

tracking the rise of eukaryotes— lipid biomarker records

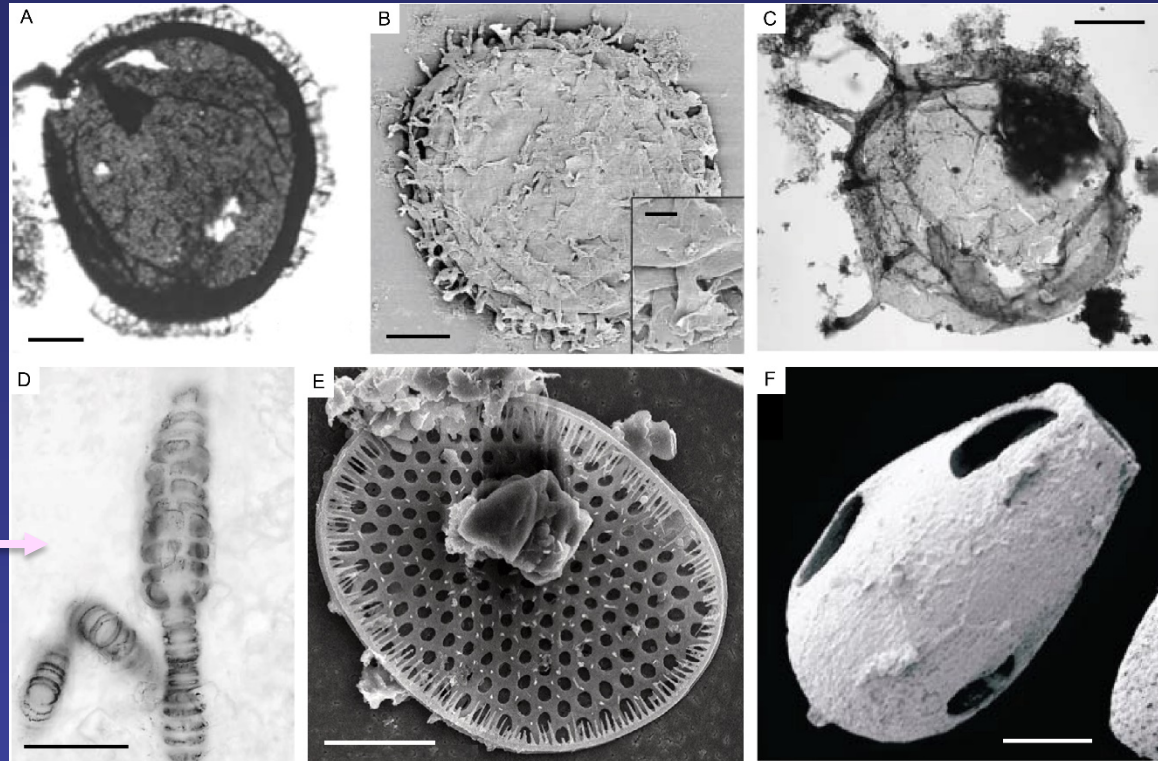
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1) When did eukaryotes become abundant and widespread in Proterozoic oceans?

Proterozoic
eukaryotic
microfossils
(1500-740 Ma)



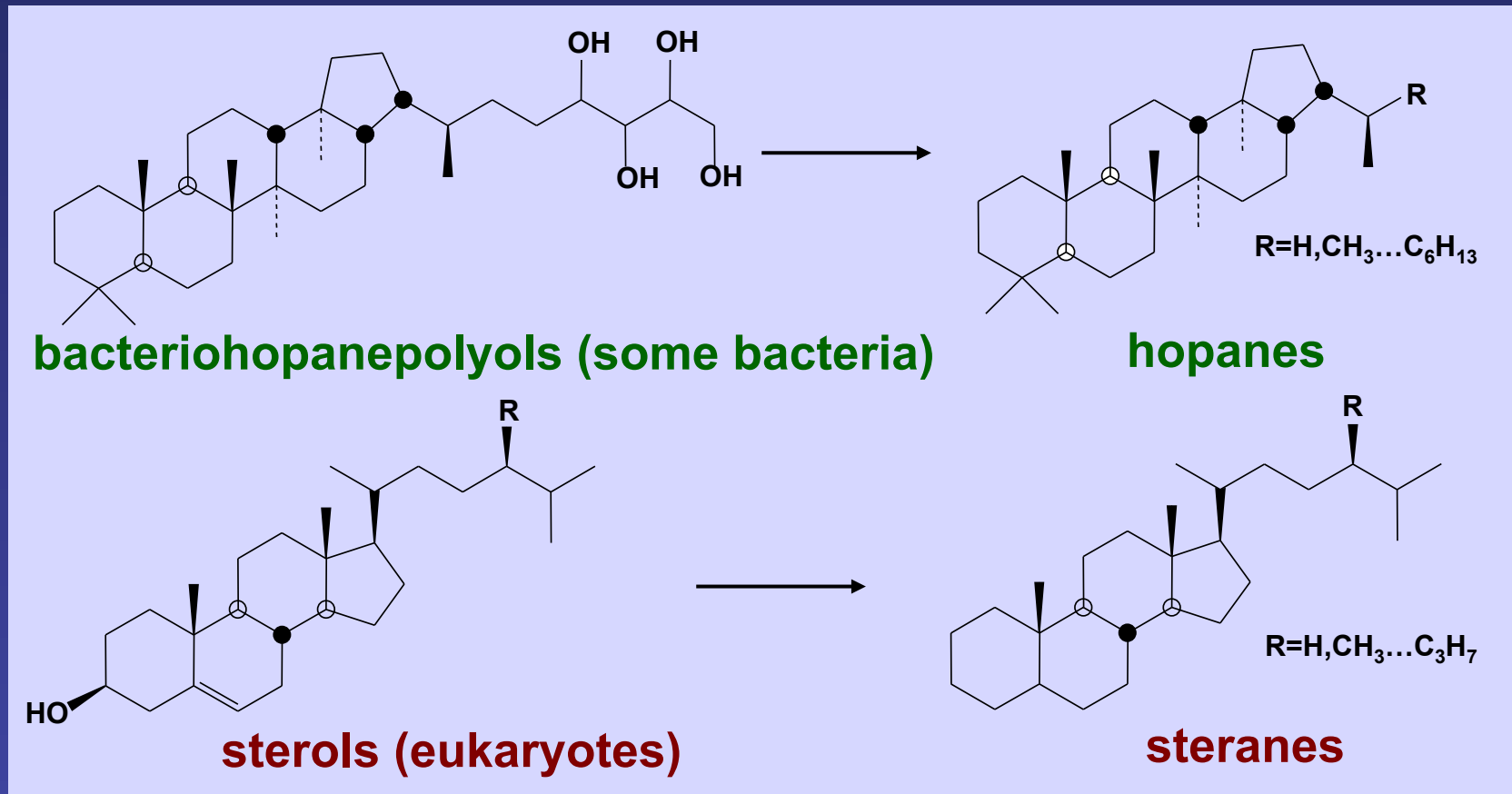
D. First evidence for
multicellular algae
& crown group
(1200 Ma Hunting Group)

Scale bars: A,B,D = 50 μm , E = 10 μm , C,F = 25 μm

Not just first appearance but when do these become abundant?

Biomarker hydrocarbons are stable over geologic timescales

precursor lipid \longrightarrow fossil hydrocarbon



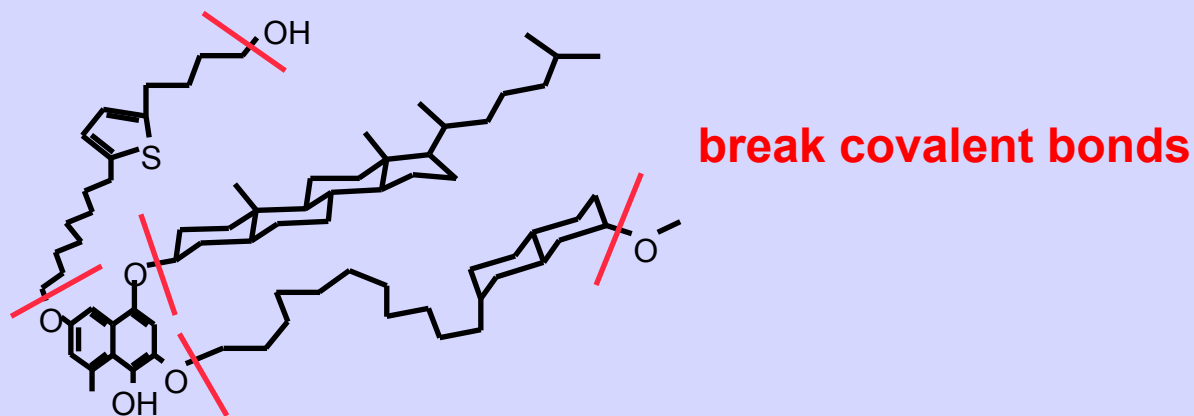
biolipids can covalently bind into geomacromolecules via functional groups

Assessing free biomarkers in ancient rocks

Discerning real signals from contaminants

- Lab procedural blanks with combusted sand
- Consistent with geological context (age, lithology) and with thermal maturity of the host sediment?
 - systematic changes in biomarker maturity ratios with depth?
- Comparison of inner vs outer core portions
 - look for suspicious concentration/compositional gradients
- Analysis of kerogen-bound biomarkers (insoluble om)
 - reliable check as common contaminants are mobile & soluble

Efficient pyrolytic release of bound biomarkers



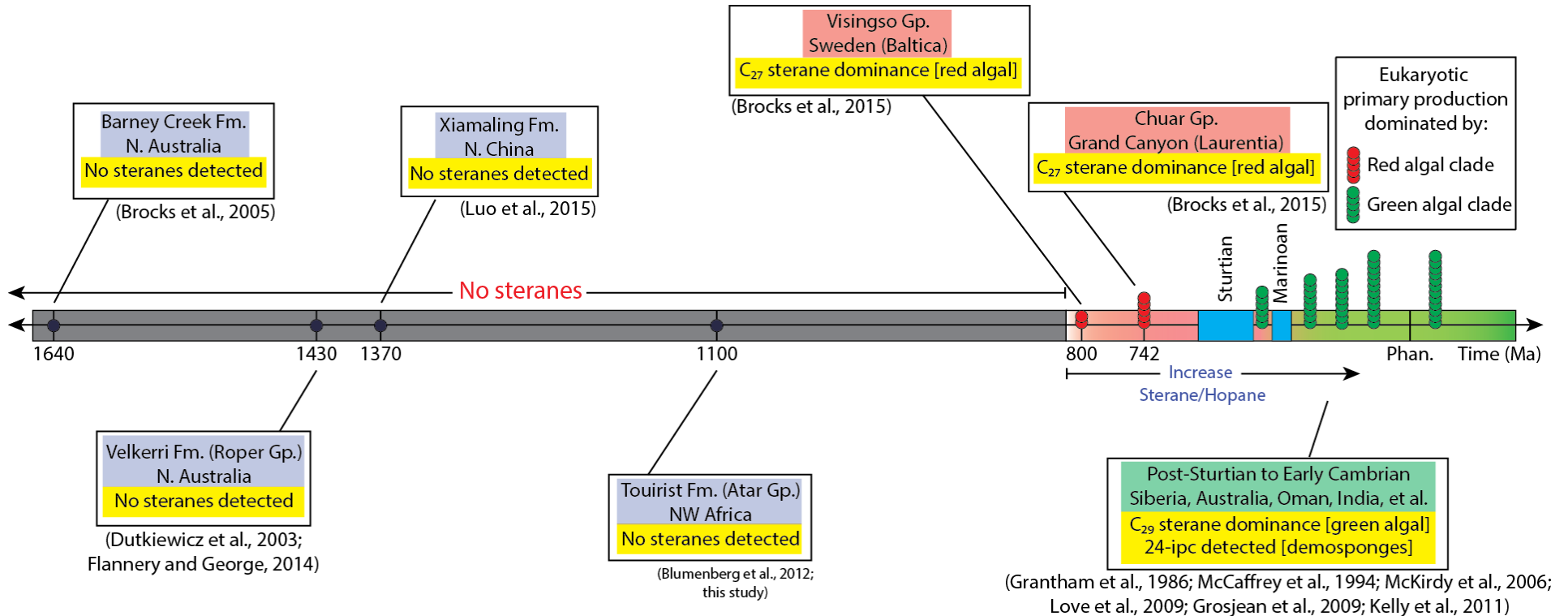
geomacromolecule

need [H] supply

GC-analysable hydrocarbons

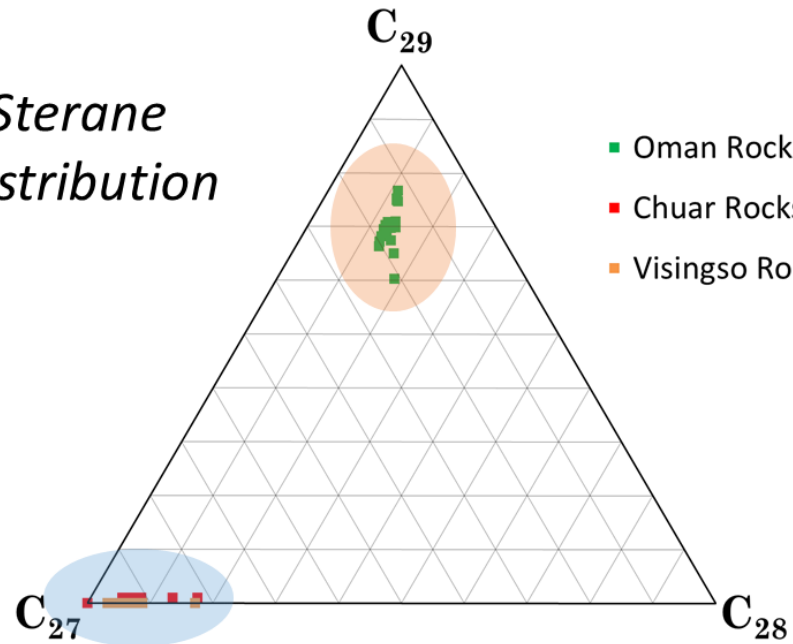
Use high H₂ pressure pyrolysis: HyPy (Love et al., 1995)

Proterozoic Sterane Biomarker Record

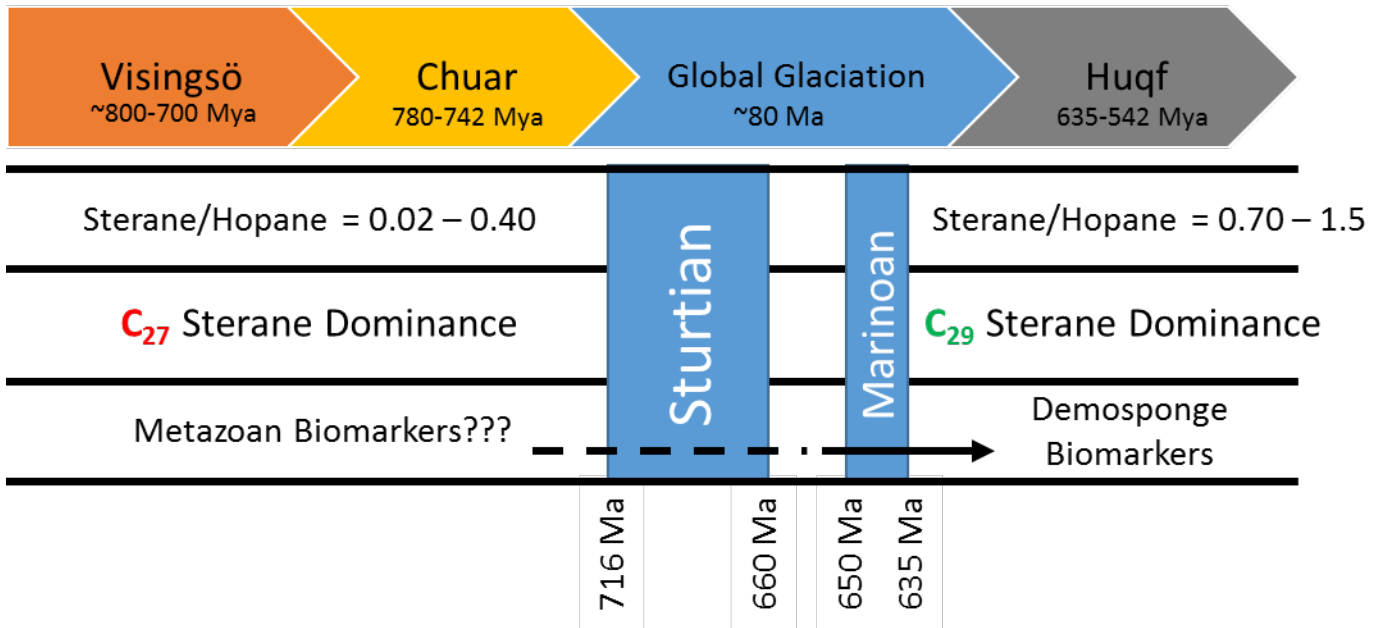


No robust reports of detectable steranes till Neoproterozoic

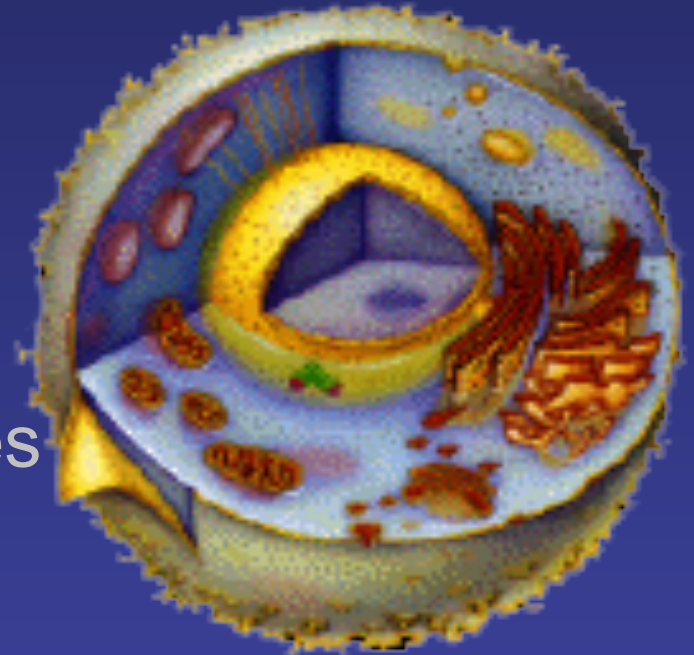
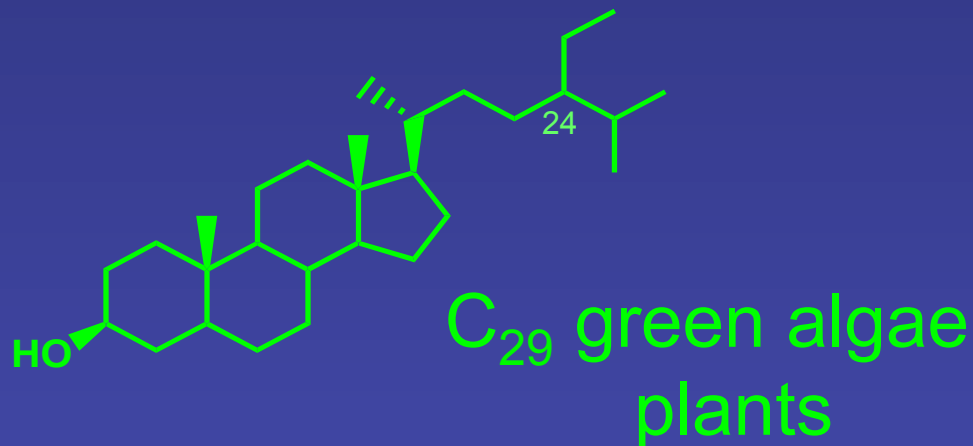
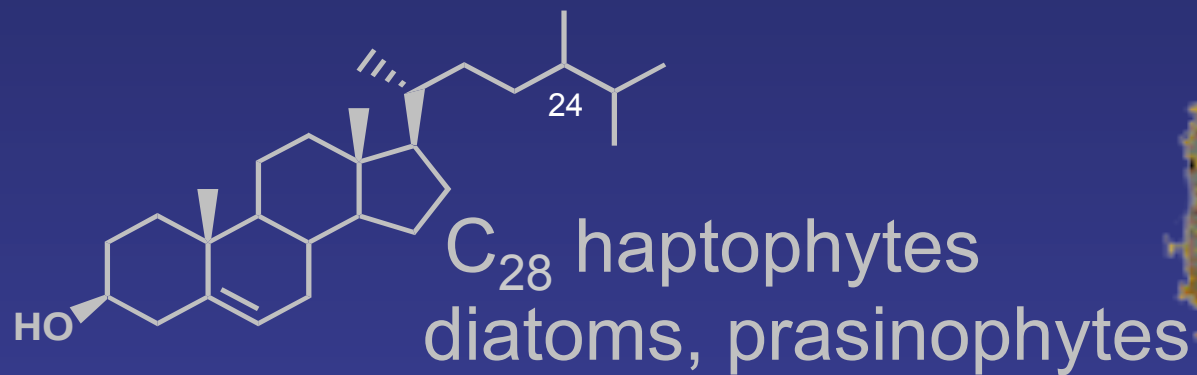
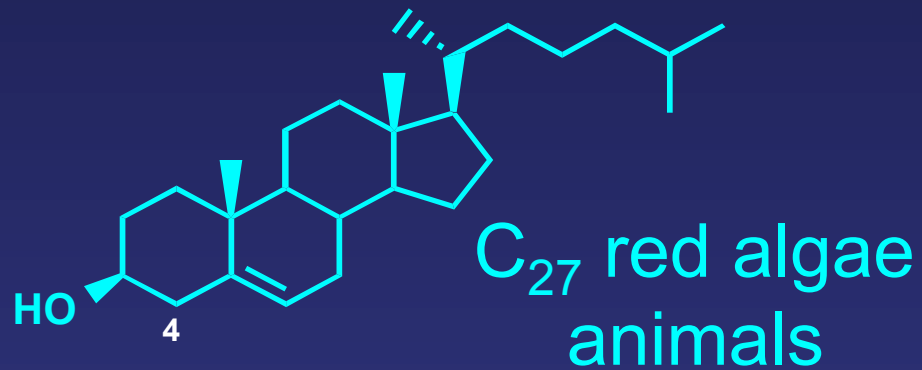
Sterane Distribution



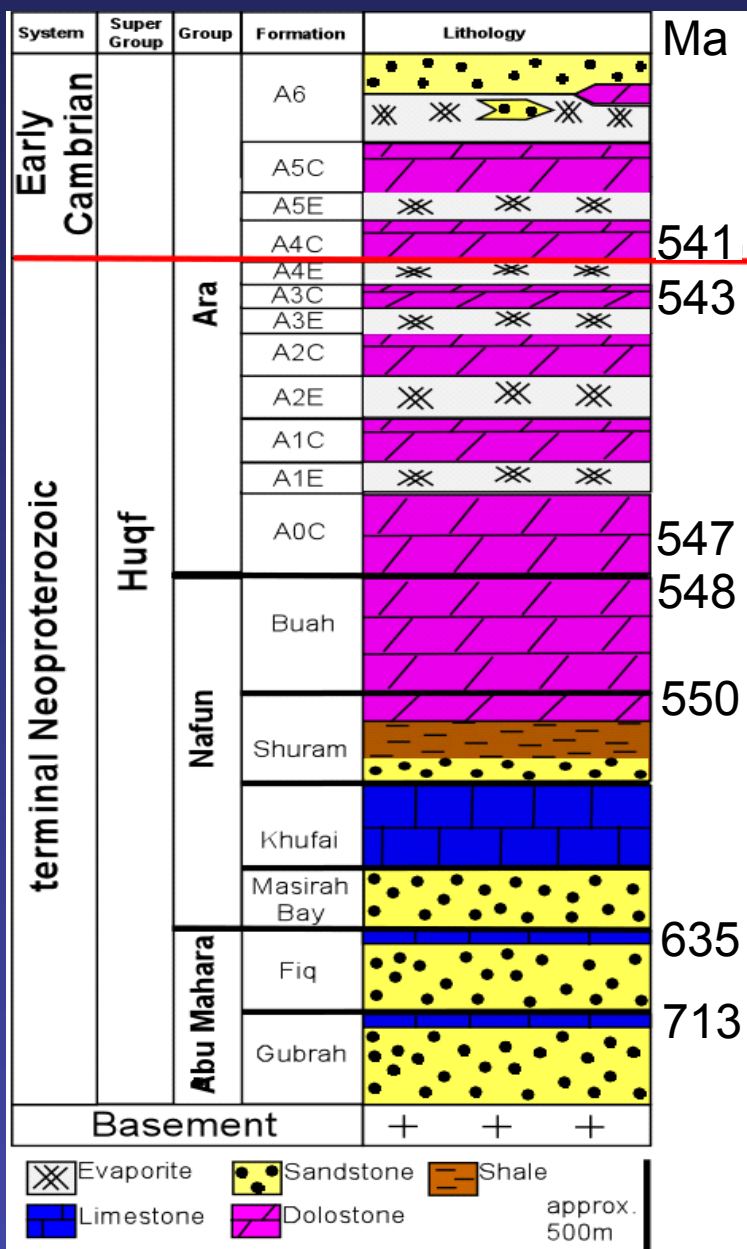
- Oman Rocks
- Chuar Rocks
- Visingsö Rocks



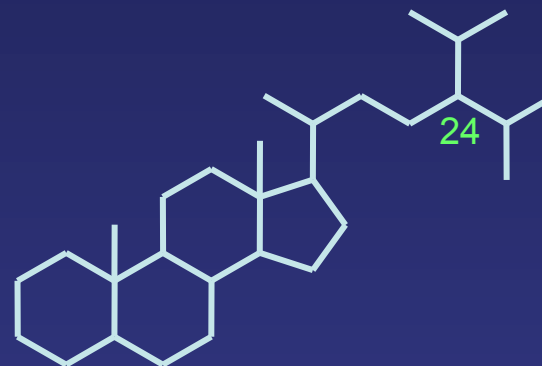
Eukaryote sterols -> steranes



South Oman Salt Basin



Demosponge sterane record



abundant 24-isopropylcholestane- (C₃₀)
(Av. 1.7% of C₂₇-C₃₀ steranes)

Continuous record of Porifera
(from >635 Ma to <542 Ma)

sample coverage

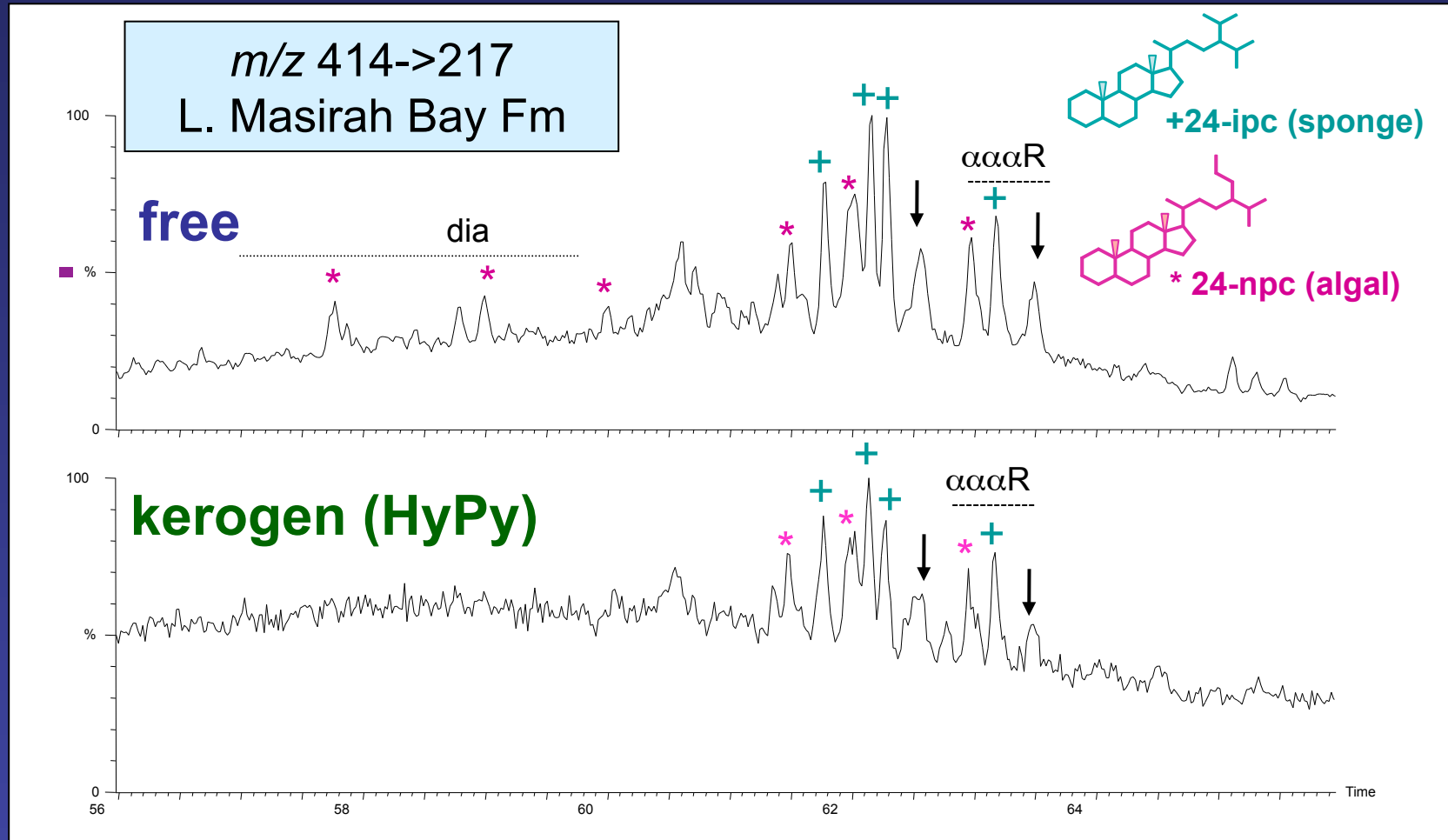
← Marinoan glaciation (635 Ma)

← Sturtian glaciation (713 Ma)

(Love et al., Nature, 2009)

64 rocks with HI = 250-700 mg/g TOC

C₃₀ sterane patterns from MRM-GC-MS free versus kerogen bound (HyPy)

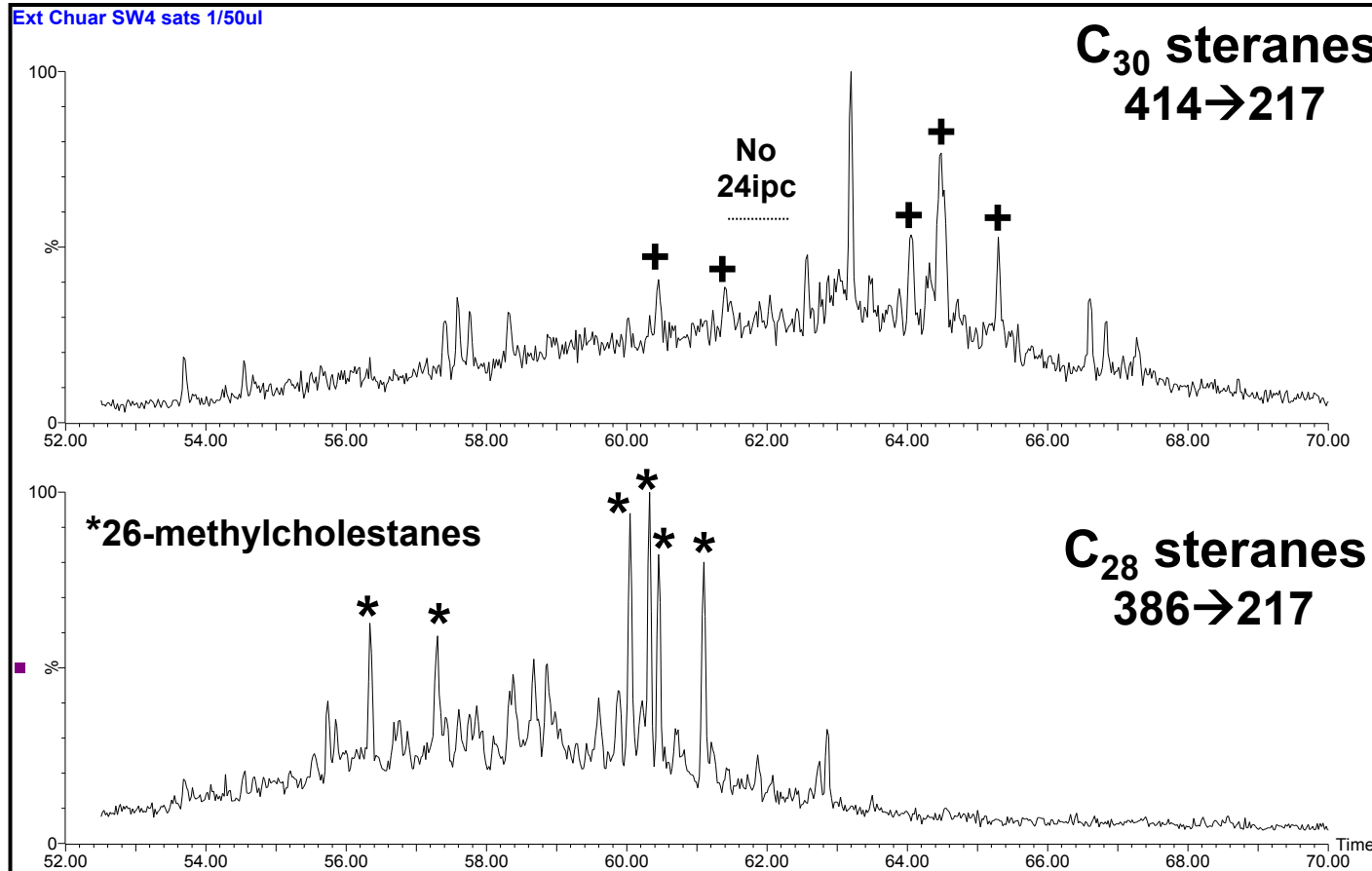


Bound sponge markers in kerogens from >635 Ma to <542 Ma

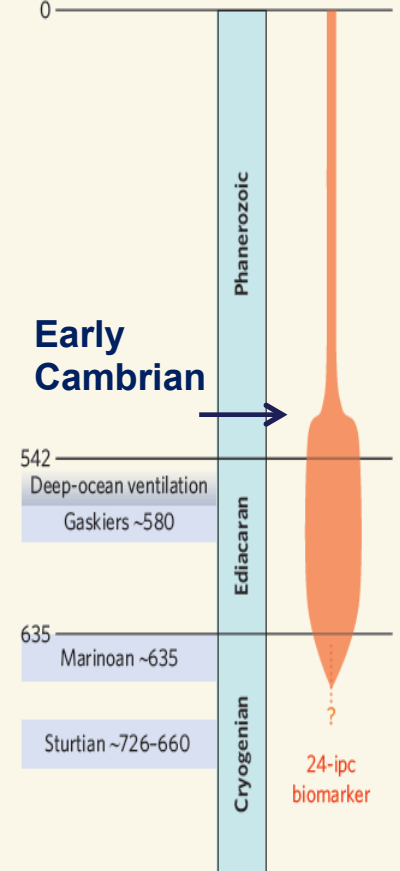
Pre-Sturtian 24-ipc biomarkers? Absent...

Chuar Group, Grand Canyon (740-770 Ma)

Ext Chuar SW4 sats 1/50ul



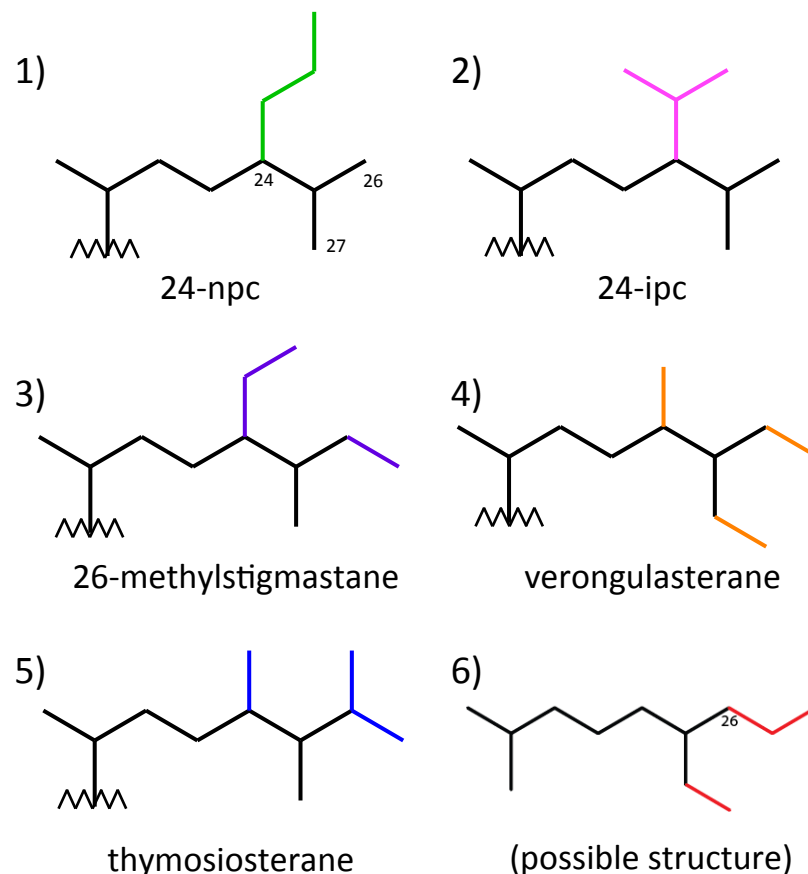
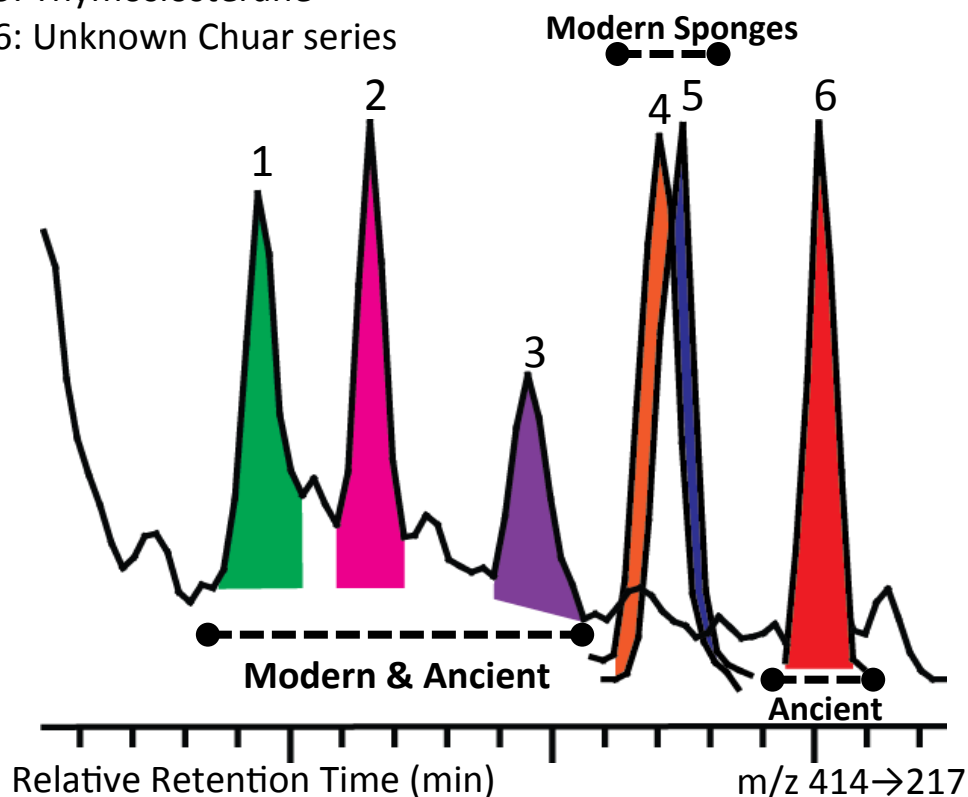
Brocks & Butterfield, 2009



Unusual C₂₈ and C₃₀ series but no 24ipc or npc (A. Zumberge)
*26-methylcholestane (“cryostane”) also reported by Brocks et al., (2015)

C_{30} Steranes [$\alpha\alpha\alpha R$] (MRM-GCMS)

- 1: 24-n-propylcholestane (24-npc)
- 2: 24-isopropylcholestane (24-ipc)
- 3: 26-methylstigmastane (???)
- 4: Verongulasterane
- 5: Thymosiosterane
- 6: Unknown Chuar series



**can resolve at least six different C_{30} steranes by MRM-GCMS;
4 found in the rock record (Alex Zumberge PhD work)**

Conclusions

- Long stem of Mesoproterozoic eukaryotes... but lack of sterane signal indicates these did not become ecologically widespread, diverse and abundant till Neoproterozoic
 - kerogen-bound sterane record from 700-800 Ma rocks
 - prokaryotes dominated oceans for >80% of Earth history
- Unusual C₂₈ & C₃₀ steranes detected in pre-Sturtian rocks from Chuar and Visingsö Gps (700-800 Ma)
 - free and kerogen-bound with terminal methylation (e.g. 26-methylcholestanes); unusual biochemistry
 - source from unicellular protist, stem metazoan, or sponge?
 - No pre-Sturtian (pre-716 Ma) finding of **24-ipc sterane**, the established demosponge biomarker (Love et al., 2009)