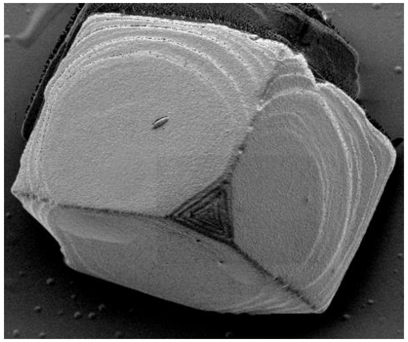
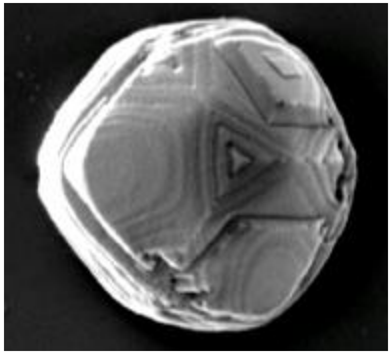
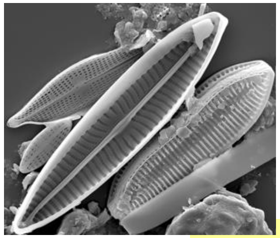
Marine biocalcification:

Origin & evolution



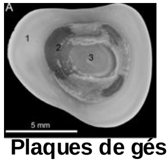




Silica

Phosphates

Halides



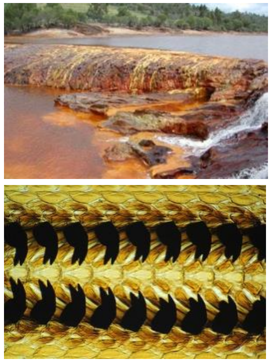
Plaques de gésiers
Gastéropodes
carnivores

Carbonates

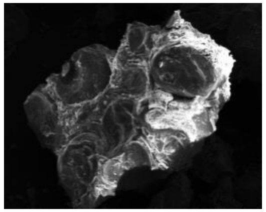
Organics

BIOMINERALS

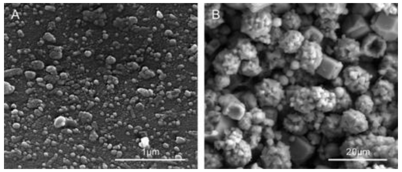
Fe oxydes



Mn oxides

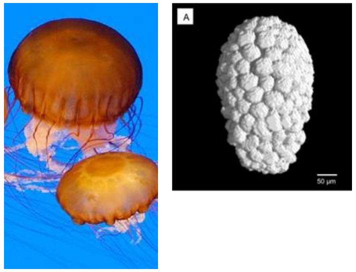


Sulfides



Oxalates

Sulphates



Biomineralization in $CaCO_3$ & carbonate cycle in the sea

Remark: surface sea water: highly supersaturated with respect to calcium carbonate

However, places where spontaneous calcium carbonate precipitation occurs are rare (Bahamas)

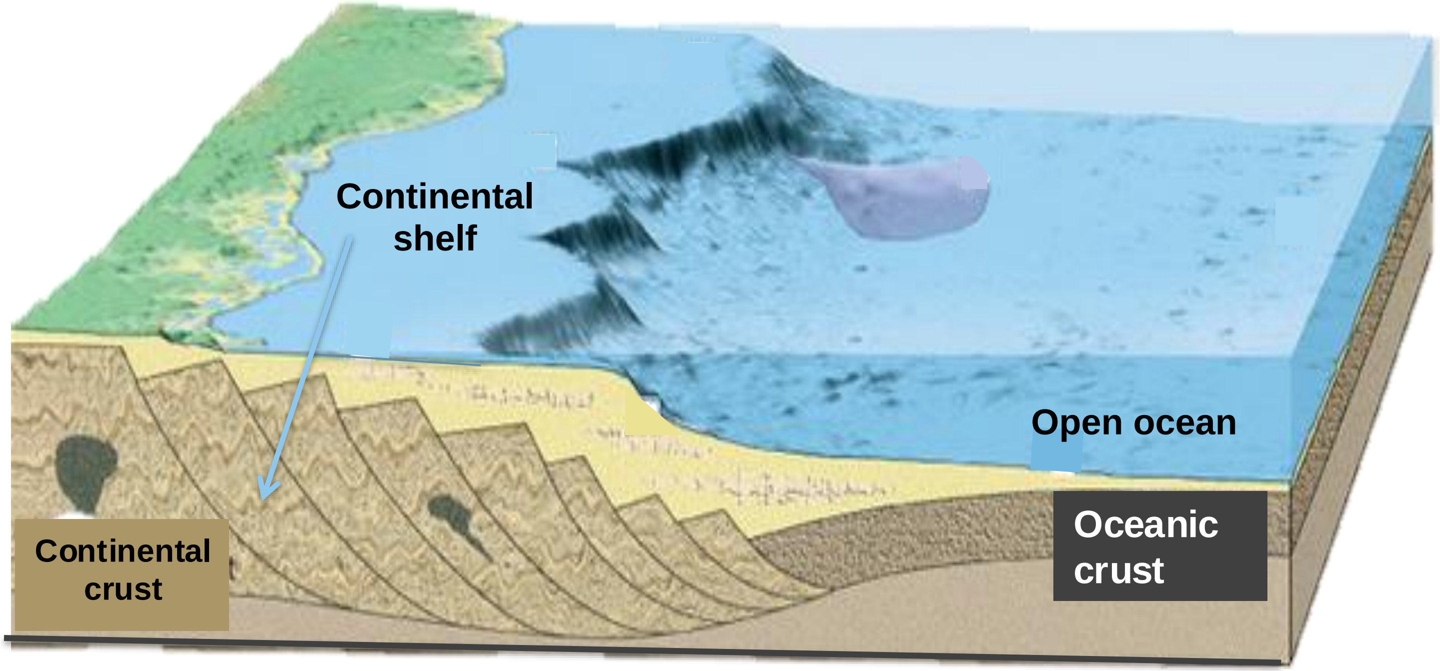
In sea water, several inhibitors of precipitation:

- *Magnesium.*
- *Organic polymers: polysaccharides, proteins…*
- *Other: phosphates, citrates…*

$CaCO_3$ = 4 % of the Earth crust

Total $CaCO_3$: 9 to $14.5.10^9$ T/y

Marine biogenic $CaCO_3$: 5 to $5.7.10^9$ T/y

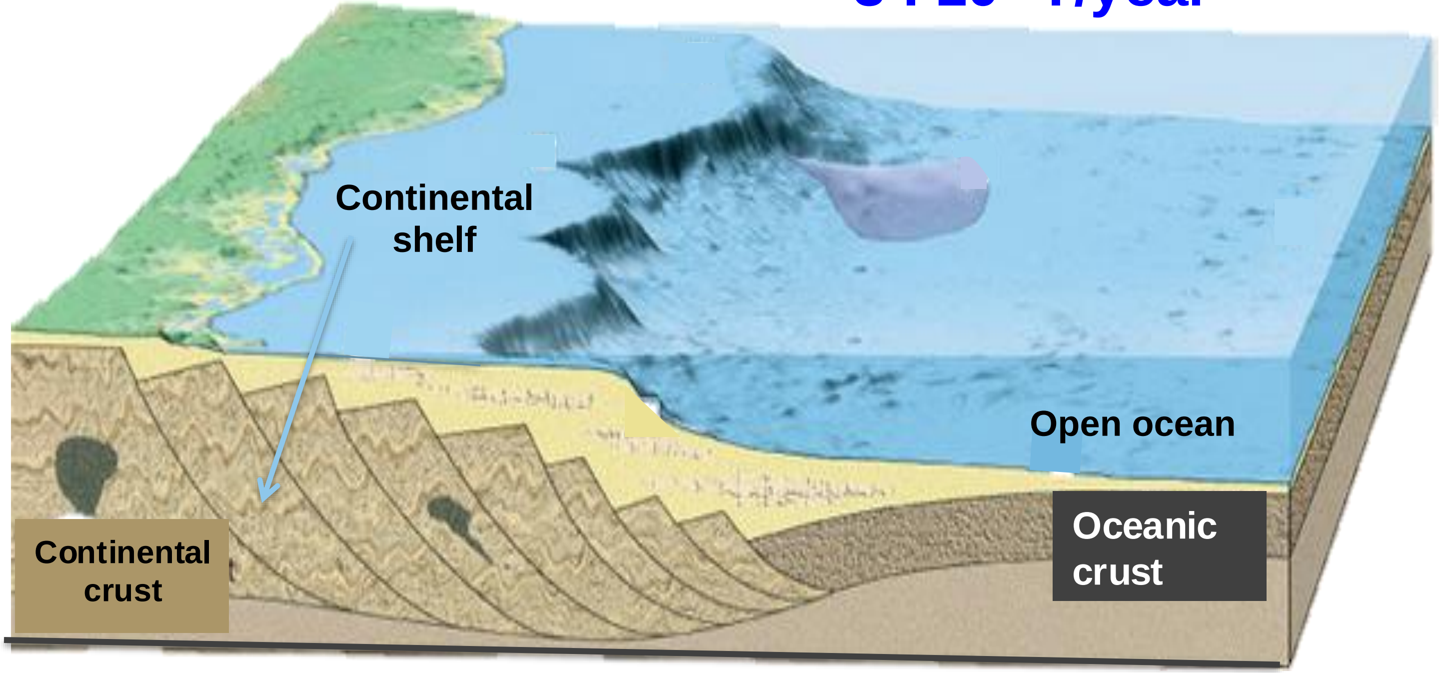


$CaCO_3$ biomineralization & the carbonate cycle

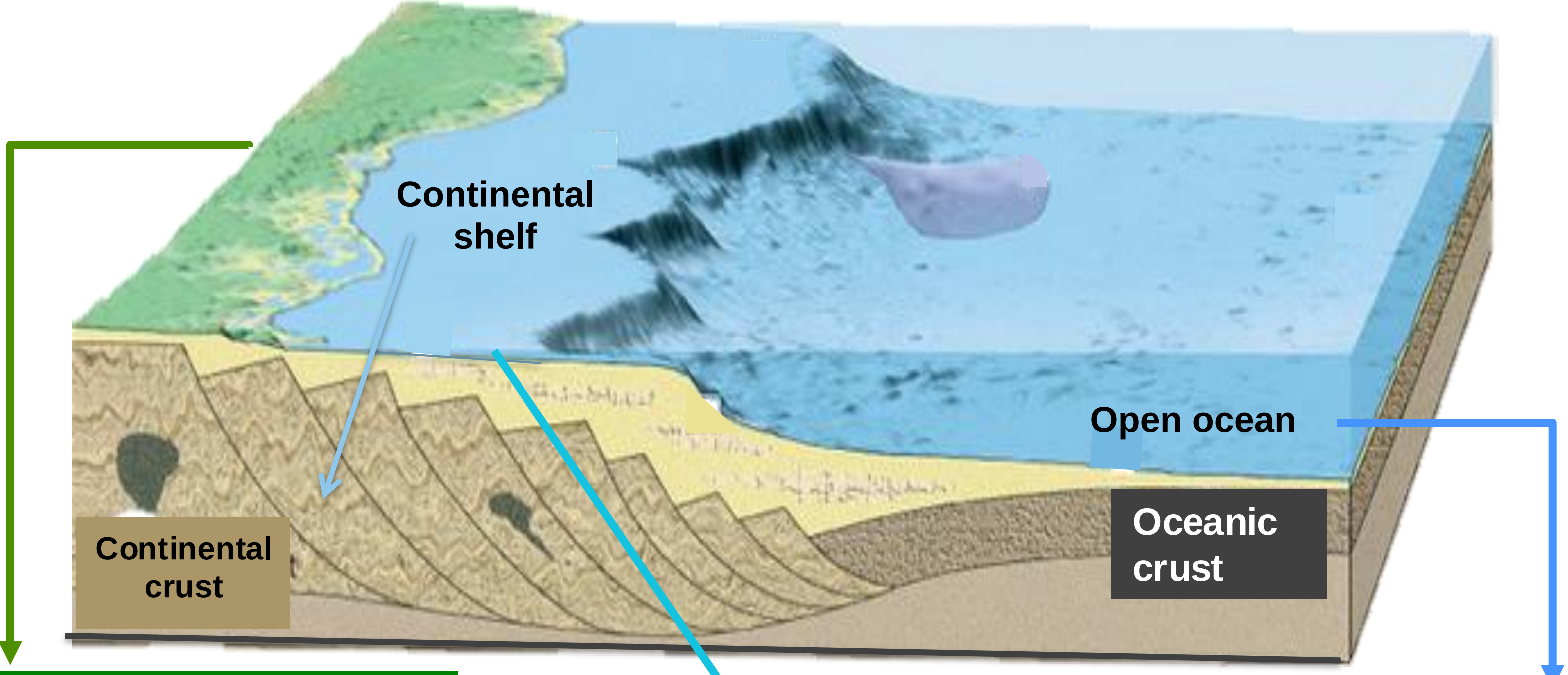
Production:
Marine $CaCO_3$
5 - 5.7.10^9 T/year
(Milliman, 1993)

40% redissolved:
2 . 10^9 T/year (CCD)

60% accumulates:
3 . 10^9 T/year



Continental carbonates not taken into account



CONTINENTS
(soils, lakes, rivers…)

Unknown production?

- Bacteria, fungi, plants, mollusks (lacustrine domains)

EPICONTINENTAL PLATFORM

Estimated production:
2,5 *10^9 T/year
(corals: 0,9 . 10^9 T/year)

- **Benthic**
- **Aragonite & (Mg) calcite**
- **Corals, foraminifera, mollusks, bryozoans, red algae, green algae**

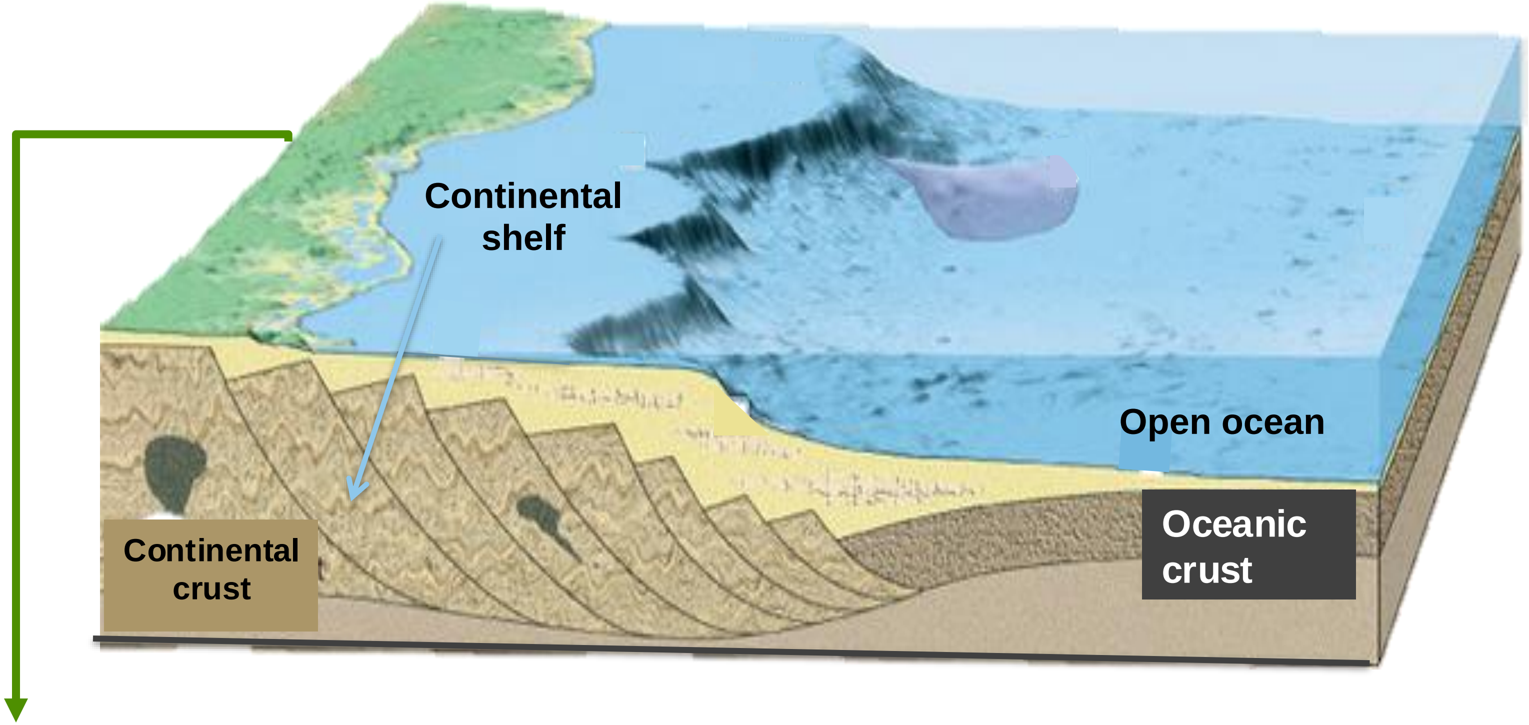
OPEN OCEAN

Estimated production:
2,4 *10^9 T/year ?

- **Planktonic**
- **Calcite**
- **Coccolithophore algae, planktonic foraminifera, 'pteropods'**

From Milliman, 1993; Wollast, 1993; Langer et al., 1997

Continental domain…



<u>**Highly variable production**</u>**:**

- **Important in lacustrine domain**
- **Almost 0 in hot deserts**
- **In temperate forests: micro-organisms (bacteria, fungi): important but poorly quantified; calcite in needles...**
- **In tropical areas: locally, can be important; example of Iroko trees**

QUESTION:

Was this « calcifying regime » constant across the geological times?

ANSWER:

NO

Macro-evolution of $CaCO_3$-based biomineralization across geological times

Geological Time Scale

-4.6 Gyr

-0.54 Gyr

Now

PRECAMBRIAN

Phanerozoic

HADEAN

ARCHEAN

PROTEROZOIC

Paleozoic

Mesozoic

Cenozoic

-3.8 Gyr

-2.5 Gyr

-2.1 Gyr

Prebiotic evolution

Earliest forms of life

1st eukaryotes (??)

Gabon Fauna
Oldest metazoans ??

'Cambrian explosion'

Biologically-induced mineralizations:
STROMATOLITES

http://www.fossilmuseum.net/Fossil_Galleries/Stromatolites/Cochabamba/Stromatolite123.htm

Cloudina

Accession of the biologically-controlled mineralizations

In the Hadean Times
(-4.6 to -4.0 Gyrs)

Where do calcium and calcium carbonate come from ?

Calcium carbonate appeared secondarily on Earth…

HADEAN EON

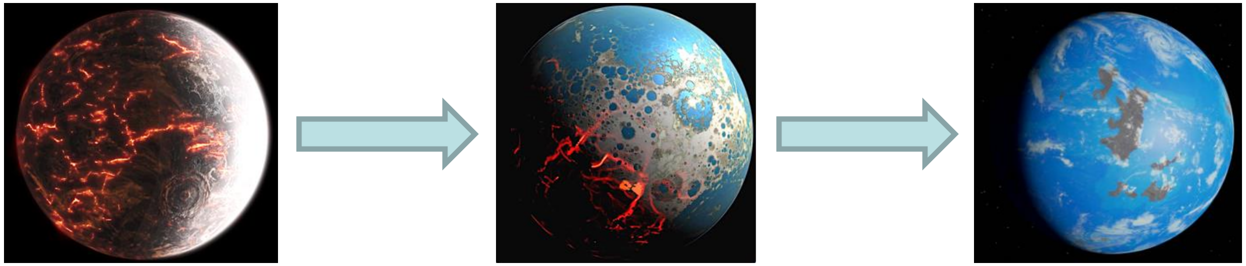
4.0 bya

ARCHEAN EON

4.6 bya

Circa 3.8 bya

3.46 bya



Early forms of life

1st stromatolites (Pilbara, AU)

Degassing => Atmospheric CO_2
Water: meteorites

Water condensation => Oceans

Weathering of silicates

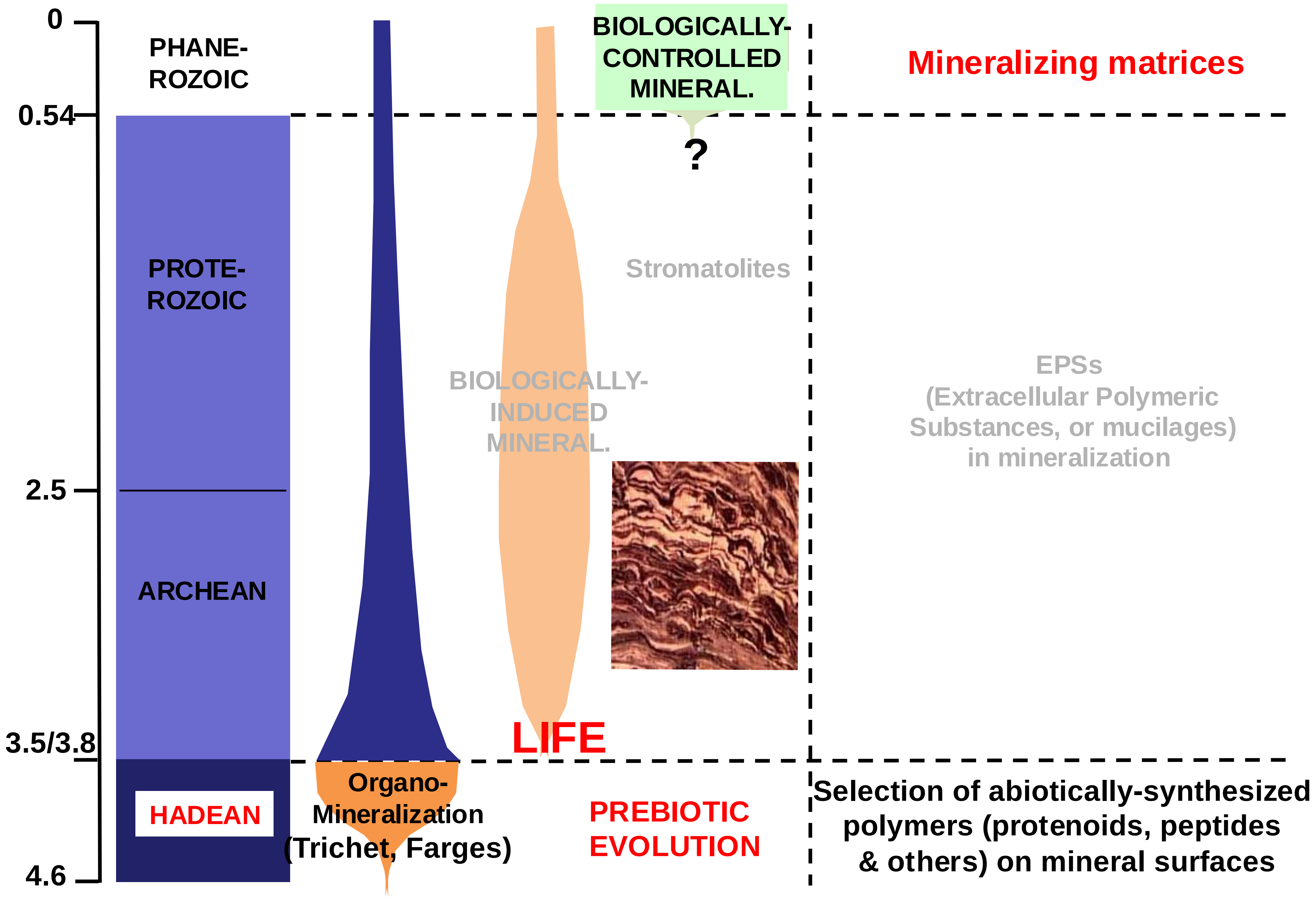
Free Ca

$CaCO_3$

Spontaneous precipitation

1^{st} biologically-induced mineralization:

- **First EPS (?)**



0

0.54

2.5

3.5/3.8

4.6

PHANE-ROZOIC

PROTE-ROZOIC

ARCHEAN

HADEAN

BIOLOGICALLY-CONTROLLED MINERAL.

?

Stromatolites

BIOLOGICALLY-INDUCED MINERAL.

LIFE

Organo-Mineralization (Trichet, Farges)

PREBIOTIC EVOLUTION

Mineralizing matrices

EPSs
(Extracellular Polymeric Substances, or mucilages)
in mineralization

Selection of abiotically-synthesized polymers (protenoids, peptides & others) on mineral surfaces

Archean & Proterozoic Times
(-4.0 to -0.54 Gyrs)

- Biologically-induced mineralizations

- First biologically-controlled mineralizations ?

Stromatolites

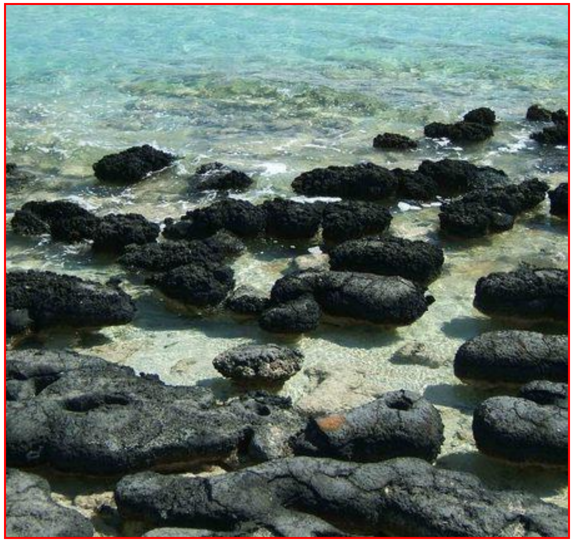
Photo Ch. Pomerol.

Oldest mineralized construction:

-3,5 billion years (ARCHEAN)

Today's stromatolites

Shark Bay, Australia



Stromatolites

Coupling between photosynthesis & biomineralization

Photosynthesis
(cyanobacteria) :

Carbon dioxide (CO_2)

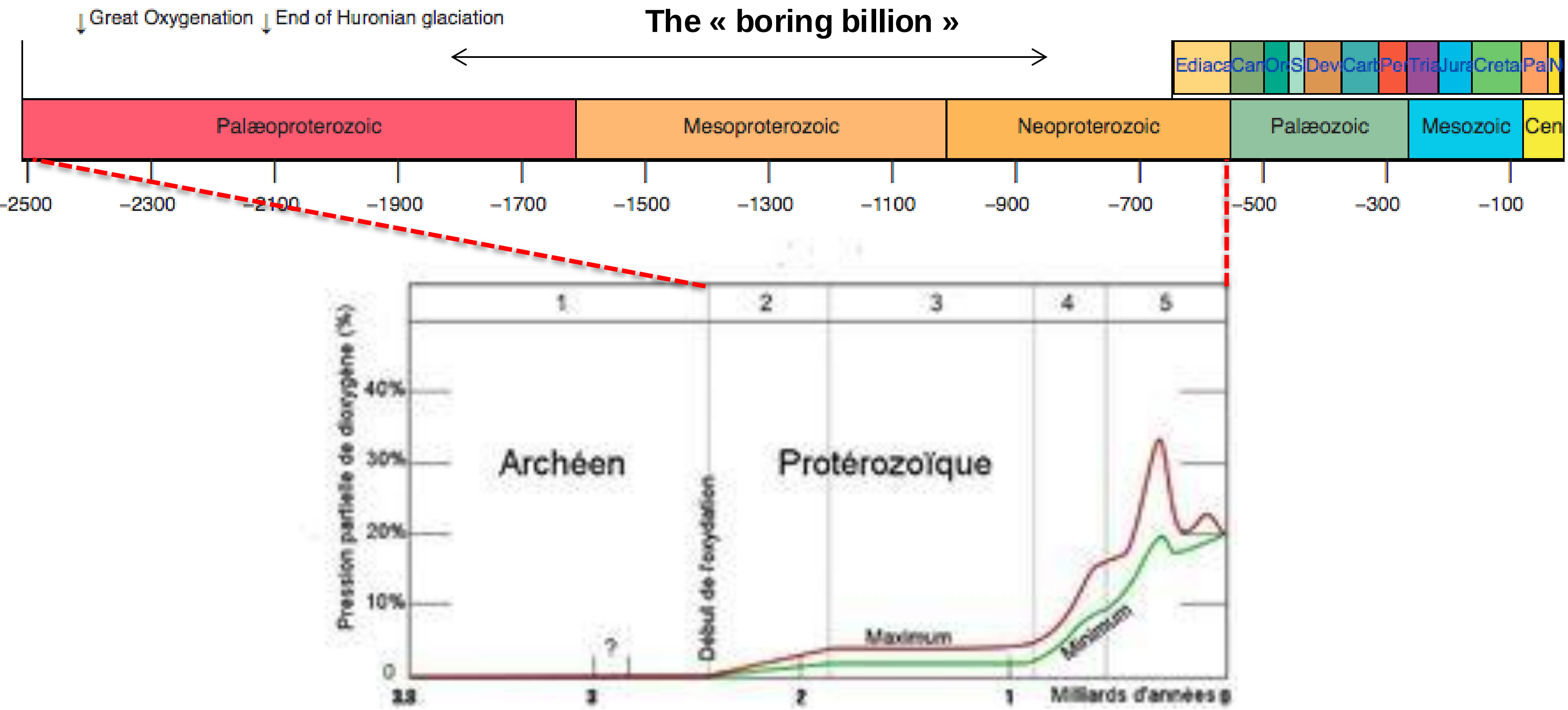
↓

Organic matter
+ oxygen (O_2)

Stromatolites played a key-role in the formation of an oxidizing atmosphere

The ‘GOE’: Great Oxidation Event

- Increase of O2 level due to photosynthesis
- 2.4 à 2.1-2 billion year ago (Paleoproterozoic)
- Extinction of anaerobic life



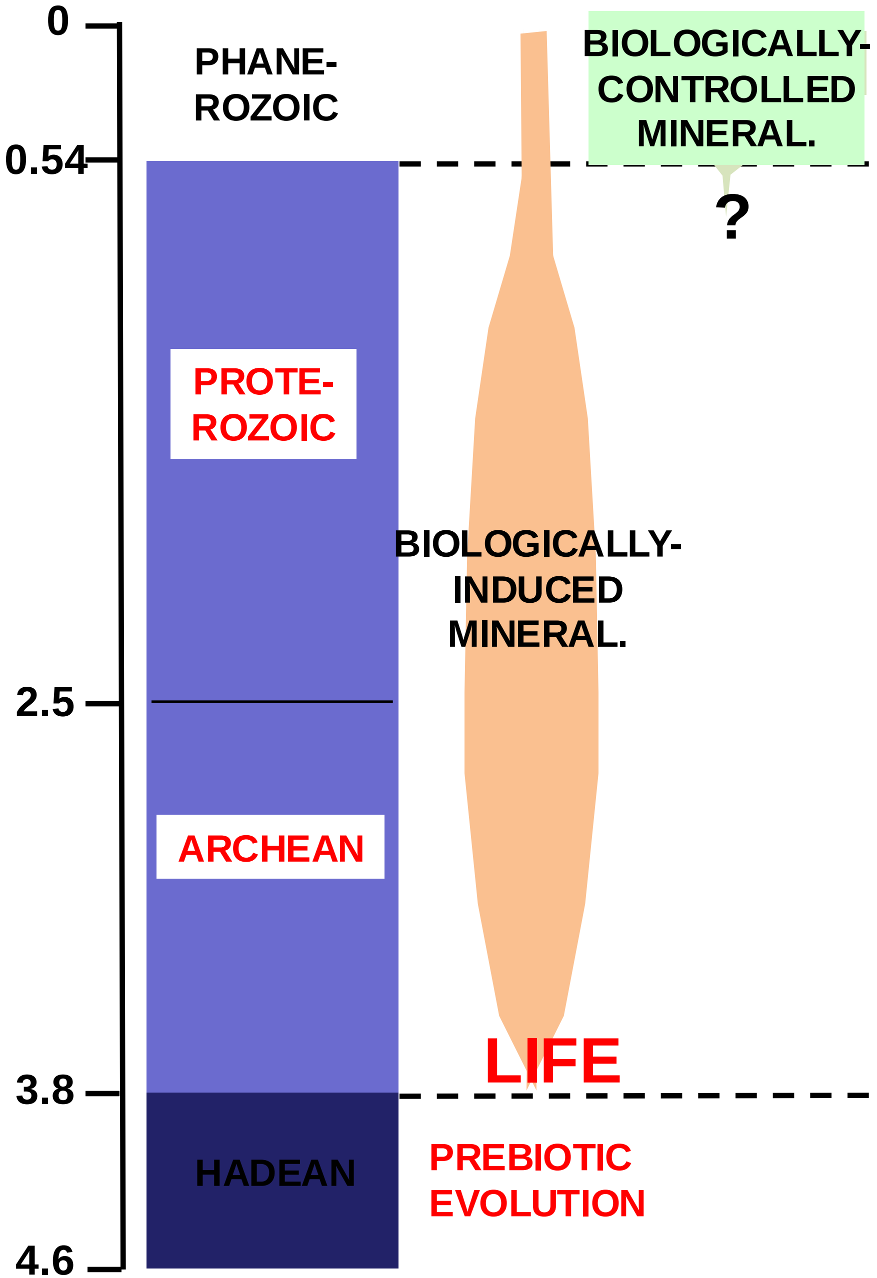
Fonction(s) of stromatolite biomineralization in cyanobacteria

- Support

- Structuring of bacterial communities

- Protection against dessiccation

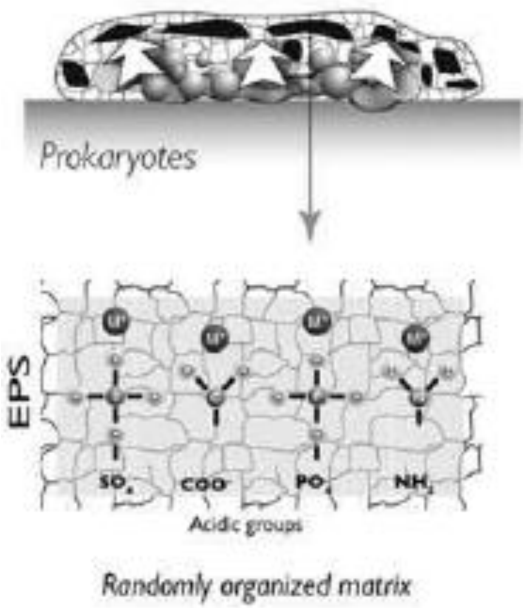
- Protection against UVs



Complex and specialized mineralizing matrices:
(fine-tuned at gene level)
Multiple molecular functions

Fundamental roles of EPS in bacterial biomineralization:

- **Peculiar micro-environment**
- **Nucleation / Template**
- **Inhibition of mineralization**
- **'Non specialized' ?**



(From Dupraz et al., 2009)

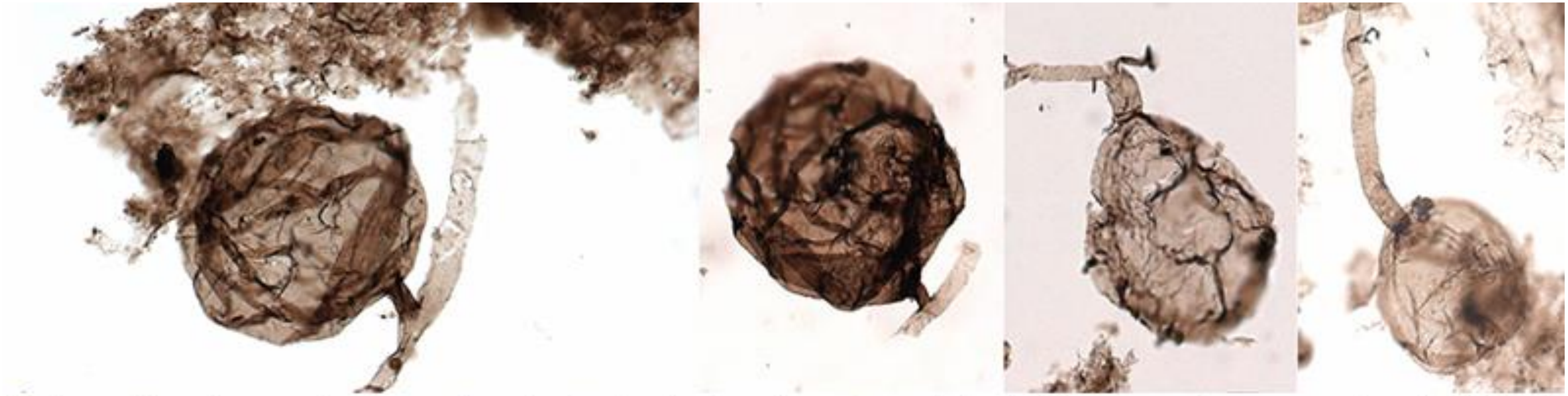
Prerequisites: - Handling of intracellular Ca fluxes – Ca, 2nd messenger
- Set up of a cytoplasmic regulatory machinery

Selection of abiotically-synthesized polymers (protenoids, peptides & others) on mineral surfaces

Multicellular eukaryotic life (fungi): 0.9 to 1 billion year old

(Loron et al., Nature, 570, 2019)

Outcrop from Canadian Arctic

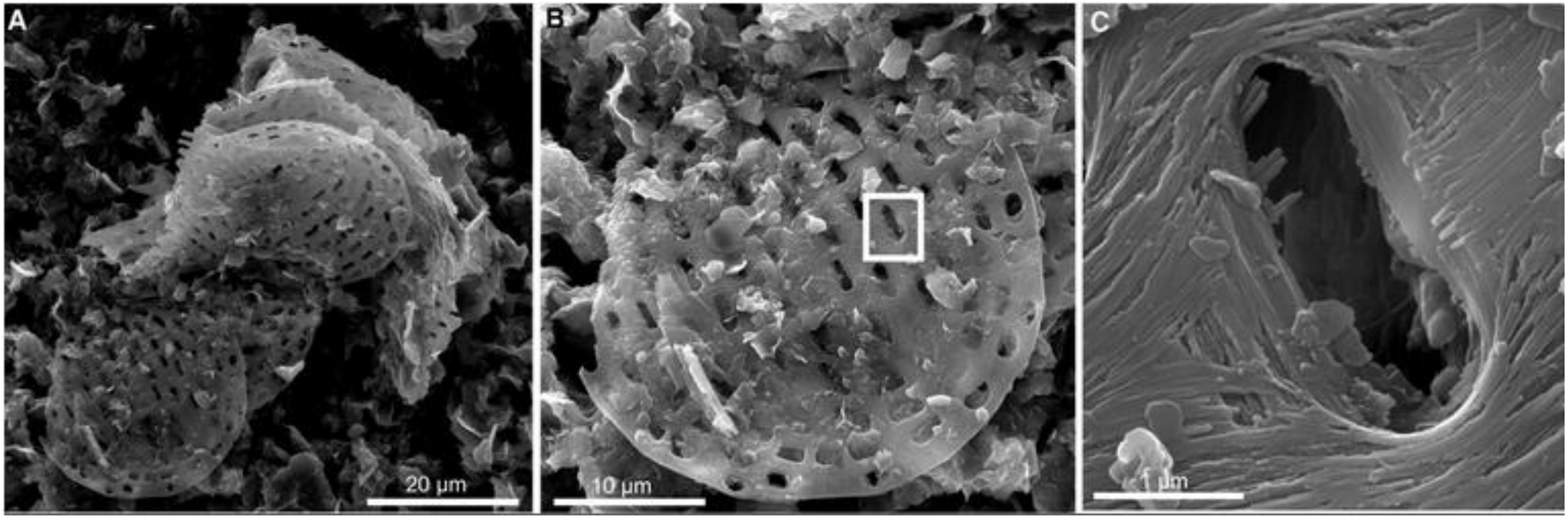


Photographies prises au microscope optique des fossiles du champignon *Ourasphaira giraldae*, un organisme eucaryote multicellulaire à paroi organique (chitine) composé de filaments en forme de "T" et segmentés (hyphes) reliés à une vésicule sphérique (spore). Les spécimens mesurent entre 30 et 80 microns de diamètre (0.03 à 0.08 mm) et sont datés entre 0.9 et 1 milliard d'années. Documents C.

➔ Chitin: one of the oldest polymers among Eukaryotes

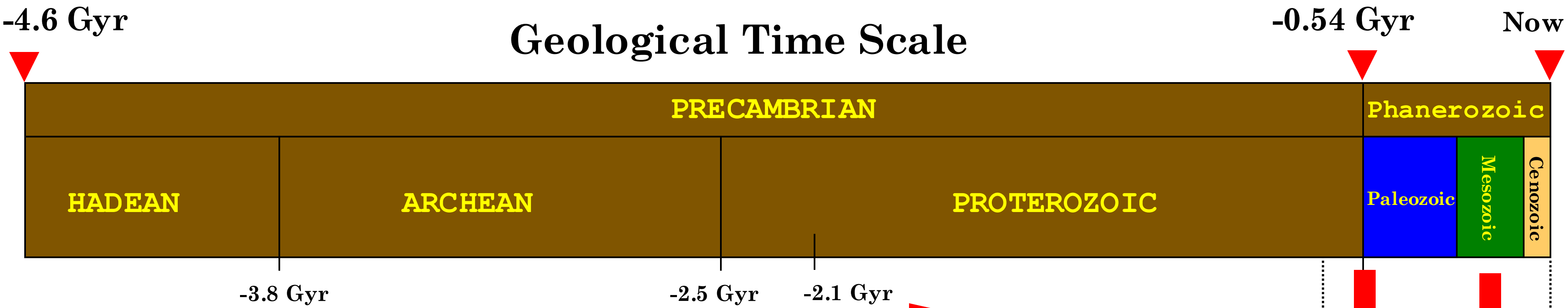
Very first complex biomineralized forms of life (Cohen et al., 2017, Science Advances)

*** Eukaryotic cells**
*** Hydroxyapatite**
*** 810 million year ago**
*** Yukon, Canada**
*** Dated by rhenium & osmium isotopes**



Macro-evolution of $CaCO_3$-based biomineralization across geological times

Geological Time Scale



Prebiotic evolution

Earliest forms of life

1st eukaryotes (??)

Gabon Fauna
Oldest metazoans ??

‘Cambrian explosion’

Biologically-induced mineralizations:
STROMATOLITES

http://www.fossilmuseum.net/Fossil_Galleries/Stromatolites/Cochabamba/Stromatolite123.htm

Cloudina

Accession of the biologically-controlled mineralizations

Around the Proterozoic / Cambrian transition

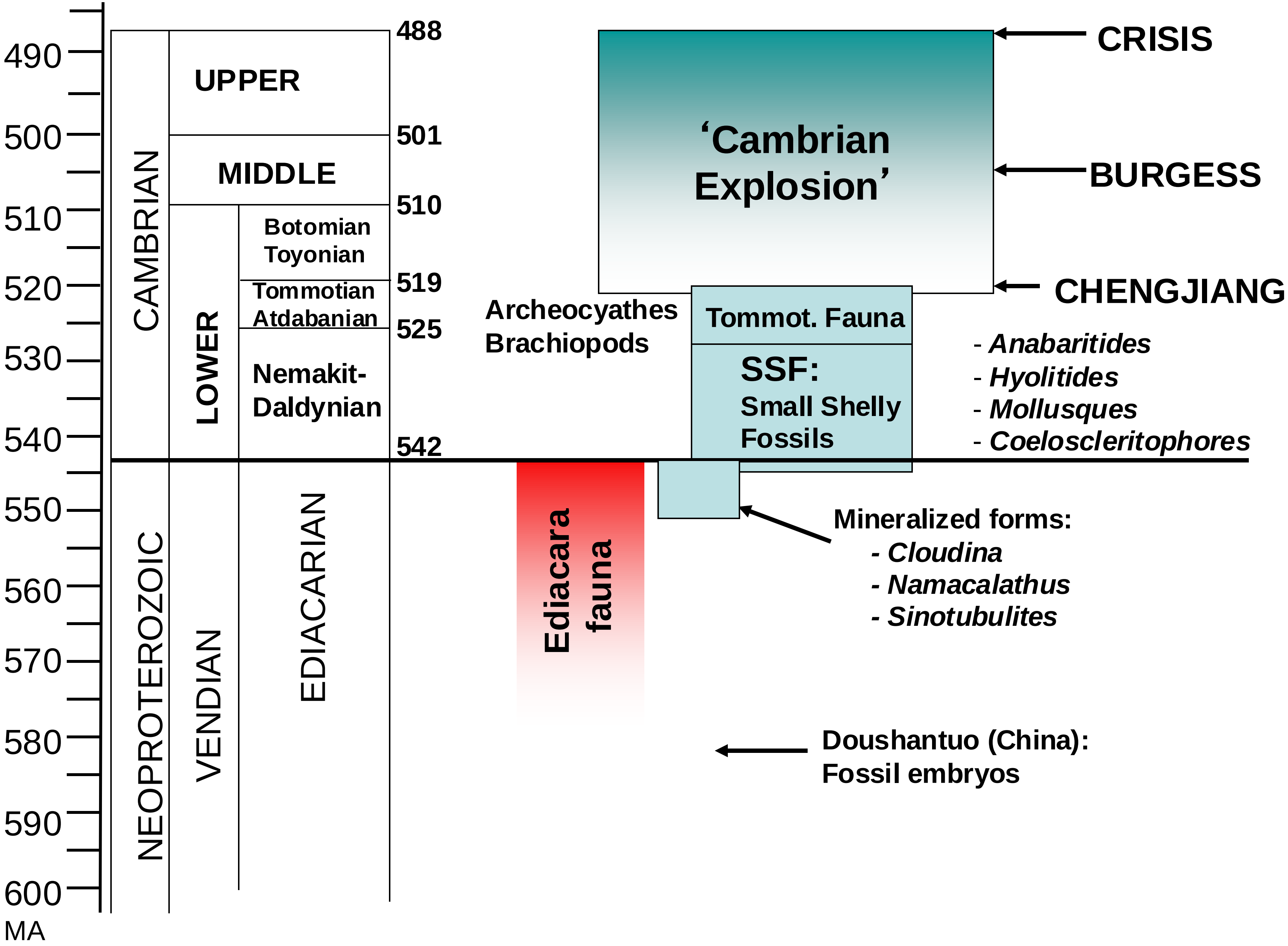
Biologically-controlled mineralization inherits the Earth

Appearance of biomineralization among metazoans =

One aspect of the « Cambrian Explosion »

What were the major steps at the Precambrian / Cambrian transition ?

P/C TRANSITION : SUCCESSION OF BIOLOGICAL EVENTS



490
500
510
520
530
540
550
560
570
580
590
600
MA

CAMBRIAN

UPPER

MIDDLE

LOWER

Botomian
Toyonian

Tommotian
Atdabanian

Nemakit-
Daldynian

488
501
510
519
525
542

NEOPROTEROZOIC

VENDIAN

EDIACARIAN

'Cambrian Explosion'

CRISIS

BURGESS

CHENGJIANG

Archeocyathes
Brachiopods

Tommot. Fauna

SSF:
Small Shelly Fossils

- *Anabaritides*
- *Hyolitides*
- *Mollusques*
- *Coeloscleritophores*

Ediacara fauna

Mineralized forms:
- *Cloudina*
- *Namacalathus*
- *Sinotubulites*

Doushantuo (China):
Fossil embryos

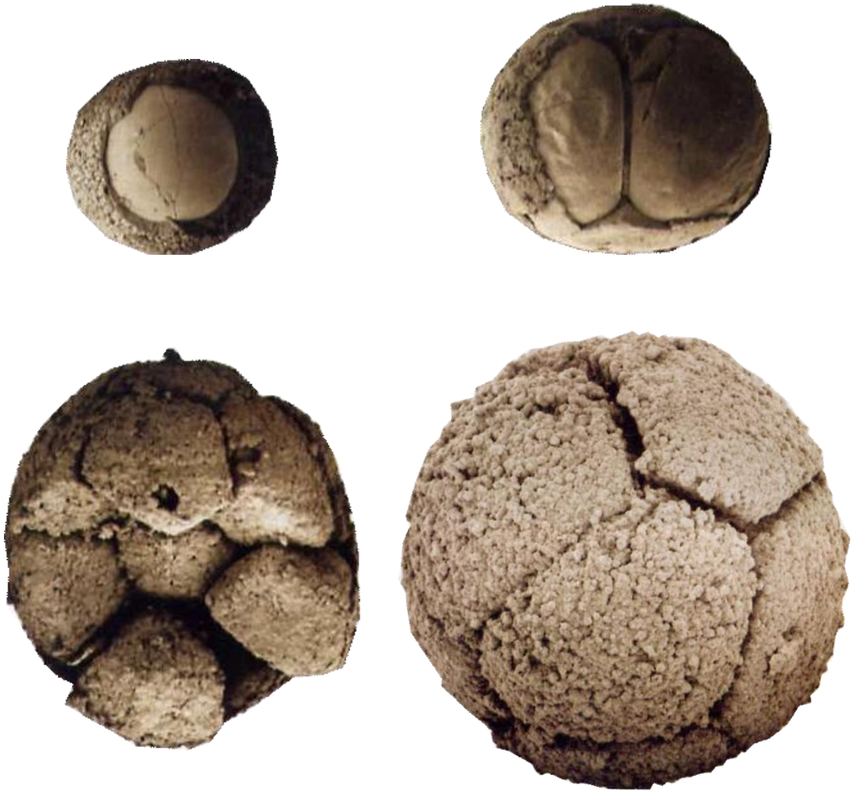
Doushantuo Formation (Chine)

1st 'fossil embryos' that are remarkably preserved:
Phosphatic deposits
Xiao, Zhang & Knoll, Nature, 391 (1998).

Age: 590 to 565 MY

Anterior or contemporary to Ediacara Fauna

- **Macro-algae**
- **Cnidarians ?**
- **Sponges ?**
- **Bilaterians ?**
- **Simple adult metazoans ?**



Ediacara fauna

P.A. Bourque, 1995

Ediacara fauna

Dickinsonia

Eoporpita

Tribrachidium

Pteridinium

Spriggina

Kimberella

Photos extraites de de http://www.ucmp.berkeley.edu/vendian/critters.html

Ediacara fauna: some features

- **Worldwide distribution: > 30 sites on the 5 continents**
  (initial discovery in South Australie in 1946)

- **Soft-bodied fauna, unmineralized**

- **Microphage, short trophic chain**

- **Adapted to a low level of O_2 : flat organisms, high surface exchange**

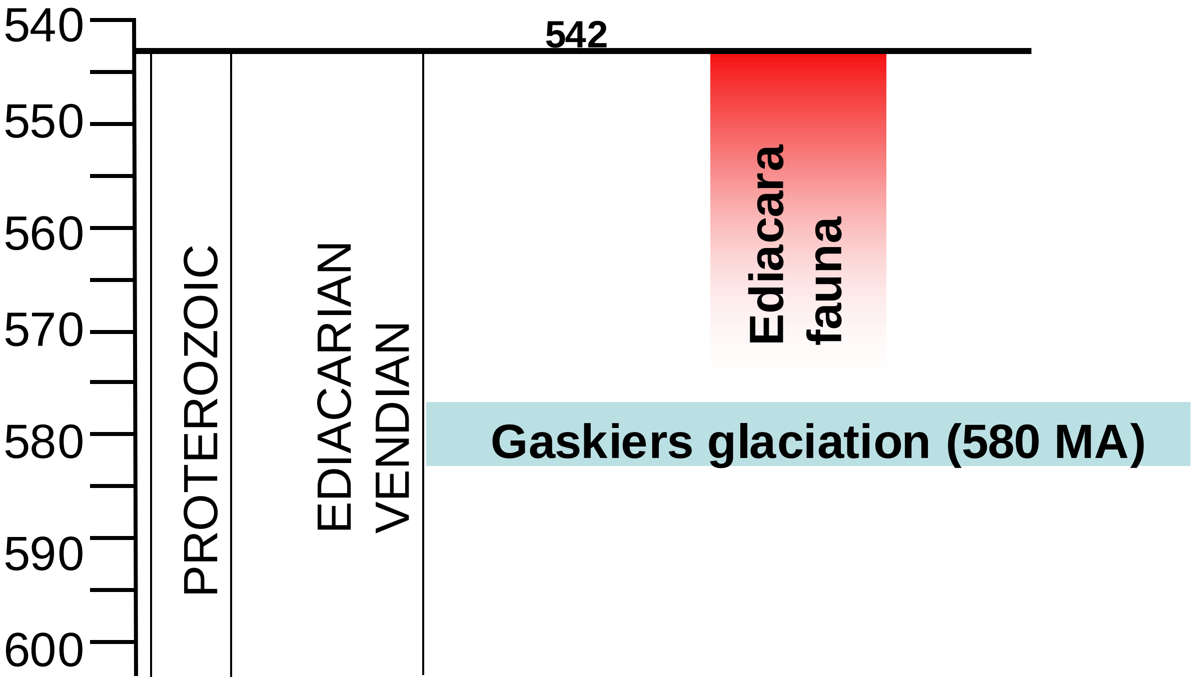
- **Increase of diversity from 570 à 545 MA**

- **Circa 70 ‘genera’ in about 100 ‘species’:**
  - ***70% cnidarian-like » = médusoid shape***
  - ***Flat worms***
  - ***Arthropods***
  - ***Unknown phylums***

Ediacara fauna & paleoenvironnemental context

***Canfield et al., Science, 315, 92-95 (2007)* :**

Late Neo-Proterozoic deep-ocean oxygenation and the rise of animal life.



Ocean oxygenation due to deglaciation ?

Ediacara fauna & its relationship with metazoans: a debated question

Ediacara has nothing to do with metazoans that appeared later = VENDOBIONTS

Aborted experiment without offsprings

Buss & Seilacher, 1994: Vendobionts = sister-group of metazoans

Ediacara fauna is a mixture of representatives of disappeared and living phylums

- ***Sponges***
- ***Cnidarians***
- ***Flat worms***
- ***Arthropods ??***
- ***Echinoderms ??***

The *Dickinsonia* case

Bobrovskiy et al., Science, 361: Sept 2018.

LIPIDIC BIOMARKERS

Cholesteroids typical of metazoans

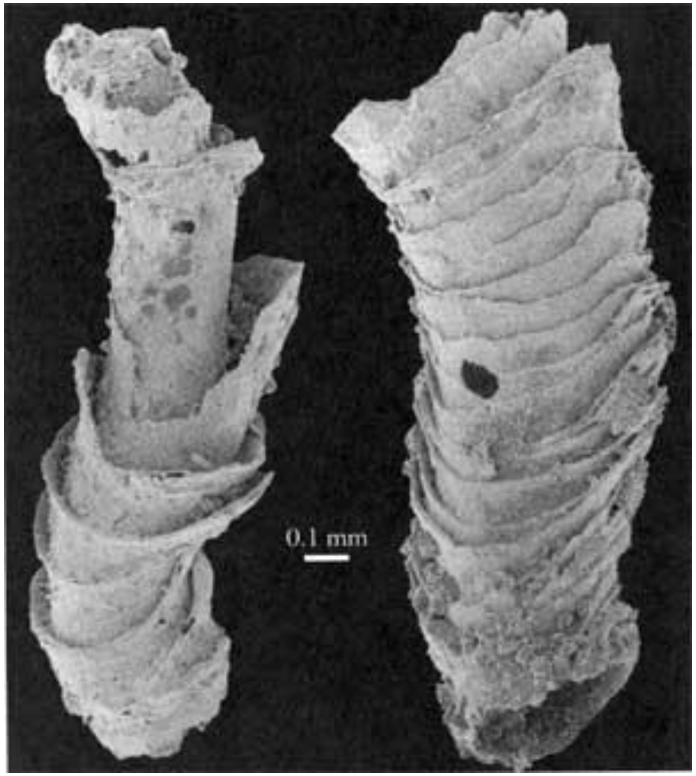
Early mineralized forms preceding the P/C transition

Cloudina:
- Germs. Am. J. Sci., 272 (1972)

- World distribution

- Calcified nested cones
- about the same age as EDIACARA

- Disappeared at the P/C transition



http://www.palaeos.com/Proterozoic/Neoproterozoic/Ediacaran/Ediacaran2.htm

Other mineralized forms:

- Namacalathus

Grotzinger et al. Paleobiology, 26 (2000)

- Namapoikia

Wood et al. Science, 296 (2002)

- Sinotubulites

1st traces of predation on Cloudina

Bengtson & Zhao. Science, 257 (1992) **Hua et al. Palaios 18 (2003)**

Small Shelly Fossils of the Lower Cambrian

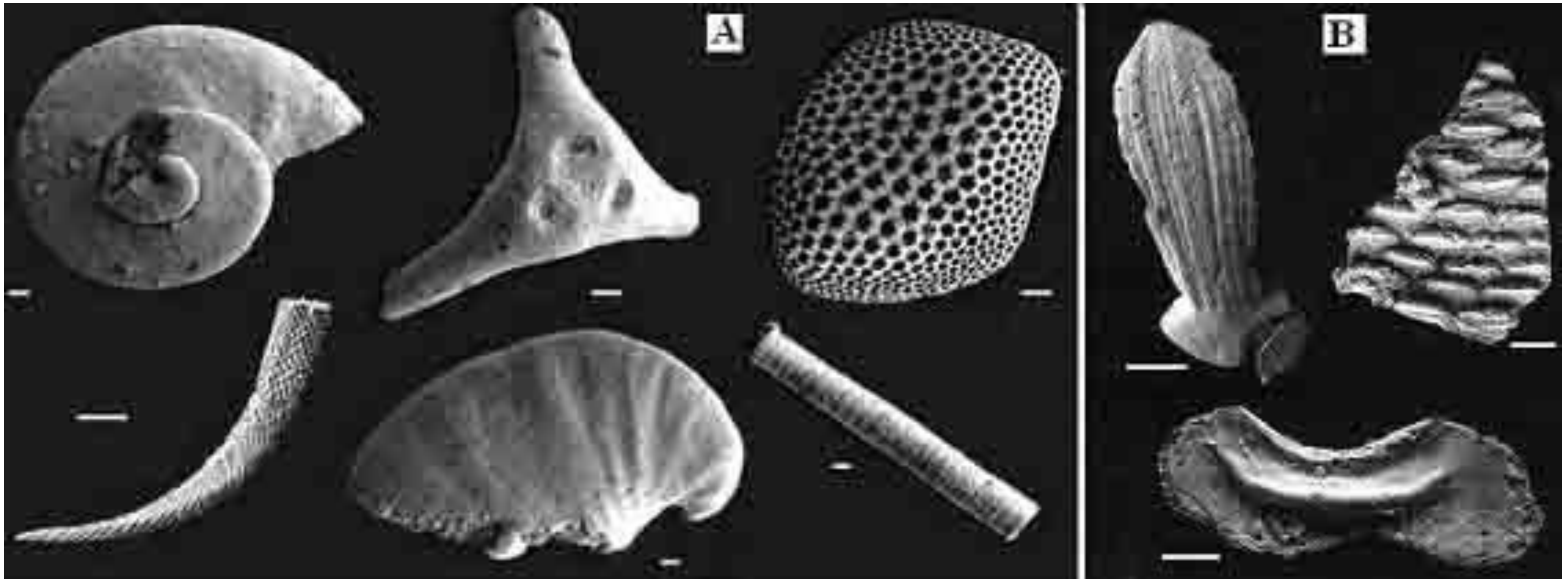
- World distribution

- Conical shapes, plates, sclérites and tubes

-1st diversification of skeleton-bearing organisms: about 40 genera

- Uncertain affinities: sponges, cnidarians, mollusks…

- 1st attested mollusk: *Helcionella*



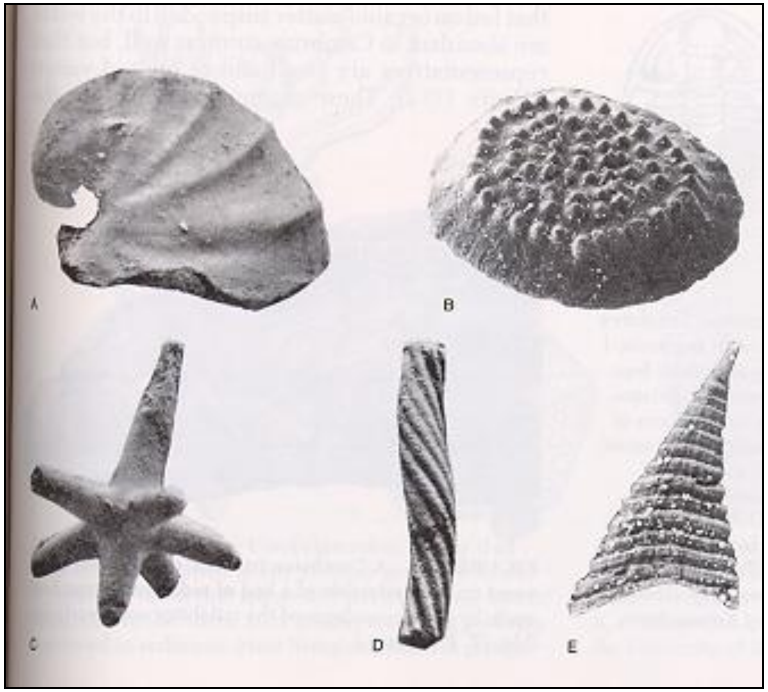
Li & Zhou, 2001

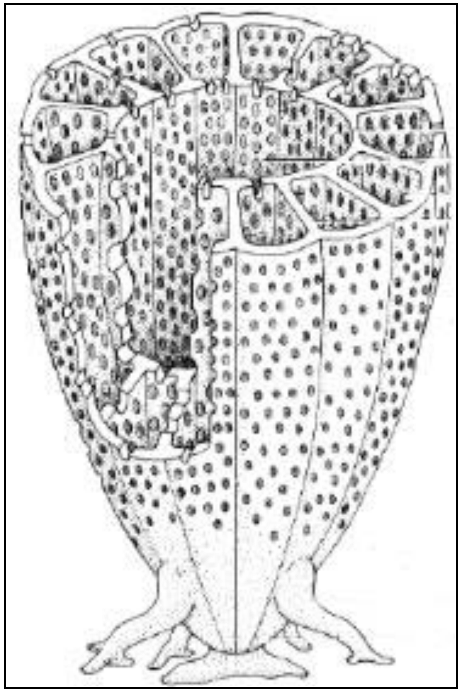
Peng *et al.*, 2001

Tommotian Fauna
(middle of Lower Cambrian)

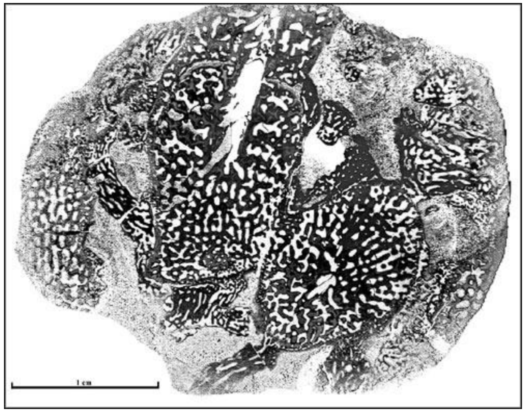
- World distribution
- Radiation of SSF

- Appearance of:
  - Archeocyatha
  - Brachiopods
  - Trilobites
  - Echinoderms





Archeocyathe



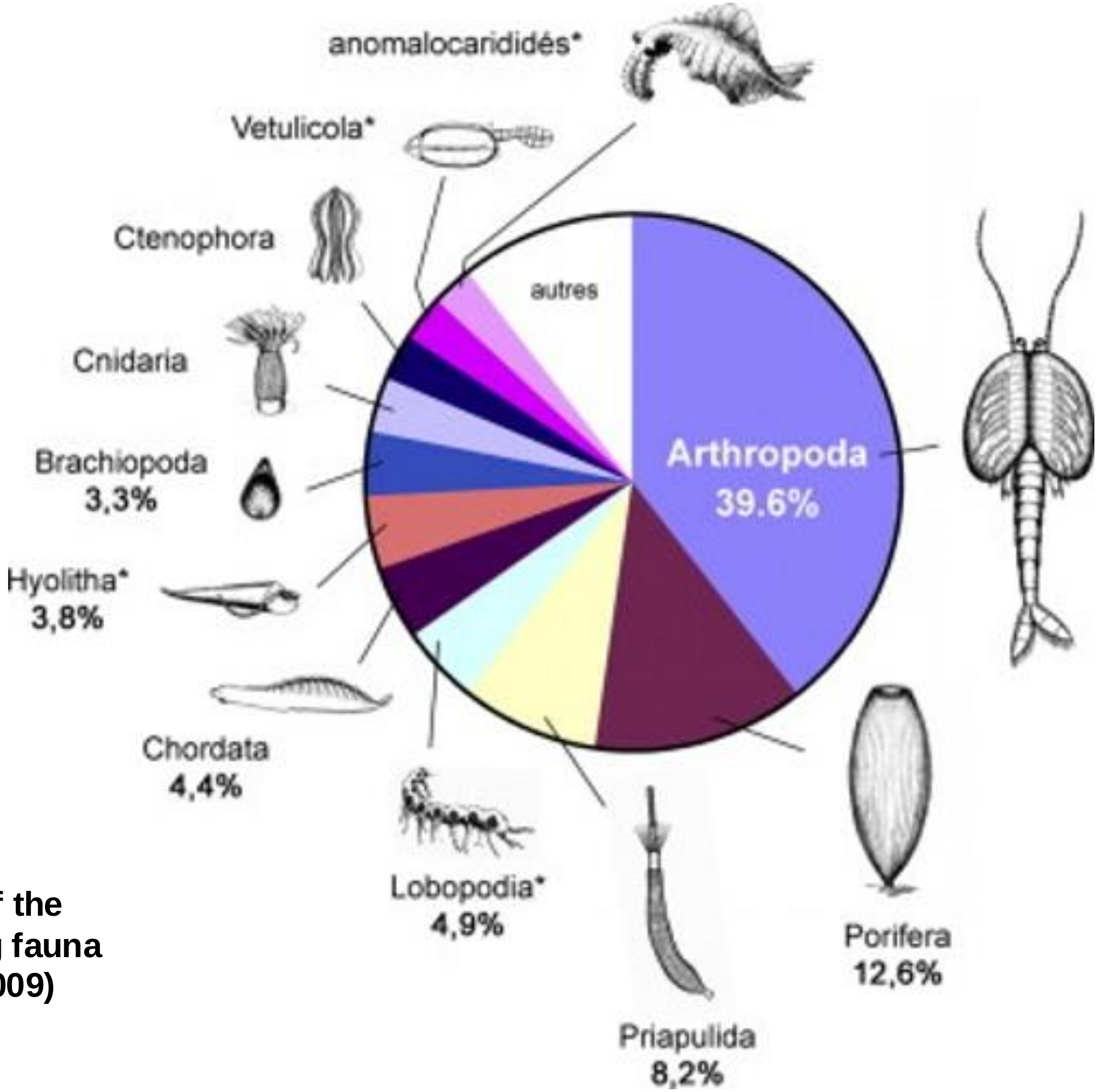
Archeocyathus atlanticus

Chengjiang Fauna: the beginning of the Cambrian Explosion

- **Age: end of Lower Cambrian (Atdabanien)**
- **< 150 species**
- **Circa 20 phylums**
- **One of the 1st modern ecosystem**

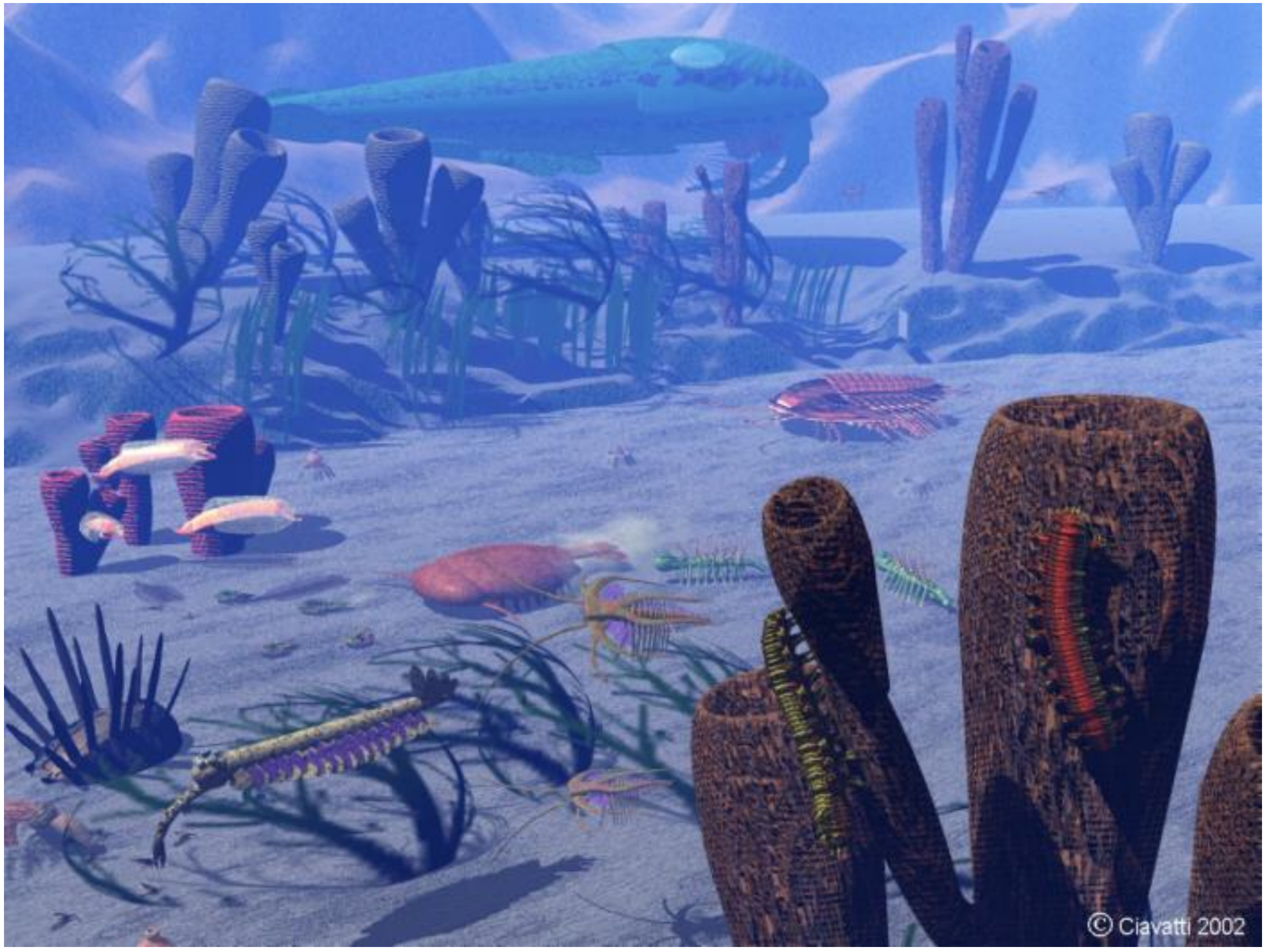
Photos J. Vannier

Chengjiang fauna: beginning of the 'Cambrian Explosion'



Diversity of the Chengjiang fauna (Vannier, 2009)

The Burgess shales fauna


© Ciavatti 2002

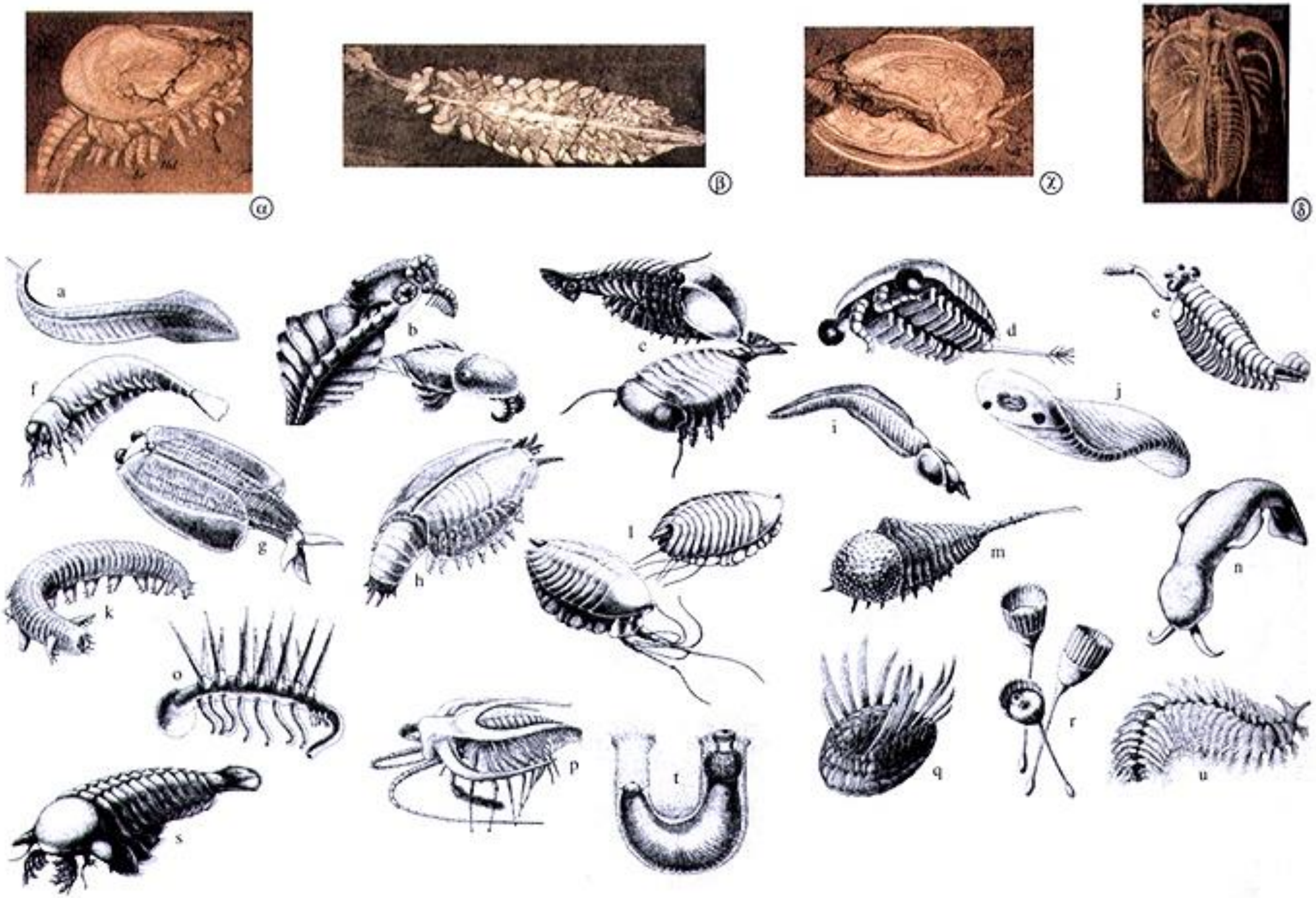
- Age : Middle Cambrian

- 37 phylums

- 70% metazoans with soft-bodies

- Sponges
- Cnidarians
- Annelids
- Priapulians
- Onychophores
- Mollusks
- Arthropods
- Echinoderms
- Chordates

Burgess Shales fauna



CARON J.-M. et coll., *Comprendre et enseigner la planète Terre*. Ophrys, 2003.

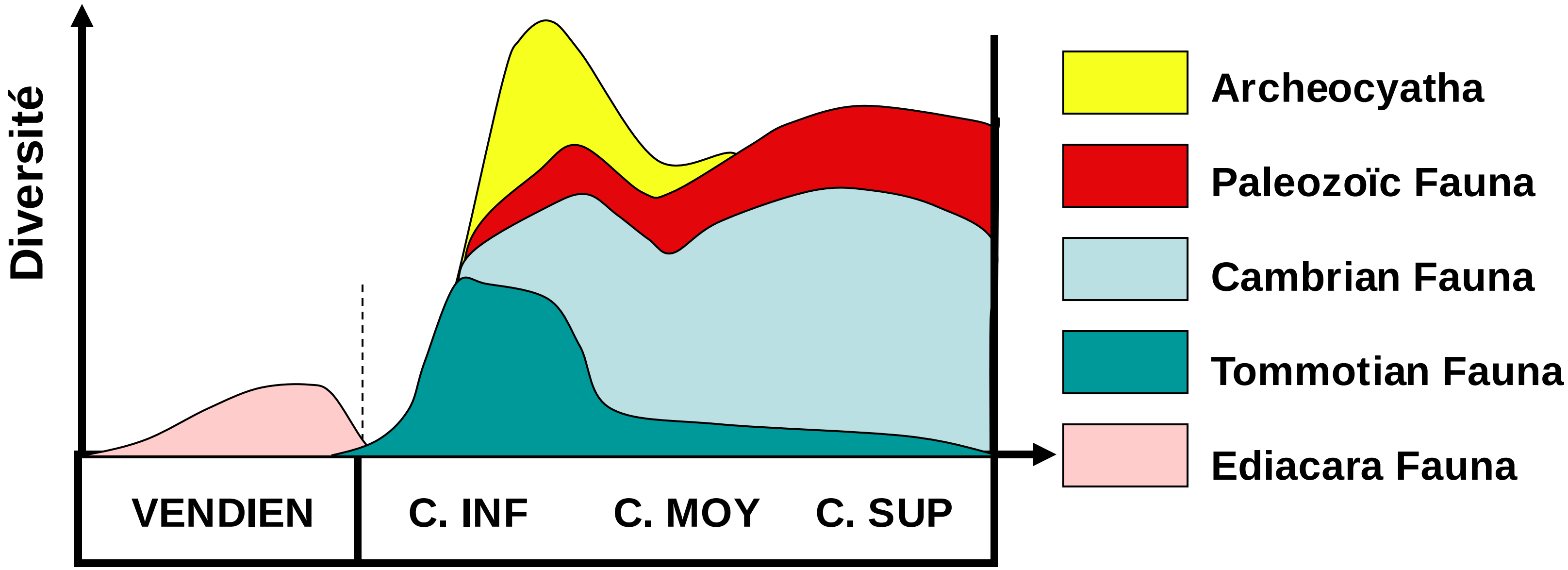
Fig. 235 La faune cambrienne de Burgess Pass (Colombie britannique).
α. *Canadaspis*. β. *Opabinia*. χ. *Leanchoilia*. δ. *Marella splendens*.

Représentations *(d'après Collins)* :
a. *Pikaia* (chordé). b. *Anomalocaris*. c. *Sidneyia*. d. *Sarotrocercus*. e. *Opabinia*. f. *Yohoia*. g. *Odaraia*. h. *Canadaspis* (malacostracé).
i. *Nectocaris*. j. *Odontogriphus*. k. *Aysheaia* (onychophore ?). l. *Leanchoilia*. m. *Habelia*. n. *Amiskwia*. o. *Hallucigenia*. p. *Marella*. q. *Wiwaxia*.
r. *Dinomischus*. s. *Sanctacaris* (arthropode chélicérate). t. *Ottoia*. u. *Canadia*.

In brief, the ‘Cambrian Explosion’ is:

- *Novel ‘bauplan’ in metazoans*
- *Increase of diversity (at all levels, specific, generic...)*
- *Modern marine ecosystems*
- *Aborted experiments: Archeocyatha*

- *APPEARANCE OF BIOMINERALIZATION*

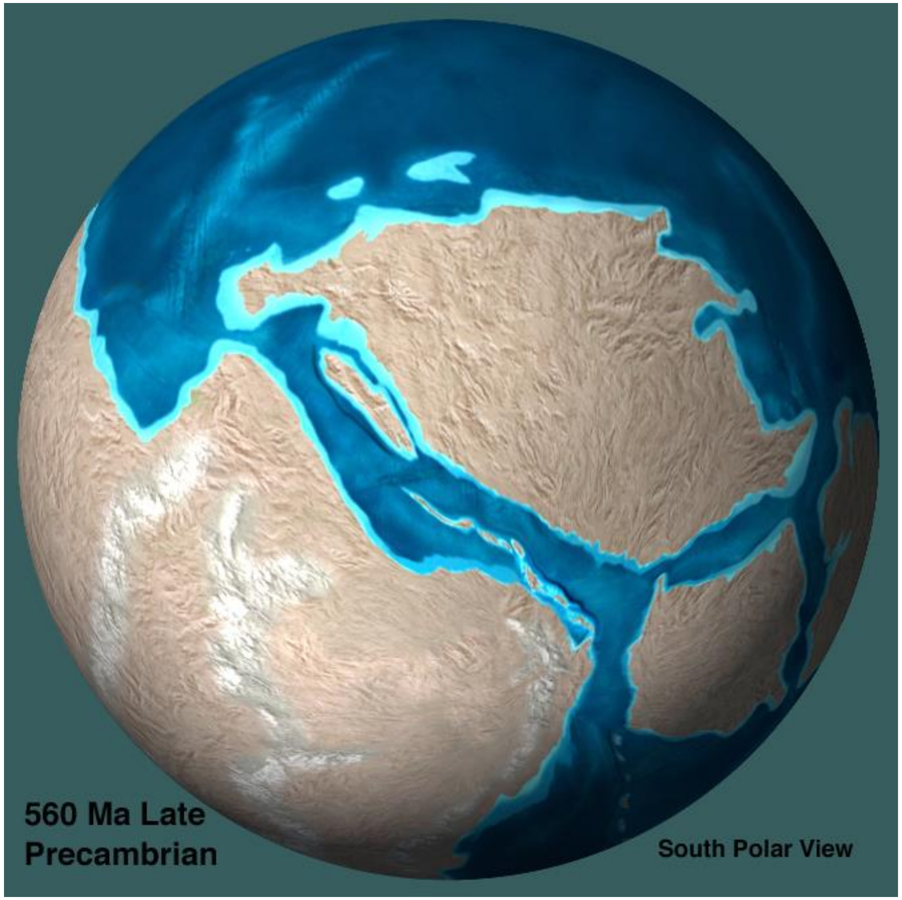


Adapted from Hallam & Wignall, 1997

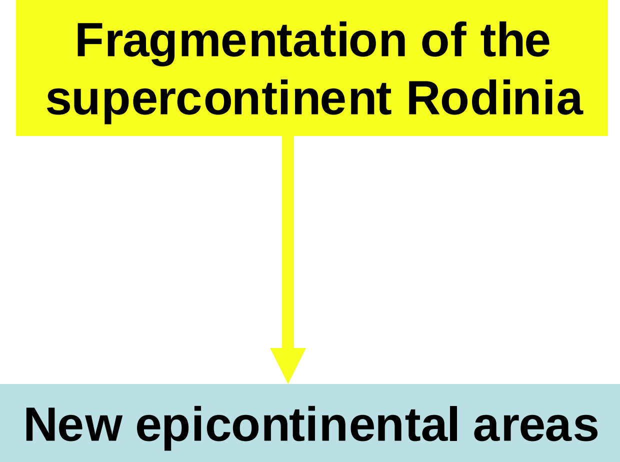
Possible causes of the ‘Cambrian Explosion’

EXTERNAL	**Tectonics** **Climat-related** O_2 **Seawater chemistry: Ca**
INTERNAL	**Physiological** **Predation** **Genetic**

Causes related to tectonics



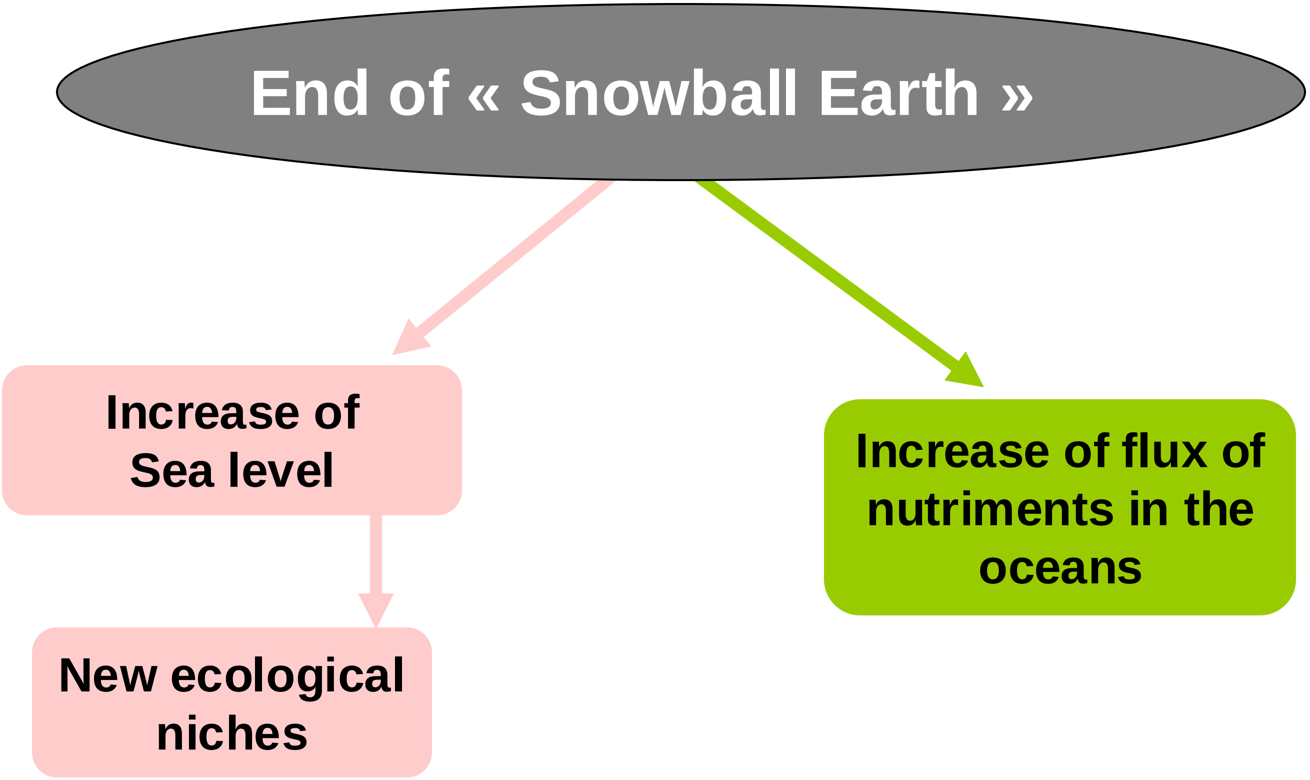
http://jan.ucc.nau.edu/~rcb7/560_LatePC_sp.jpg



Fragmentation of the supercontinent Rodinia

New epicontinental areas

Climatic causes



End of « Snowball Earth »

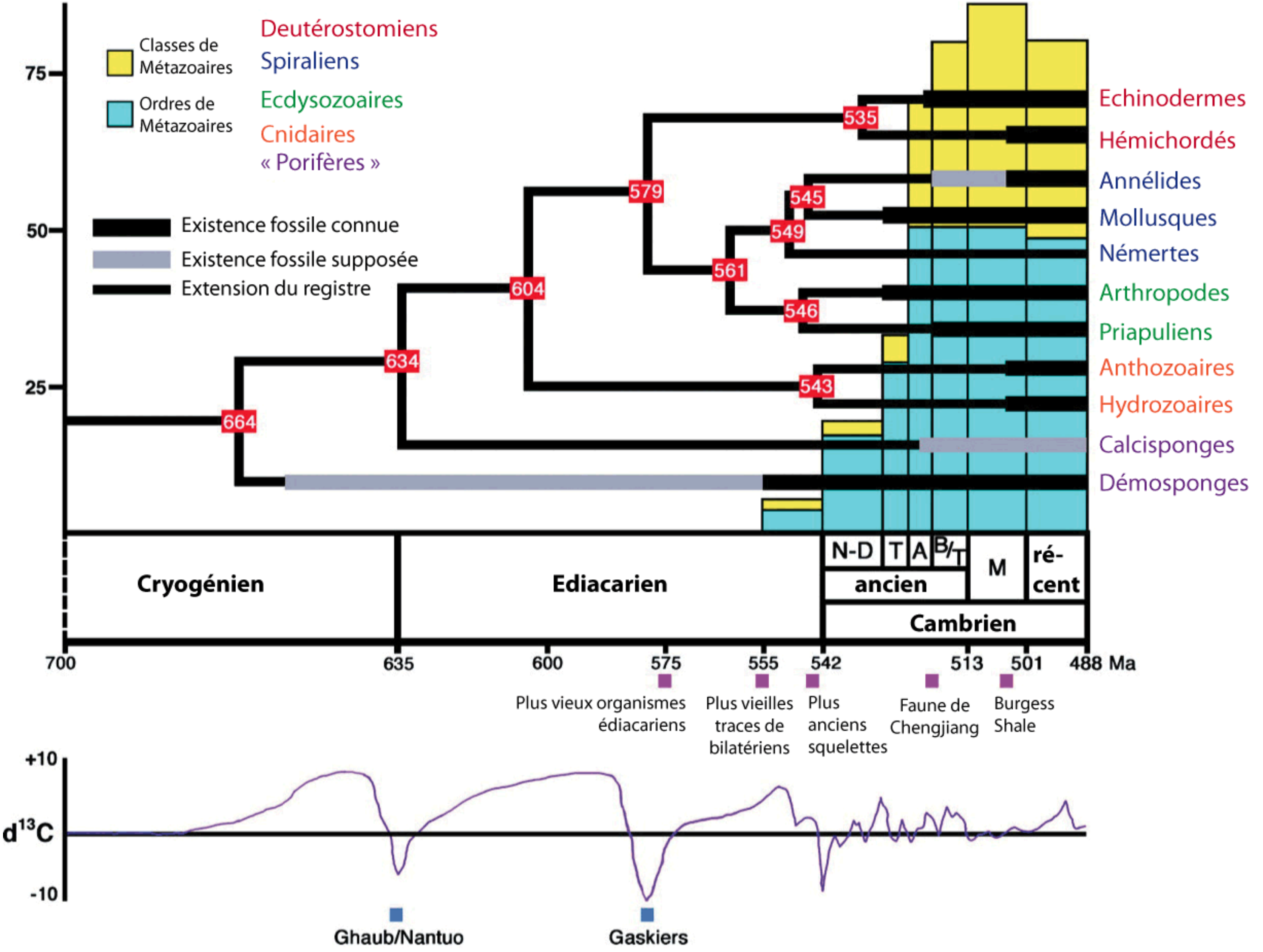
Increase of Sea level

New ecological niches

Increase of flux of nutriments in the oceans

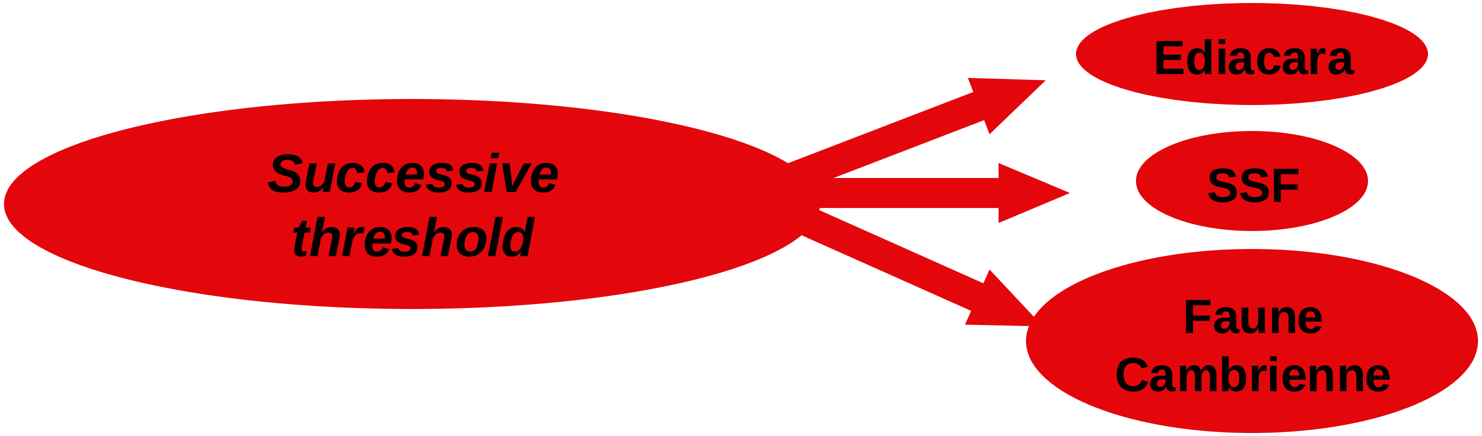
End of Snowball : due to a massive release of CO2 ? (Pierrehumbert, Nature, 2004)

Climatic causes



Oxygen-related causes

Old hypothesis of Towe (1970) : O_2 & collagen



Successive threshold

Ediacara

SSF

Faune Cambrienne

Raff & Raff. Nature, 228 (1970)

Kaufman & Knoll. Precamb. Res., 73 (1995)

Canfield. Nature, 396 (1998)

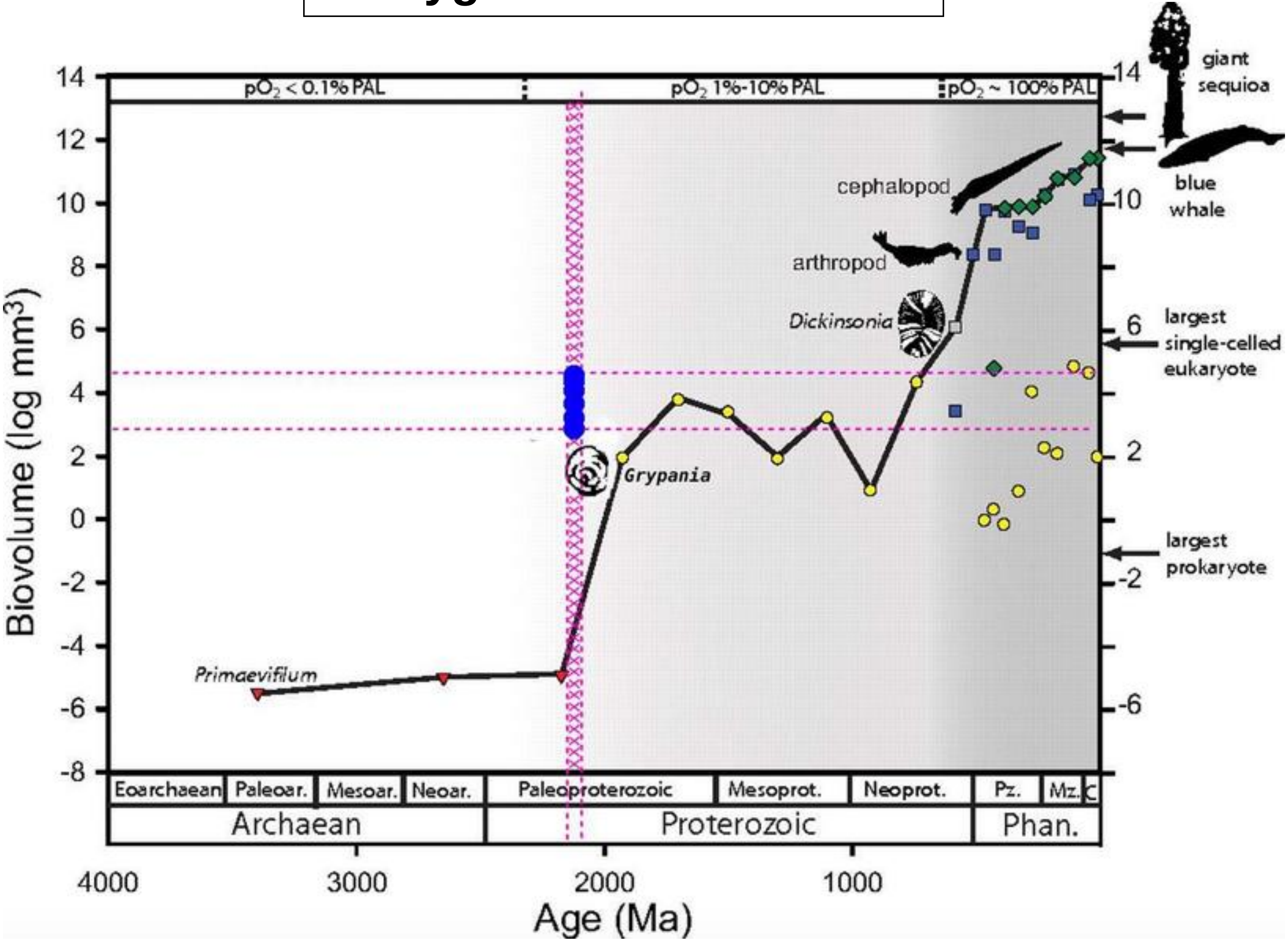
Shield. Terra Nova, 17 (2005)

Raymond & Segre. Science, 311 (2006)

Fike et al. Nature, 444 (2006)

Canfield et al. Science, 315 (2007)
Deep anoxic ocean until Gaskiers episode, then oxic ocean

Oxygen-related causes



Causes related to the chemistry of oceans

Hypercalcified bacteria of the Neoproterozoic, in Spitzberg:
Knoll et al. Palaios, 8 (1993)

NEOPROTEROZOIC OCEANS
SUPERSATURATED WITH RESPECT TO $CaCO_3$

Without growth inhibitors, spontaneous precipitation

Fraiser et al. Palaios, 18 (2003)

Brennan et al. Geology, 32 (2004)

Corsetti & Grotzinger, Palaios, 20 (2005)

Kovalevych et al. Prec. Res., 144 (2005)

Decrease of the Mg^{2+}/Ca^{2+} ratio
Riding. Nature, 299 (1982)

Hardie, Geology, 31 (2003)

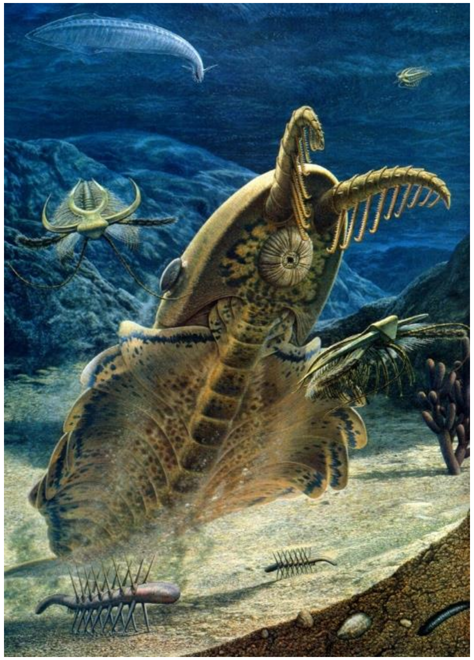
Stanley, P^3, 232 (2006)

Porter, Science, 316 (2007)

Ecological causes

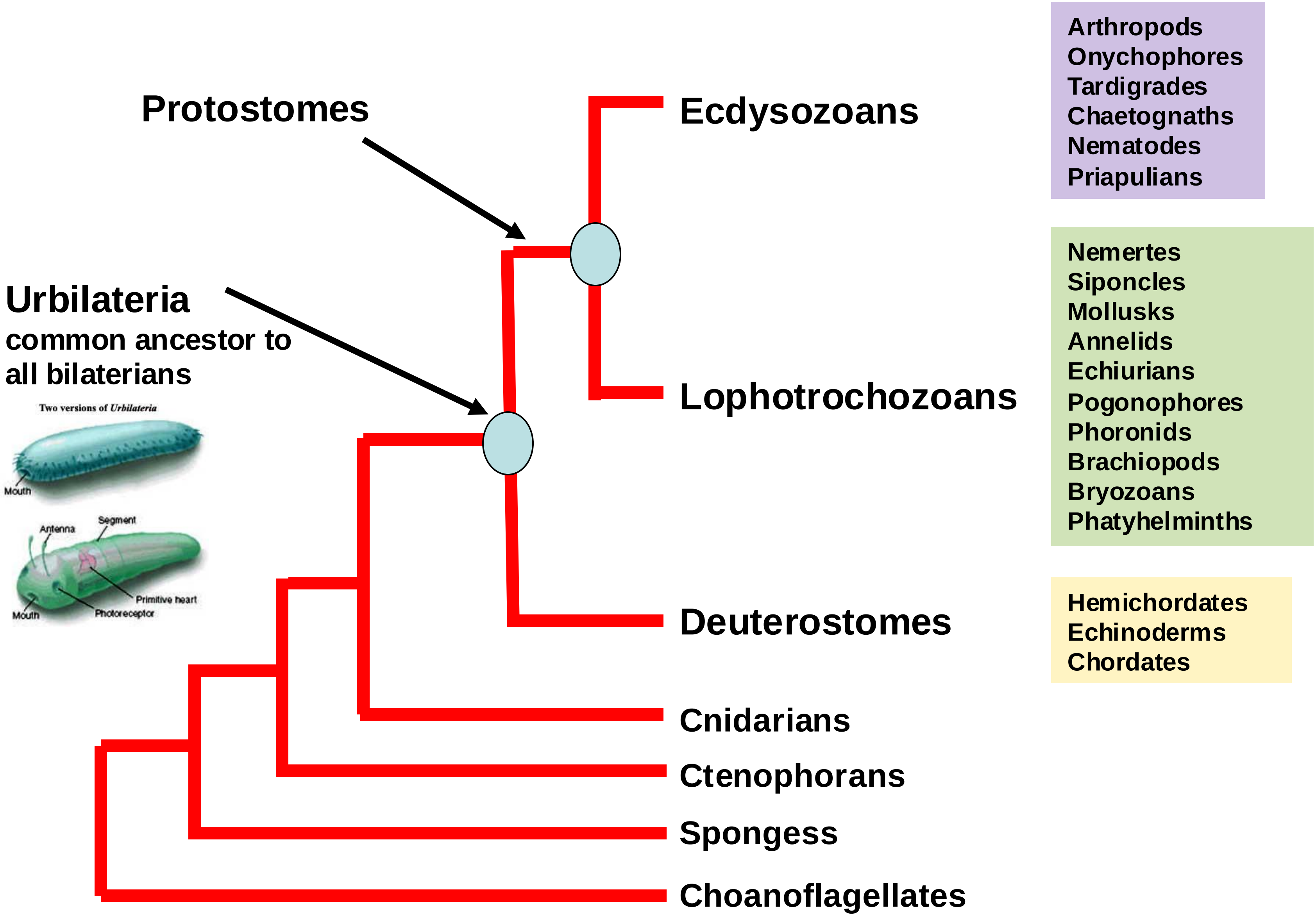
Appearance of predation

Traces of predation on trilobites: Nedin, Geology, 27 (1999)



***Anomalocaris*, the killer of Cambrian seas !!!**

Genetic causes: novel ‘bauplan’



Protostomes

Urbilateria
common ancestor to
all bilaterians

Ecdysozoans

Lophotrochozoans

Deuterostomes

Cnidarians

Ctenophorans

Spongess

Choanoflagellates

Arthropods
Onychophores
Tardigrades
Chaetognaths
Nematodes
Priapulians

Nemertes
Siponcles
Mollusks
Annelids
Echiurians
Pogonophores
Phoronids
Brachiopods
Bryozoans
Phatyhelminths

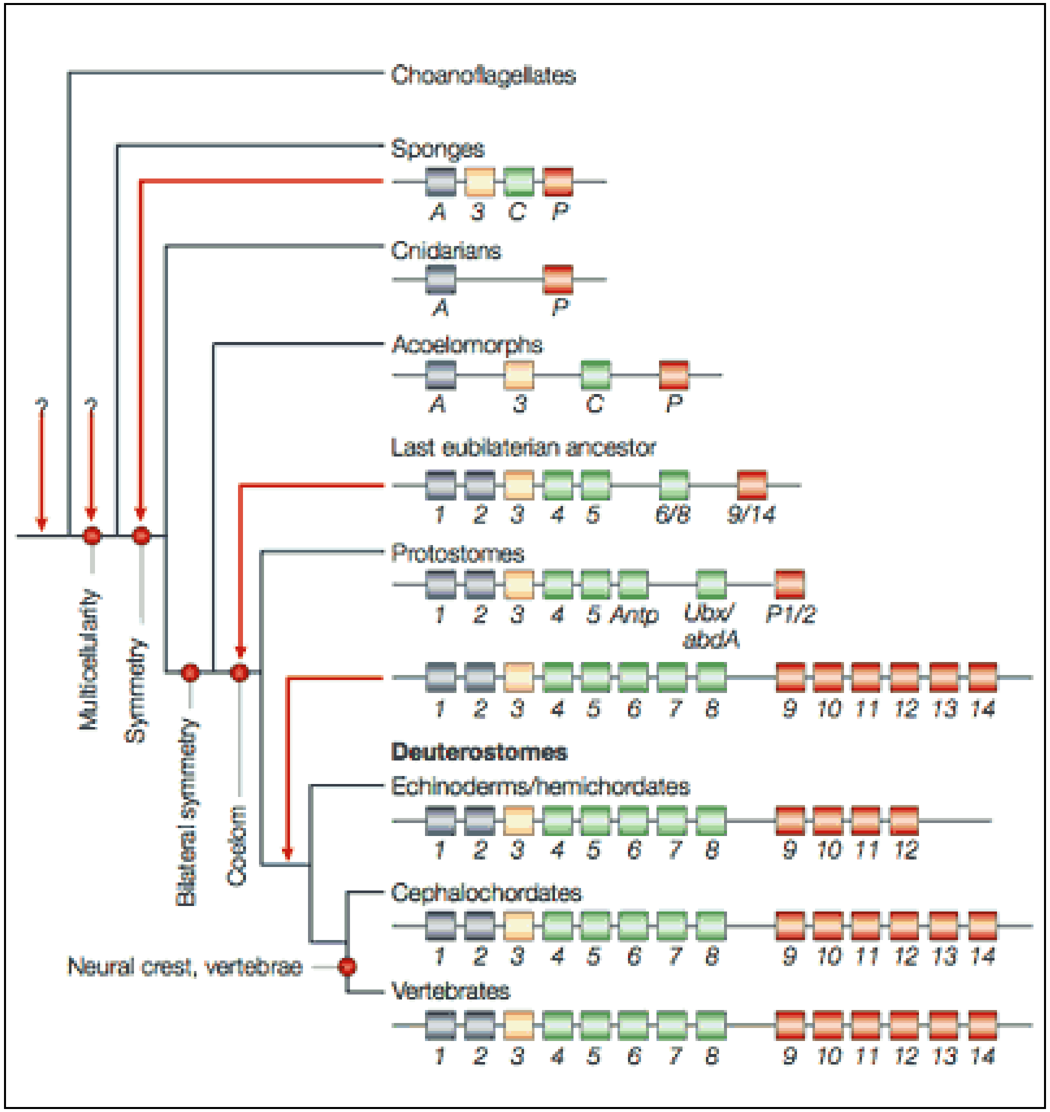
Hemichordates
Echinoderms
Chordates

Genetic causes: novel 'bauplan'

Role of Hox genes

- **Hox genes code for transcription factors**
- **They control the expression of other genes**
- **Development genes, structuring the antero-posterior axis**

- **Grouped in clusters (colinearity)**
- **Evolved by gene duplication**



Garcia-Fernandez, Nature Reviews Genetics, *6*, 881-892 (2005)

Anti-calcification:

Marin et al. PNAS, 96 (1996)

Supersaturated ocean with respect to $CaCO_3$

Requirement of inhibitors to avoid overgrowth of crystals

Anticalcifying mucus may have played this role

At P/C transition, mucus inhibitors would have played another function: to keep crystallization in check

Ediacara-type fauna

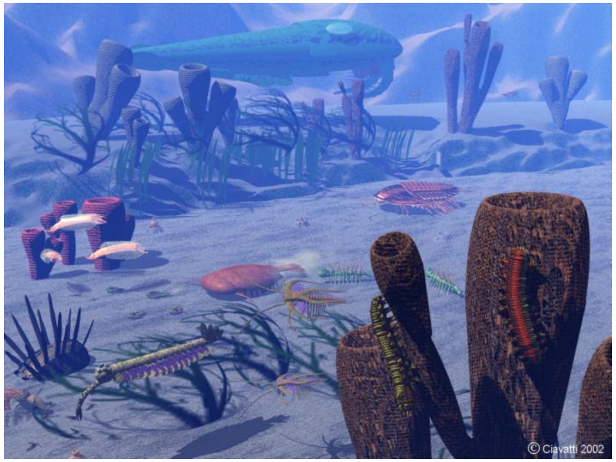
Appearance of biologically-controlled mineralization: what it implies

Proterozoic ecosystem

P.A. Bourque, 1995

Soft-bodied fauna

Cambrian ‘modern’ ecosystem’



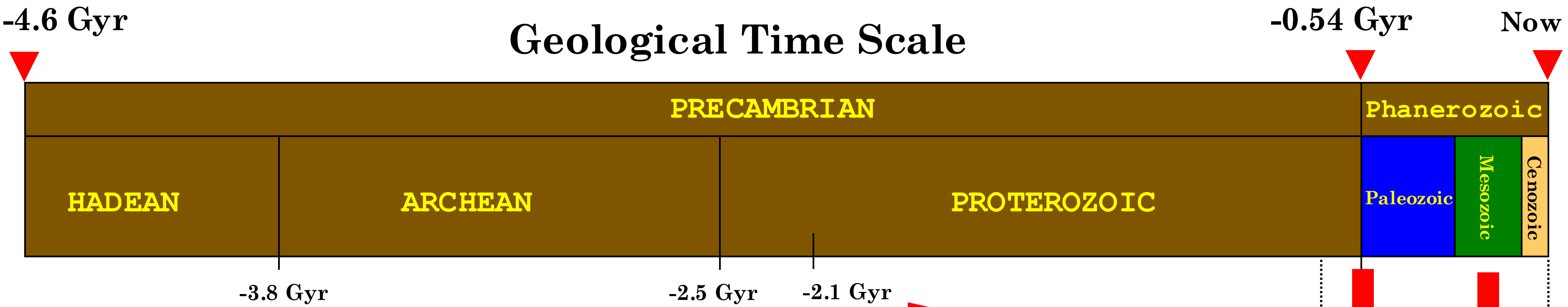
Mineralized fauna

Emergent properties

Controlled biomineralization → HIERARCHY

Controlled biomineralization → SPECIALIZED ORGANIC MATRIX

Macro-evolution of $CaCO_3$-based biomineralization across geological times



Prebiotic evolution

Earliest forms of life

1st eukaryotes (??)

Gabon Fauna
Oldest metazoans ??

'Cambrian explosion'

Biologically-induced mineralizations: STROMATOLITES

http://www.fossilmuseum.net/Fossil_Galleries/Stromatolites/Cochabamba/Stromatolite123.htm

Cloudina

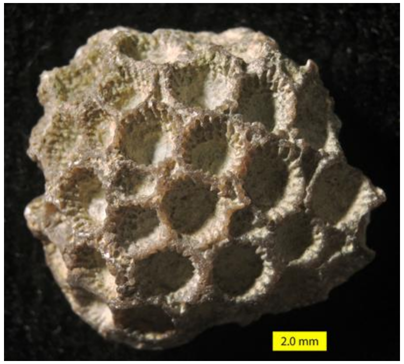
Accession of the biologically-controlled mineralizations

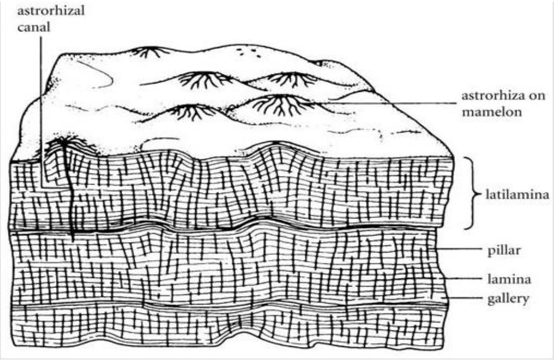
During the Paleozoic times

At world scale, biomineralizations dominated by reef systems in a ‘calcitic’ ocean: Paleozoic corals

-Tabulate corals
-Rugosans

-Stromatoporoids (sponge-like)



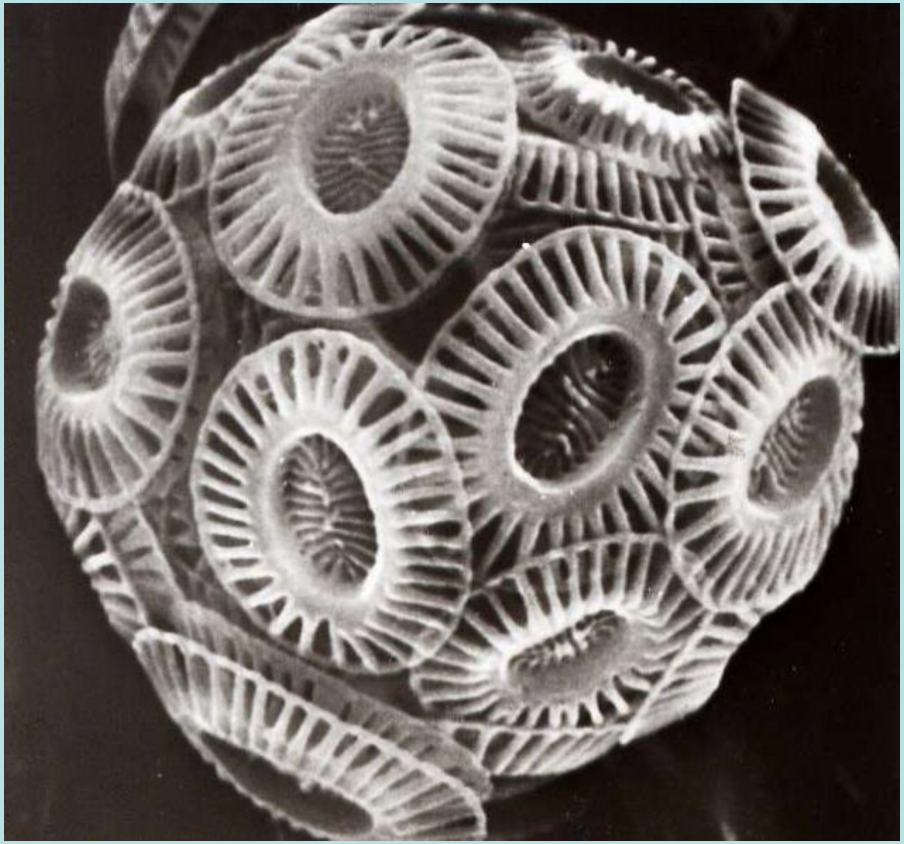


Extinction at the P/T crisis, 250 MY ago

During the Mesozoic times:

Emergence of planktonic organisms as important providers of biogenic calcium carbonate: the case of coccolithophore algae

Coccolithophore algae



Photos P. Westbroek

Photos P. Westbroek

Photos P. Westbroek

Accumulation of coccolithes: chalk cliffs

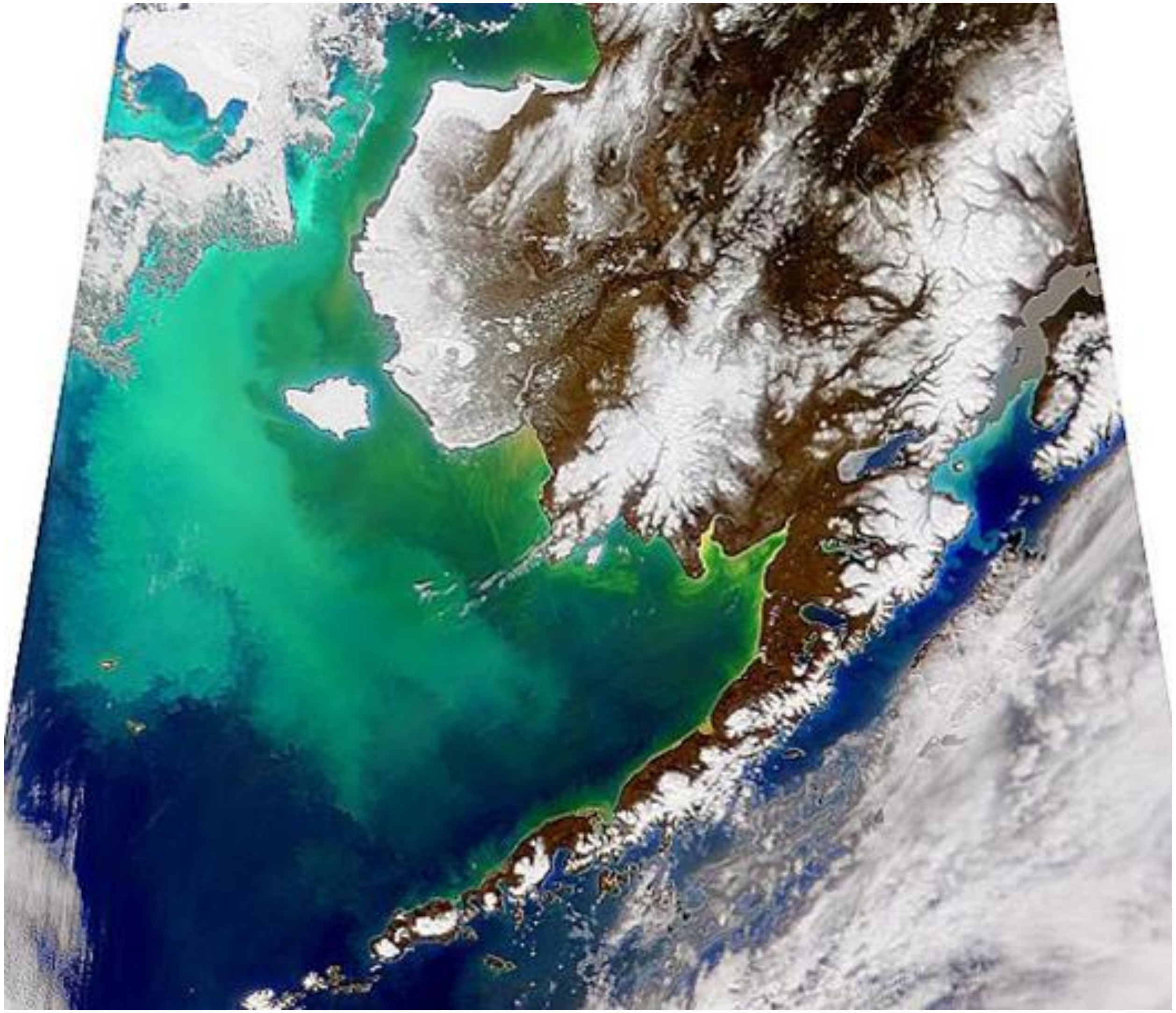
Etretat cliffs

Cretaceous period

Accumulation of coccolithes: chalk cliffs

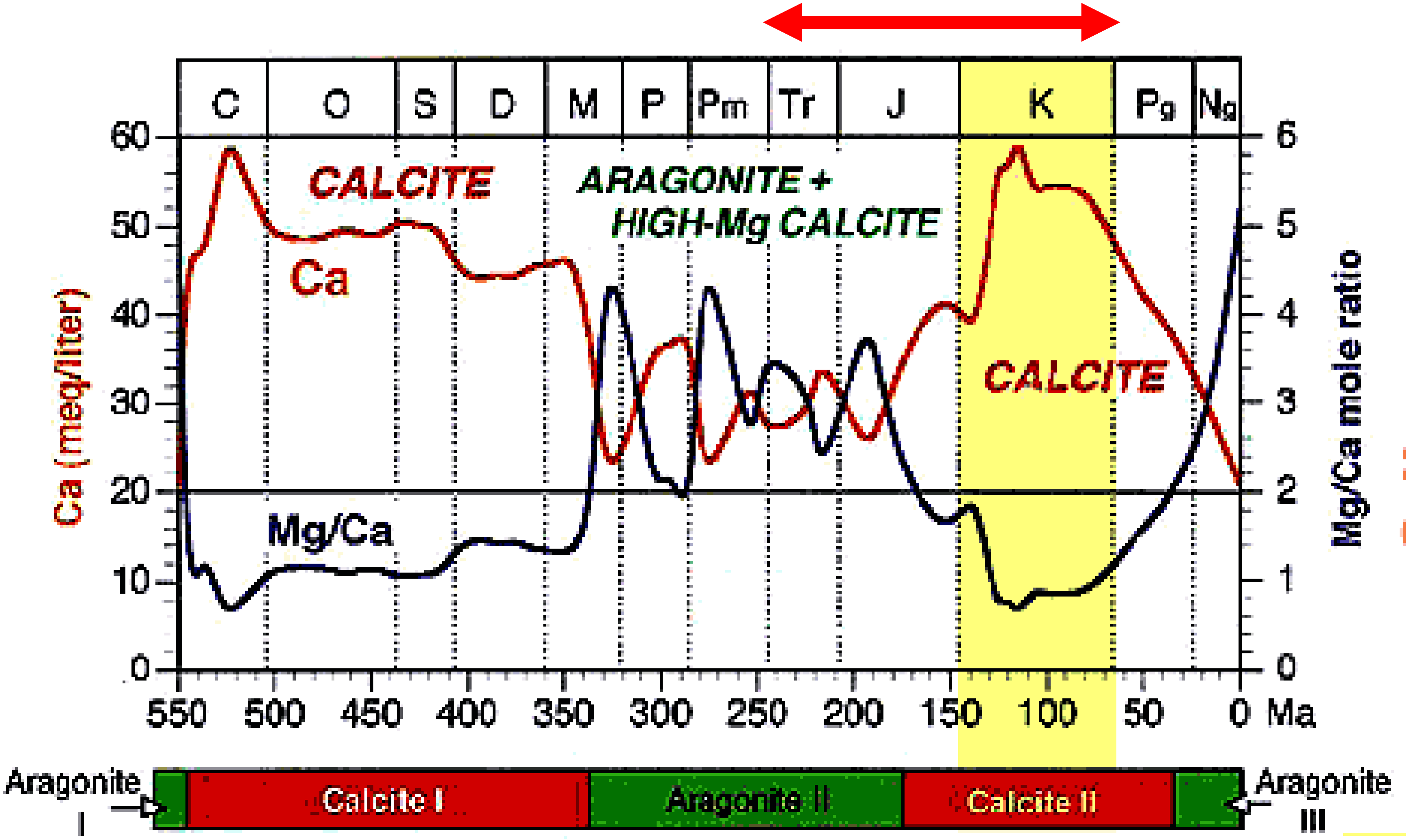
Seven Sisters, Sussex
(P. Standing, Geograph.org)

Today's bloom of coccolithophore algae



During the Mesozoic times:

Fluctuation of Mg/Ca ratio: High => Aragonite
Low => Calcite



During the Mesozoic times:

While calcifying planktonic organisms emerged, reef systems continued to develop during the Trias, the Jurassic and the Lower Cretaceous: from 250 to 120 MY. They were dominated by Scleractinian corals (like today's corals)

**Yonne Valley,
Upper Jurassic**

In the Upper Cretaceous, reef systems were dominated by rudists, a clade of highly specialized bivalves

Photo Schumann & Steuber

© 2007 - S Mohd NurAhmed

The take-away message

In brief:

Biologically-induced calcifications:
STROMATOLITES: Archean to Proterozoic

I. Biologically-controlled mineralization

- ***Cambrian Explosion: 544 My***
  - ***Benthic fauna***
  - ***Neritic domain***

- ***Mesozoic revolution (Jurassic)***
  - ***Takeover by planktonic protists***
  - ***Open oceanic domain***