

# 12.158 Lecture 8

## Pigment-derived Biomarkers

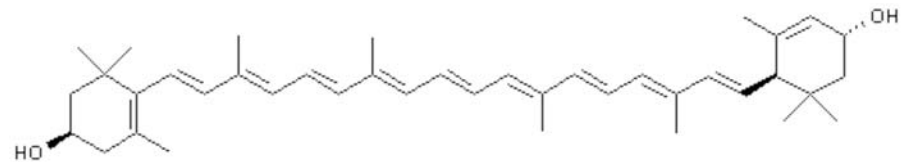
- (1) Colour, structure, distribution and function**
- (2) Biosynthesis**
- (3) Nomenclature**
- (4) Aromatic carotenoids**
  - **Biomarkers for phototrophic sulfur bacteria**
  - **Alternative biological sources**
- (5) Porphyrins and maleimides**

Many of the figures in this lecture were kindly provided by Jochen Brocks, RSES ANU

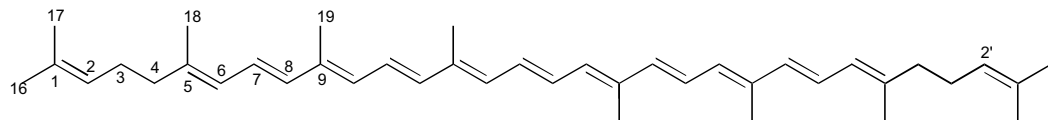
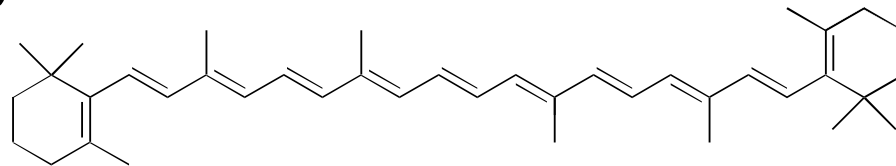
# Carotenoid pigments

- Carotenoids are usually yellow, orange or red coloured pigments

lutein



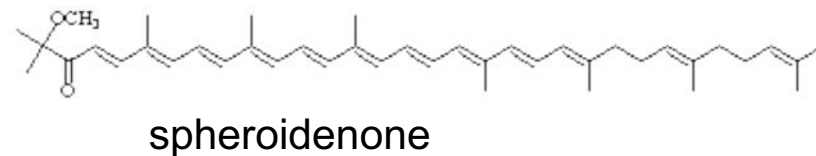
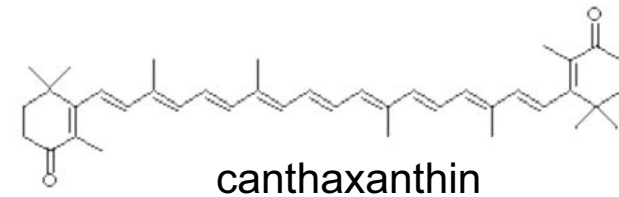
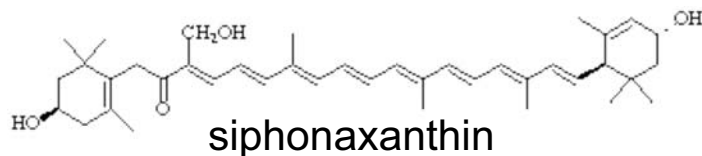
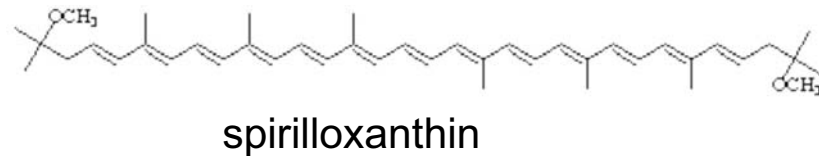
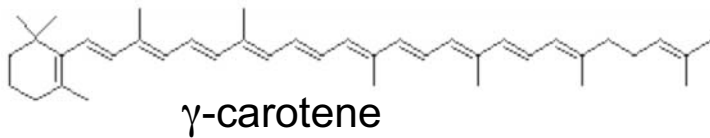
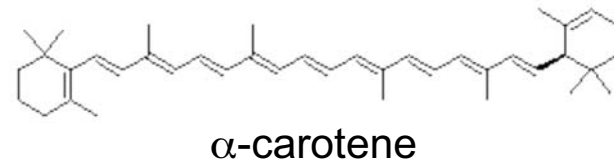
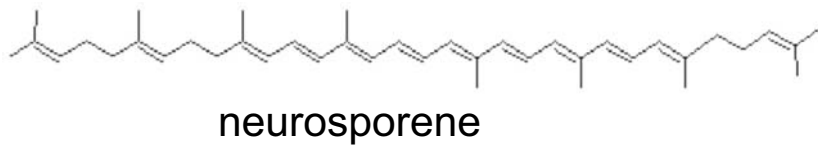
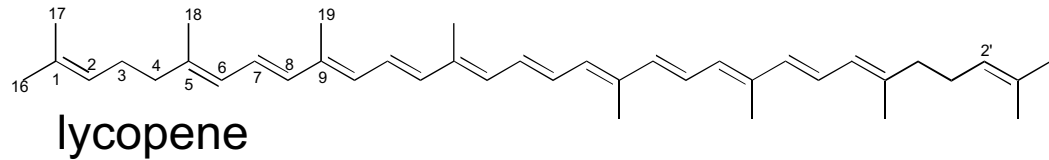
$\beta$ -carotene



lycopene

# Structural diversity

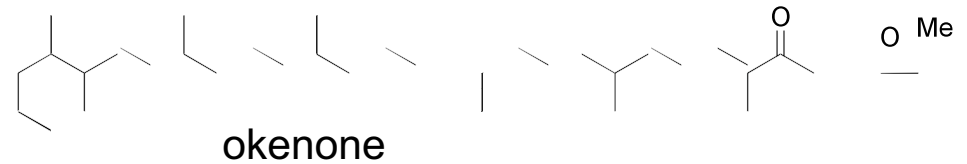
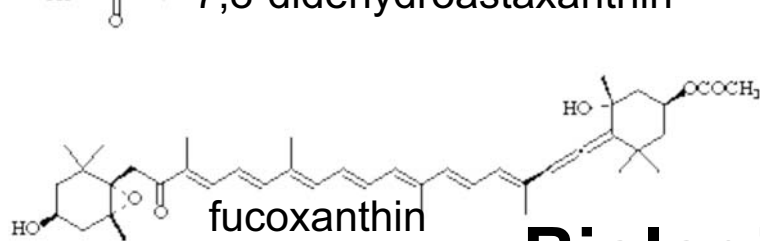
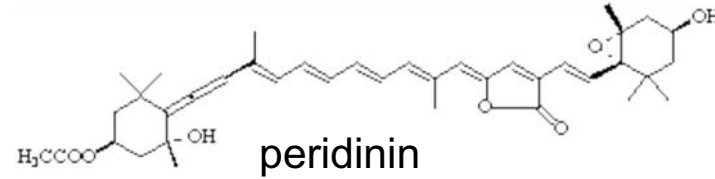
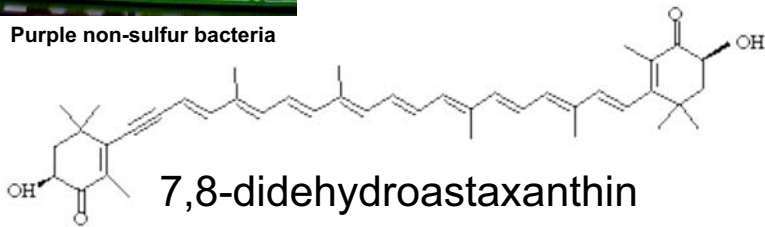
- More than 600 different natural structures are known,
- They are derived from the C<sub>40</sub> carotenoid lycopene by varied hydrogenation, dehydrogenation, cyclization and oxidation reaction





Purple non-sulfur bacteria

# Structural diversity



# Biological distribution

- Carotenoids are biosynthesized *de novo* by all phototrophic bacteria, eukaryotes and halophilic archaea
- They are additionally synthesized by a large variety of non-phototrophs
- Vertebrates and invertebrates have to incorporate carotenoids through the diet, but have often the capacity to structurally modify them

# Carotenoid function

## **(1) Accessory pigments in Light Harvesting Complex (LHC)**

(annual production by marine phytoplankton alone: 4 million tons)

e.g. LH-II

Red and blue: protein complex

Green: chlorophyll

Yellow: lycopene

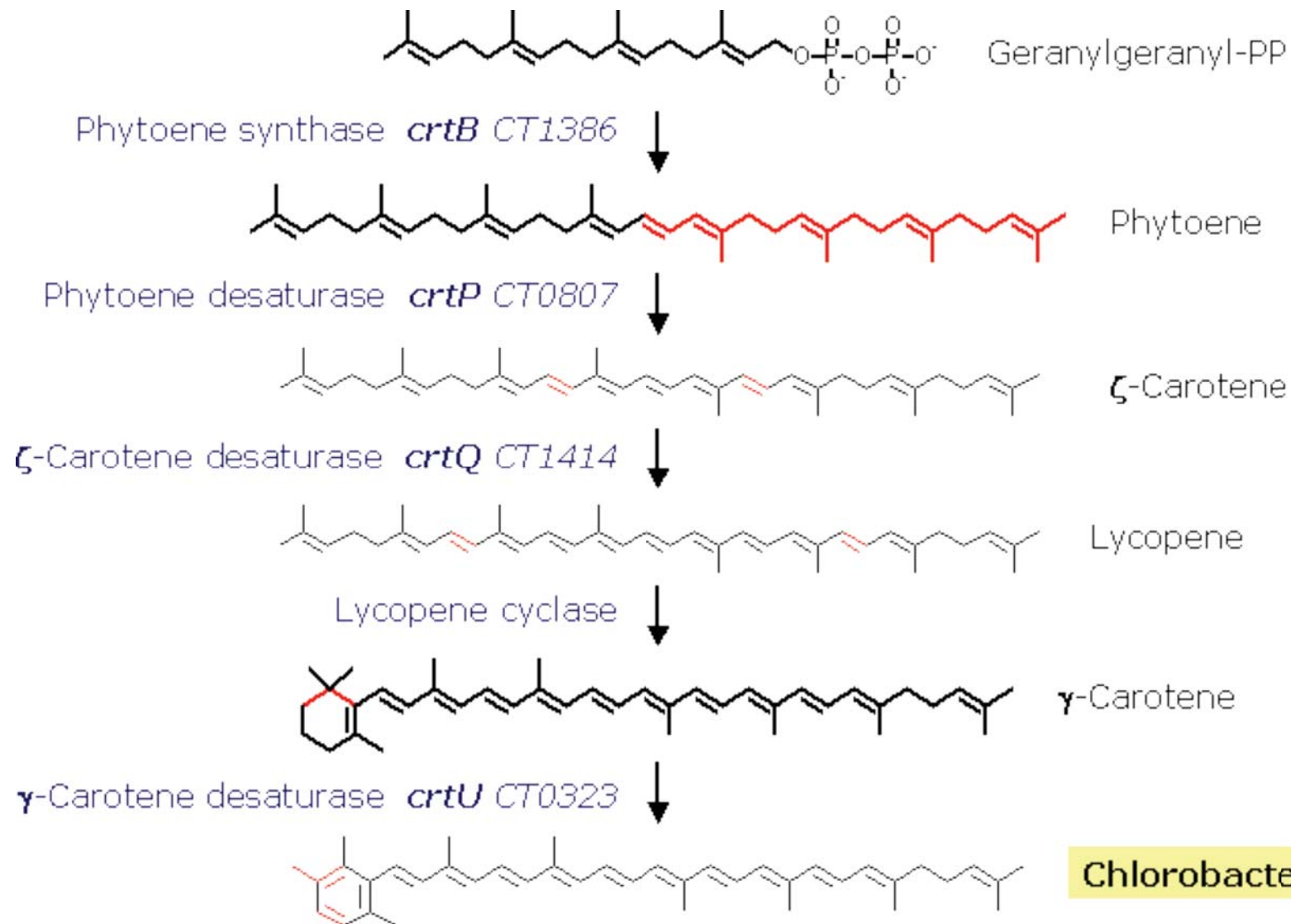
## **(2) Photoprotection**-----

### **(3) photoreceptors for phototropism and phototaxis**

Halobacteria in a saltern  
(carotenoid bacterioruberin)

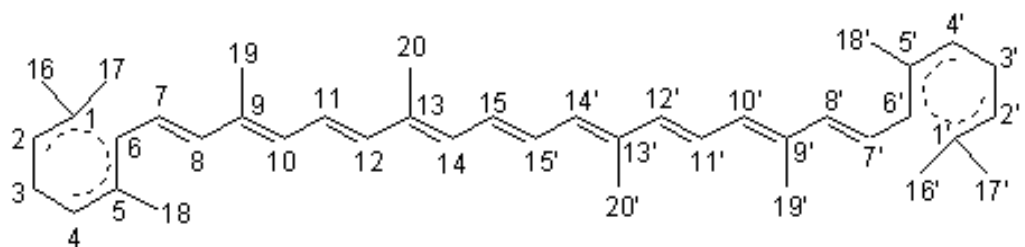
### **(4) Coloration of plants, fungi and animals**

### **(5) Vision**

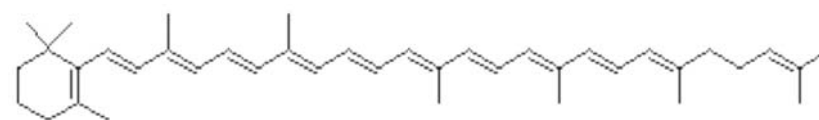
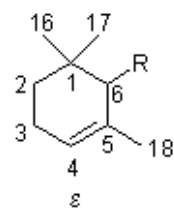
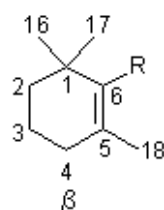
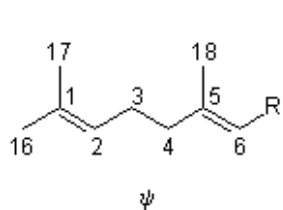


# Carotenoid nomenclature

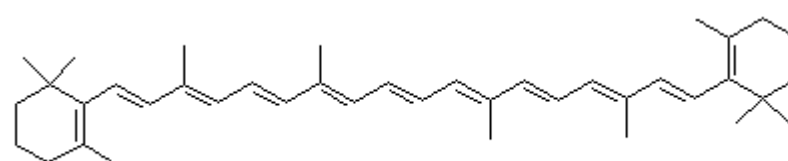
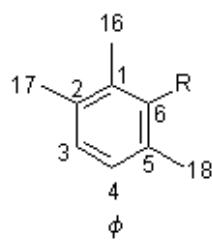
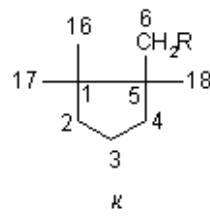
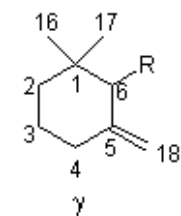
## (1) Numbering



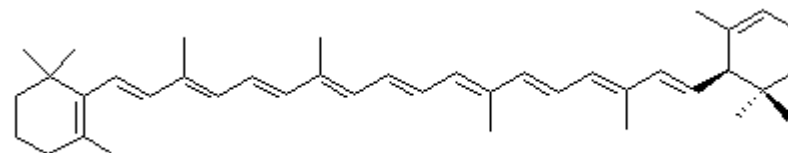
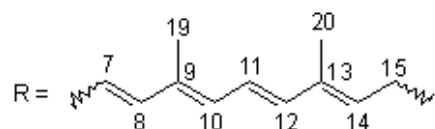
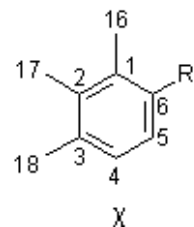
## (2) The greek alphabet of hydrocarbon endgroups



$\beta, \psi$ -carotene ( $\gamma$ -carotene)

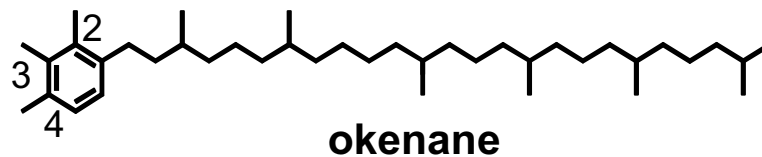
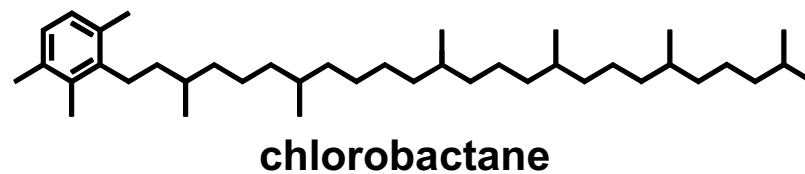
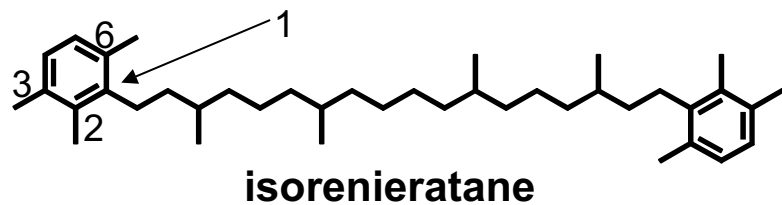


$\beta, \beta$ -carotene ( $\beta$ -carotene)

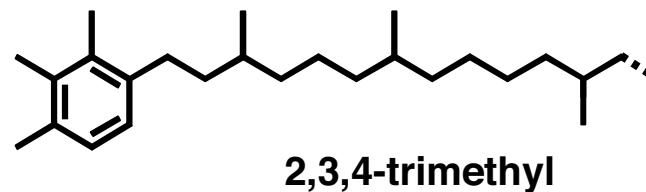
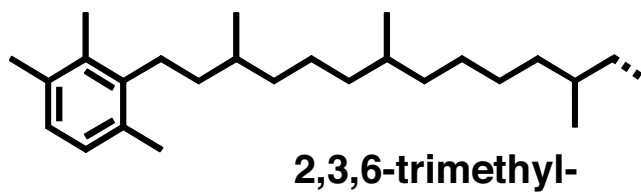


$\beta, \epsilon$ -carotene ( $\alpha$ -carotene)

# Aromatic Carotenoids

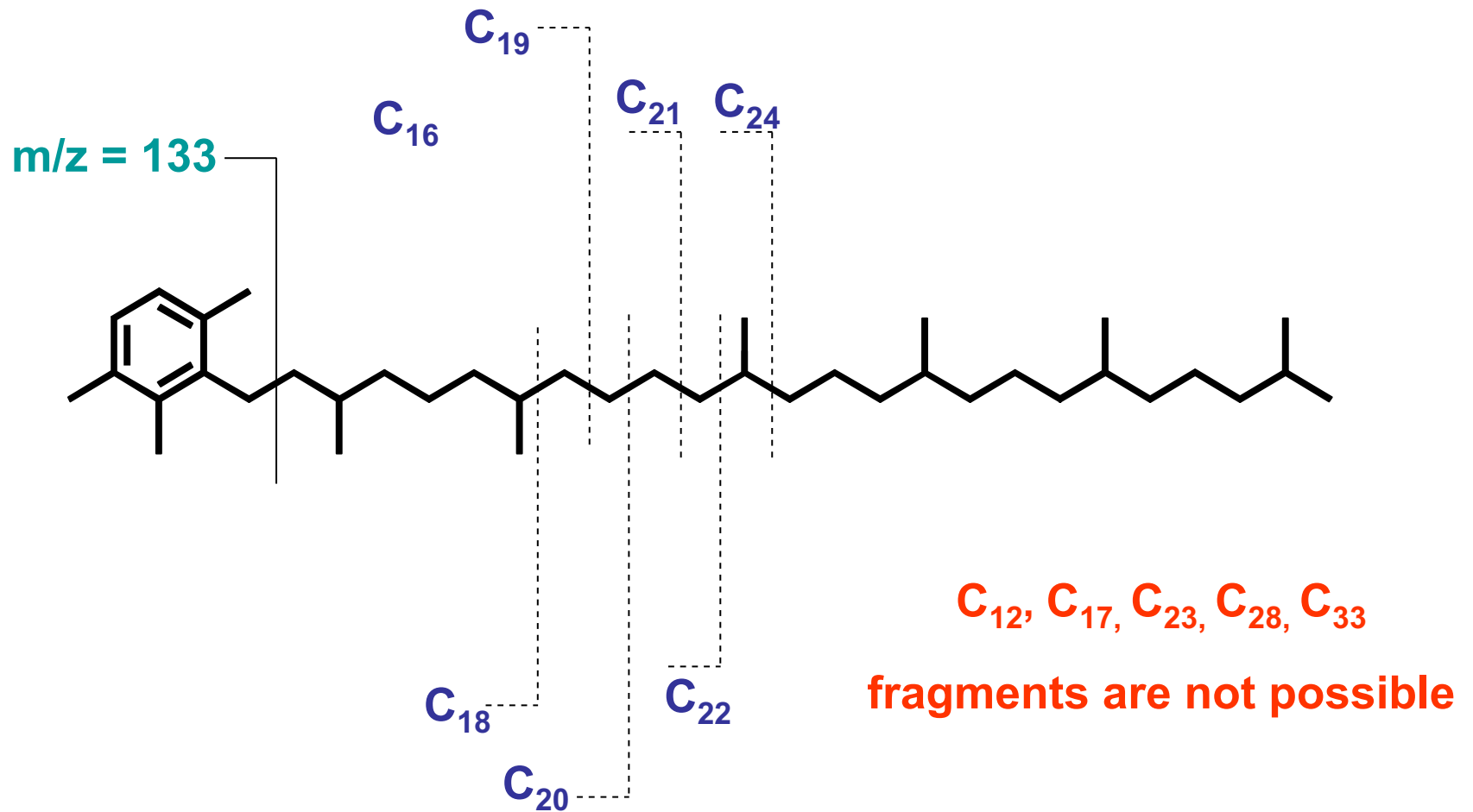


# Arylisoprenoids



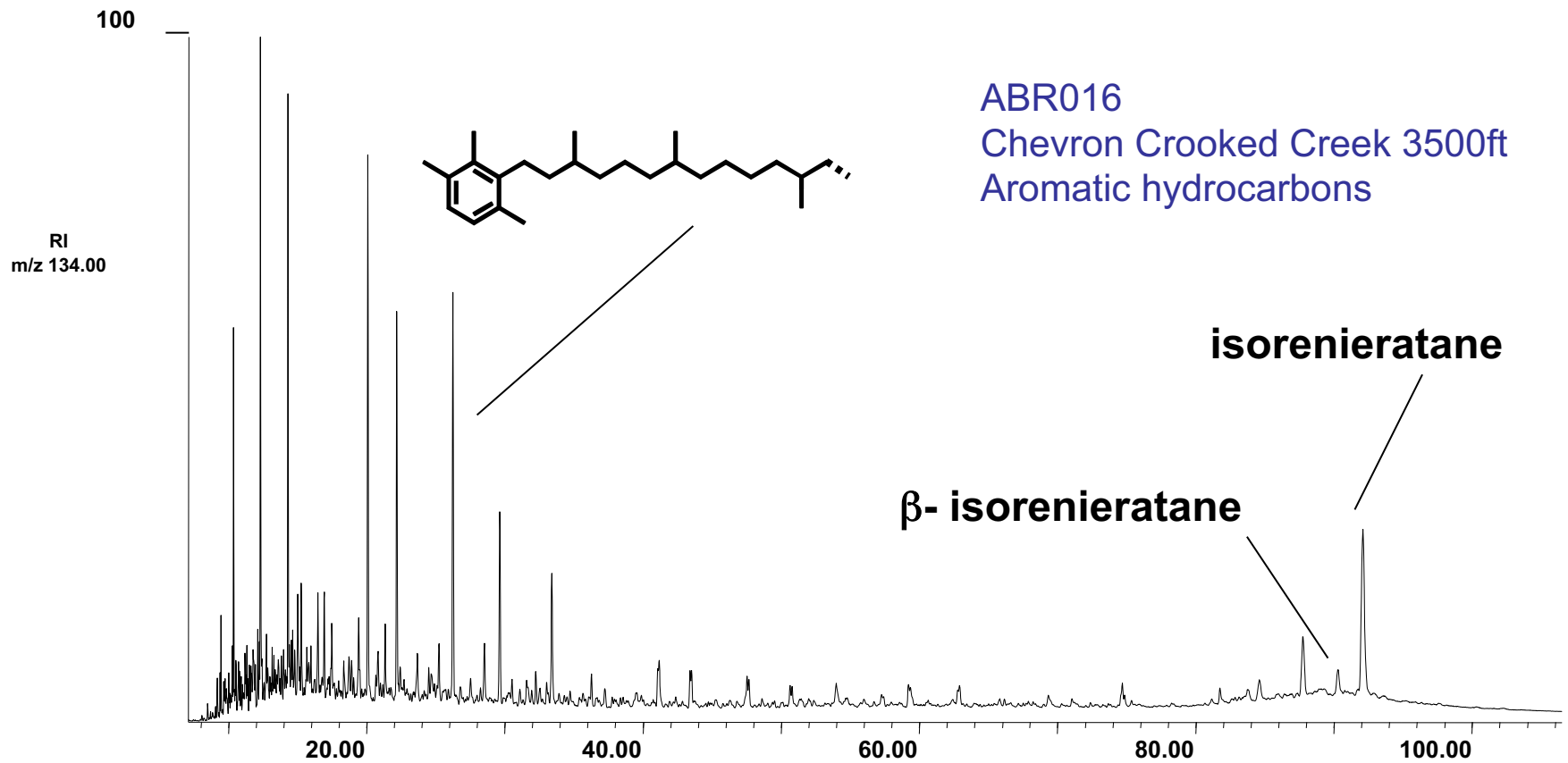


# Arylisoprenoids



Monitoring of  $m/z = 133.1$  and  $134.1$  in GC-MS SIR

# Aryl isoprenoids present in 7 samples from 4 wells at the *H. parvus* level of the Montney Fm



# Identification of Isorenieratane in Hovea-3

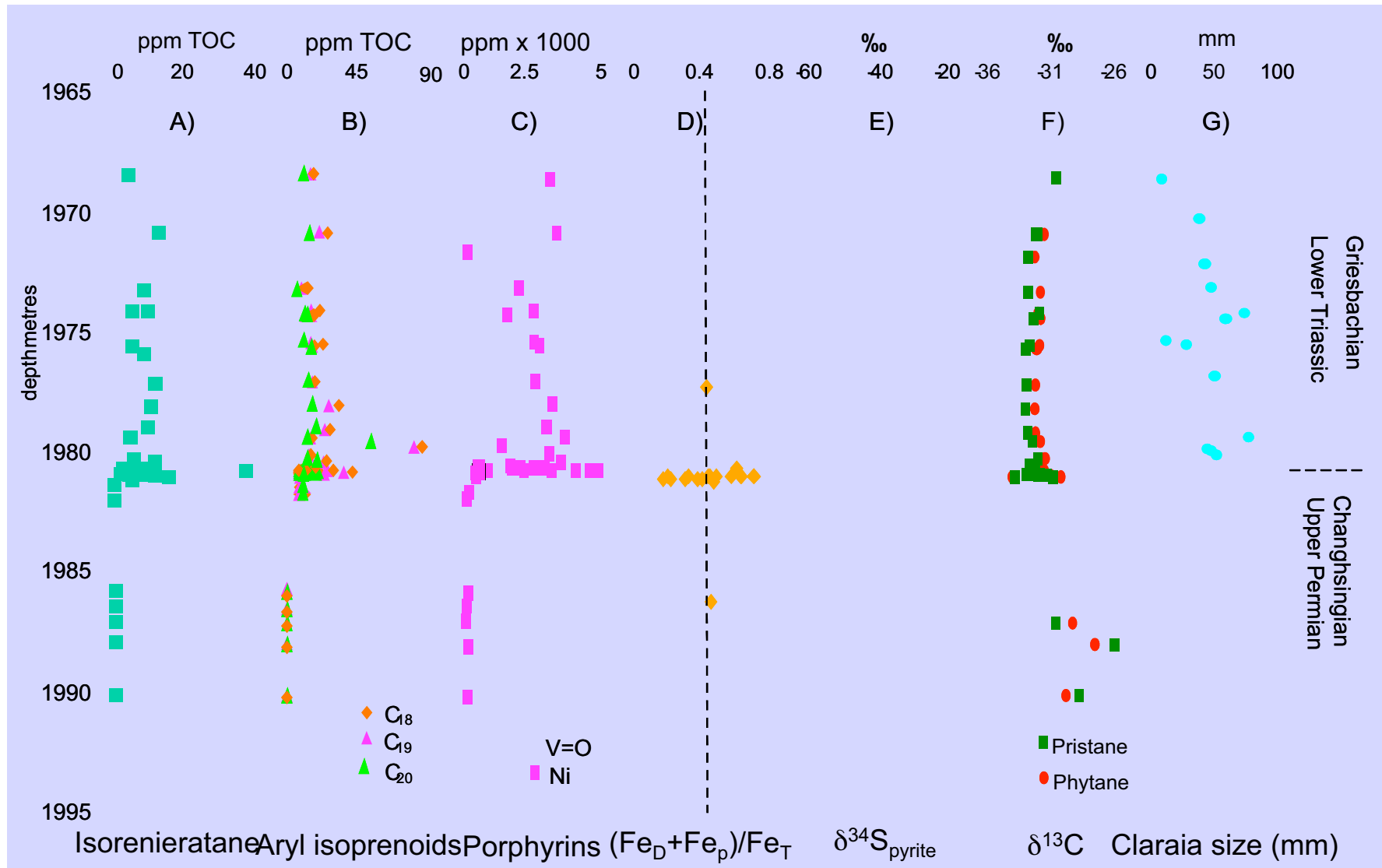
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Isorenieratane indicative of 'brown pigmented' Green Sulfur Bacteria & H<sub>2</sub>S 20  
-100m from surface

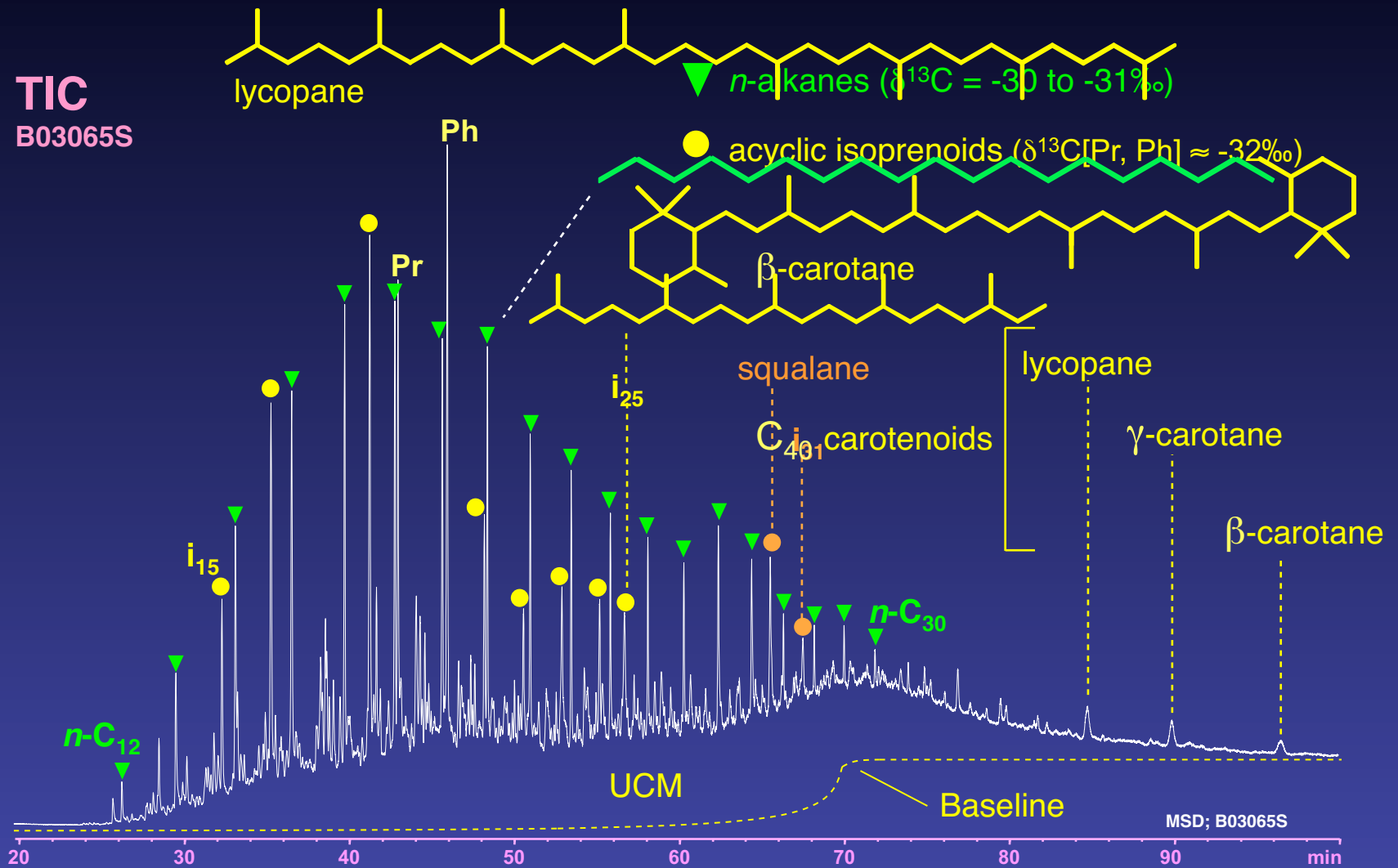
Identical Series of Arylisoprenoids and Isorenieratane in Core and Outcrop from  
Meishan

Grice K., Cao C., Böttcher M.E., Twitchett R.J., Grosjean E., Summons R.E., Turgeon S.C,  
Dunning W. and Jin Y., 2005. Anaerobic Photosynthesis in an Early Triassic Sea: Sluggish  
Ocean Circulation in a Greenhouse World. *Science* 307, 706-709.

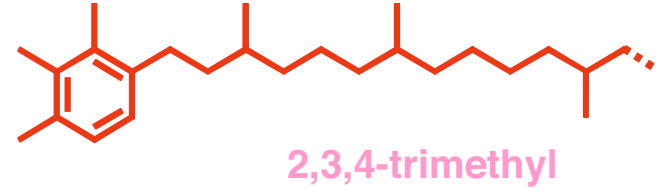
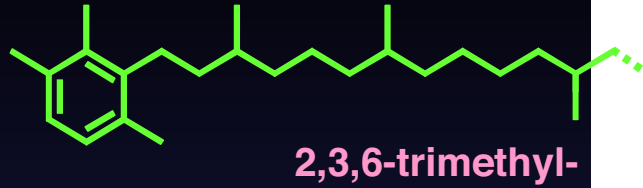
# Biogeochemical Proxies at Hovea-3



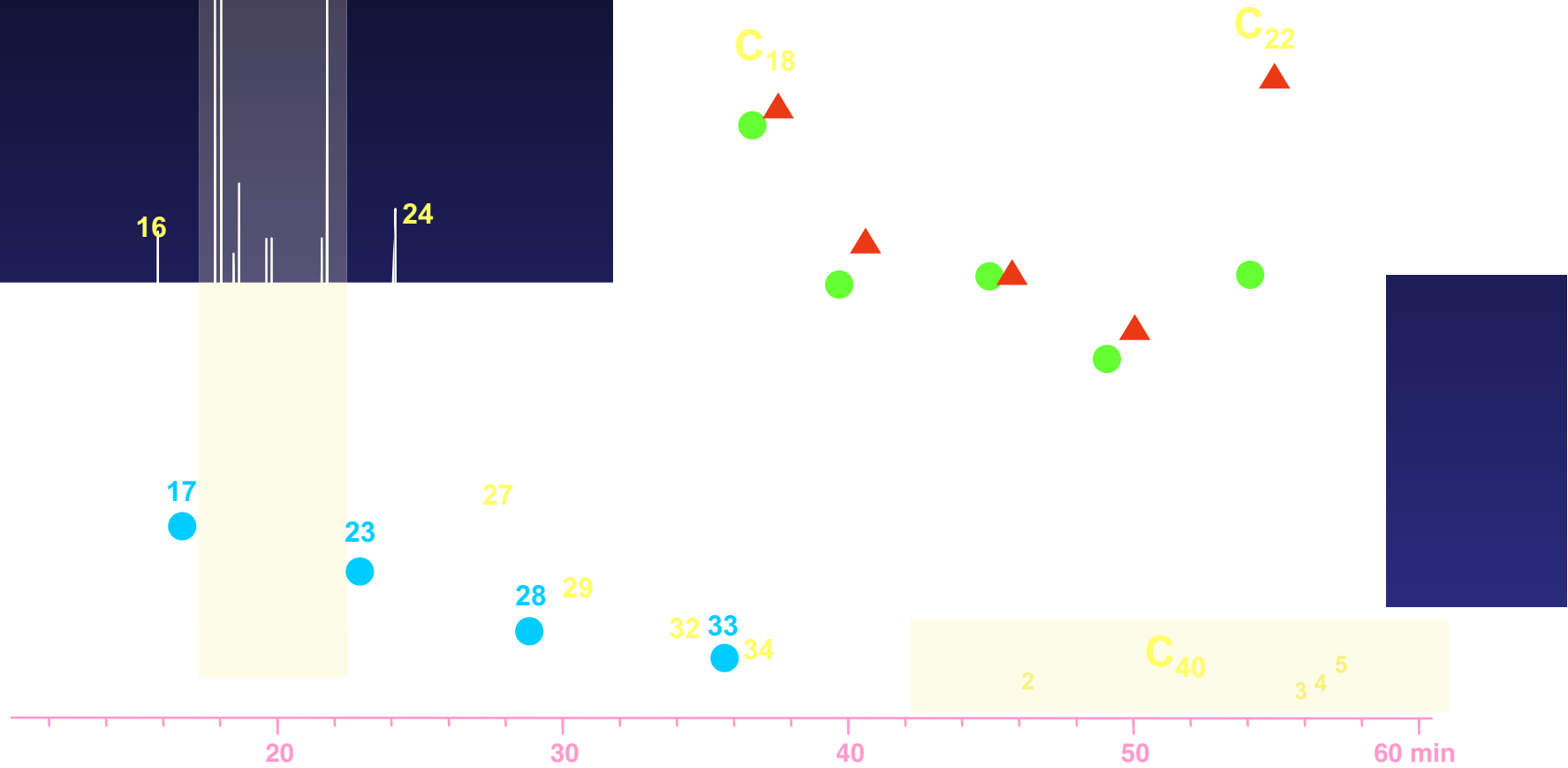
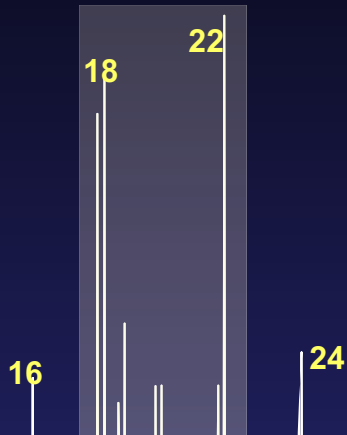
# Saturated hydrocarbon fraction of the Barney Creek Fm.



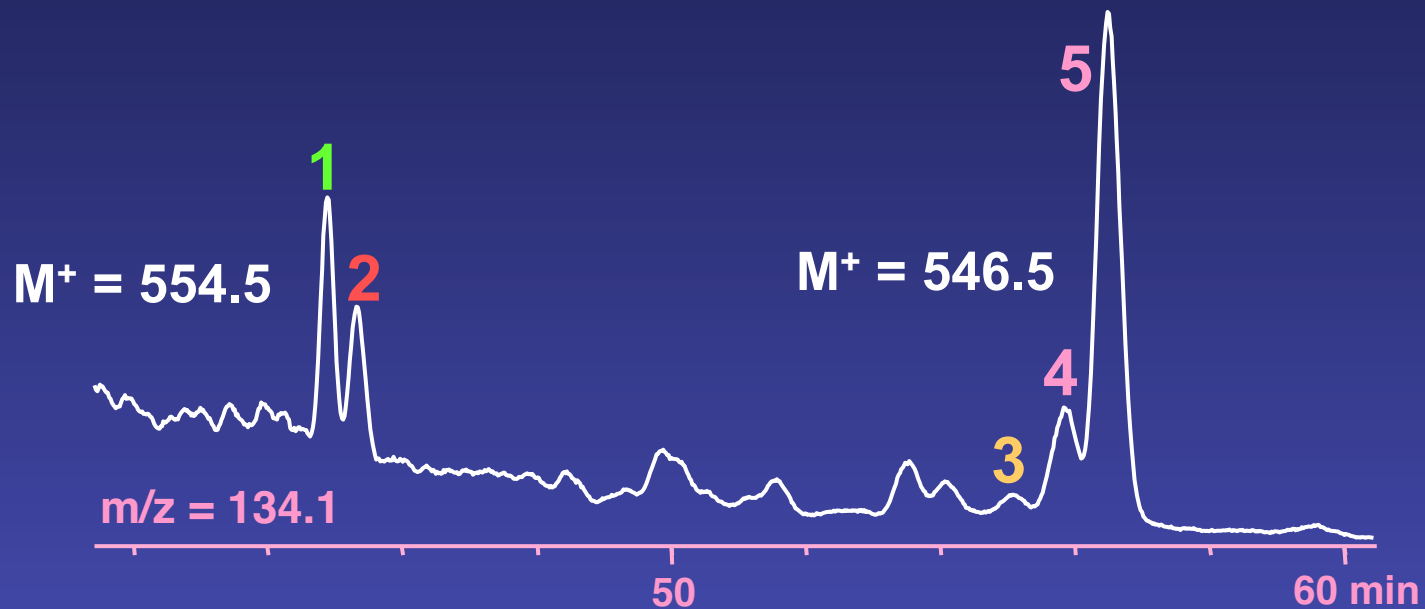
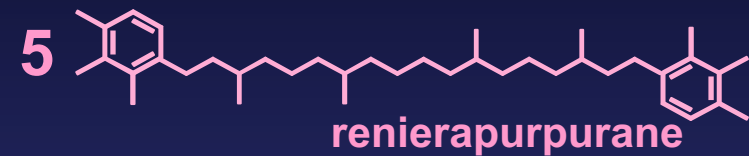
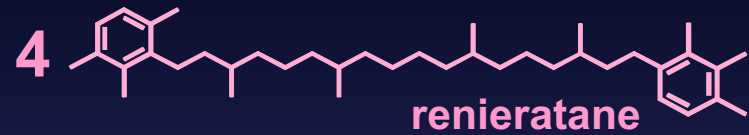
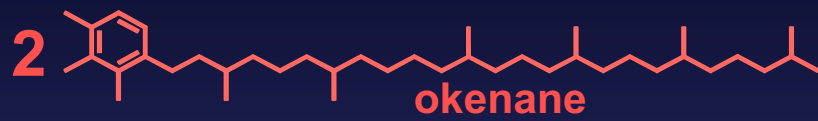
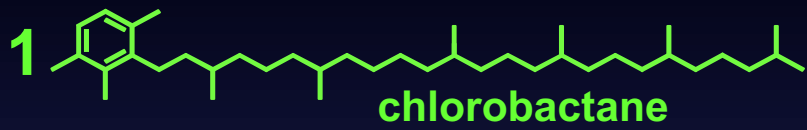
# Arylisoprenoids in the Barney Creek Formation

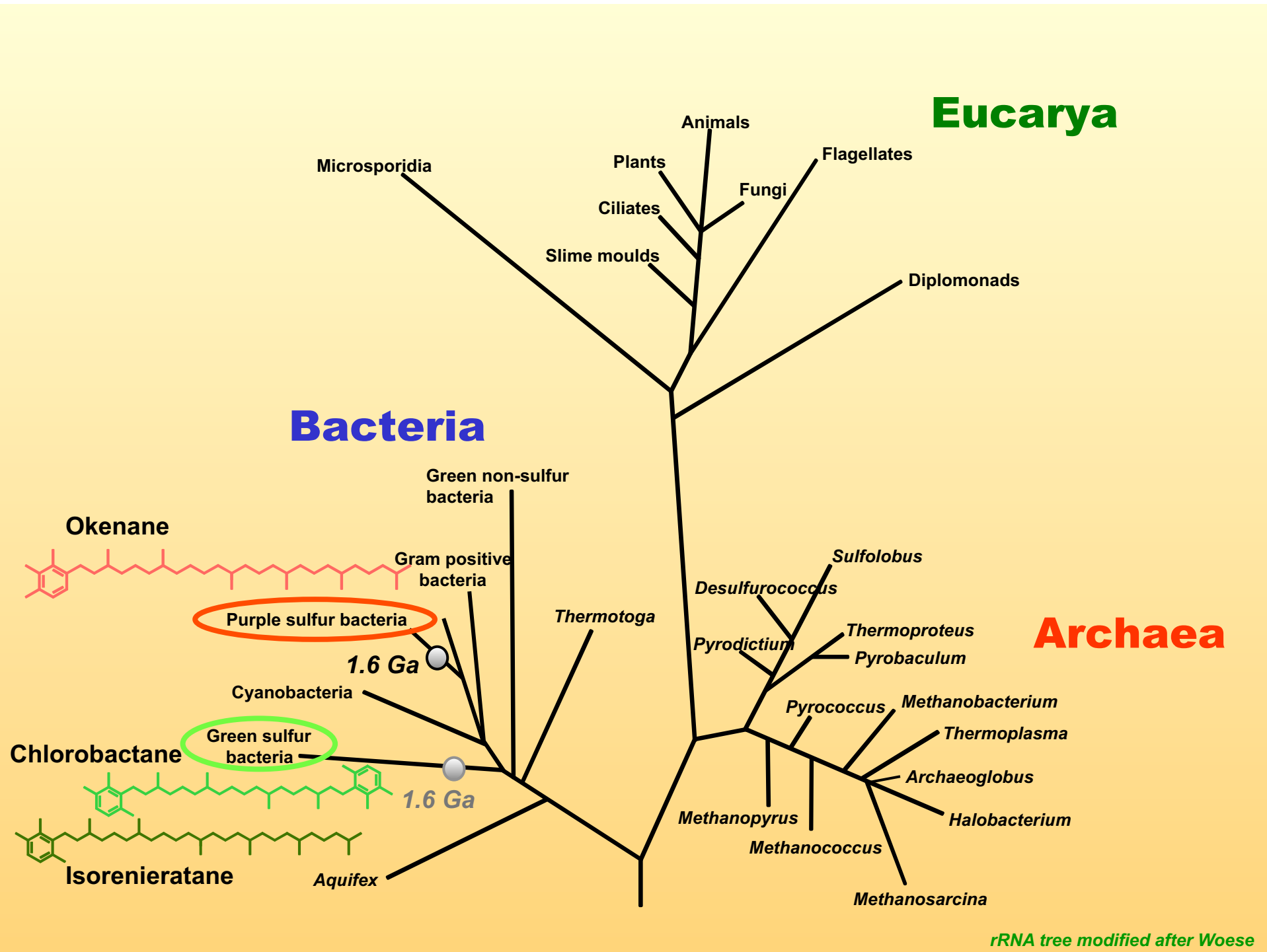


SIR  
m/z = 134.1



# C<sub>40</sub> Arylisoprenoids

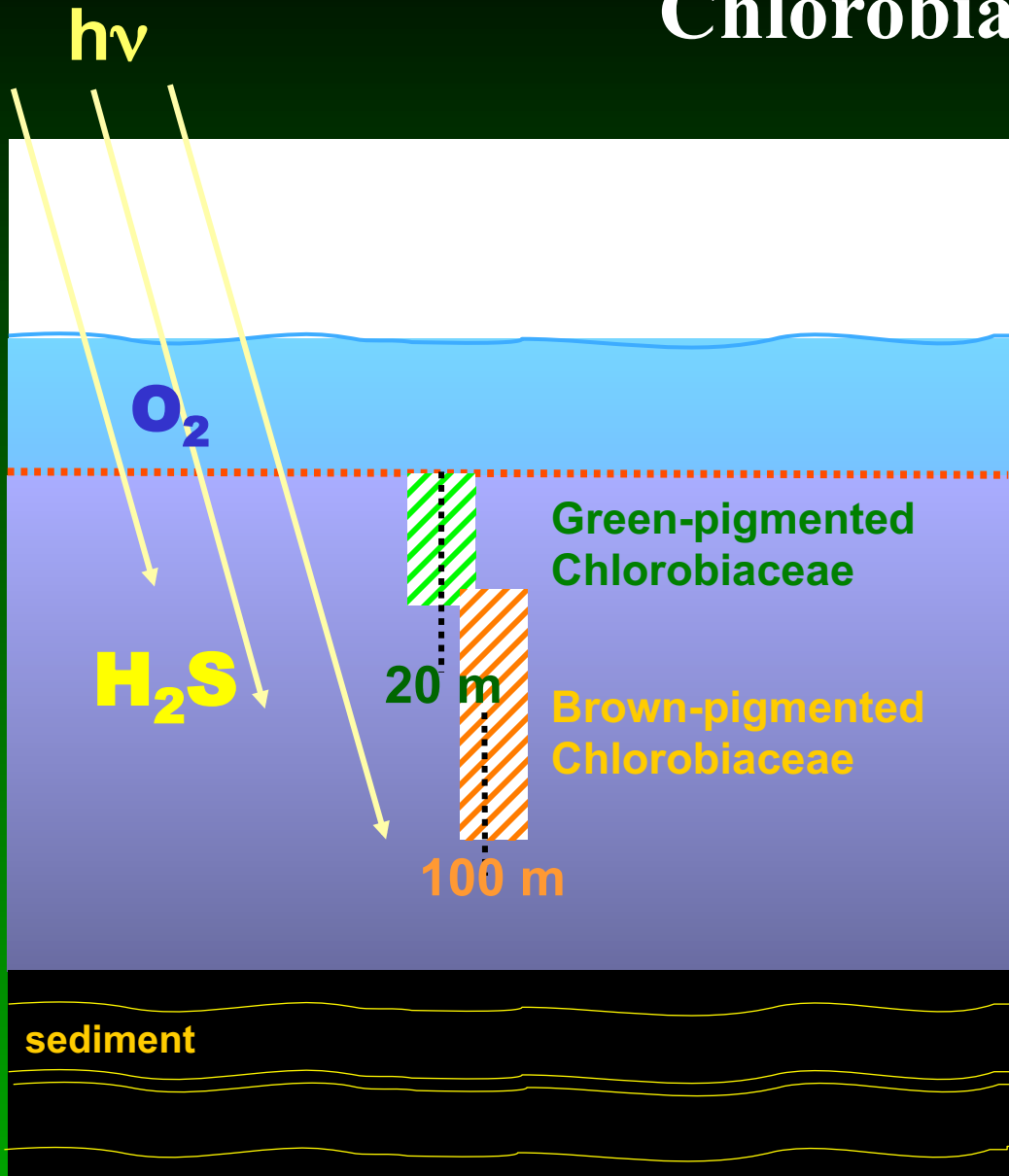






# Green sulfur bacteria

## Chlorobiaceae



### *Anoxygenic photosynthesis*



$h\nu$



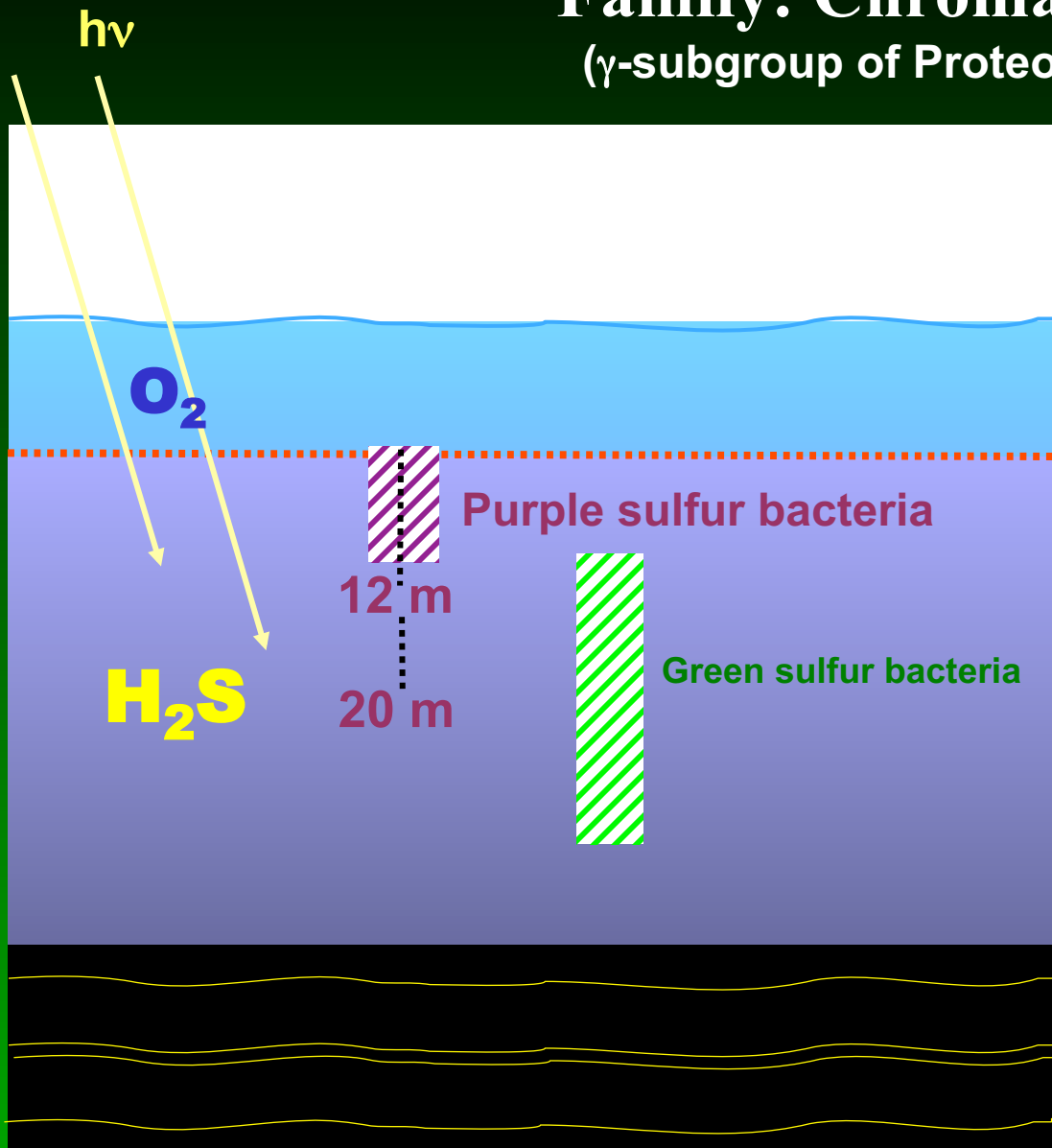
- require reduced sulfur
- require light
- strictly anaerobic





# Purple sulfur bacteria

Family: Chromatiaceae  
( $\gamma$ -subgroup of Proteobacteria)



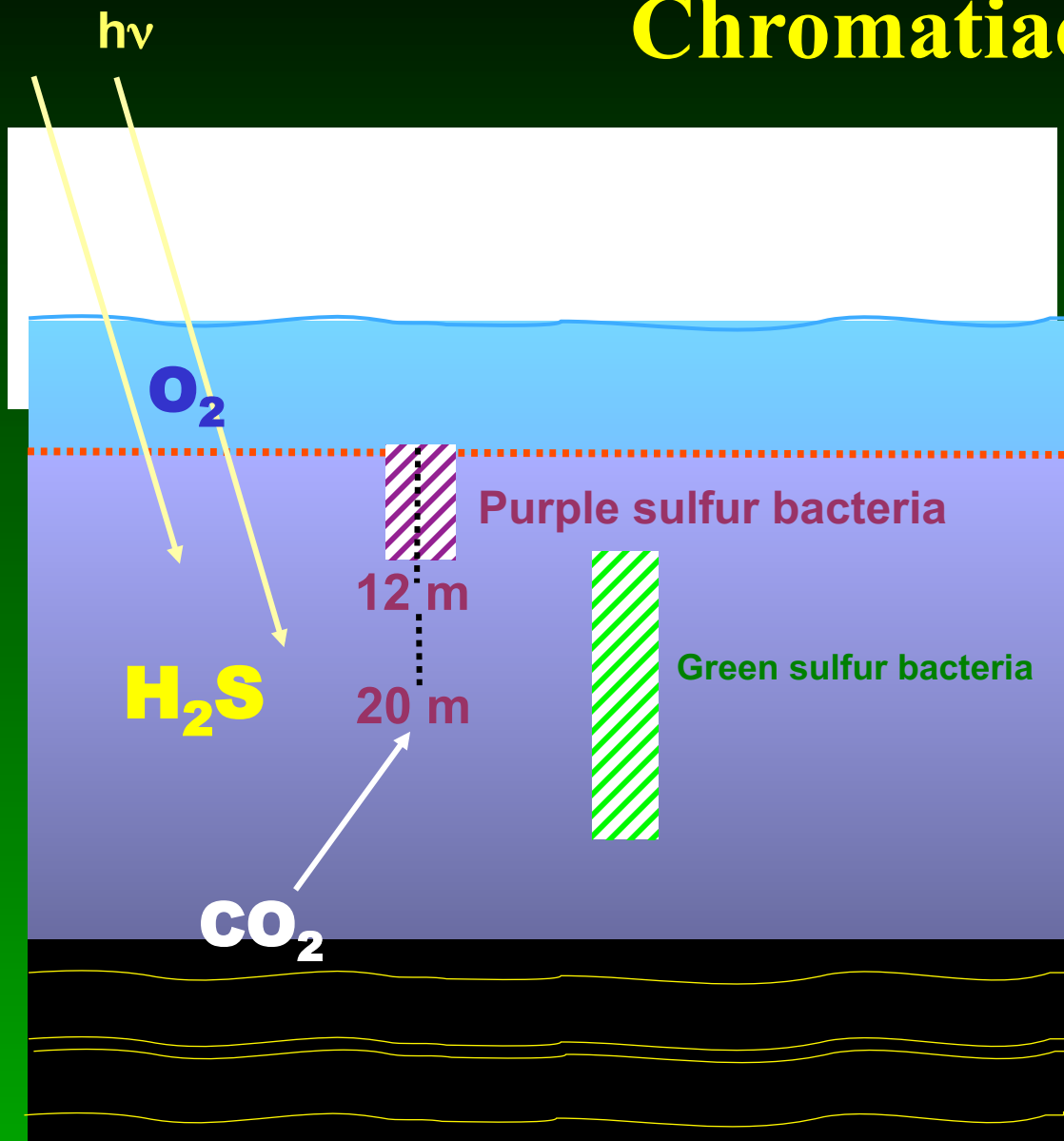
Similar requirements to  
Chlorobiaceae

- reduced sulfur
- light
- anoxic conditions



# Purple sulfur bacteria

## Chromatiaceae

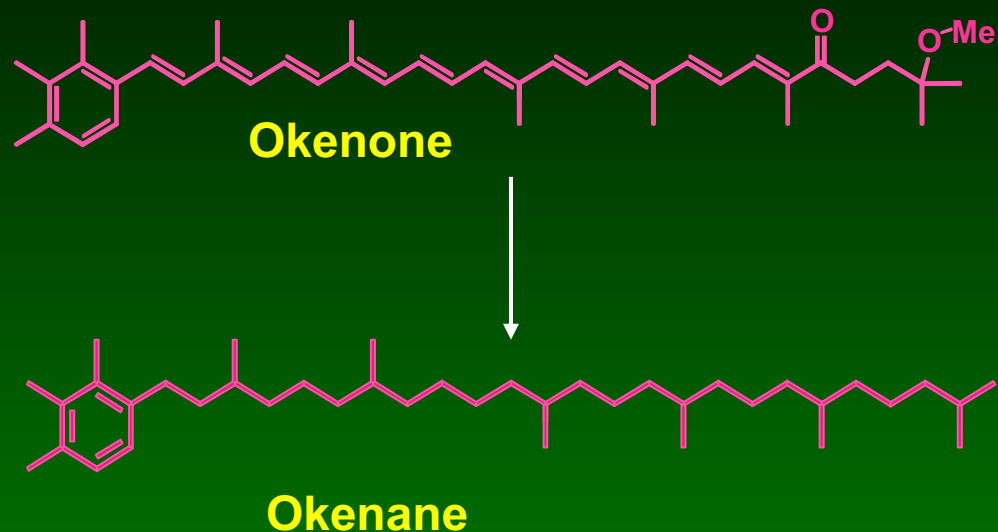
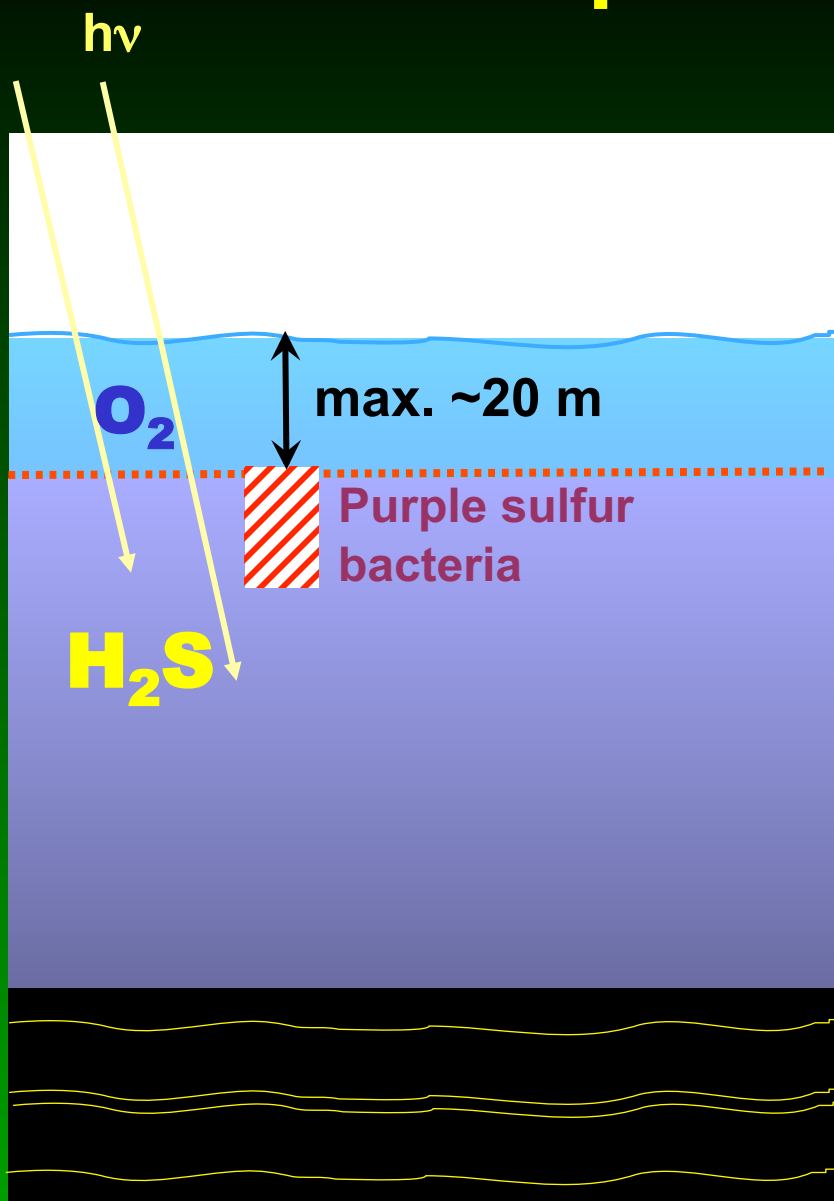


As in oxygenic phototrophs,  
carbon fixation follows the  
**Calvin Cycle**

However, isotopically light  $CO_2$   
sources might be utilized

⇒ Biomass is commonly  
somewhat *depleted* in  $^{13}C$   
relative to oxygenic phototrophs.

# Interpretations: okenane

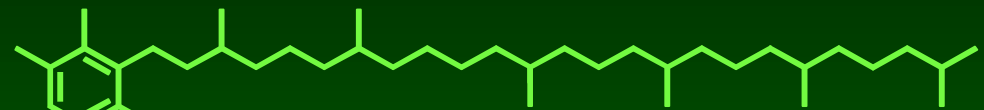
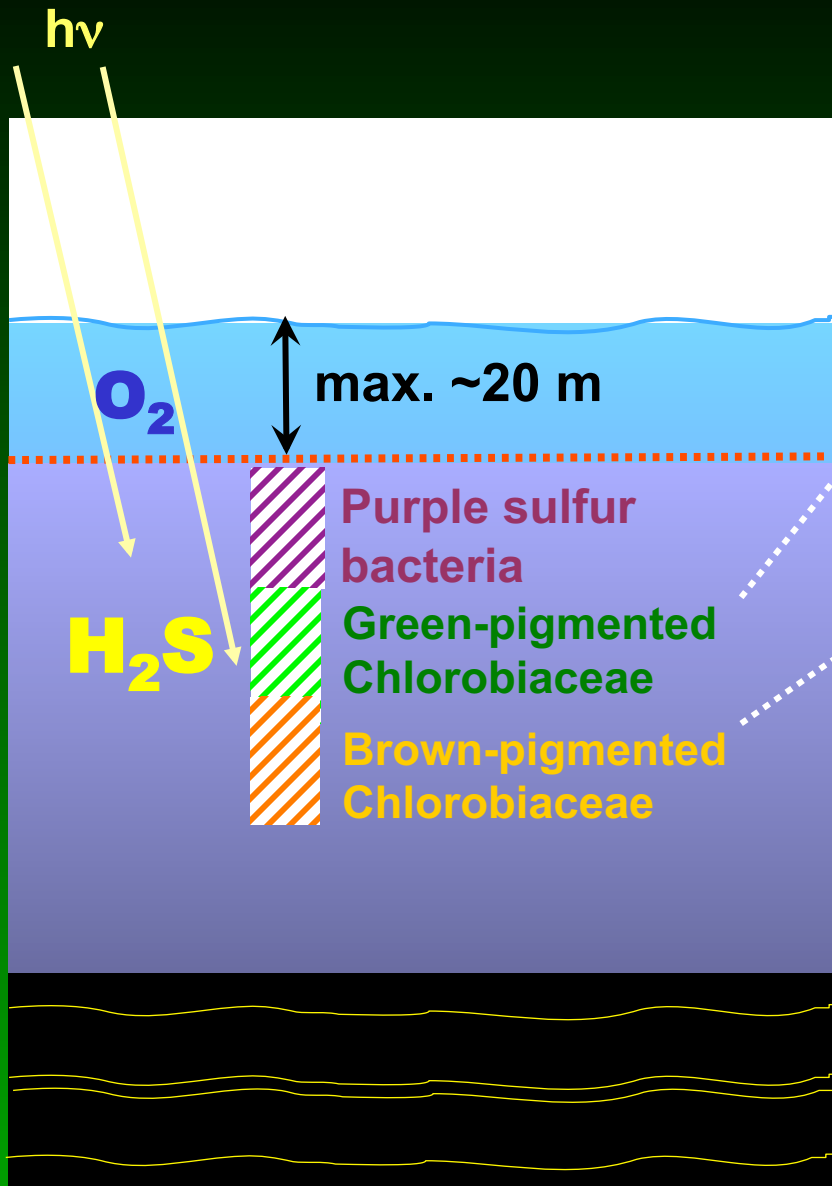


Okenane is a new  
(and the first!)  
biomarker for  
purple sulfur bacteria

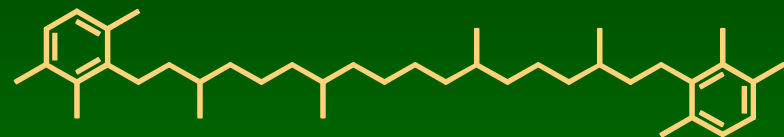




# Chlorobactane & Isorenieratane



Chlorobactane



Isorenieratane

Layers below Chromatiaceae  
were inhabited by  
Chlorobiaceae

Carbon isotopic data is required to  
confirm this interpretation

# Aromatic carotenoids in Lake Cadagno, Schweiz

Schaeffer et al. (1997), Tetrahedron Lett., 38, p.8413-16

The lake is meromictic, i.e. permanently stratified

Carbon isotopic measurement of hydrogenated extracts from the lake sediment

<b>Isorenieratane</b>	<b>-27‰</b>
<b>Chlorobactane</b>	<b>-28‰</b>
<b>β-Isorenieratane</b>	<b>-27‰</b>
<b>Okenane</b>	<b>-45‰</b>
<b>β-Renieratane</b>	<b>-42‰</b>

⇒ **Biomass of Chlorobiaceae and Chromatiaceae might be both strongly *depleted* in  $^{13}\text{C}$  by assimilation of  $\text{CO}_2$  sourced in remineralized OM**

The lake is 850x430x21m size; meromictic with sulfate rich bottom waters from leached host rocks & topped with freshwater; 6 month ice covered at 1920m altitude (Behrens et al (2000) GCA, 64, 3327)

# Restricted utility of arylisoprenoids

## North Sea oil

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$\beta$ -isorenieratane

isorenieratane

Koopmans et al., *GCA*, 2003

# Restricted utility of arylisoprenoids

Koopmans et al., *GCA*, 2003

**Laboratory generation of  $\beta$ -isorenieratane by partial hydrogenation with  $\text{PtO}_2/\text{H}_2$  and subsequent dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone**

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**Q: Is this a realistic simulation of a natural processes?**

**Q: Is there an alternative explanation for the isotopic values in the North Sea oil?  
How could you test it?**

**Q: Could okenane be generated this way starting with  $\gamma$ -carotene?**

$\beta$ -isorenieratene

# Alternative sources of arylisoprenoids

Mediterranean sapropel

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Hopmans, Rijpstra, Rohling, Cane, Sinninghe Damste (2003) *IMOG Poster*

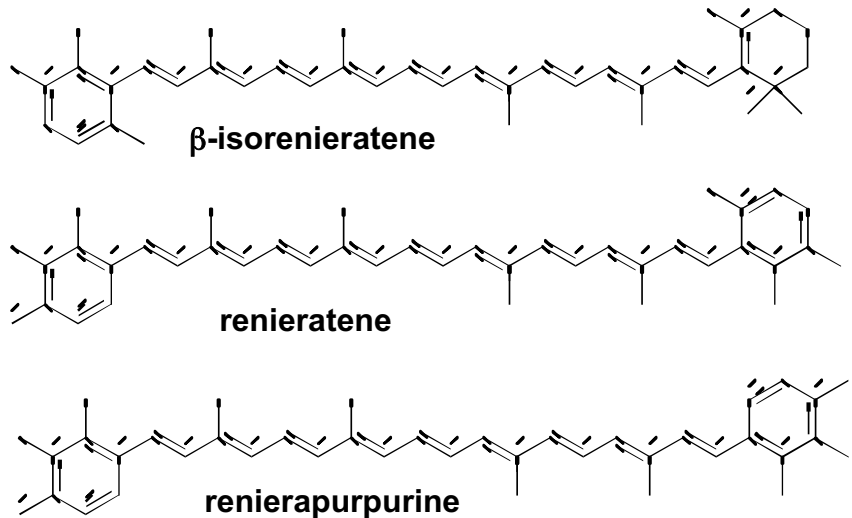
**! Isorenieratene also occurs in actinomycetes ( *Mycobacterium*, *Streptomyces* ).**

**Q: What is the preferred habitat of actinomycetes? Using this additional bit of information, give an alternative explanation for the above data.**

**Q: How could you test the new hypothesis?**

# Alternative sources of arylisoprenoids

A variety of aromatic carotenoids also occurs in sponges:  
isorenieratene,  $\beta$ -isorenieratene,  
renieratene, renierapurpurine



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***Reniera fulva***  
(Orangener Polsterschwamm)

**Q: What are the possible biosynthetic sources of these carotenoids?**  
**Q: How could you test what the source is?**

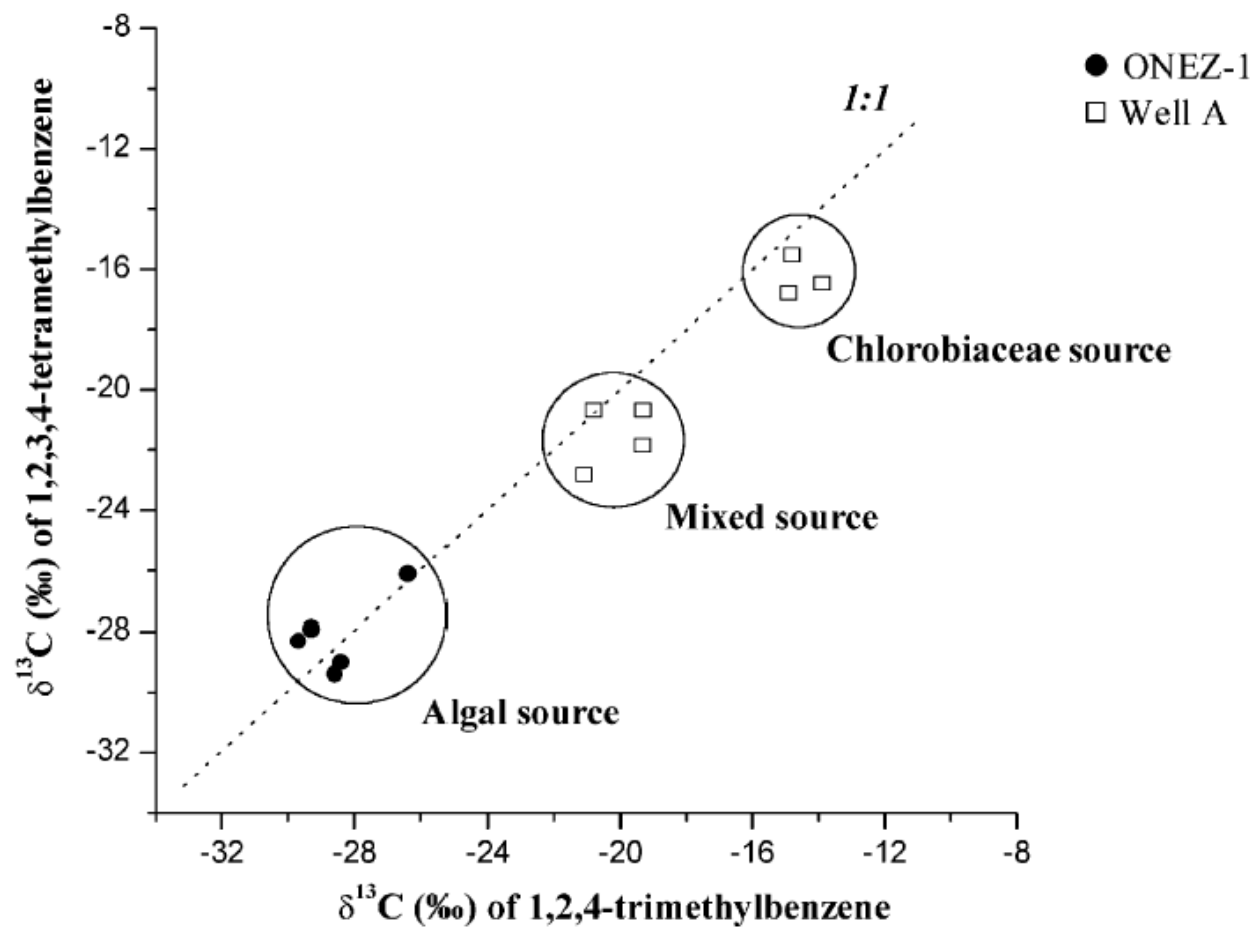
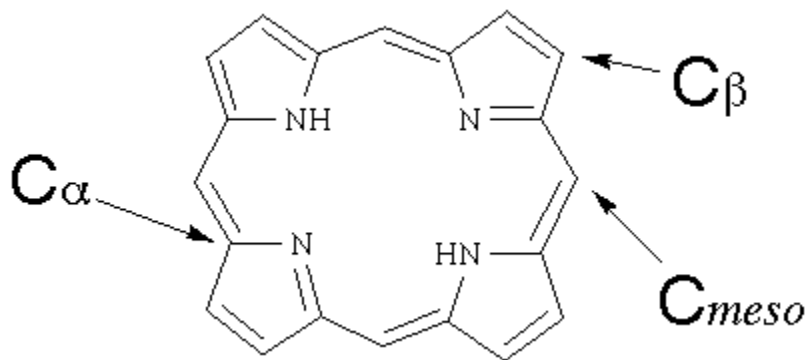


Fig. 4.  $\delta^{13}\text{C}$  of 1,2,4-TriMB plotted against  $\delta^{13}\text{C}$  of 1,2,3,4-TetraMB from hexane/dichloromethane extract of off-line pyrolyzates from ONEZ-1 well in Gabon and Well A in the Kwanza Basin.

Courtesy Elsevier, Inc., <http://www.sciencedirect.com>. Used with permission.

# Porphyrins

Porphyrins are a ubiquitous class of naturally occurring compounds with many important biological representatives including hemes, chlorophylls, and several others. There are additionally a multitude of synthetic porphyrinoid molecules that have been prepared for purposes ranging from basic research to functional applications in society. All of these molecules share in common the porphyrin macrocyclic substructure. The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges as shown in the following illustration:





# Porphyryns

- Metal and S contents of bitumen decreases with maturity
- Virtually all the metal bound in organics is Ni and VO in porphyrin
- Non-marine oils with high terrigenous organic matter contents show high wax, low sulfur and very low metals contents
- Marine carbonates & siliciclastics show low wax, moderate to high-S, high overall nickel and vanadium but a low ( $<1$ ) Ni/V ratio.
- Lacustrine oils show high wax, low-S, moderate Ni and V and high ( $>2$ ) Ni/V ratio
- Sediment redox state determines whether Ni or VO sequestered by porphyrin

# Geoporphyrins

Emmanuelle Grosjean

# Outline

- **Definition, structures**
- **Precursors, diagenesis**
- **Analytical methods**
- **Biological markers : depositional conditions, maturity, correlation parameters**

## References :

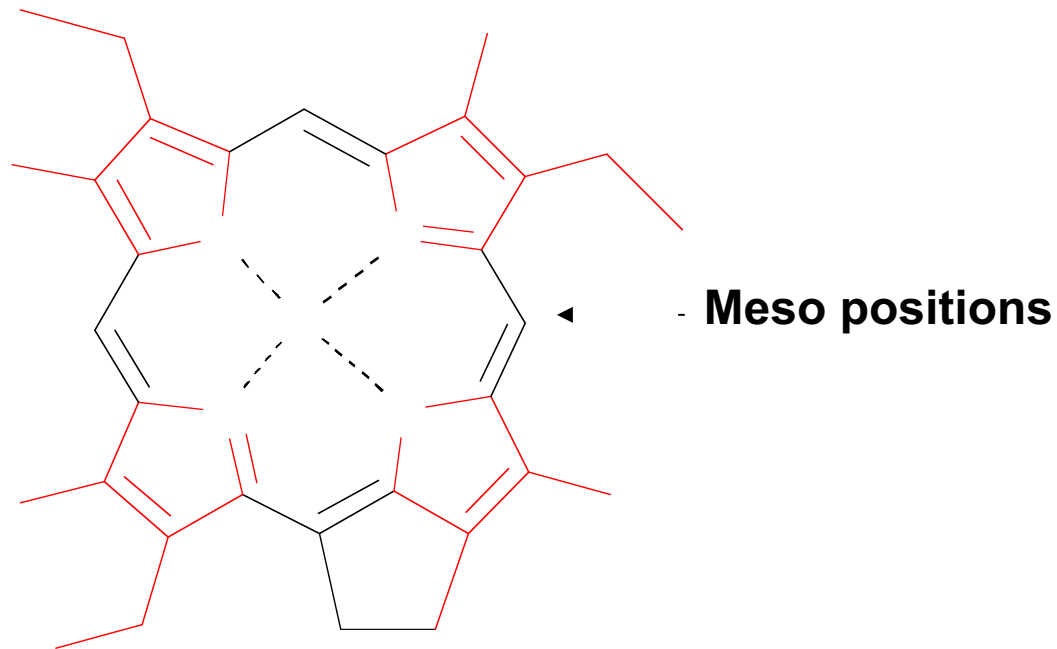
**Callot H.J. and Ocampo R.**

**Geochemistry of porphyrins, The porphyrin Handbook, volume 1, pp 349-398**

**Peters and Moldowan, The Biomarker Guide**

# Structure

- **cyclic tetrapyrrole structure: 4 pyrrole rings (red) joined by 4 methine bridges**

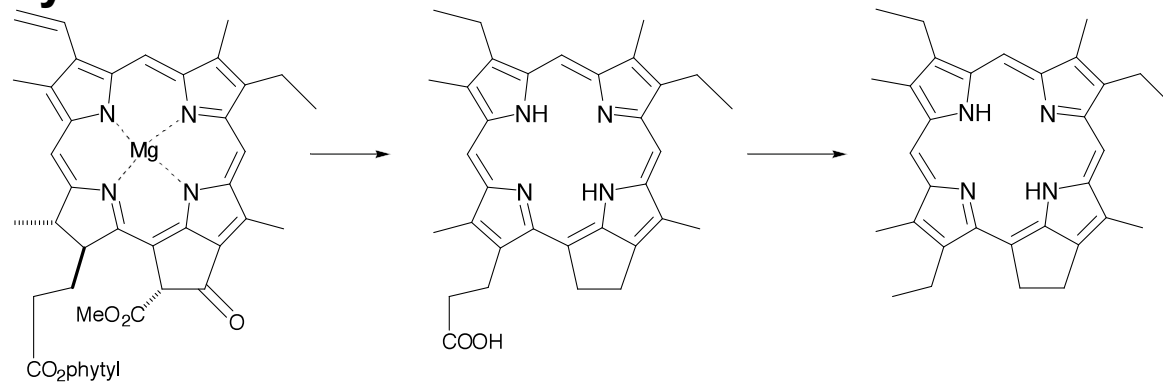


## Deoxophylloerythroetioporphyrin DPEP

- **Cavity allows the insertion of a metallic ion : red pigments**

# Fossil porphyrins

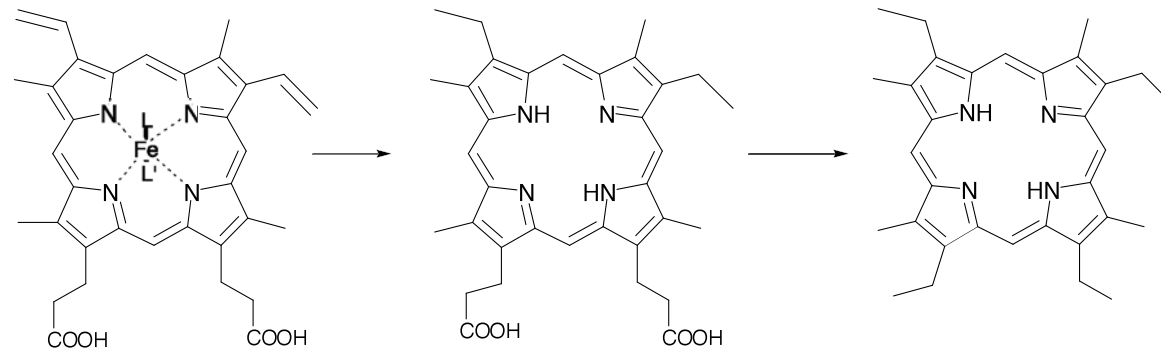
- First structural elucidation by Alfred Treibs in 1934
- First to propose a biological origin : father of the organic geochemistry



**Chlorophyll a**

**Deoxophylloerythrin**

**Deoxophylloerythroetioporphyrin  
DPEP**



**Heme**

**Mesoporphyrin IX**

**Etioporphyrin III**

# Fossil porphyrins

- **Fossil porphyrins : geoporphyrins, petroporphyrins, sedimentary porphyrins**
- **Found in source rocks, oil shales, crude oils, coals,...**
- **Porphyrins separated spontaneously from the organic matter as a crystal (Green River oil shale) : described as a mineral, abelsonite**
- **Most porphyrins are metallated : these metals interfere with the processing of oil, have to be eliminated by hydrometallation.**

# Metals in geoporphyrins

- **Most abundant metalloporphyrins:**
  - **Vanadium(IV) as vanadyl (V=O) complexes**
  - **Nickel(II)**
  
- **Fe, Ga (coal), Cu, Mn less frequent**
  
- **Metals different from the ones found in tetrapyrrolic biomolecules:**
  - **Magnesium in chlorophylls**
  - **Iron in hemes**
  
- **Predominance of nickel and vanadyl porphyrins due to:**
  - **stability of the nickel and vanadyl porphyrin complexes**
  - **availability of nickel and vanadium in the sediments**

**Magnesium complexes unstable towards traces of acids:  $Mg^{2+}$  is lost during the earliest stages of chlorophyll transformation in the water column**

# Metals in geoporphyrins

**Factors influencing the insertion of a metallic ion in the tetrapyrrolic cavity:**

- **availability of the metallic ion : concentration of metal, solubility of the metal compounds, oxidation level**
- **relative rates of insertion of the metal ions**
- **relative stability of the porphyrin complexes: nature of the metal-nitrogen bond, fitting of the metal ion in the cavity**

**Examples:**

▪ **Aluminum abundant in sediments + aluminum porphyrin very stable**

**BUT aluminum ions non available in sediments (sequestered in aluminosilicates)**

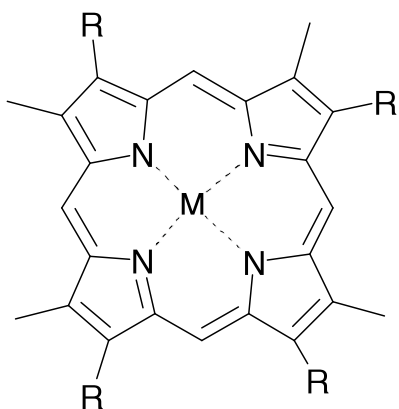
▪ **Platinum porphyrins very stable**

**BUT low concentration of these metals + slow metallation kinetics**



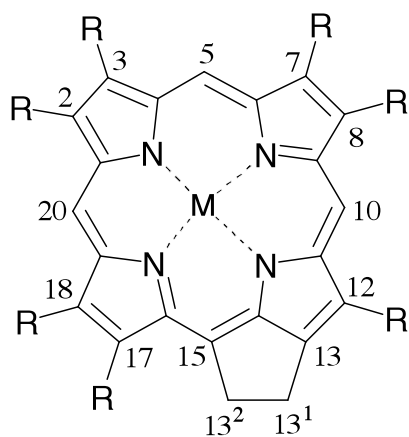
# Series

- **Etioporphyrins or etio: polyalkylporphyrins**
- **“DPEP”** often used to designate all porphyrins containing an additional ring fused to the aromatic nucleus (with “diDPEP” in the case of two rings) but **cycloalkanoporphyrins (CAP)** is now preferred.

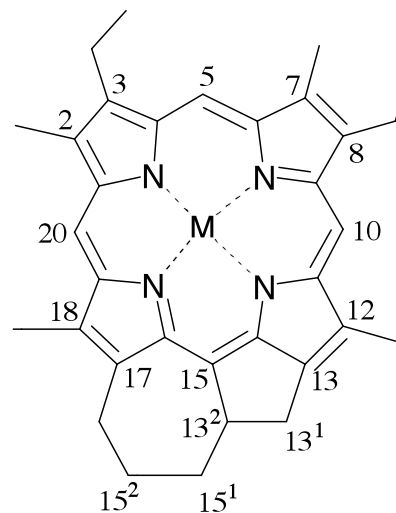


R = H, Me, Et  
M = Ni, V=O

**Etio series**



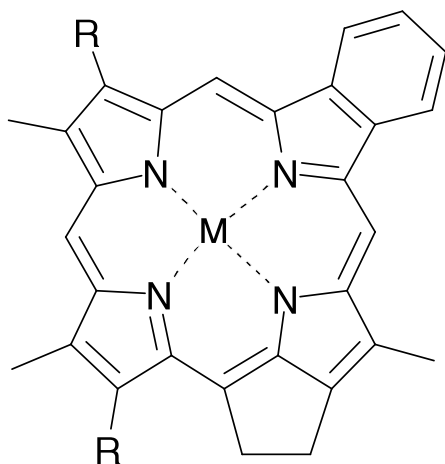
**“DPEP” series**



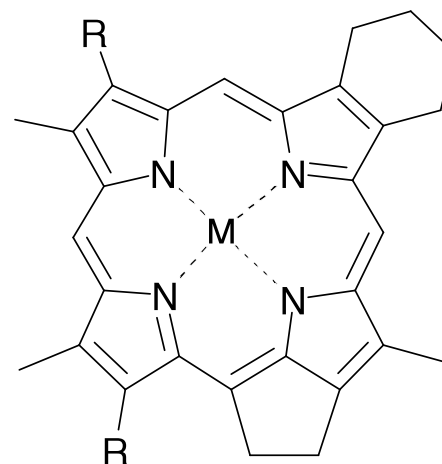
**diDPEP**

## Series

- **Benzoporphyrins (rhodoporphyrins)**
- **Tetrahydrobenzoporphyrins**



**Benzoporphyrin**



**Tetrahydrobenzoporphyrin**

# Biological precursors

➤ **Principal chlorophylls : convert solar energy into chemical energy**

- Chlorophyll *a* : higher plants, algae, cyanobacteria
- Bacteriochlorophyll *a* : photosynthetic bacteria
- Bacteriochlorophyll *c, d, and e* : ***Chlorobium* bacteria**

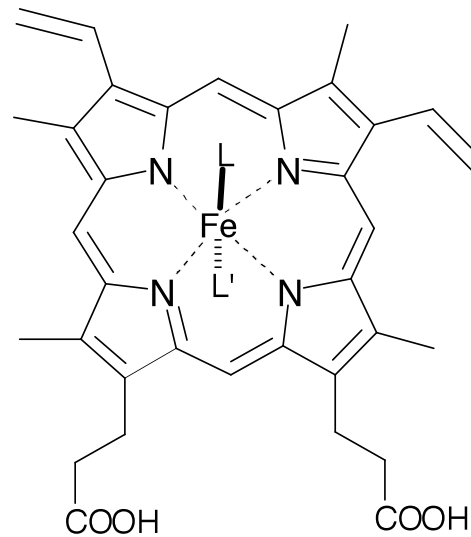
➤ **Secondary co-occurring chlorophylls : broaden the spectrum of light absorbed during photosynthesis**

- Chlorophyll *b* : higher plants, green algae
- Chlorophyll *c* : several algae including diatoms, dinoflagellates, prymnesiophytes
- Bacteriochlorophyll *b* : purple non-sulfur bacteria

# Biological precursors

## ➤ Hemes :

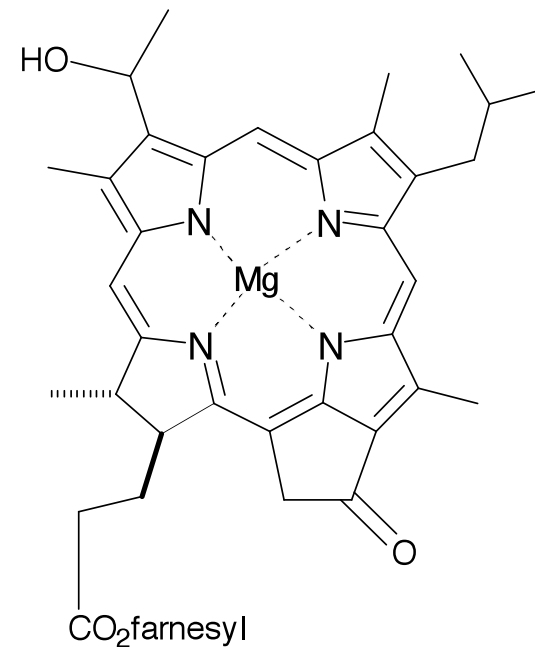
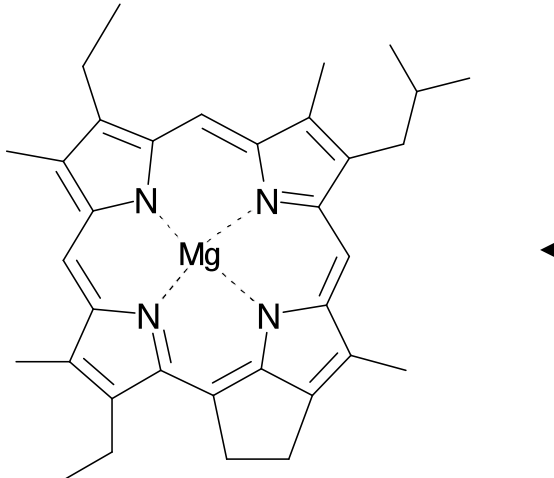
- Much lower contribution in terms of biomass : chlorophyll/heme  
=  $10^5$



# Biological precursors

➤ **unspecific biological precursors : C<sub>32</sub> DPEP can be derived from Chl *a*, Chl *b*, Chl *c*<sub>1</sub> and *c*<sub>2</sub>, BChl *a*, BChl *b***

➤ **specific biological precursors :**



**BChl *d***

➤ **Some geoporphyrins are “orphan” :**

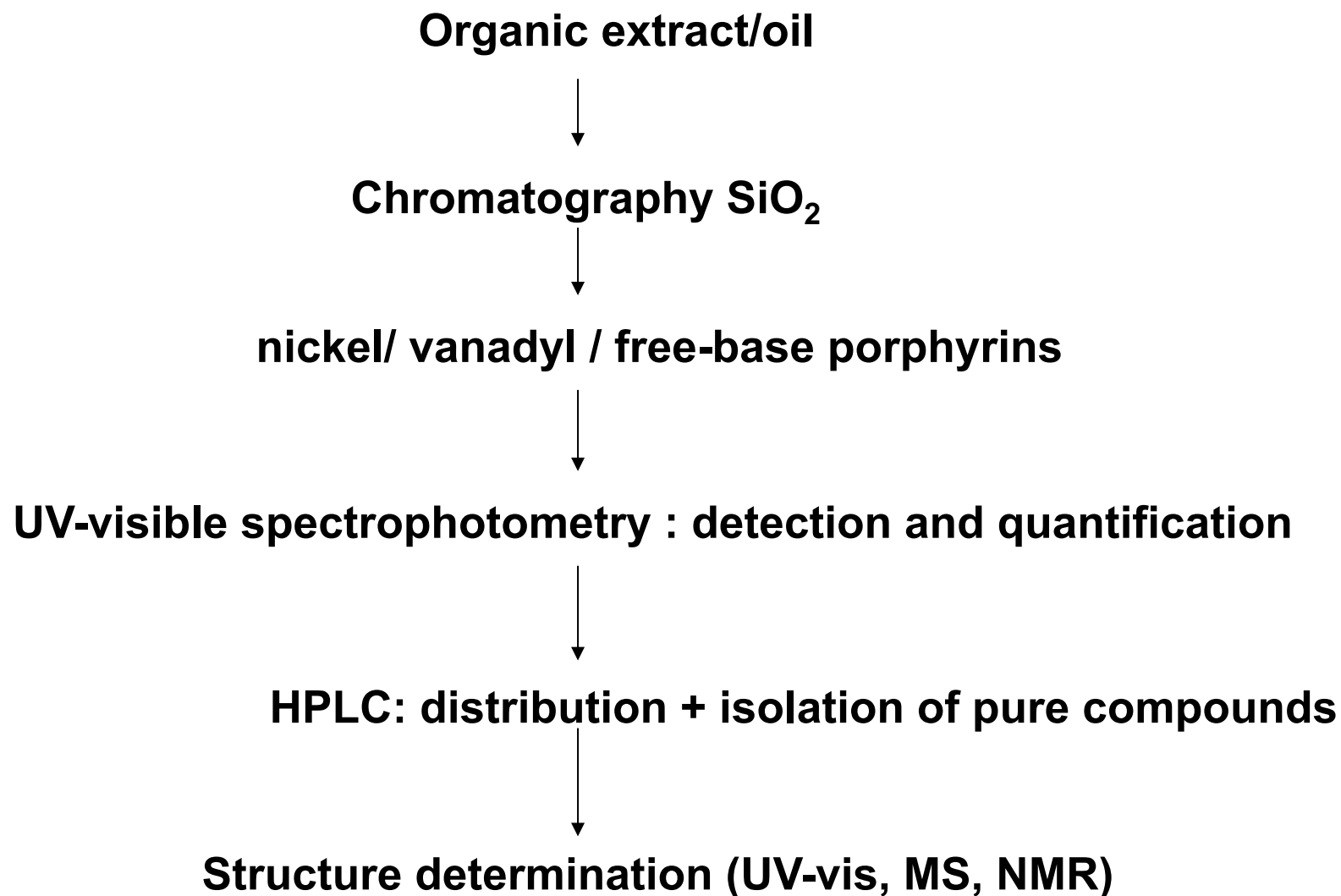
**Tetrahydrobenzoporphyrins and rhodoporphyrins : no precursors known**

# Diagenesis

**Possible transformations for the conversion of chlorophylls:**

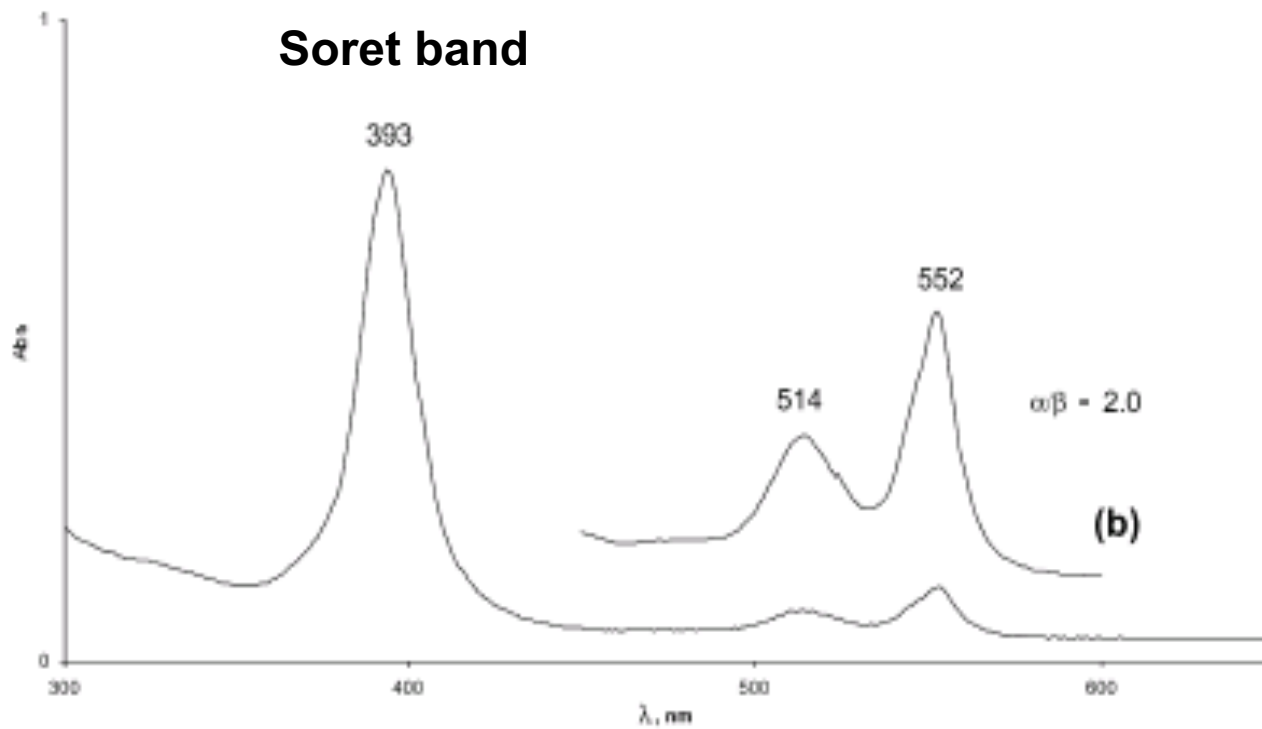
- **Demetallation: free-base porphyrins**
- **Decarboxylation**
- **Loss of the phytyl chain**
- **Reduction of oxygenated functions and olefinic bonds**
- **Aromatization: gives more stable fully aromatic systems**
- **Dealkylation**
- **Metallation by metallic ions**

# **Porphyrin isolation analytical procedure**



# Analytical methods

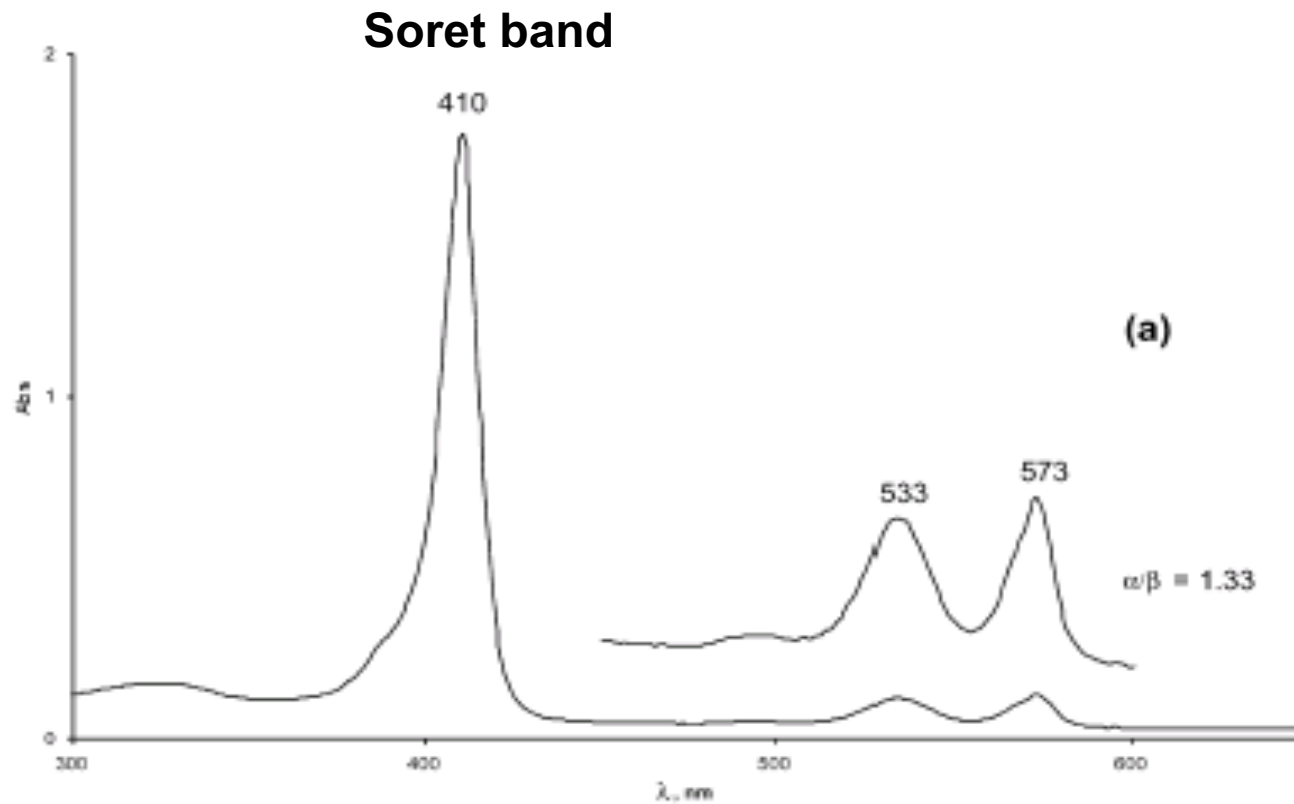
## ➤ UV-visible spectrophotometry: Nickel porphyrins





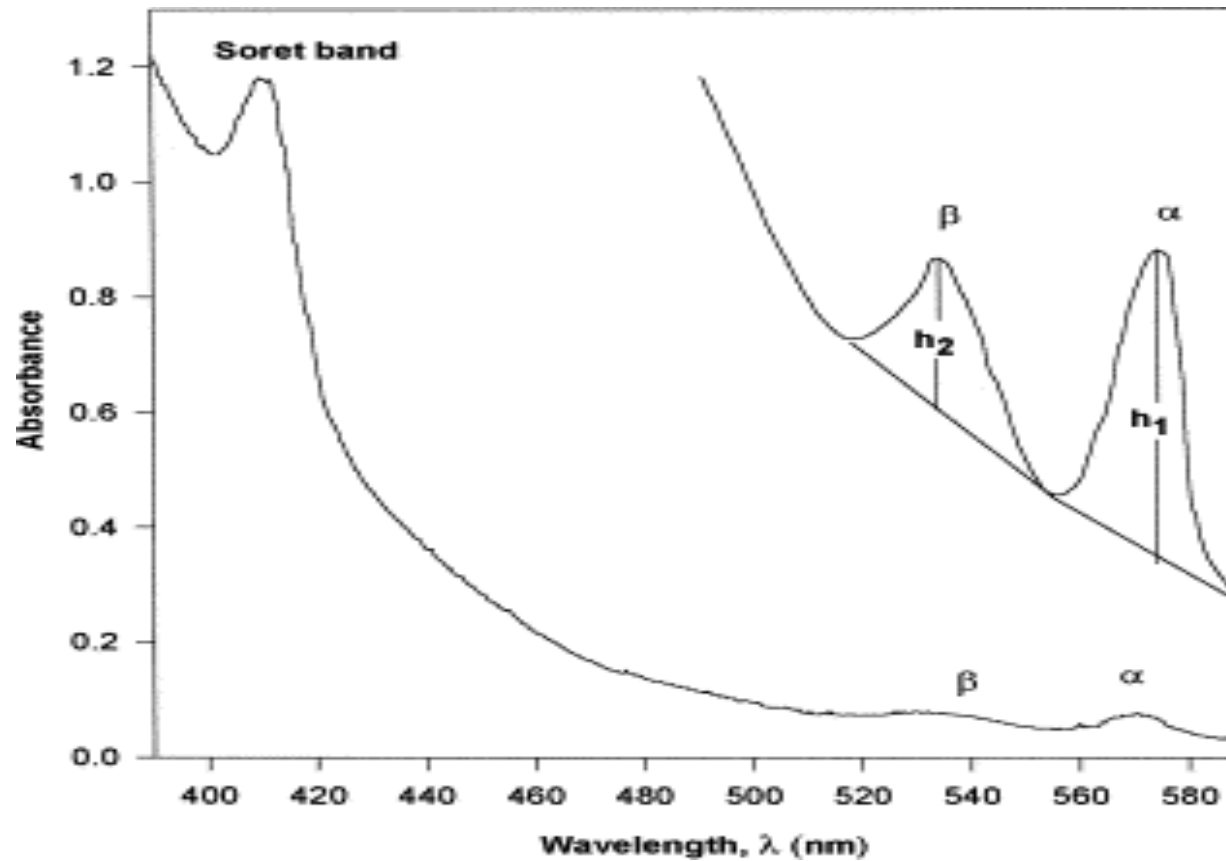
# Analytical methods

## ➤ UV-visible spectrophotometry: Vanadyl porphyrins



# Analytical methods

## ➤ UV-visible spectrophotometry : total fraction



# Analytical methods

- **High Performance Liquid Chromatography (HPLC) linked to a UV-vis detector**
- **Gas chromatography : hampered by low volatility of porphyrins**
  - **Derivatization of porphyrins into silyl complexes (R<sub>3</sub>Si) 2Si(porphyrin)**
  - **Use of high temperature GC columns (> 400 C)**
- **Mass spectrometry :**
  - **GC-MS: limited**
  - **Direct inlet mass spectrometry**
  - **El: big molecular ion, almost no fragmentation**
  - **LC-MS**

# Bound porphyrins

- **Bound to the sediment via ester bonds, released by acid or base hydrolysis (Huseby and Ocampo, 1997)**
- **Sulfur-bound porphyrins released by desulfurization : nickel boride preferred to Raney nickel (destruction of porphyrins or artificial metallation) (Schaeffer and Ocampo, 1993)**
- **Hydrous pyrolysis (Sundararaman, 1993; Huseby et al., 1996)**

# **Geoporphyrins as biological markers for geological studies and oil exploration**

- **Parameters for depositional environment : redox conditions**
- **Thermal maturity parameters**
- **Oil-source rock parameters**

## Indicators of depositional redox conditions

Proportions of nickel and vanadyl porphyrins governed by redox conditions during the early diagenesis (Lewan, 1984):

$\text{VO}^{2+}$  and  $\text{Ni}^{2+}$  compete for chelation with free-base porphyrins

- Regime I: oxic +  $\text{pH} > 7$  : V non available because of its quinquivalent state ( $\text{V}_4\text{O}_{12}^{4-}$ ,  $\text{V}_2\text{O}_7^{4-}$ ,  $\text{VO}_4^{3-}$ ) whereas Ni present as  $\text{Ni}^{2+}$ :  
 $\text{V}/(\text{Ni}+\text{V}) < 0.1$ , Nickel porphyrins predominate

- Regime II: normal oxic conditions: both  $\text{Ni}^{2+}$  and  $\text{VO}^{2+}$  ions available  
Presence of sulfide or hydroxide ions may hinder the availability of Ni or V for bonding  
 $0.1 < \text{V}/(\text{Ni}+\text{V}) < 0.9$

- Regime III: low Eh conditions:  $\text{H}_2\text{S}$  formed by sulfate-reducing bacteria:  
precipitation of nickelous ion as nickel sulfide:  
 $\text{VO}^{2+}$  favoured,  $\text{V}/(\text{Ni}+\text{V}) > 0.5$

## **Indicators of depositional redox conditions**

**V/(V+Ni) porphyrins ratio can be used to assess source rock depositional environment:**

**Low V/(V+Ni) : oxic to suboxic conditions**

**High V/(V+Ni): euxinic sedimentation**

# Maturity parameters

**With increasing thermal maturity, DPEP/etio porphyrins ratio decreases.**

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**DPEP/Etio < 1 in some crude oils and sediments**

**Contradiction with the distribution of the corresponding precursors where chlorophyll/heme =  $10^5$**



## Maturity parameters

- **DPEP/Etio porphyrin ratio decrease with maturity due to :**
  - **Thermal cleavage of ring E**
  - **Release of etio porphyrins from kerogen during catagenesis : dilution of DPEP**
  
- **Maturity parameters used in oil exploration (determined by HPLC or LC-MS) :**
  - **DPEP/Etio or DPEP/(DPEP+Etio): involves many compounds**
  - **Porphyrin Maturity Parameter ((Sundararaman et al., 1988)**

$$\text{PMP} = \text{C}_{28} \text{ etio} / (\text{C}_{28} \text{ etio} + \text{C}_{32} \text{ DPEP})$$

# Oil-source rock correlation parameters

- **Geoporphyrins distributions give complementary data to those given by classical biomarkers (steranes, hopanes)**

Ocampo *et al.*, 1993 :

**Steranes and hopanes distributions of Ponte Dirillo and Gela oils are very similar to the potential source rock (Piano Lupo).**

**But based on porphyrin distributions, Piano Lupo source rock for Ponte Dirillo oil but not for Gela oil**

- **Geoporphyrins resistant to biodegradation : can therefore be used as correlation parameters in case of biodegraded oils**

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# Weathering

➤ **Geoporphyrins sensitive to weathering**

**Grosjean *et al.*, 2003 (in press):**

**Study of an outcrop core (Paris basin, Lower Toarcian)**

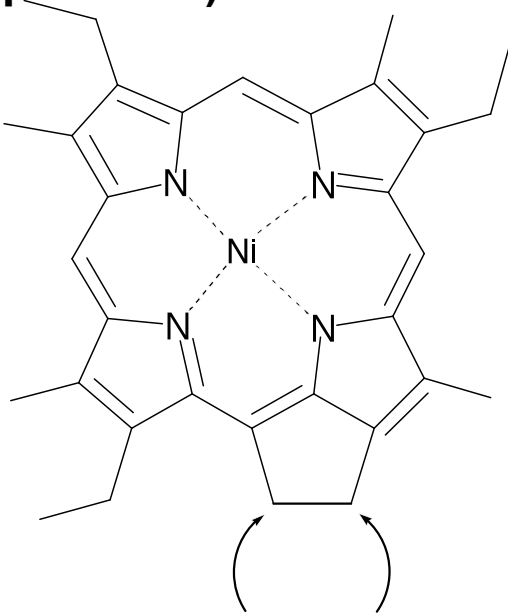
**Concentrations of Ni and VO porphyrins undergo a depletion of 99% and 90 % at the surface**

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**DPEP porphyrins more sensitive than etio porphyrins**

## **Weathering**

**Degradation mechanism proposed :  
Abiotic oxidation  
(confirmed by an oxidation experiment)**



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# **Maleimides: palaeoenvironmental conditions**

**Grice *et al.*, 1996**

**BChl *c*, *d* and *e* highly specific for *Chlorobiaceae* but corresponding fossil porphyrins uneasy to analyse (use of LC-MS required)**

**These bacteriochlorophylls may undergo oxidative degradation to maleimides.**

**Maleimides derived from BChl *c*, *d* and *e* have specific alkyl substituents**

# Maleimides: palaeoenvironmental conditions

Methyl isobutyl maleimide diagnostic of *Chlorobiaceae*

**GC-IRMS:**

$\delta^{13}\text{C}$  MeiBuMaleimide enriched by 10-11‰ relative to MeEt maleimide  
(typical for the reverse TCA cycle used by Chlorobiaceae)

MeiBumaleimide indicative of euxinic conditions

# Porphyrins

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**Porphyrin numbering**

**Phytoporphyrin  
(from chlorophyll d series)**

<http://www.chem.qmul.ac.uk/iupac/tetrapyrrole/TP2.html#p21>

# Porphyrins

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## Figure 2

Chemical structure of chlorophyll a and its derivatives in sediments: the chlorophyll found in plants (1) and vanadyl DPEP porphyrin (2) found in oils possess the same tetrapyrrolic nucleus. This observation led Treibs (1934) to infer that petroleum was of biological origin. The alteration of chlorophyll in sediments by rupture of the phytol side chain and saturation of its fragments, also leads to the formation of isoprenoid hydrocarbons (3). After Bordenave *et al.* (1993). *With permission of Éditions Technip.*

***Oil & Gas Science and Technology – Rev. IFP, 58 (2003) pp. 203-231***  
**Copyright © 2003, Éditions Technip A History of Organic Geochemistry B. Durand**



# Chlorophyll Precursors

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<http://www.chem.qmul.ac.uk/iupac/tetrapyrrole/app1.html>

# More Chlorophyll Precursors

Eight bacteriochlorophyll (BChl)-d homologs and epimers were isolated from a strain of the green sulfur bacterium *Chlorobium vibrioforme*. By a combination of mass spectrometry and <sup>1</sup>H-NMR spectroscopy using the chemical shifts of meso- and 3(1)-protons and <sup>1</sup>H-<sup>1</sup>H NOE correlations, the molecular structures were determined as (3(1)R)-8-ethyl-12-methyl, (3'R)-8-ethyl-12-ethyl, (3(1)R)-8-propyl-12-methyl, (3(1)S)-8-propyl-12-methyl, (3(1)R)-8-propyl-12-ethyl, (3(1)S)-8-propyl-12-ethyl, (3(1)S)-8-isobutyl-12-methyl and (3(1)S)-8-isobutyl-12-ethyl.

**Photochem Photobiol Sci. 2002 Oct;1(10):780-7**

**Isolation and structure determination of a complete set of bacteriochlorophyll-d homologs and epimers from a green sulfur bacterium *Chlorobium vibrioforme* and their aggregation properties in hydrophobic solvents.**

**[Mizoguchi T](#), [Saga Y](#), [Tamiaki H](#).**

# Other chlorophyll Precursors

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<http://www.chem.qmul.ac.uk/iupac/tetrapyrrole/app1.html>

# Parent skeletons

11 unsaturations

10 unsaturations

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10 unsaturations

9 unsaturations

<http://www.chem.qmul.ac.uk/iupac/tetrapyrrole/app1.html>

# Porphyryns

Abelsonite, a crystalline nickel porphyrin with the probable composition  $C_3H_{32}N.Ni$ , has been found in eight drill cores in or near the Mahogany Zone oil shale of the Green River Formation in Uintah County, Utah. Associated authigenic minerals include orthoclase, pyrite, quartz, dolomite, analcime, and a K-Fe micaceous mineral. Abelsonite occurs as aggregates of platy crystals, as much as 3 mm long, that range in color from pink-purple to dark reddish-brown. The crystals are very soft («3 on Mohs scale) and have a semi metallic to adamantine luster. Probable cleavage is (111). In transmitted light the color is red or reddishbrown, with intense absorption to reddish-brown. Its reaction with high-index liquids and its strong absorption prevented determination of optical characteristics. Abelsonite is triclinic, space-group aspect  $P^*$ , with cell dimensions (Weissenberg),  $a = 8.44$ ,  $b = 11.12$ ,  $C = 7.28A$ ,  $a = 90^\circ 53'$ ,  $\beta = 113^\circ 45'$ ,  $\gamma = 79^\circ 34'$ ; volume  $613.8A^3$ , calculated density (for  $Z = 1$ ) = 1.45 g/cm<sup>3</sup>. The five strongest lines of the X-ray powder pattern ( $d$  value in A, relative intensity, indices) are 10.9 (100) 010, 3.77 (80) 111, 7.63 (50) 100, 5.79 (40) 110, 3.14 (40) 012. Ultraviolet, visible, and infrared spectra indicate that abelsonite is a deoxophylloerythroetioporphyrin, presumably a chlorophyll derivative. The mineral is named in honor of Philip H. Abelson, President, Carnegie Institution of Washington.

# Porphyrins

*Preliminary separations:* In contrast to other biomarkers discussed, porphyrins are polar compounds and difficult to analyse by GCMS

The presence of porphyrins in bitumen is often evident from the presence of coloured bands in LC separations of SAP fractions.

Aromatic (Ni-P) and Polar (VO-P) fractions can be re-chromatographed as follows:

Nickel porphyrins elute from silica gel with cyclohexane-chloroform (2:1v/v).

Vanadyl porphyrins elute from silica gel with benzene-acetone.

These fractions can then be analysed by LCMS

# Porphyrins

ANALYTICAL SCIENCES 2001, VOL.17 SUPPLEMENT i1511

2001 © The Japan Society for Analytical Chemistry

**Practical Approach to Chemical Speciation of Petroporphyrins**

**Koichi SAITOH†, Hideaki TANJI, and Yazhi ZHENG**

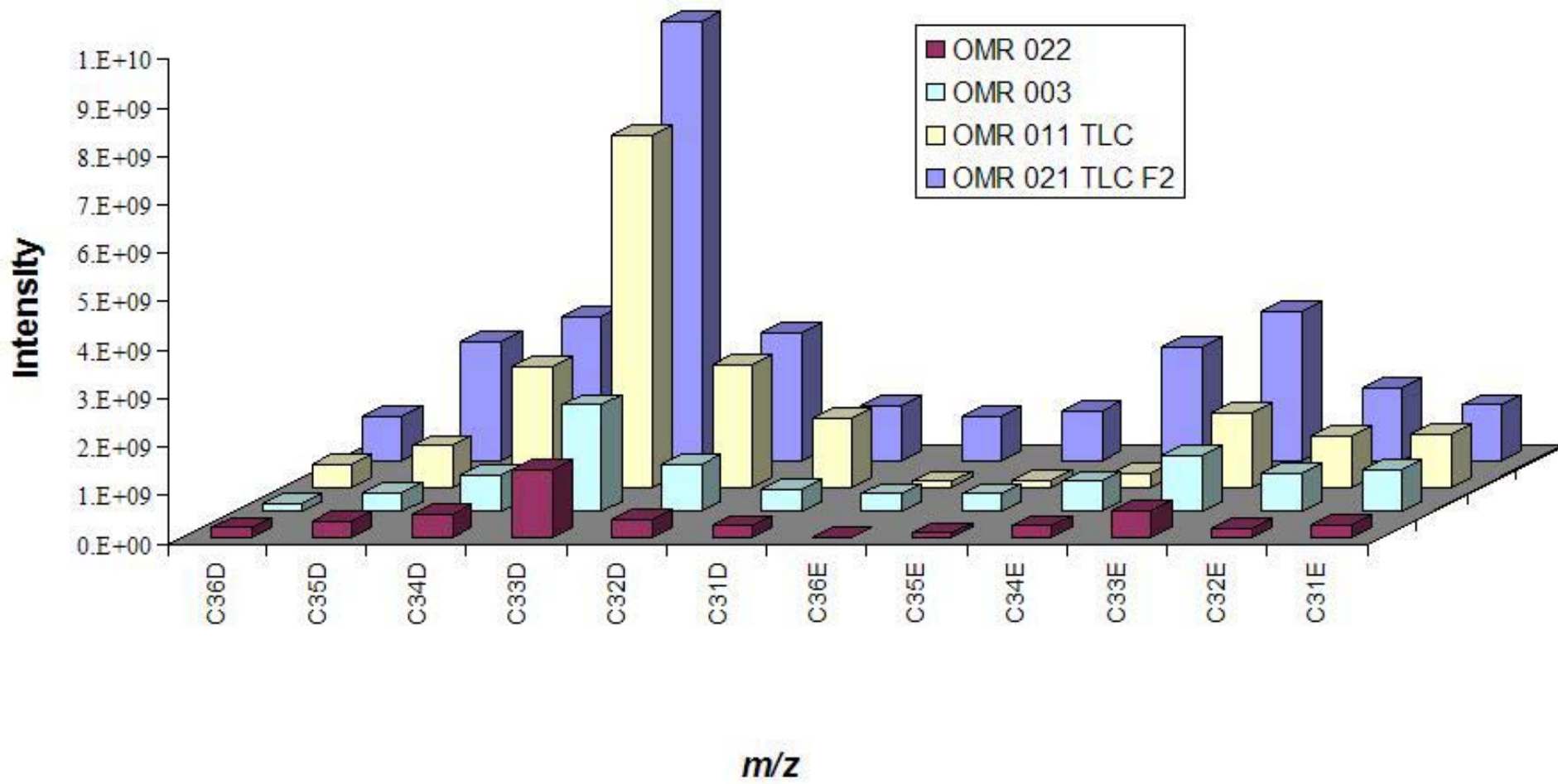
desoxophylloerythroaetioporphyrin  
(DPEP)

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copyright restrictions.

Etio-type: Ni-Etio(n) = 366 + 14 n  
DPEP-type: Ni-DPEP(n) = 392 + 14 n

Etio-type: VO-Etio(n) = 375 + 14 n  
DPEP-type: VO-DPEP(n) = 401 + 14 n

# Thuleilat Comparison





**GeochimCosmochim Acta.**

1994 58(17):3691-701.

## **Porphyrin and chlorin distributions in a Late Pliocene lacustrine sediment.**

**[Keely BJ](#), [Harris PG](#), [Popp BN](#), [Hayes JM](#), [Meischner D](#), [Maxwell JR](#).**

**The tetrapyrroles in a highly immature Late Pliocene lacustrine sediment (Willershausen, Germany) show a simple distribution of both chlorin and porphyrin components as the free bases. The major components are C32 desoxophylloerythroetioporphyrin (DPEP), a C33 bicycloalkano porphyrin, the chlorin analogue of the latter, and desoxophylloerythrin and its chlorin counterpart. The structure of the novel bicycloalkano chlorin was determined using a combination of two-dimensional phase-sensitive COSY NMR and nOe studies. Measurements of delta 13C and other data indicate that DPEP and the bicycloalkano porphyrin were derived from the chlorophyll(s) of photosynthetic organisms utilising a common source of CO<sub>2</sub>, probably diatoms. The occurrence of DPEP and other minor alkyl porphyrins indicates that the chlorophyll defunctionalisation pathway leading to these components can occur at low temperature and was probably biologically mediated, as was the condensation leading to the fused ring components.**

## Maleimides

Grice 2001 via Peters et al, The Biomarker Guide 2005, p606

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# Maleimides

Grice et al GCA, 60, 3913, 1996

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12.158 Molecular Biogeochemistry  
Fall 2011

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