams

Radiolaria

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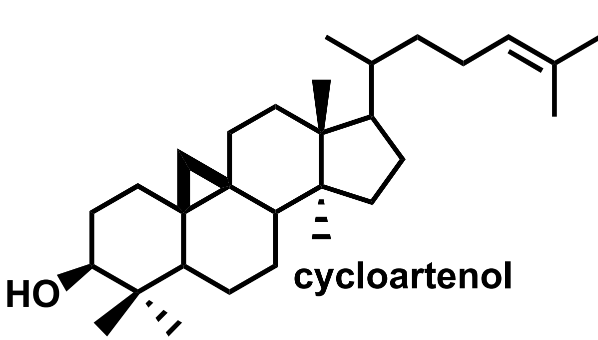
Keeling et al. 2005

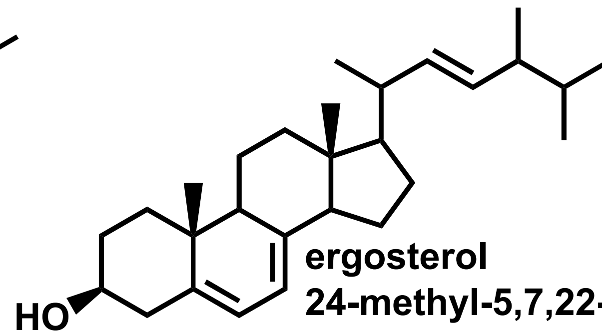
Phytosterols

Whereas vertebrates and fungi synthesize sterols from epoxysqualene through the lanosterol, plants cyclize epoxysqualene to cycloartenol as the initial sterol.

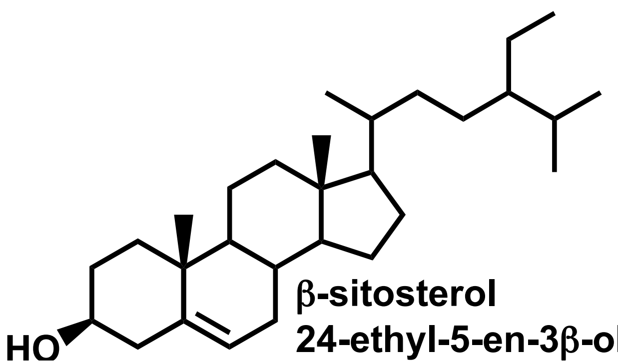
Q. Presumably lanosterol biosynthesis predates cycloartenol biosynthesis? What might have driven the lanosterol-cycloartenol bifurcation?



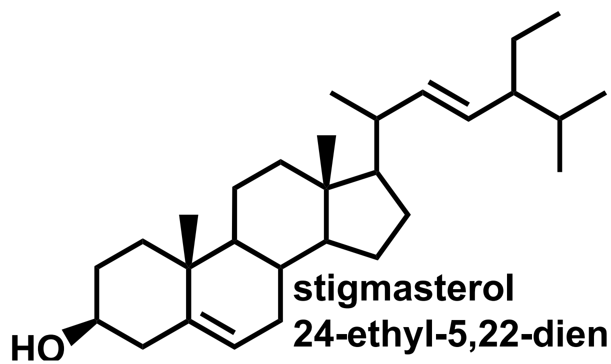
cycloartenol



ergosterol
24-methyl-5,7,22-trien-3β-ol



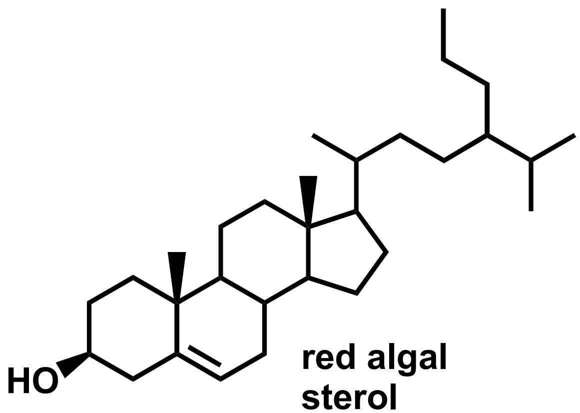
β-sitosterol
24-ethyl-5-en-3β-ol



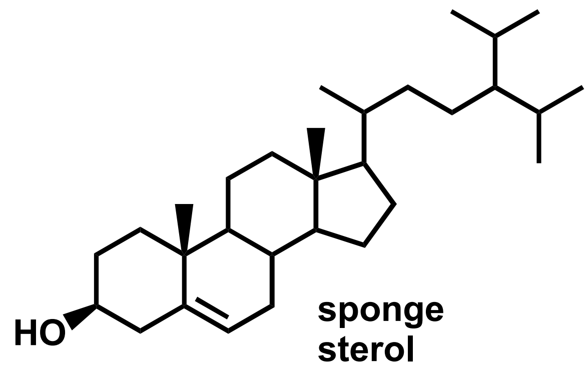
stigmasterol
24-ethyl-5,22-dien-3β-ol

Phytosterols

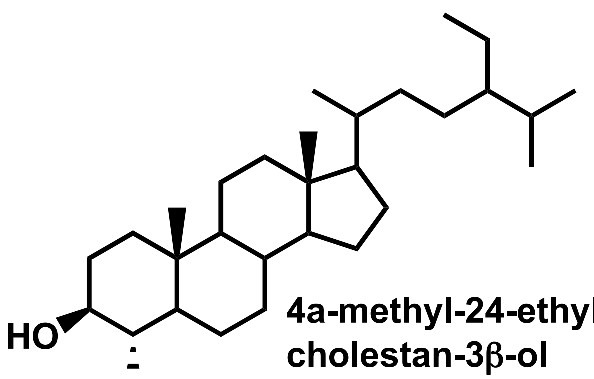
C_{30} sterols are generally minor components of organisms and immature sediments. However, when they occur, they have distinctive structures that are easily recognised in the ancient record.



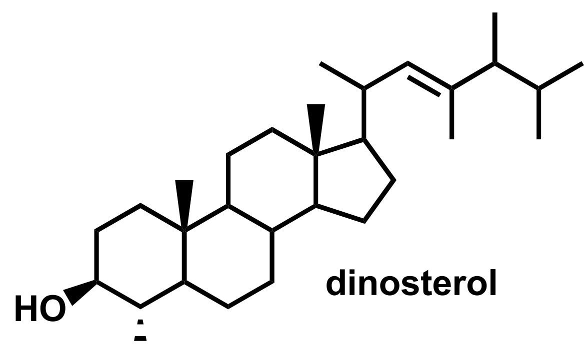
red algal sterol



sponge sterol



4a-methyl-24-ethyl-cholestan-3β-ol



dinosterol

Oxidosqualene Cyclase Alignment

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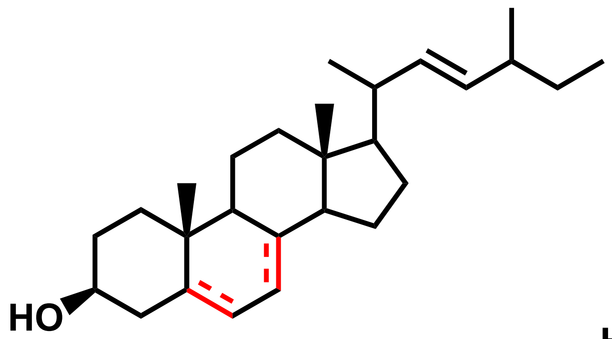
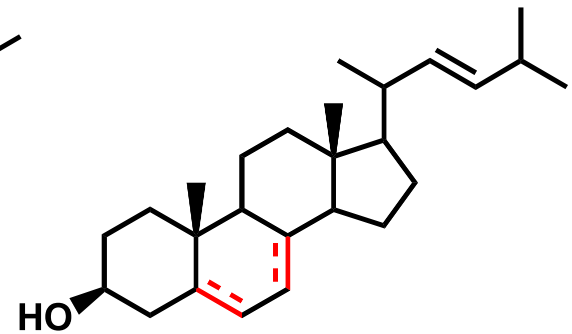
Microorganism	Major or common sterols
Microalgae	
Bacillariophyceae	C28D5,22, C28D5,24(28), C27D5, C29D5, C27D5,22
Bangiophyceae	C27D5, C27D5,22, C28D7,22
Chlorophyceae	C28D5, C28D5,7,22, C28D7,22 C29D5,22, C29D5
Chrysophyceae	C29D5,22, C29D5, C28D5,22
Cryptophyceae	C28D5,22
Dinophyceae	4Me-D0, dinosterol, C27D5, C28D5,24(28)
Euglenophyceae	C28D5,7,22, C29D5, C28D7, C29D5,7, C28D7,22
Eustigmatophyceae	C27D5 (marine) or C29D5 (freshwater)
Haptophyceae	C28D5,22, C27D5, C29D5,22, C29D5
Pelagophyceae	C30 D5,24(28), C29D5,22, C29D5, C28D5,24(28)
Prasinophyceae	C28D5, C28D5,24(28), C28D5
Raphidophyceae	C29D5, C28D5,24(28)
Rhodophyceae	C27D5, C27D5,22
Xanthophyceae	C29D5, C27D5
Cyanobacteria:	C27D5, C29D5, C27D0, C29D0 (evidence equivocal)
Methylotrophic bacteria	4Me-D8
Other bacteria	C27D5
Yeasts and fungi	C28D5,7,22, C28D7, C28D7,24(28)
Thraustochytrids	C27D5, C29D5,22, C28D5,22, C29D5,7,22

The nomenclature is CxDy where x is the total number of carbon atoms and y indicates the positions of the double bonds. In general, C28 sterols have a methyl group at C-24, and C29 sterols have a 24-ethyl substituent. Table adapted from data in Volkman (1986); Jones et al. (1994) and Volkman et al.

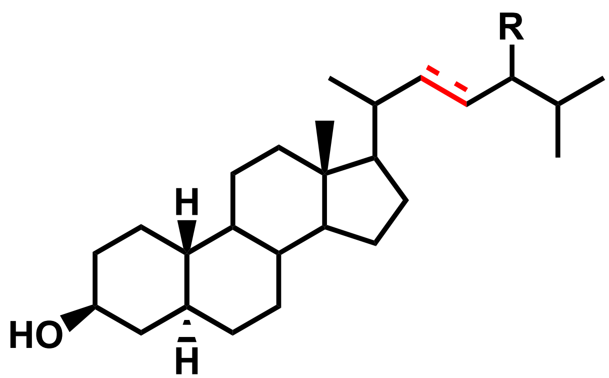
Uncommon Marine Sterols



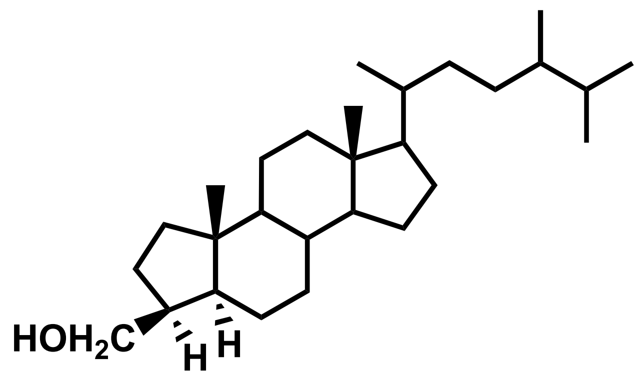
24-methyl-27-nor sterols and stanol known in sponges: C27 compounds



24-nor sterols a range of algae & invertbrates: C26

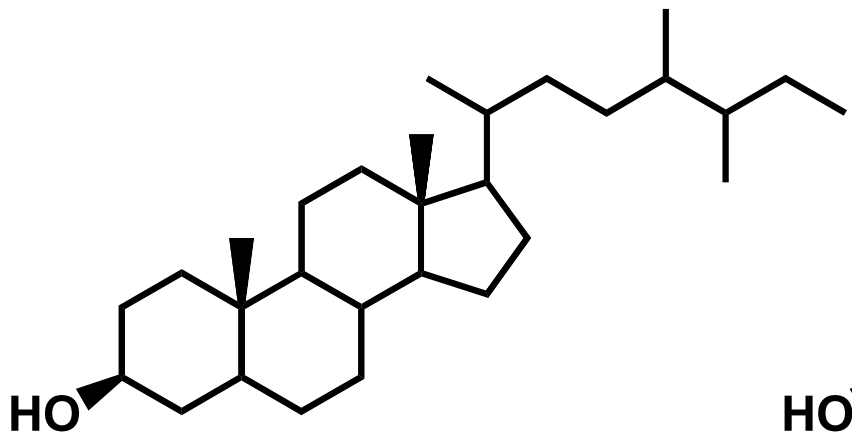


19-nor sterols
R=H, CH_3, C_2H_5, methylene
Δ22 trans unsaturation probably formed by de-alkylation of algal sterols

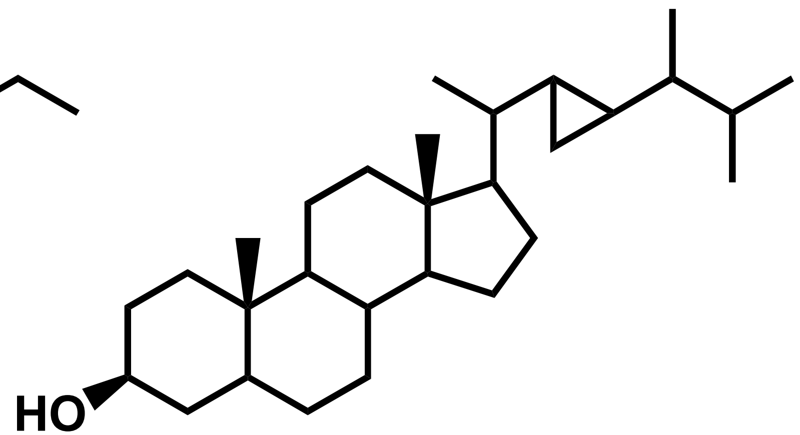


A-nor sterols sponges

Uncommon Marine Sterols (2)



Aplysterol



Gorgosterol

How to identify sterols by GC-MS of TMS and acetate derivatives

- **Relative Retention Times of Nematode Sterols**
- **Mass Spectra of Nematode Sterols**
- Mass Spectral Data for Nematode Sterols, Analyzed as Steryl Acetate Derivatives*a*
  Steryl acetate Mass spectrum (*m/z*, relative intensity to base peak) Cholesta-5,7,9(11)-trienol 424 (5), 364 (100), 349 (33), 251 (31), 209 (64), 197 (43), 195 (52)Cholest-8(14)-enol 428 (100), 413 (18), 368 (6), 353 (13), 315 (16), 288 (7), 273 (6), 255 (21), 229 (42), 213 (43), 81 (80), 55 (83)Cholesterol 368 (100), 353 (14), 260 (15), 255 (13), 247 (18), 213 (14), 147 (48), 145 (37), 81 (74), 55 (71) Cholestanol430 (12), 415 (2), 370 (33), 355 (16), 316 (3), 276 (28), 275 (18), 257 (4), 230 (17), 215 (100), 201 (18), 147 (32), 81 (53)

Sterol Reading #1

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Please see
http://www.springerlink.com/content/q05172k241v60328

Reconstruction of past biota

Biomarkers and Fossils what can they can say:

Who are the major groups of marine primary producers today?

Which groups dominated at different periods in the geologic past?

How is plankton growth recorded in rocks – and oil?

What factors influence the completeness of the fossil record of marine plankton?

How has long-term ecological succession of marine plankton affected the evolution of other organisms and biogeochemical cycles?

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Marine Primary Producers

Today, 2 major groups:

Acquired photosynthesis by secondary endosymbiosis

Were preceded by red/green algae & prokaryotic phototrophs

Left a rich body & molecular fossil record

Rose to ecological prominence relatively recently

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Picocyanobacteria

Prochlorococcus/

Marine *Synechococcus*

Chl *a*+c Phytoplankton

Diatoms

Dinoflagellates

Coccolithophorids

Eukaryote Diversity & Chloroplast Endosymbiosis

Anaerobes stem of tree?

Algae

Forams

Radiolaria

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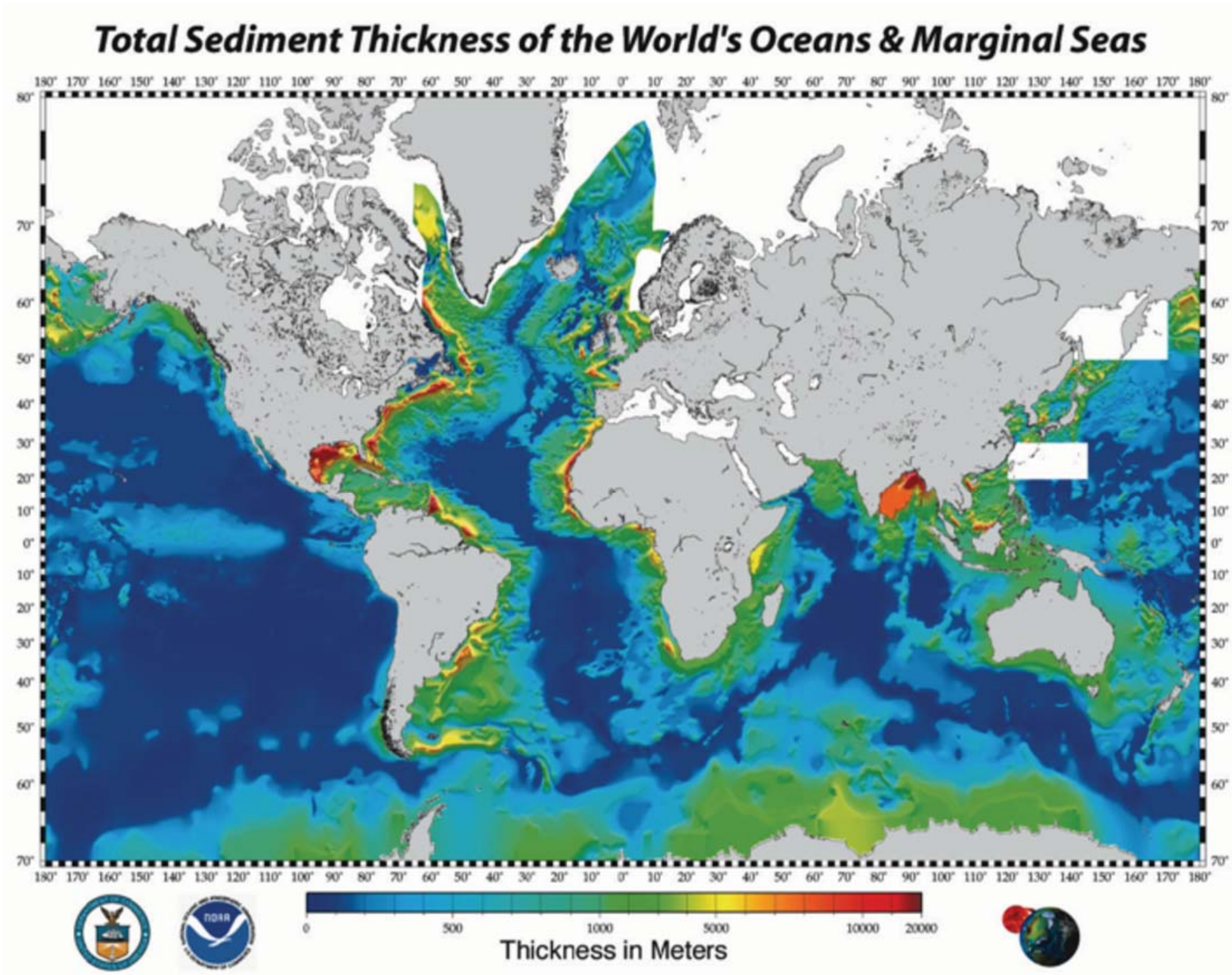
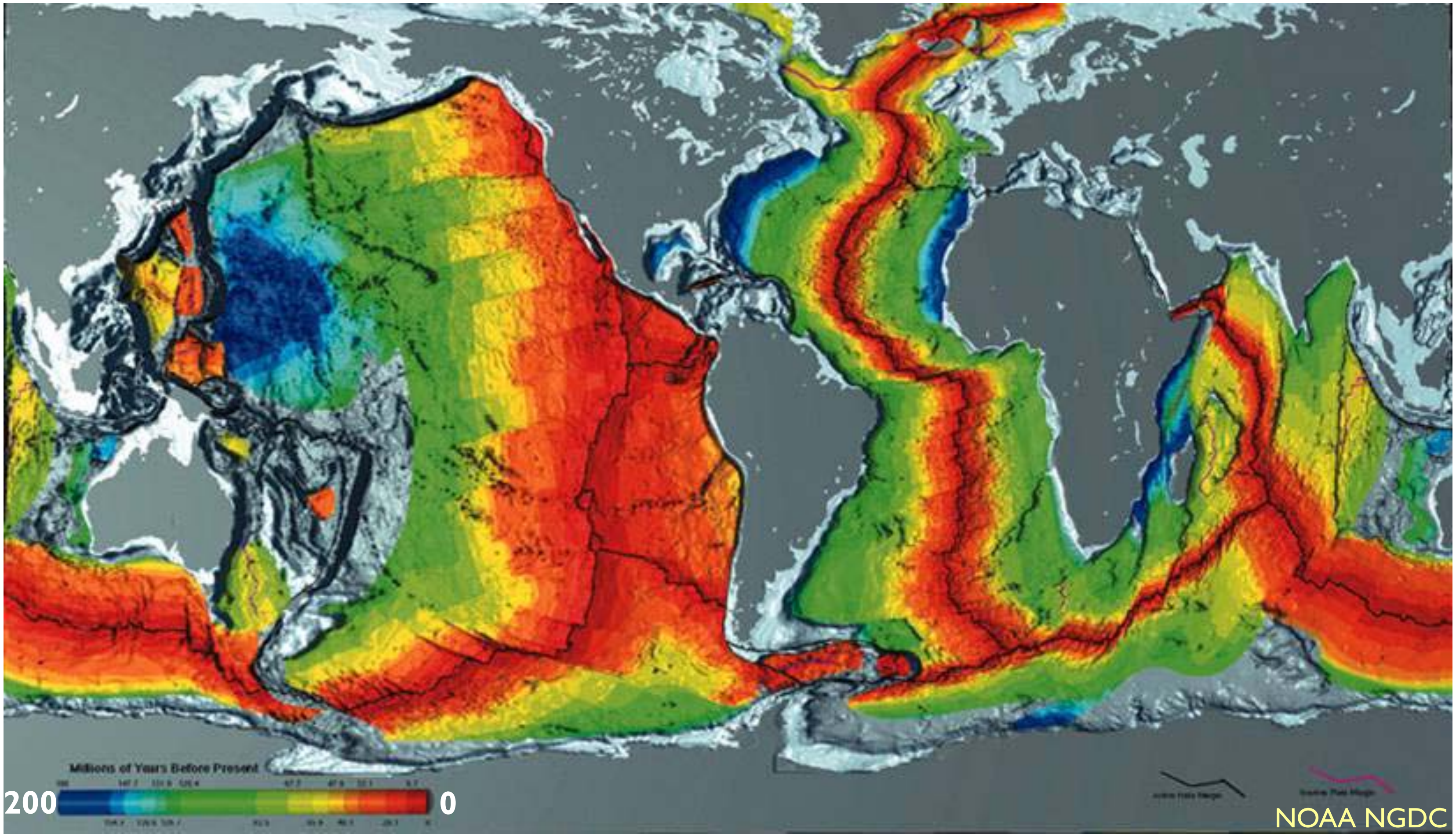
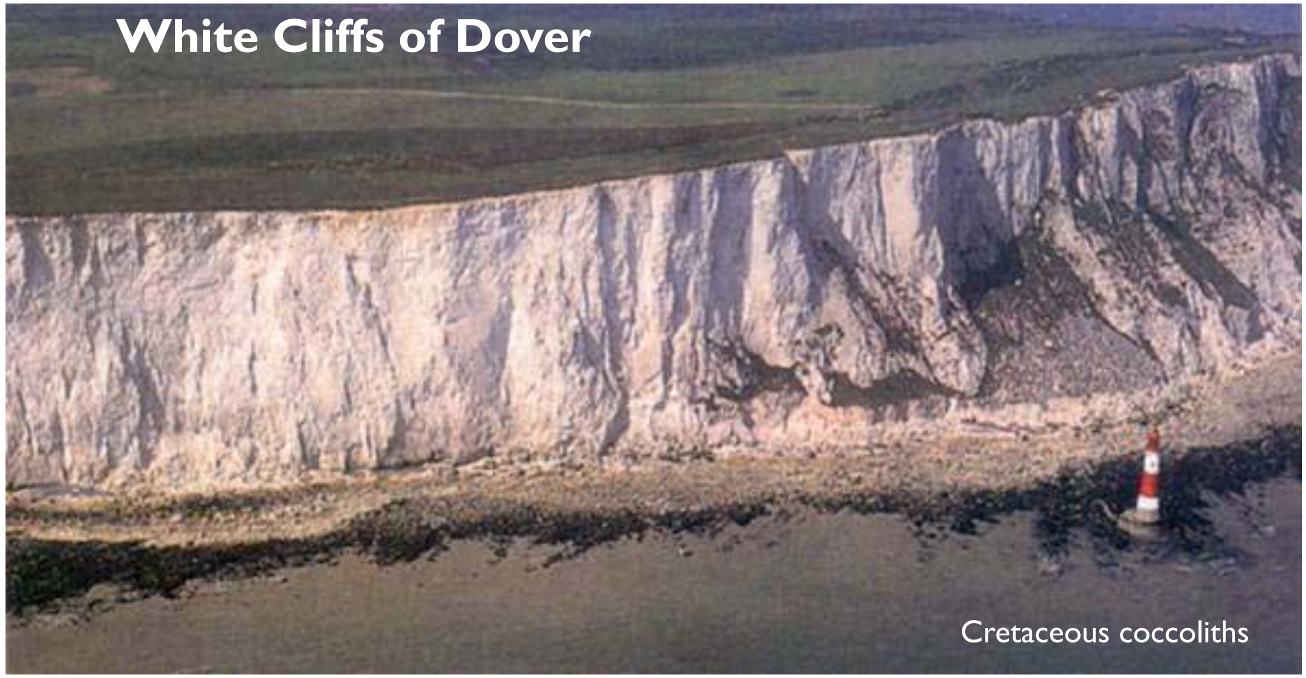
Keeling et al. 2005

The Fossil Record of Phytoplankton - one form of bias: where sediment is deposited



Another form of Bias: Age of the Ocean Floor

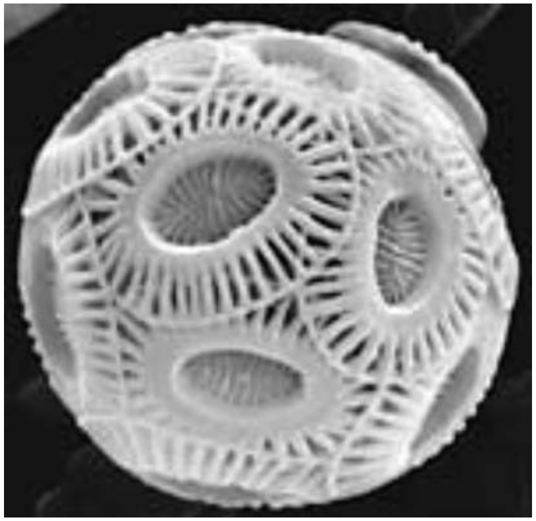




Grace Muilenburg, Kansas Geol. Surv.

Courtesy of Organic Geochemistry Group, Universitat Bremen. Used with permission.

Succession in the Photosynthetic Plankton of the Ocean: A Perspective Drawn from Chemical Fossils



Roger E. Summons & Jacob R. Waldbauer (MIT)
Andrew H. Knoll (Harvard University)
John E. Zumberge (GeoMark Research)

Successions in Biological Primary Productivity in the Oceans. In Falkwoski P. and Knoll A.H. (eds) The Evolution of Photosynthetic Organisms in the Oceans, 2006.

Evolutionary Trends from Rocks & Oils: Present-day sample localities

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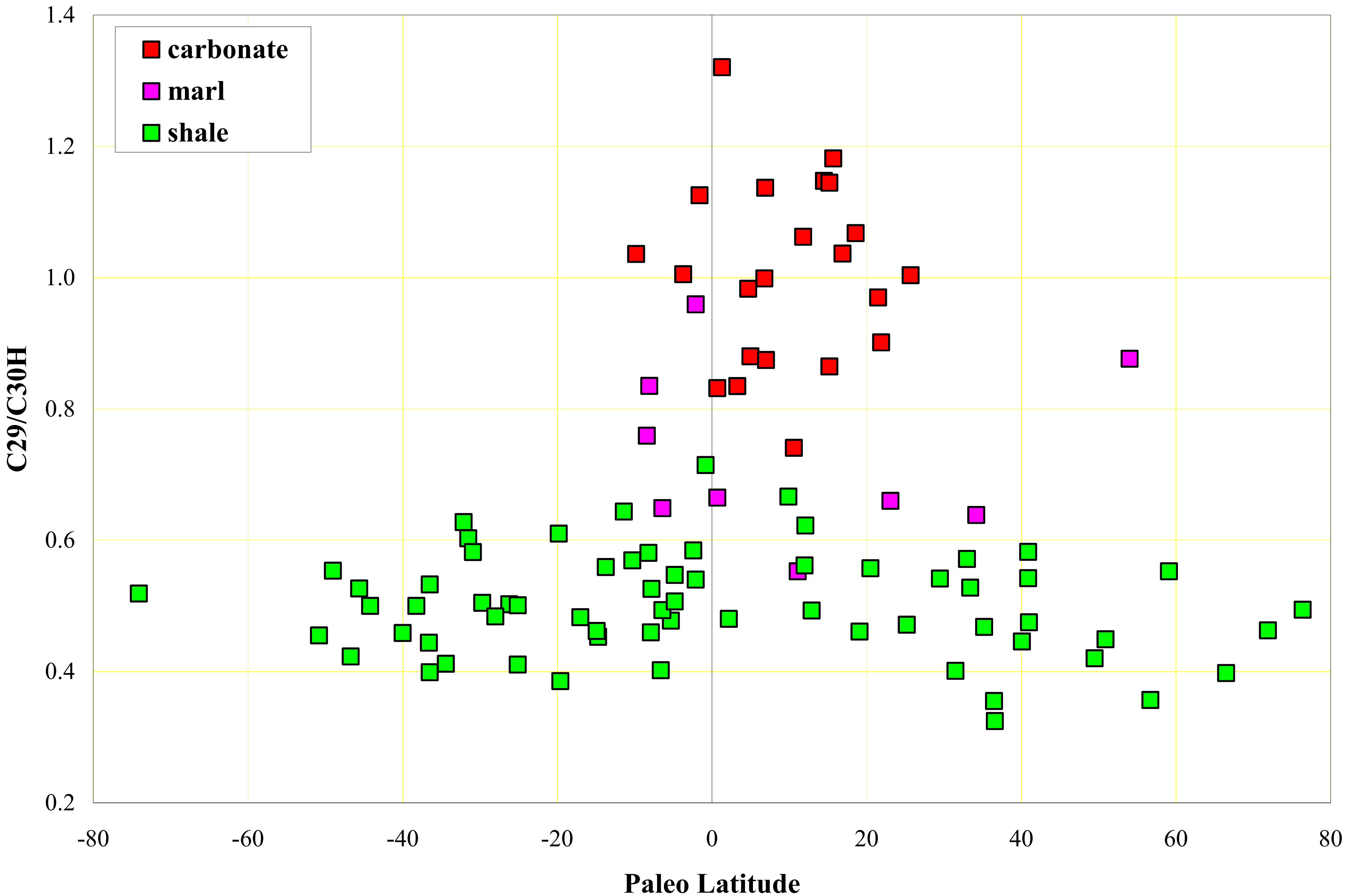
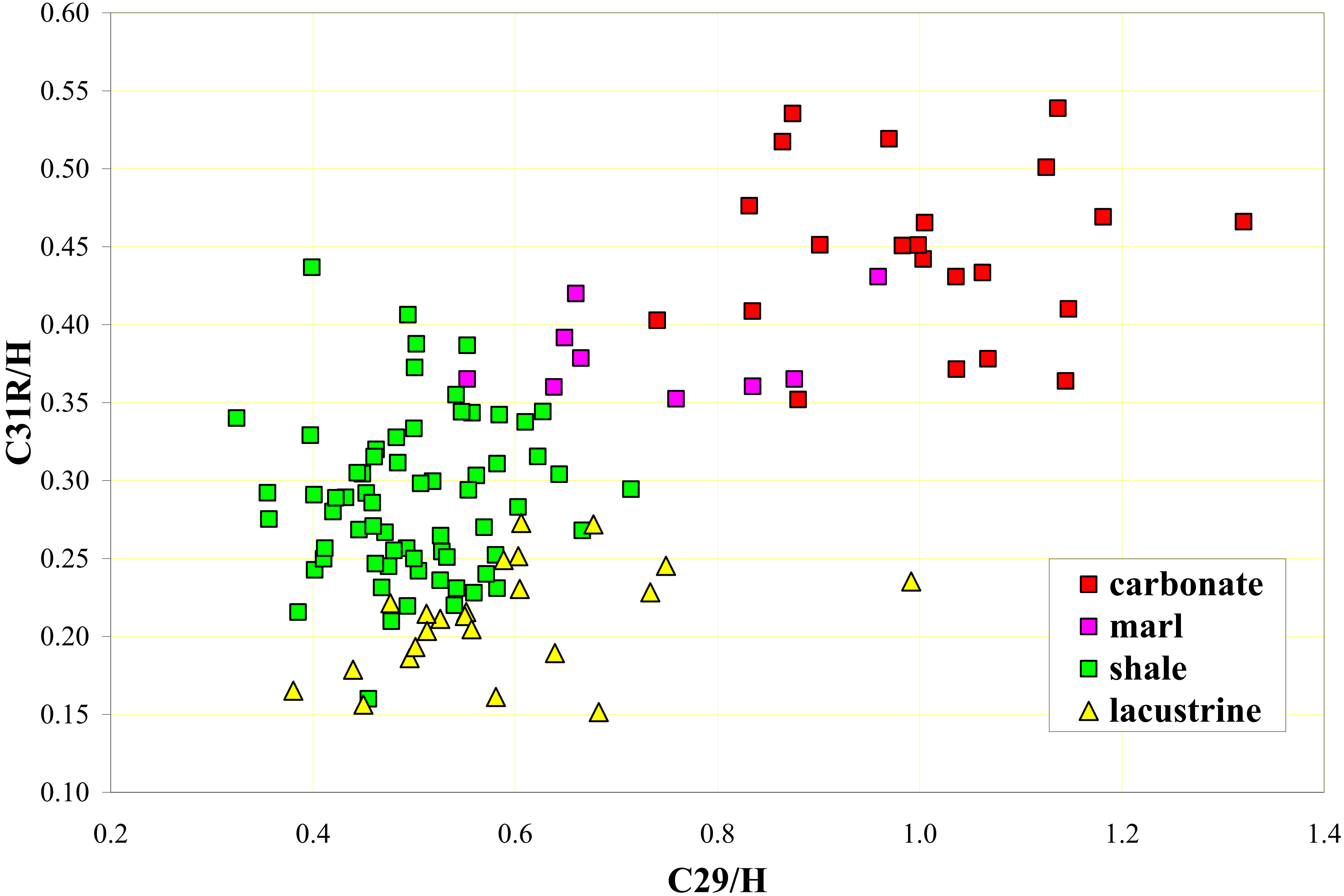
Evolutionary Trends from Rocks & Oils

- Sedimentary organic matter is the direct geologic legacy of primary production
- Massive accumulations of organic matter in petroleum systems worldwide record ocean biogeochemistry
- Oils are widely available, accessible, abundant & carry the same kind of evolutionary information that is buried in sediments
- Oils reflect the natural 'average' in the variation in source rock organofacies
- GeoMark Database: Biomarker parameters from over 1800 microbial-sourced oils (no terrigenous input) have been averaged to obtain 133 petroleum systems from the Neoproterozoic to Miocene
- The source rock type and age for many of the oils in GeoMark's database are known based on extensive integration of geological and geochemical frameworks

PaleoLatitude vs Carbonate-Sourced Oils

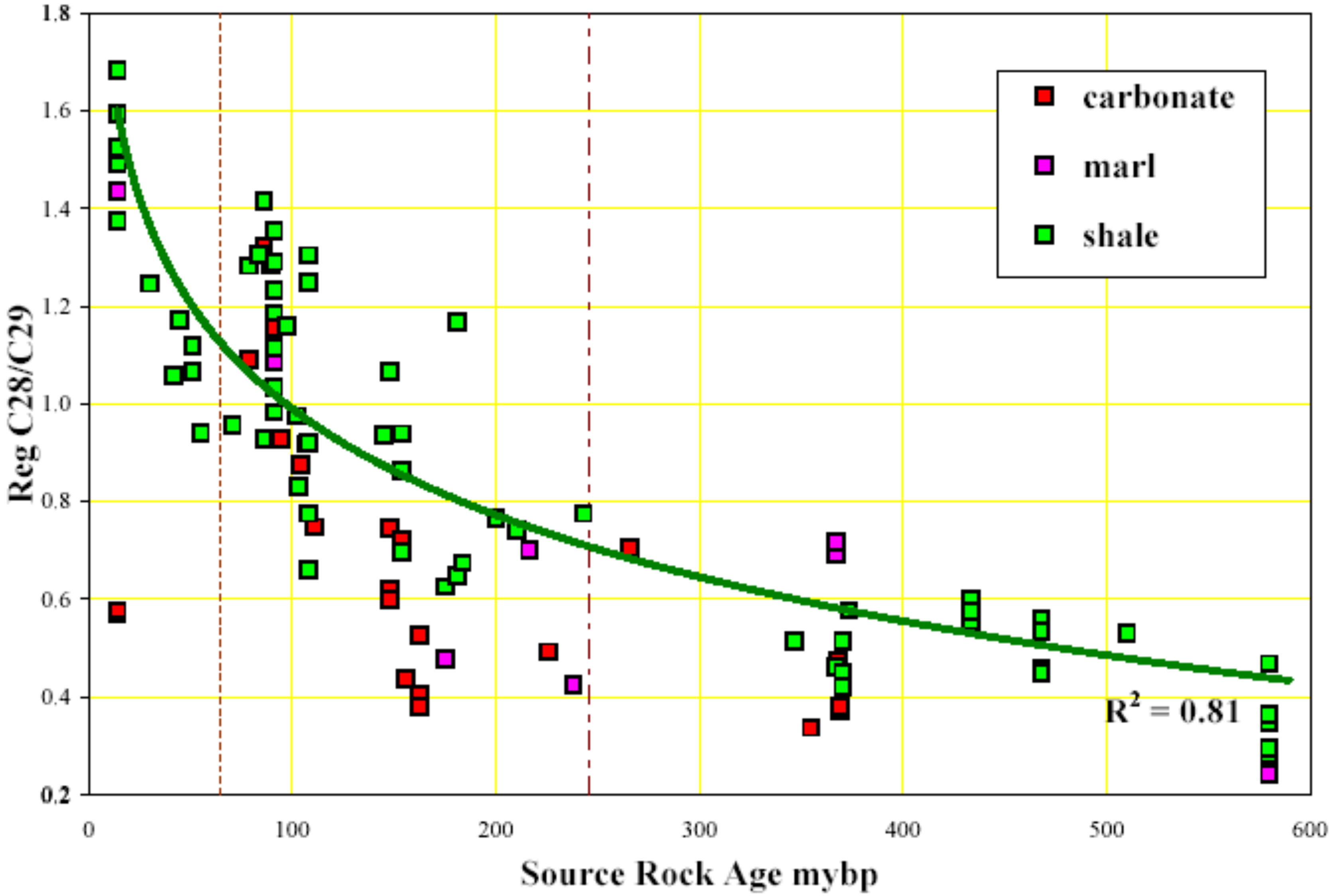


Pentacyclic Terpane Ratios

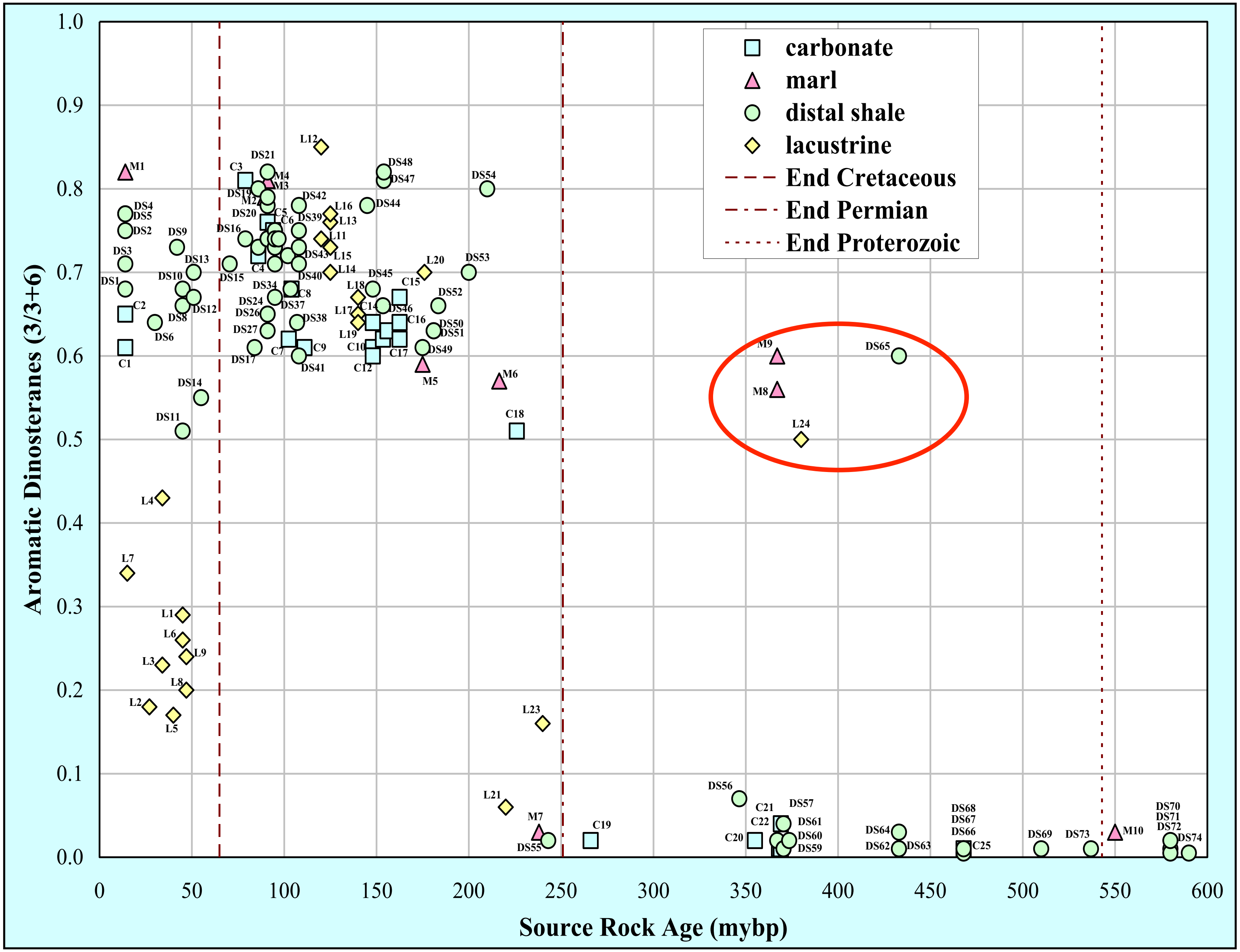


- Clearly, these groups rise to paleontological prominence in Mesozoic and Cenozoic oceans, but…
- Is there an earlier, “cryptic” evolutionary history?
  - Unmineralized or poorly mineralized stem diatoms or coccolithophorids?
  - Non-diagnostic fossils of dinos (sans archeopyle) among older acritarchs??
  - Help from molecular clocks??
  - Sedimentary record: Biomarker molecules are most informative

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



Dinoflagellate Biomarkers-Petroleum Record



Aromatic dinosteroids/2+3-methyls

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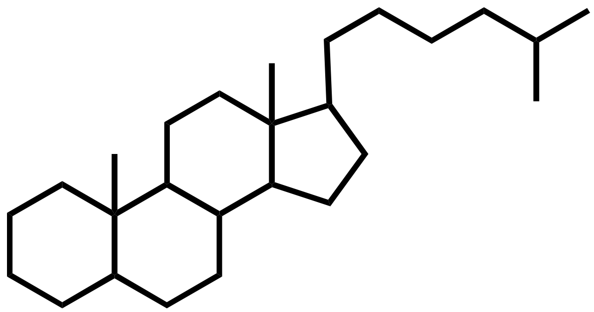
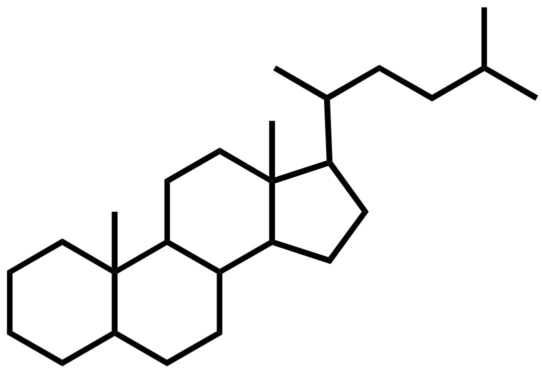
Distribution of dinosteroids in Phanerozoic sediments

Moldowan and Talyzina
Science 281,168-1170, 1998

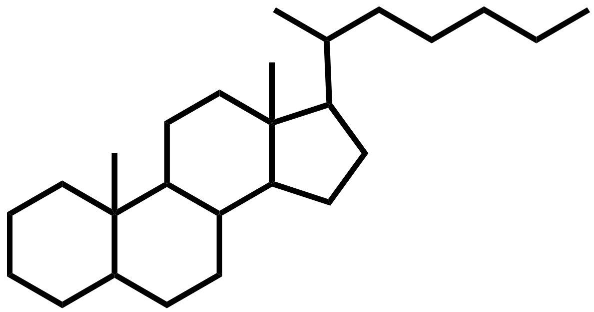
C_{26} steranes



21-nor Unknown source



24-nor Unknown source

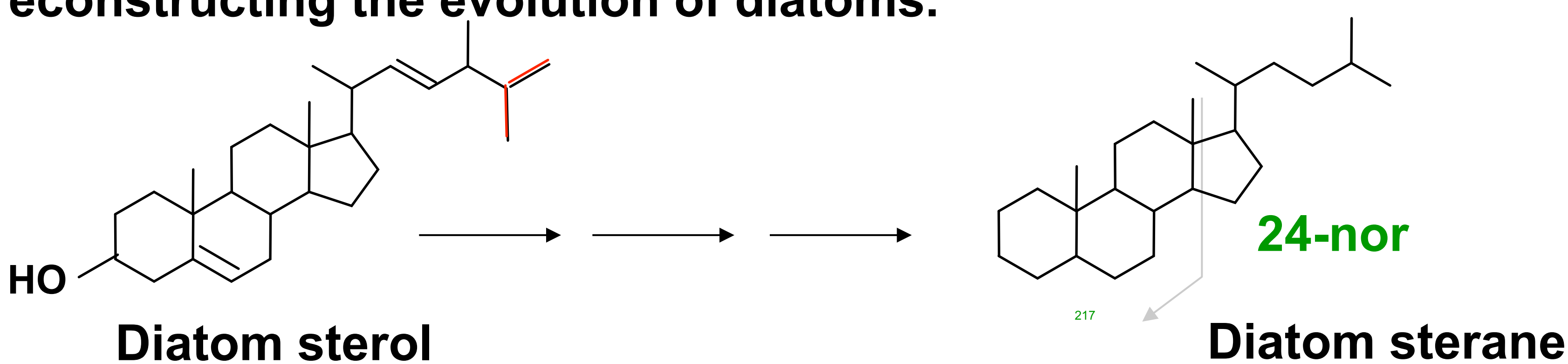


27-nor Unknown source

Secular Change in C_{26} Sterane Abundance

Application of 24-norcholestanes for constraining source age of petroleum
A. G. HOLBA et al. Org. Geochem. 29,1269 -1283, 1998

Rampen et al., AGU 2004:……………..Another specific biomarker is 24-norsterol. Its value as an age diagnostic biomarker was already reported (3), but the source of this sterol was still unknown although a diatomaceous source was assumed. We have now found this sterol in the diatom species *Thalassiosira aff. Antarctica*. In combination with the knowledge that the 24-norsterol production increased substantially during the Cretaceous this may provide a tool to predict the mutation rate of the Thalassiosirales. Our data show that molecular paleontology can assist in obtaining more reliable estimates of the molecular clock rate and thus be an important tool in reconstructing the evolution of diatoms.



C_{26} steranes elution pattern

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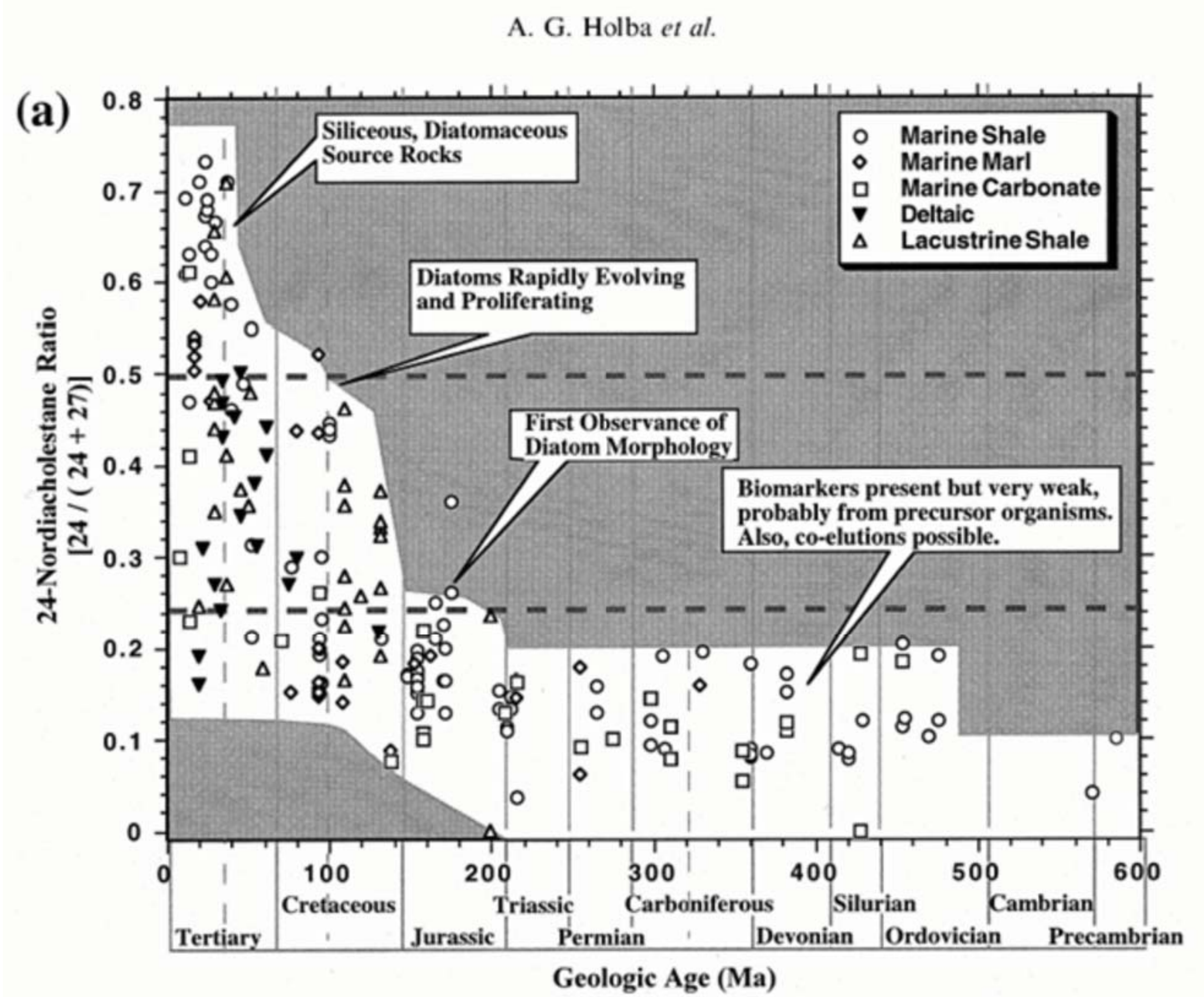
Moldowan et al GCA 55, 1065, 1991

Secular Change in C_{26} Sterane Abundance

Application of 24-norcholestanes for constraining source age of petroleum
A. G. HOLBA et al. Org. Geochem. Vol. 29, pp. 1269 -1283, 1998



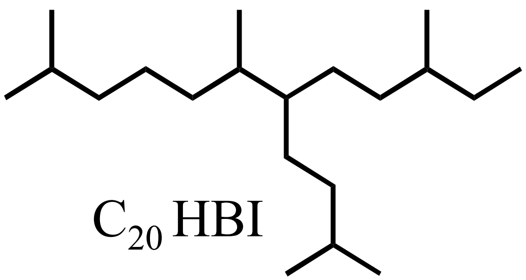
Diatom-specific HBI & their Geologic Occurrence

Highly branched acyclic isoprenoid alkenes and alkanes

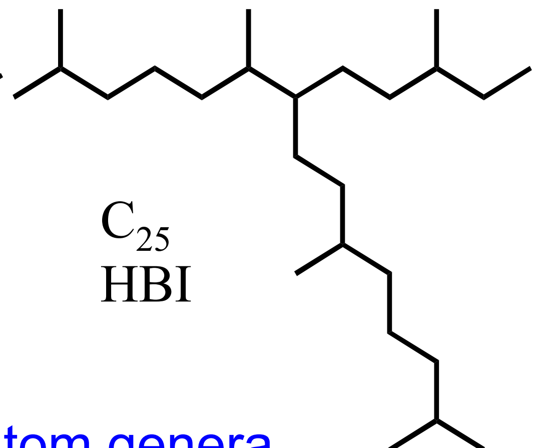
The Rise of the Rhizosolenid Diatoms

Jaap S. Sinninghe Damsté, Gerard Muyzer, Ben Abbas,
Sebastiaan W. Rampen, Guillaume Massé, W. Guy Allard,
Simon T. Belt, Jean-Michel Robert, Steven J. Rowland,
J. Michael Moldowan, Silvana M. Barbanti, Frederick J. Fago,
Peter Denisevich, Jeremy Dahl, Luiz A. F. Trindade and Stefan Schouten

23 APRIL 2004 VOL 304 SCIENCE



C_{20} HBI



C_{25} HBI

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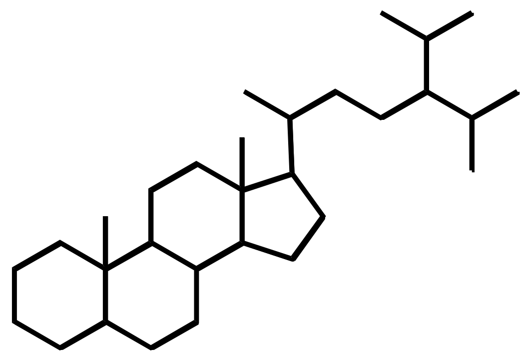
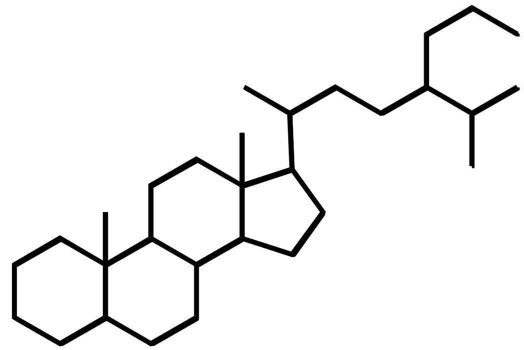
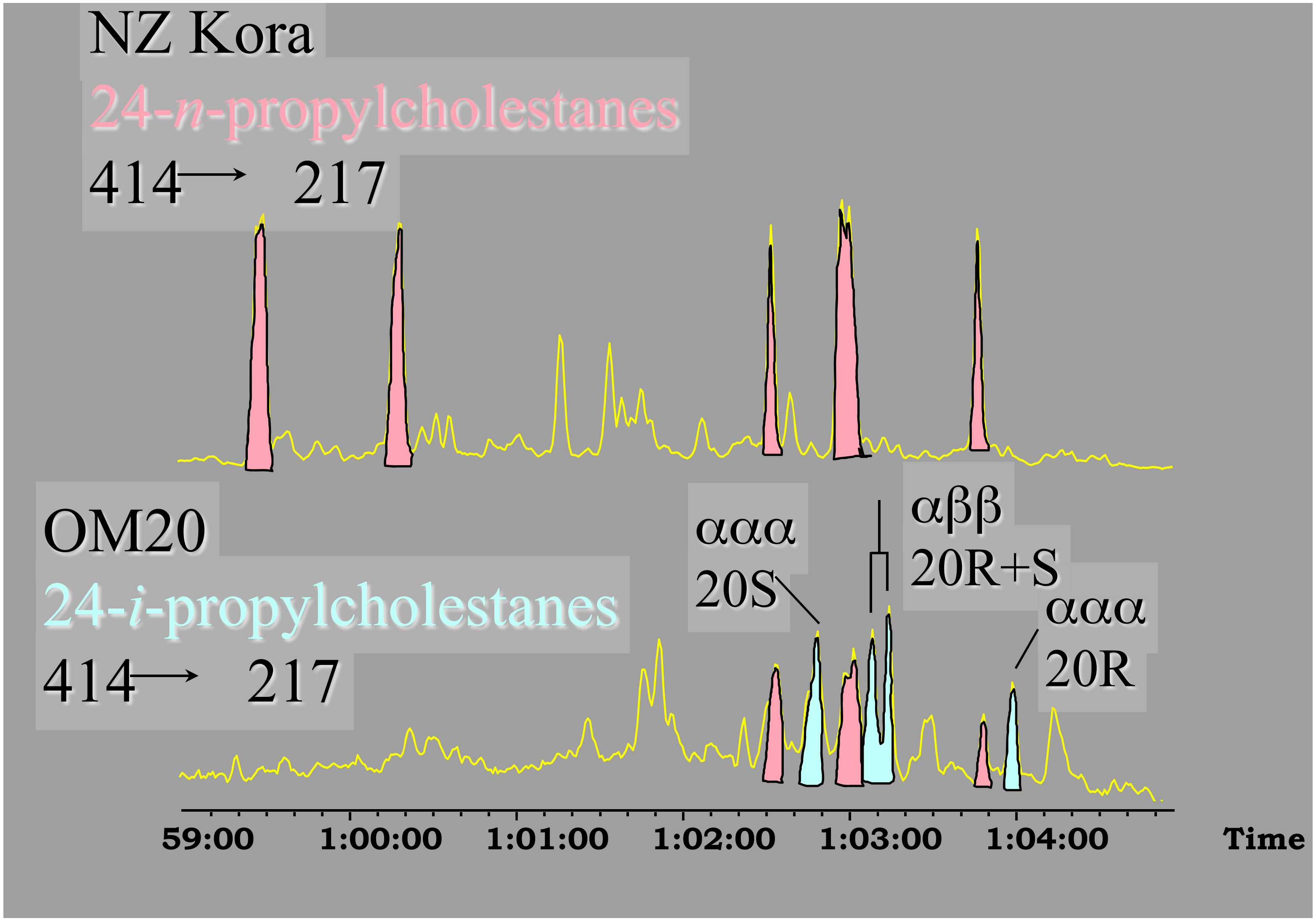
- Identified in the diatom genera *Rhizosolenia, Haslea, Navicula*, and *Pleurosigma* only
- Biological products have 1-6 unsaturations; fossils fully saturated

C_{30} Desmethylsteranes

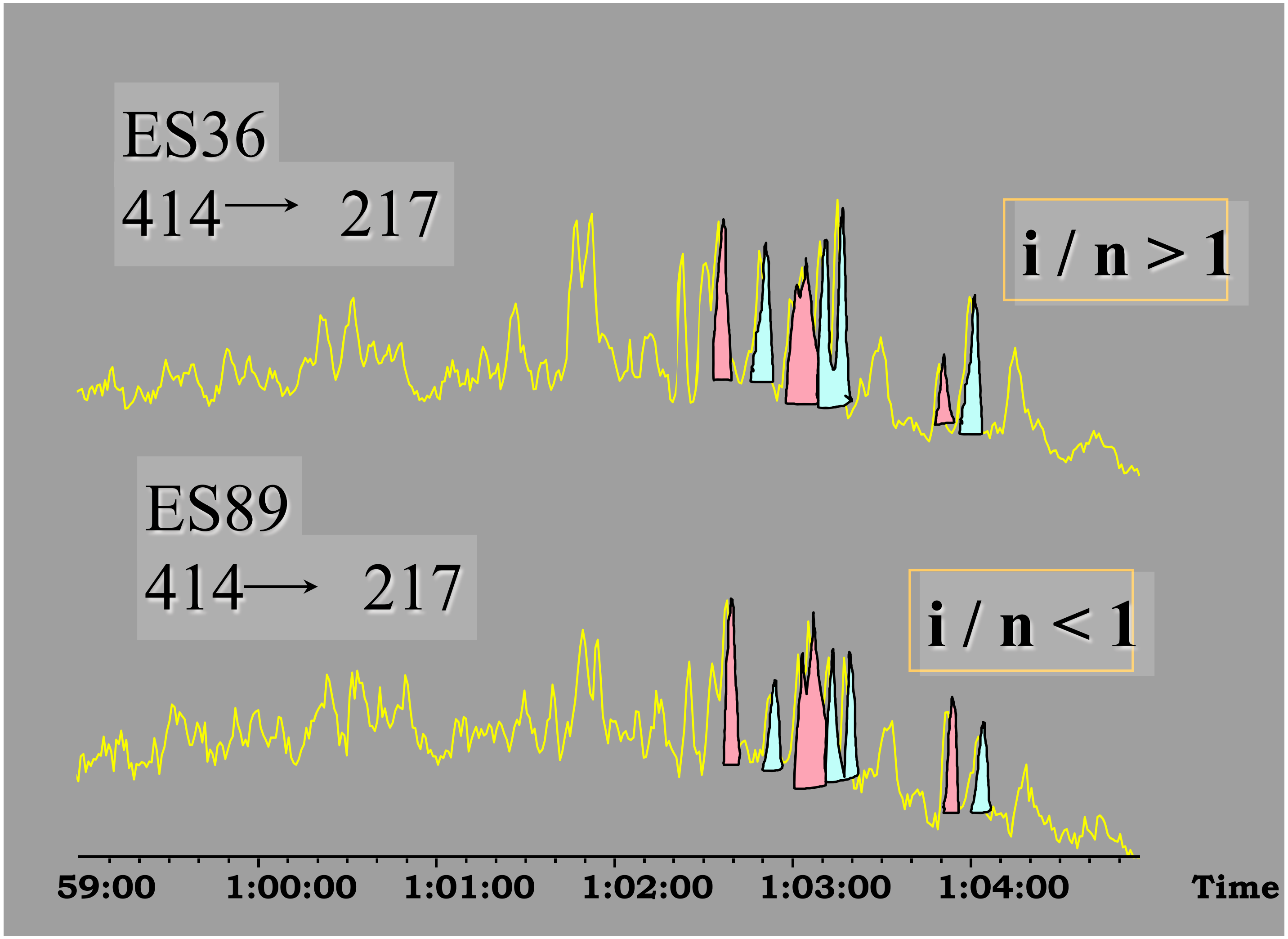




C_{30} Desmethyl Steranes
Oil from Southern Oman



C_{30} Desmethyl Steranes Eastern Siberia Oils



Stratigraphic column of Huqf Supergroup withrepresentativ e lithology, biostratigraphy and geochronologica l constraints.

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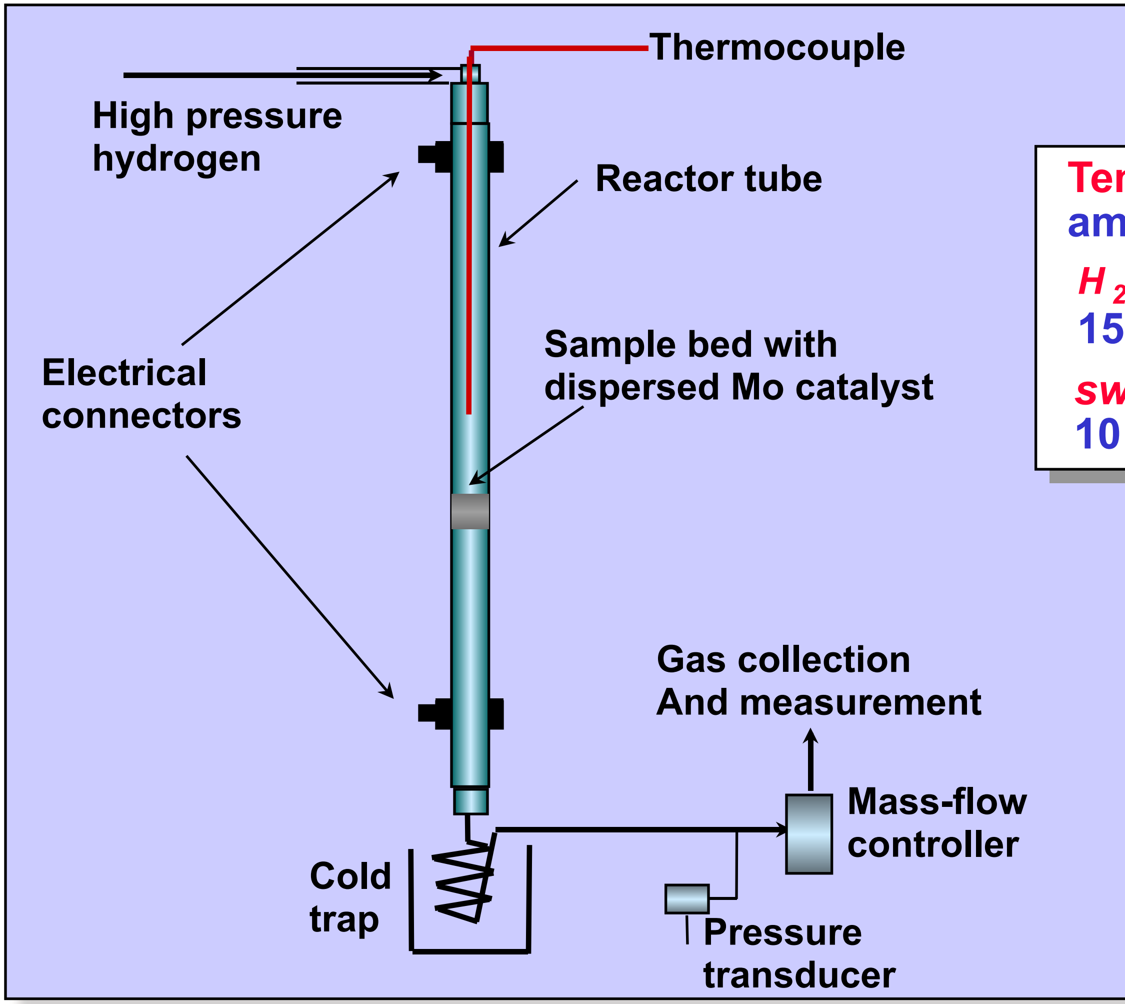
GD Love *et al.* *Nature* 457, 718-721 (2009) doi:10.1038/ nature07673

Catalytic hydropyrolysis (HyPy)
biomarker geochemistry applications

- Pyrolysis assisted by high H_2 pressure (15 MPa) and a molybdenum catalyst (active phase is MoS_2)
- A powerful tool for releasing bound biomarkers
  - high yields of biomarker hydrocarbons
  - less structural/stereochemical alteration
  - Love *et al*. (1995) *Org. Geochem*. 23, 981
  - info on bonding (D_2)

Hydropyrolysis apparatus

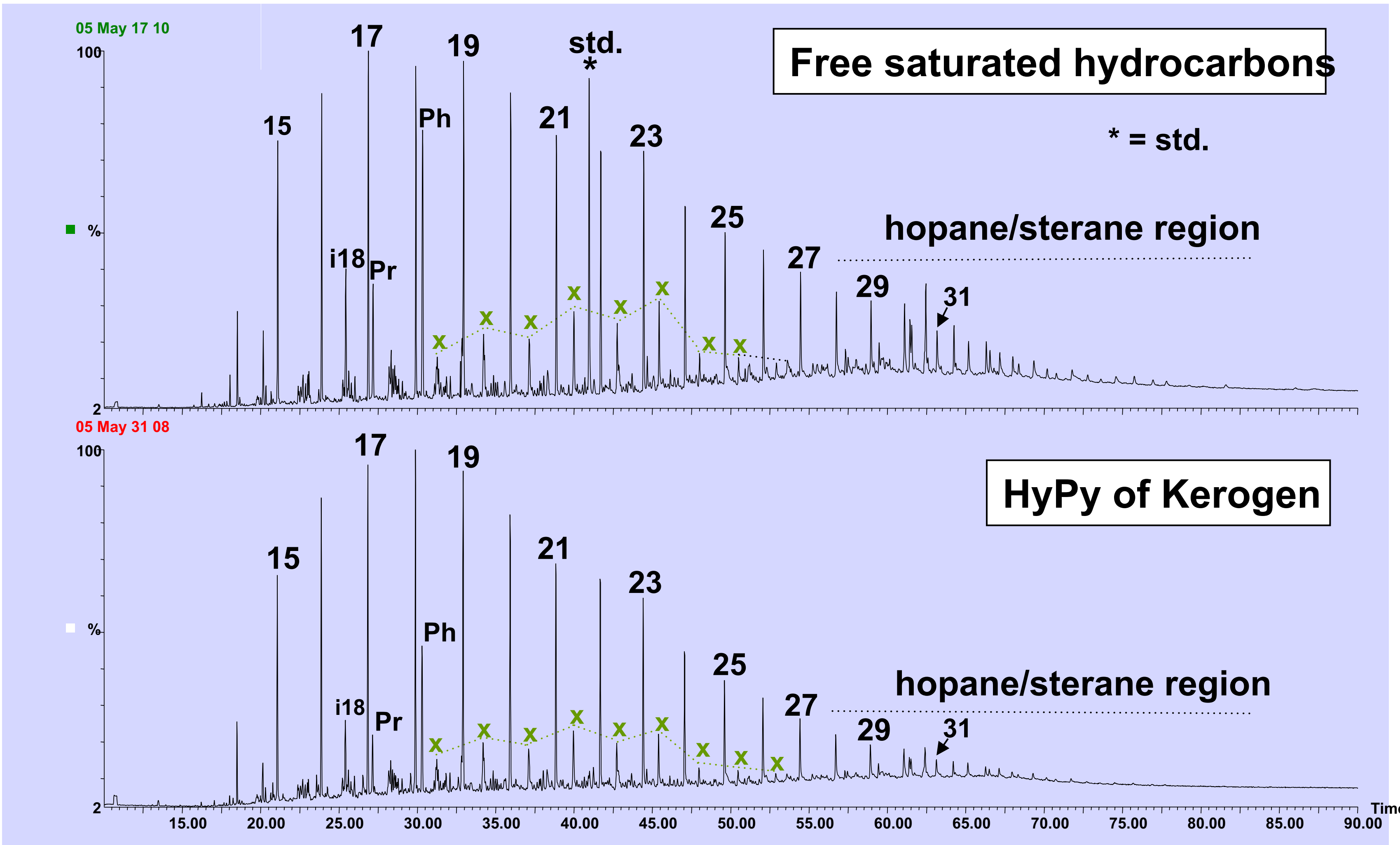


Temp prog.
amb. – 500°C @ 8°C/min

H_2 pressure
15 MPa

sweep gas flow
10 dm^3/min

Comparison of free and kerogen-bound hydrocarbons TICs of saturates for a Minassa-1(A1C) sample



X= series of mid-chain methylalkanes (unknown origin)

MRMGC-MS ion chromatograms of C_{26}–C_{30} desmethylsteranes released from catalytic hydropyrolysis of a Masirah Bay Formation (JF-1) and a Ghadir Manquil Formation (GM-1) kerogen.

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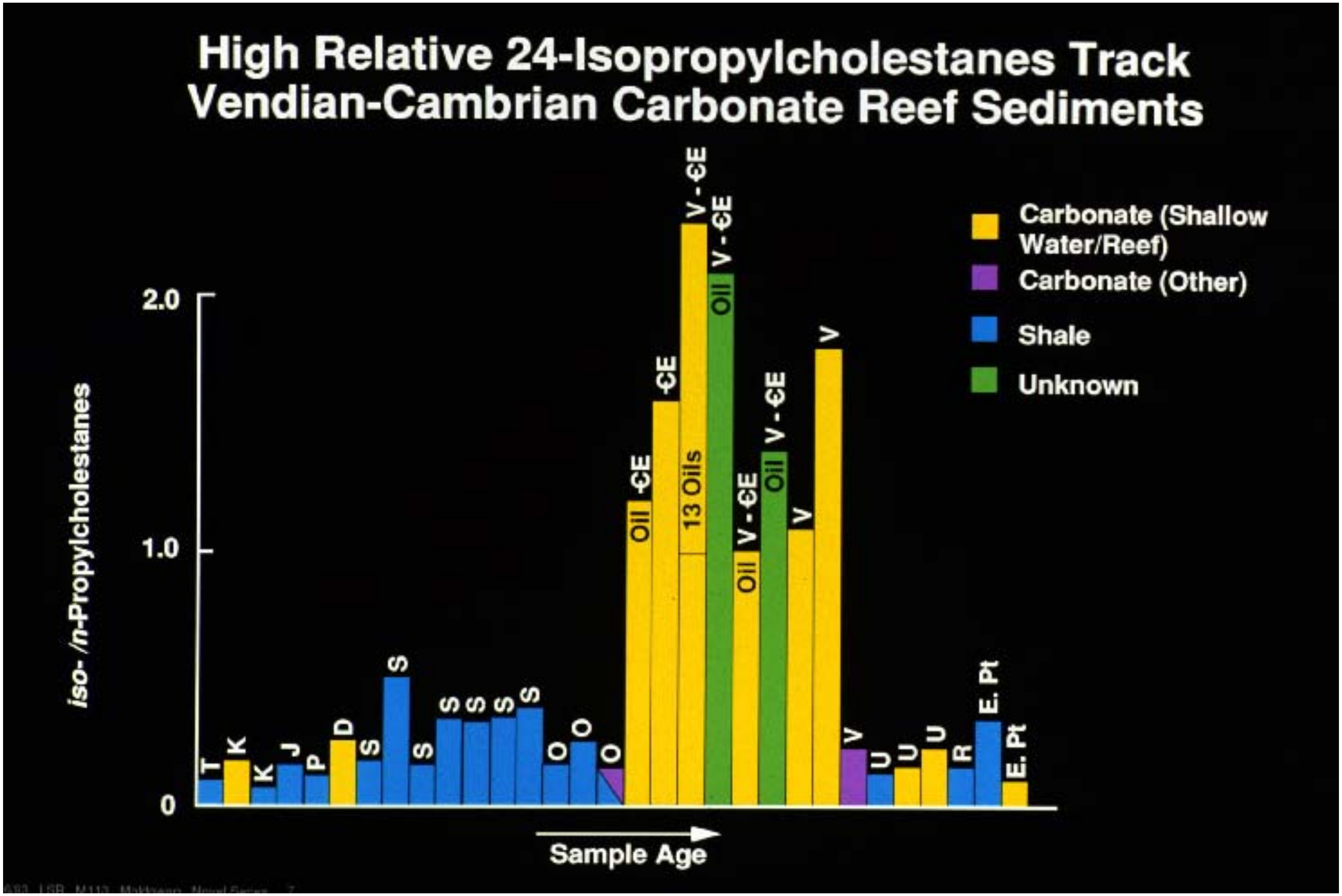
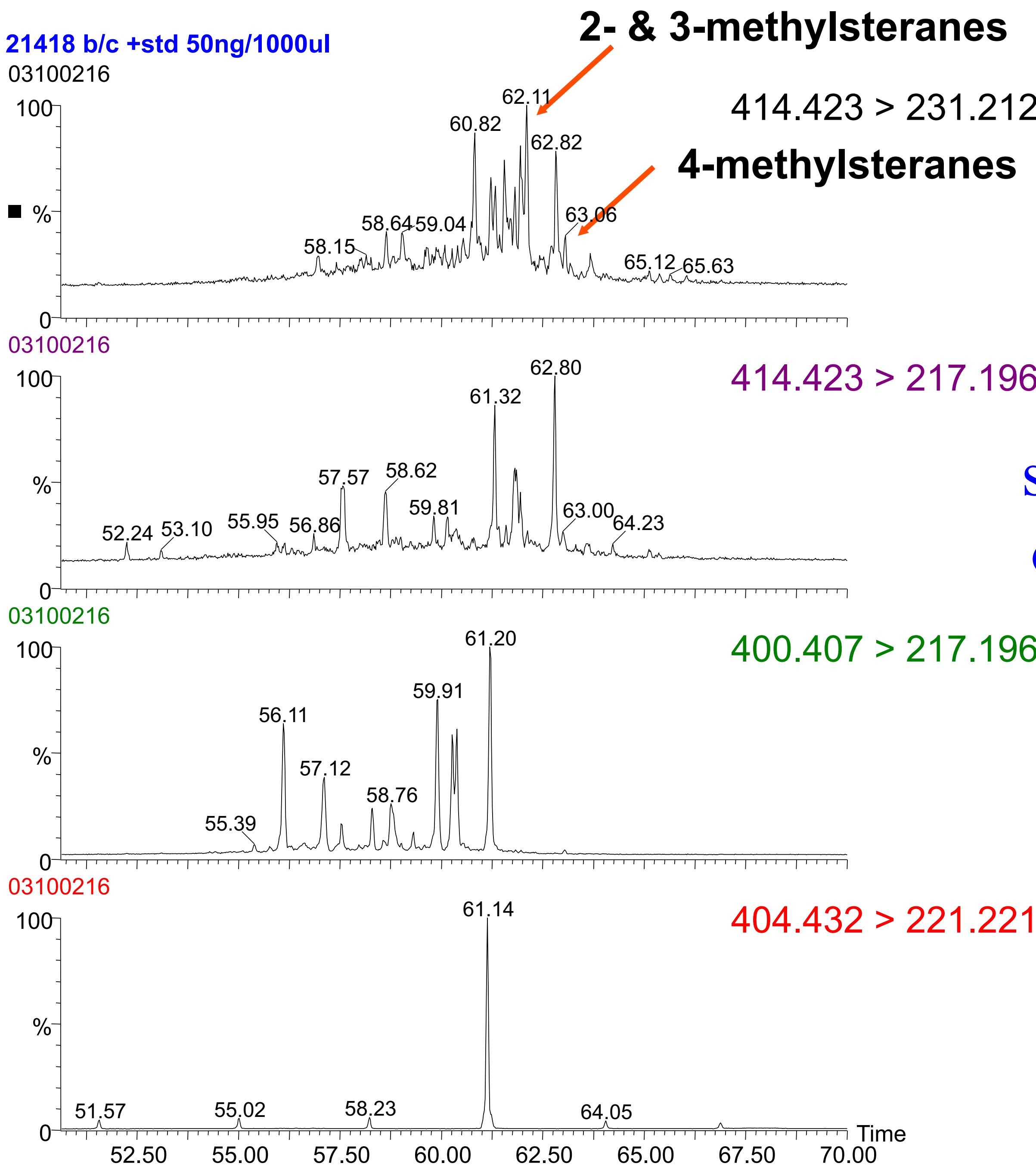
GD Love *et al. Nature* 457, 718-721 (2009) doi:10.1038/ nature07673


High Relative 24-Isopropylcholestanes Track
Vendian-Cambrian Carbonate Reef Sediments
iso- /n-Propylcholestanes
2.0
1.0
0
Sample Age
Carbonate (Shallow Water/Reef)
Carbonate (Other)
Shale
Unknown
T
K
K
J
P
D
S
S
S
S
S
S
S
O
O
O
Oil -ЄE
-ЄE
V - ЄE
13 Oils
Oil V - ЄE
Oil V - ЄE
Oil V - ЄE
V
V
V
U
U
U
R
E. Pt
E. Pt

MRM –GCMS showing C_{30} steranes of a marine sediment



2- & 3-alkylsteranes

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Note the exact co-elution of the four synthetic isomers with the equivalent peaks of the Phosphoria oil

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2- & 3-alkylsteranes

Note the different isomer preference for marine vs lacustrine sediments

12.158 Molecular Biogeochemistry
Fall 2011