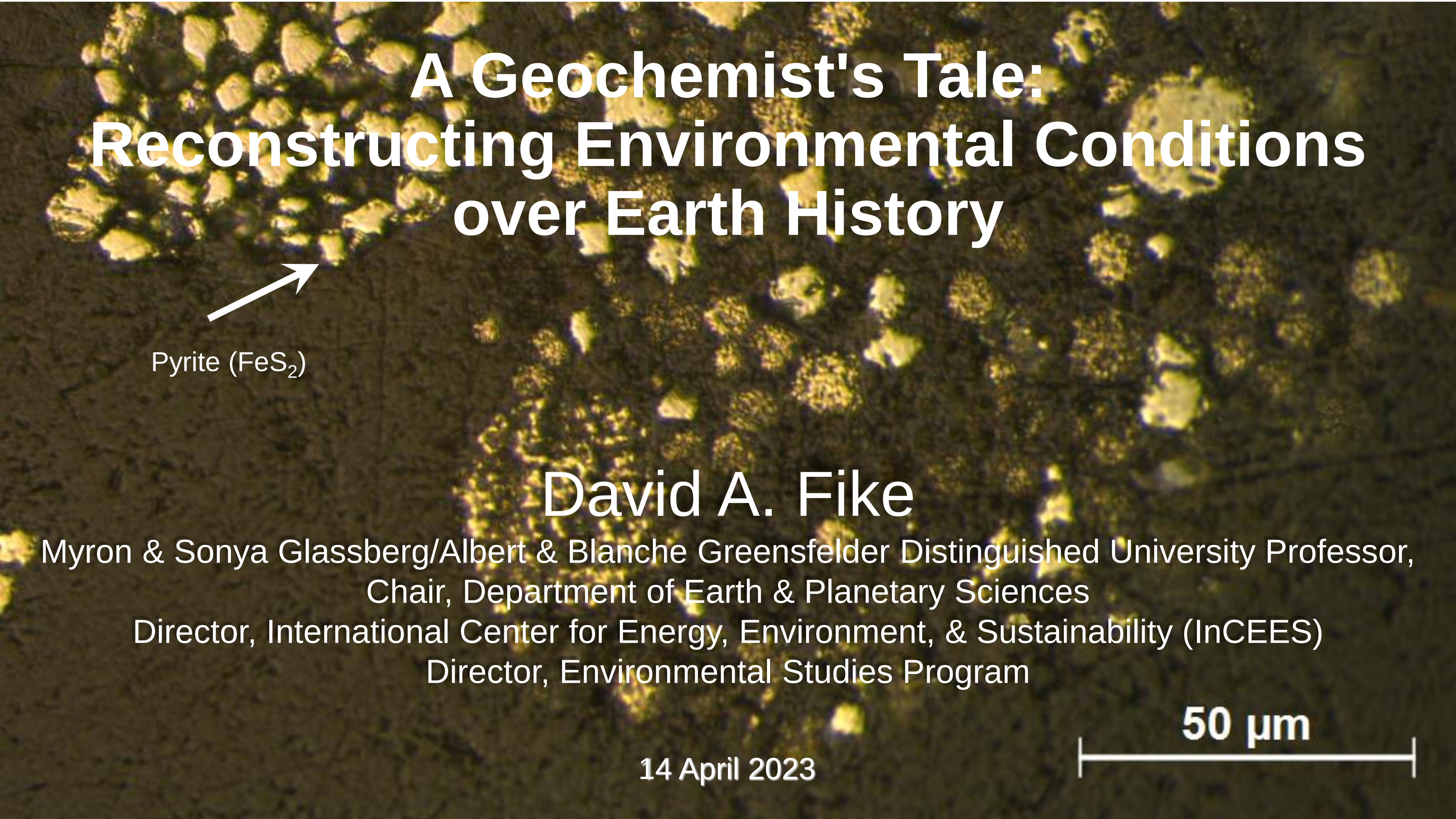
A Geochemist's Tale: Reconstructing Environmental Conditions over Earth History



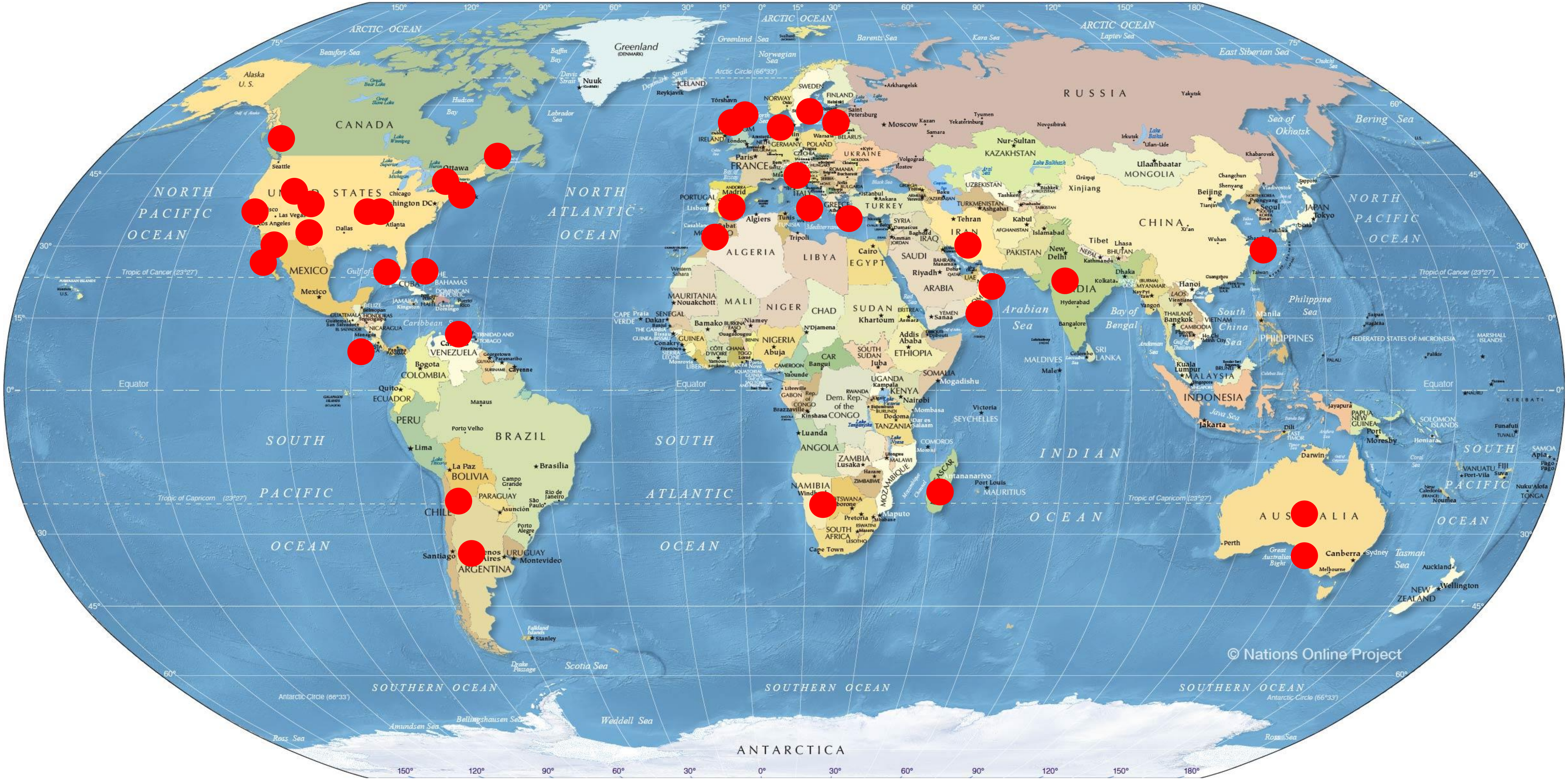
David A. Fike

Myron & Sonya Glassberg/Albert & Blanche Greensfelder Distinguished University Professor,
Chair, Department of Earth & Planetary Sciences
Director, International Center for Energy, Environment, & Sustainability (InCEES)
Director, Environmental Studies Program

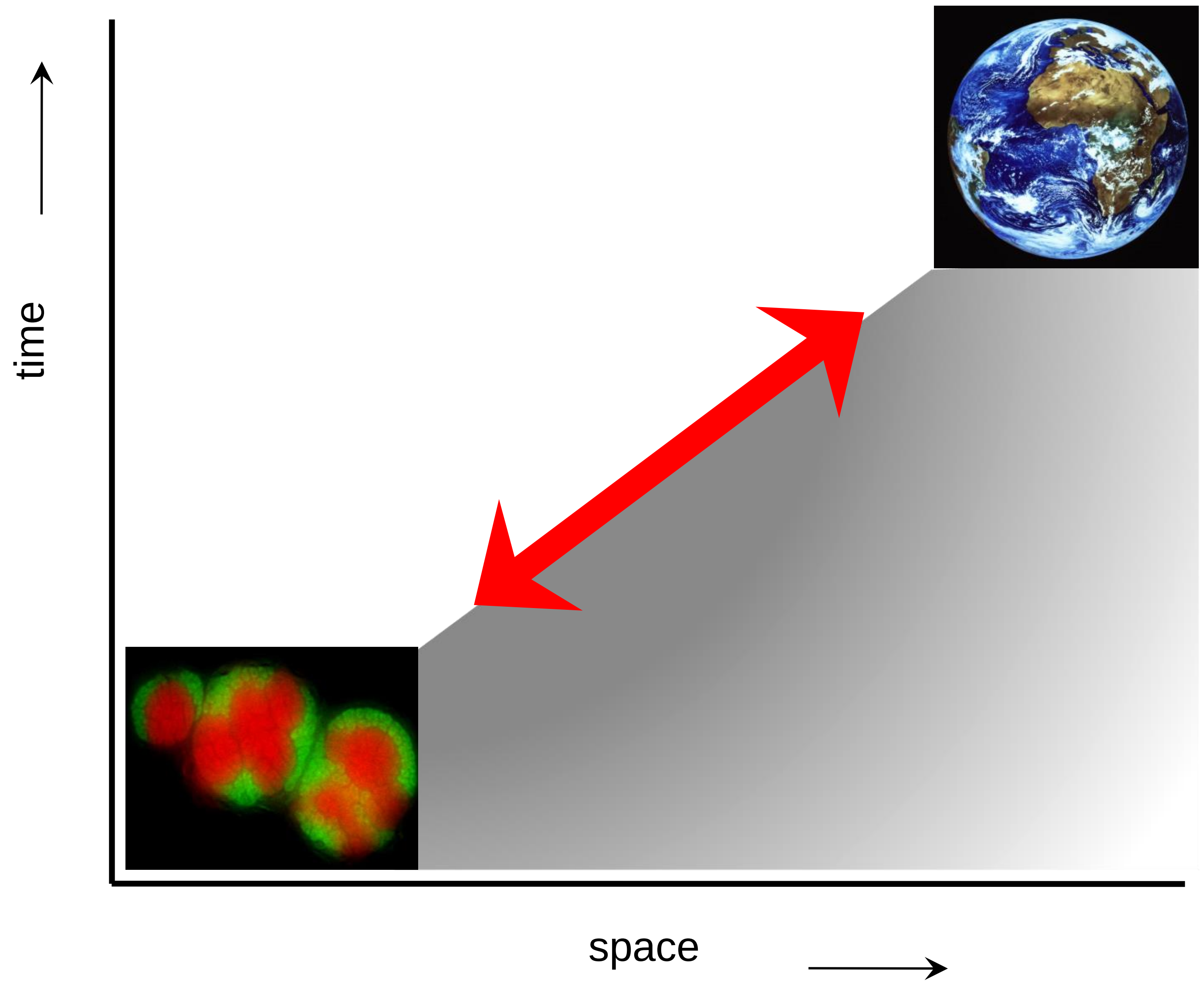
14 April 2023


Lab Group 2022

Exploring the World’s Modern & Ancient Environments



Geobiology



Geobiology

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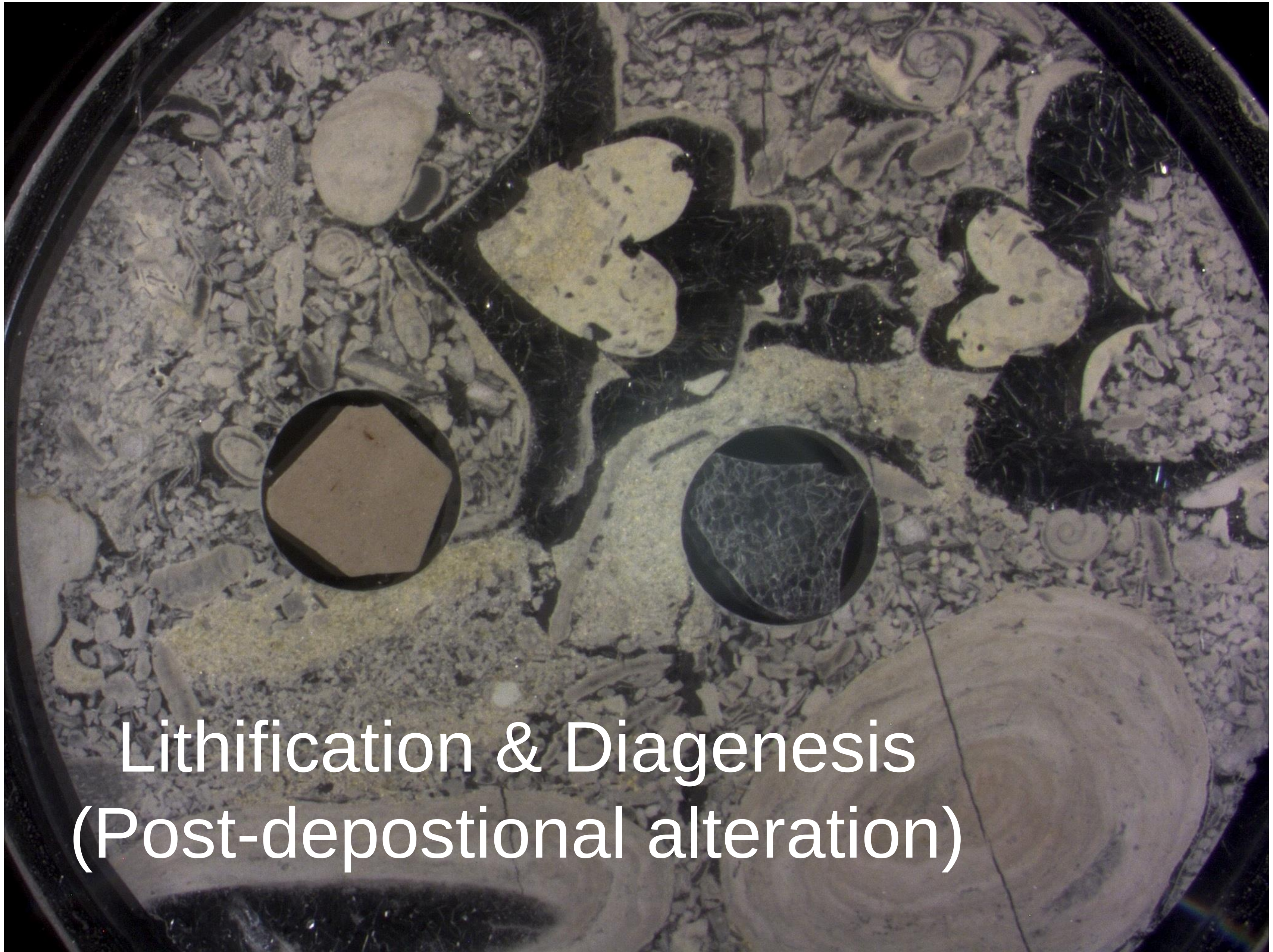
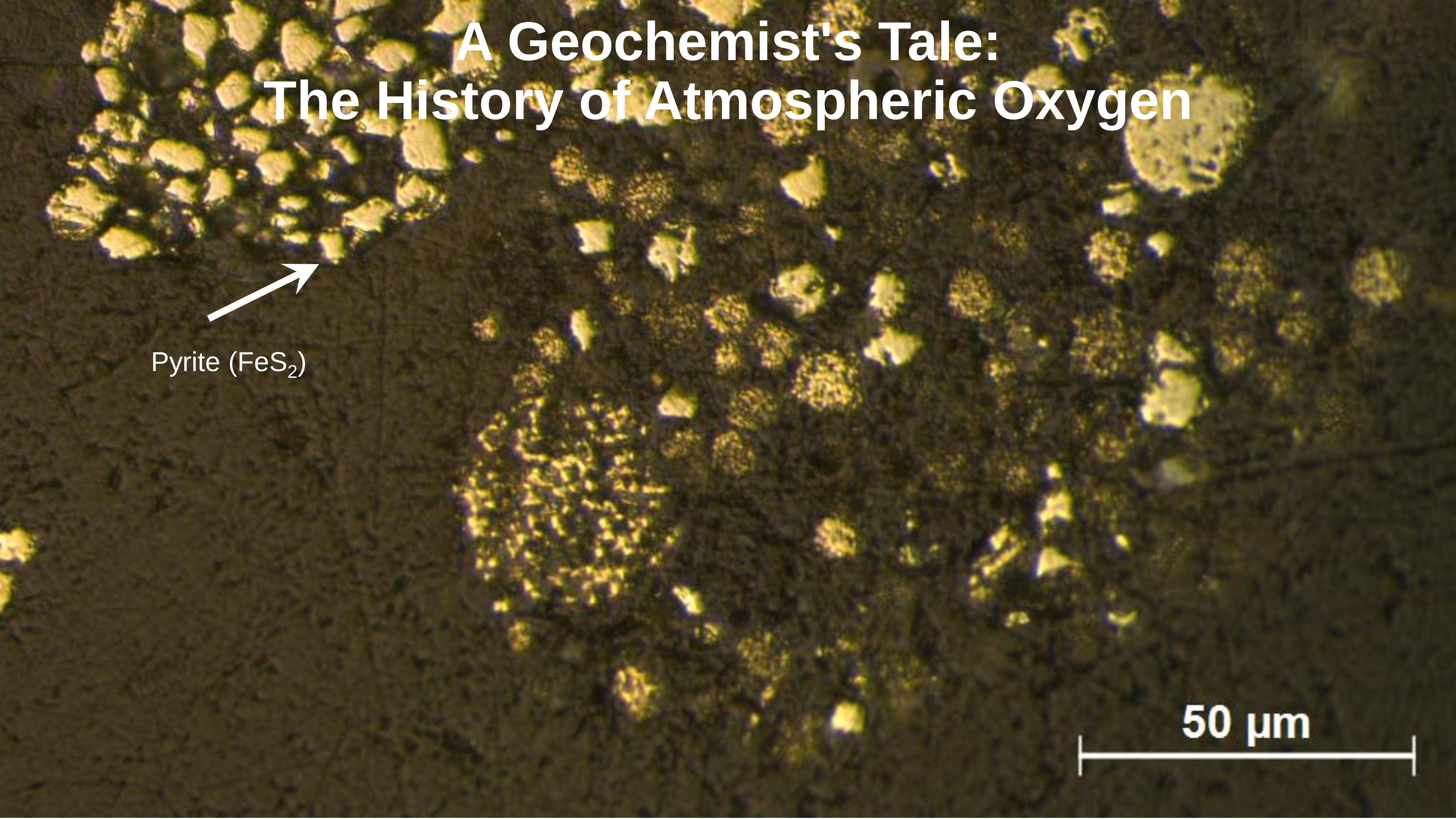


A Geochemist's Tale: The History of Atmospheric Oxygen



Air

- What is it?
- How did it get there?

Air

- N_2: 78%
- O_2: 21%
- Ar: 0.9%
- CO_2: 0.04% = 400 ppmv = parts per million (by volume)
- CH_4: 1.866 ppmv = 1866 ppbv = parts per billion (by volume)

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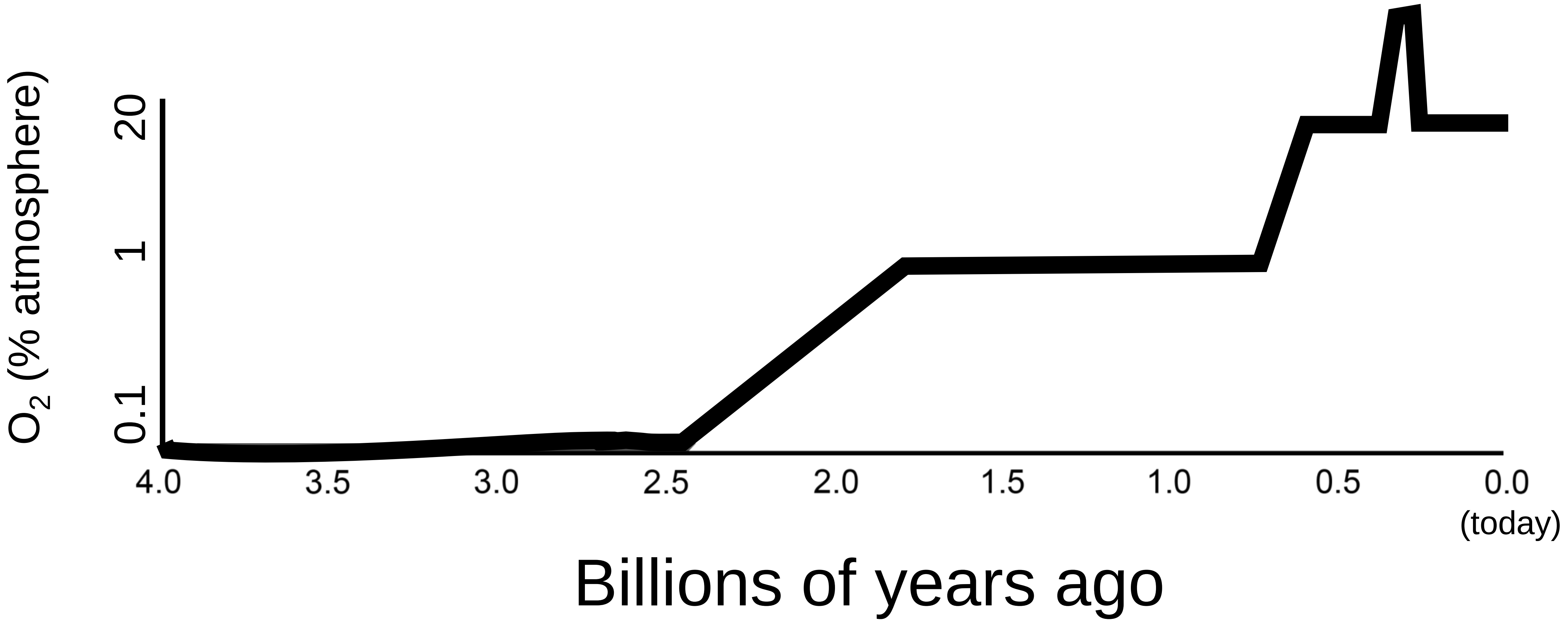
The History of Oxygen in the Atmosphere



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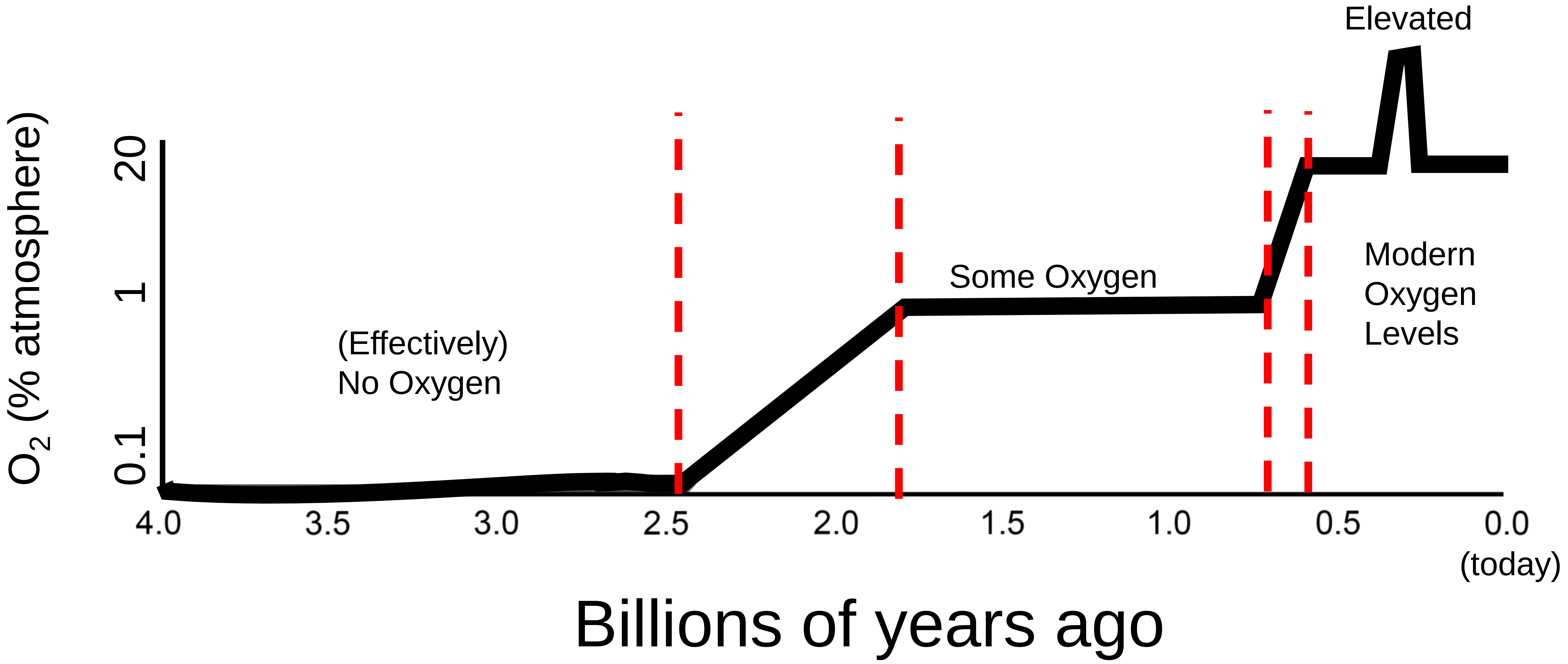
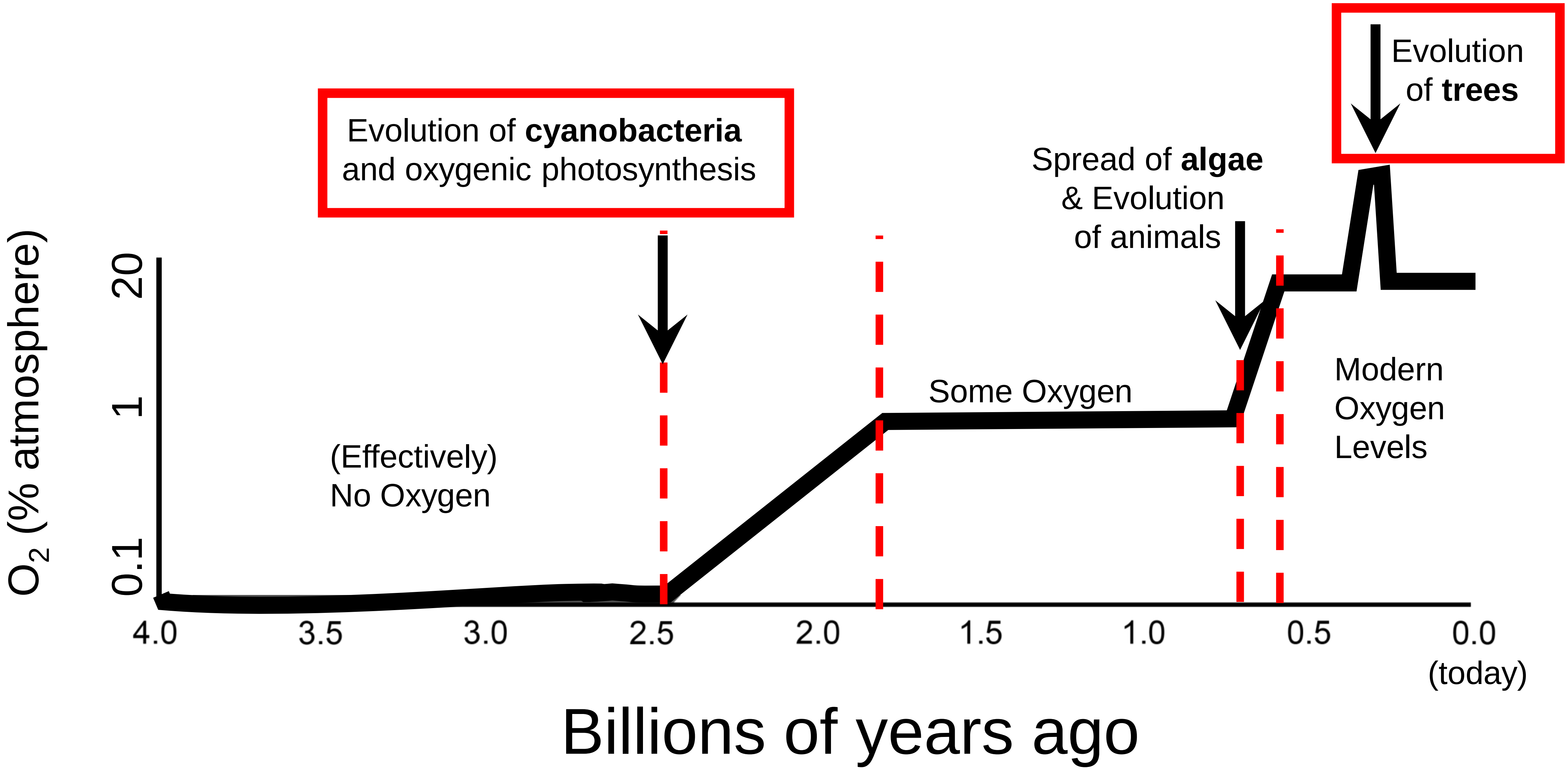
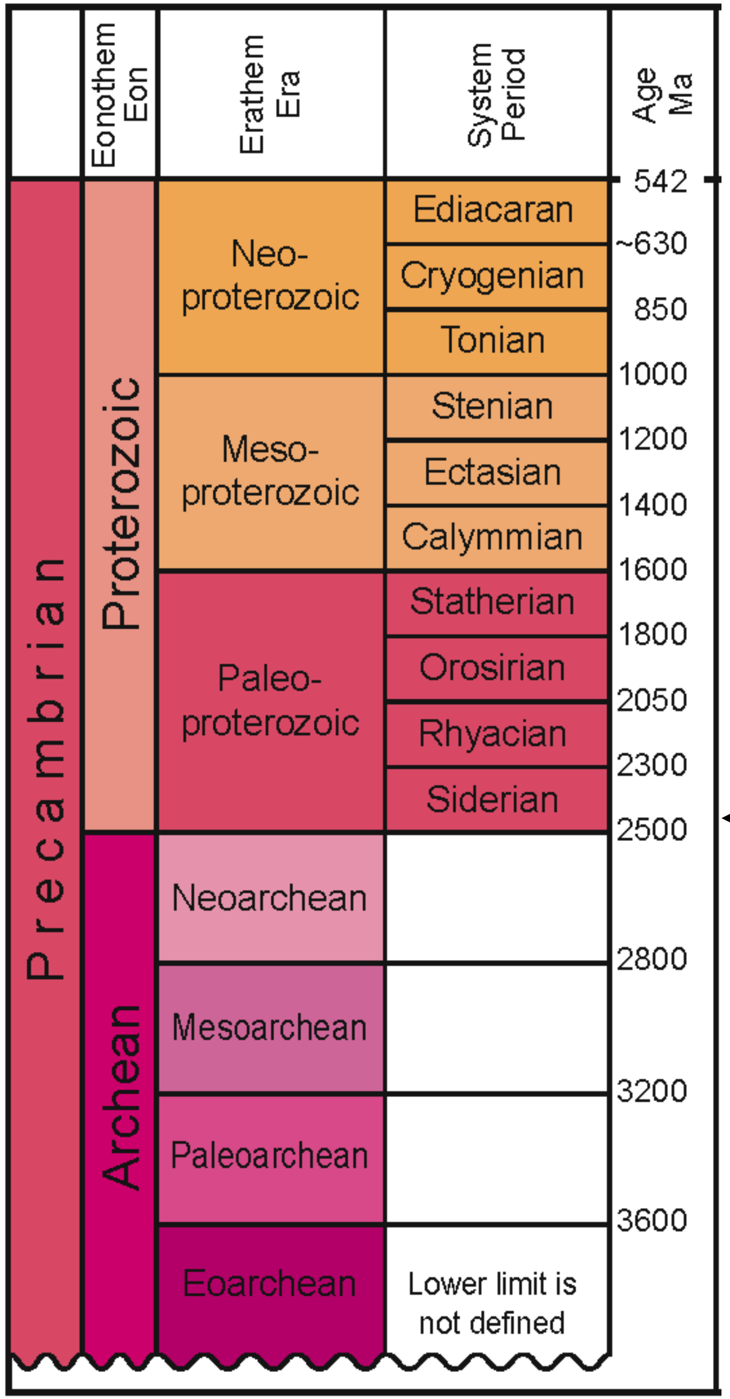


The History of Oxygen in the Atmosphere

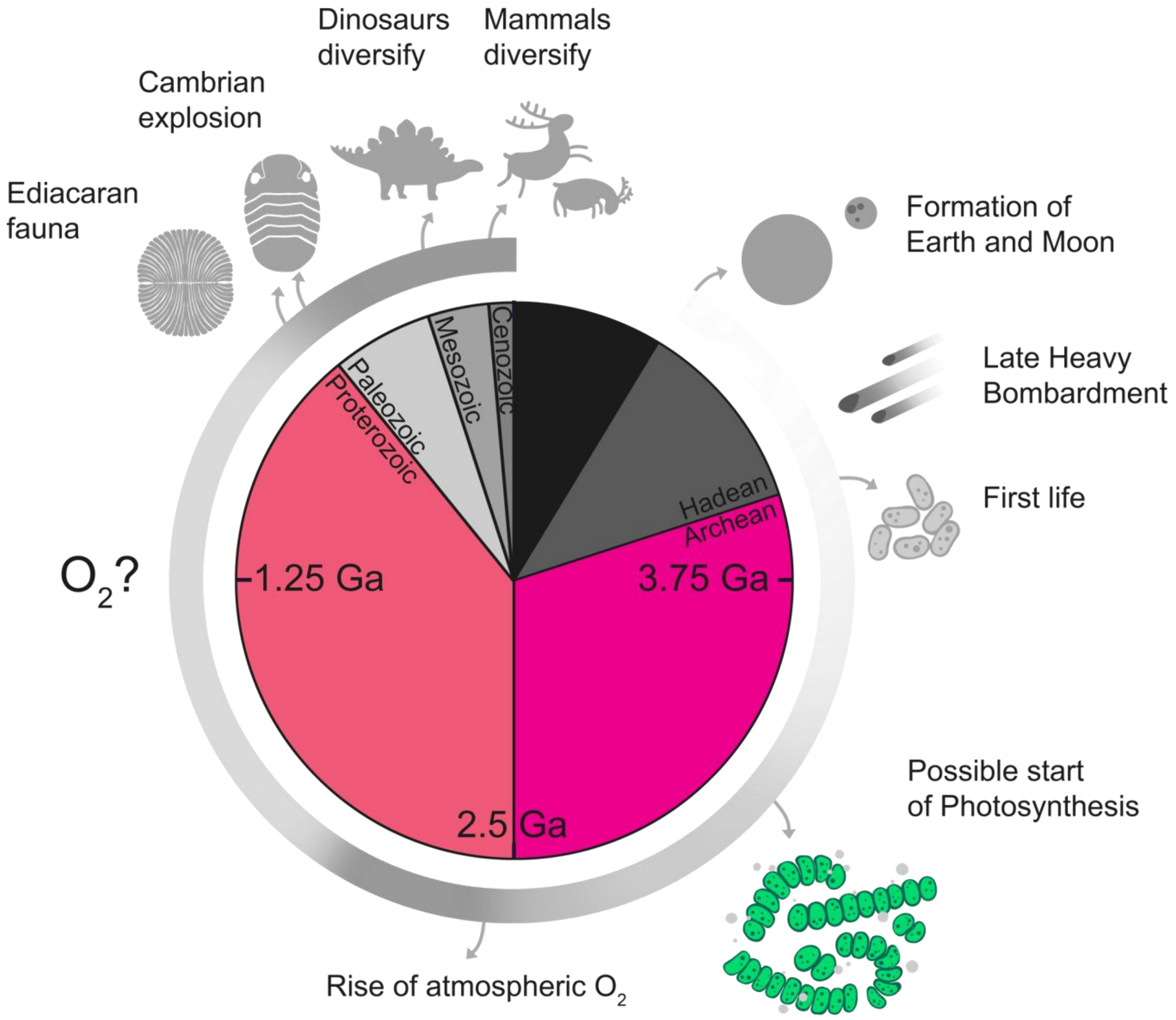


Changes in oxygen levels associated with major geological transitions

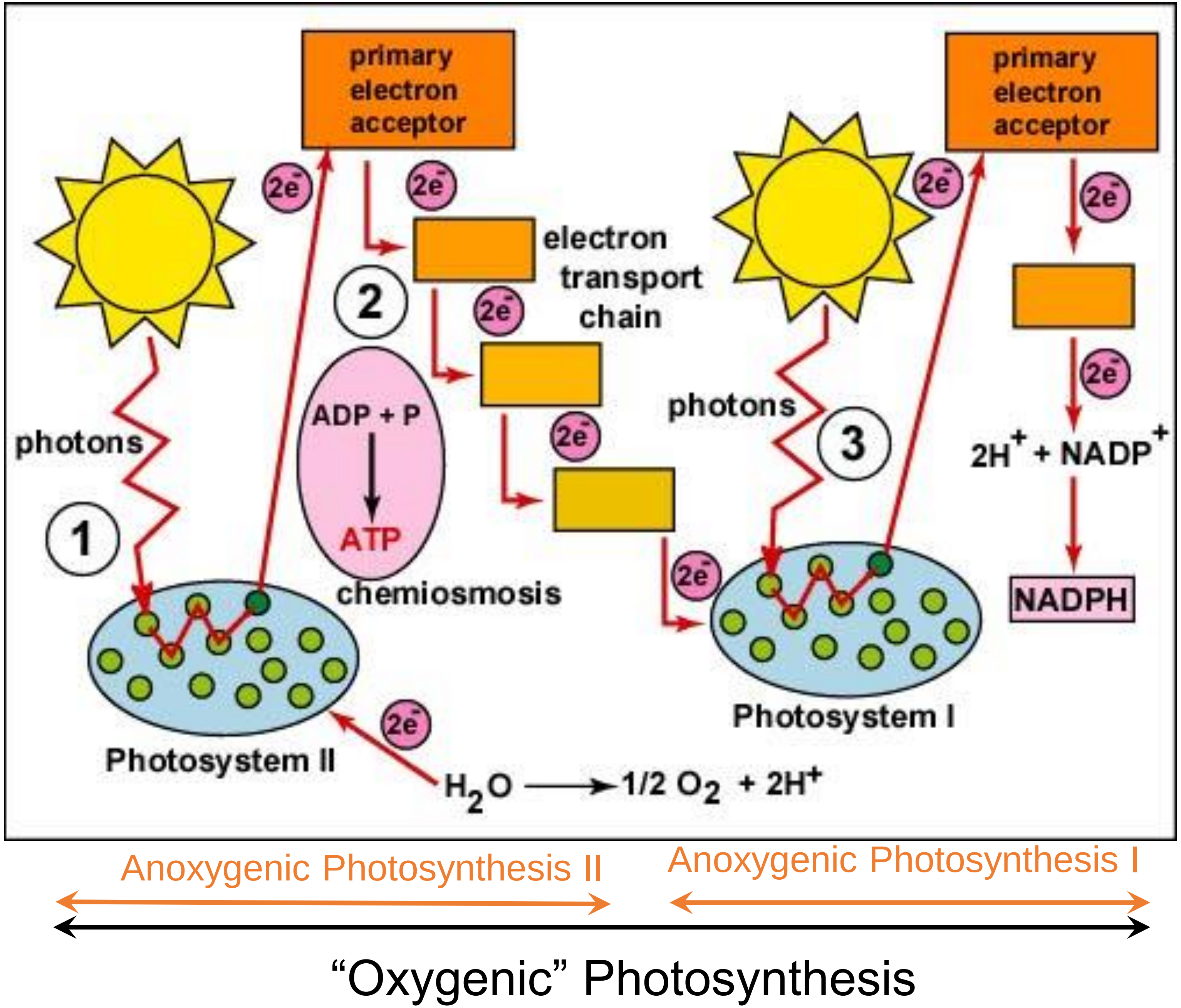


Second rise of oxygen

Initial rise of oxygen

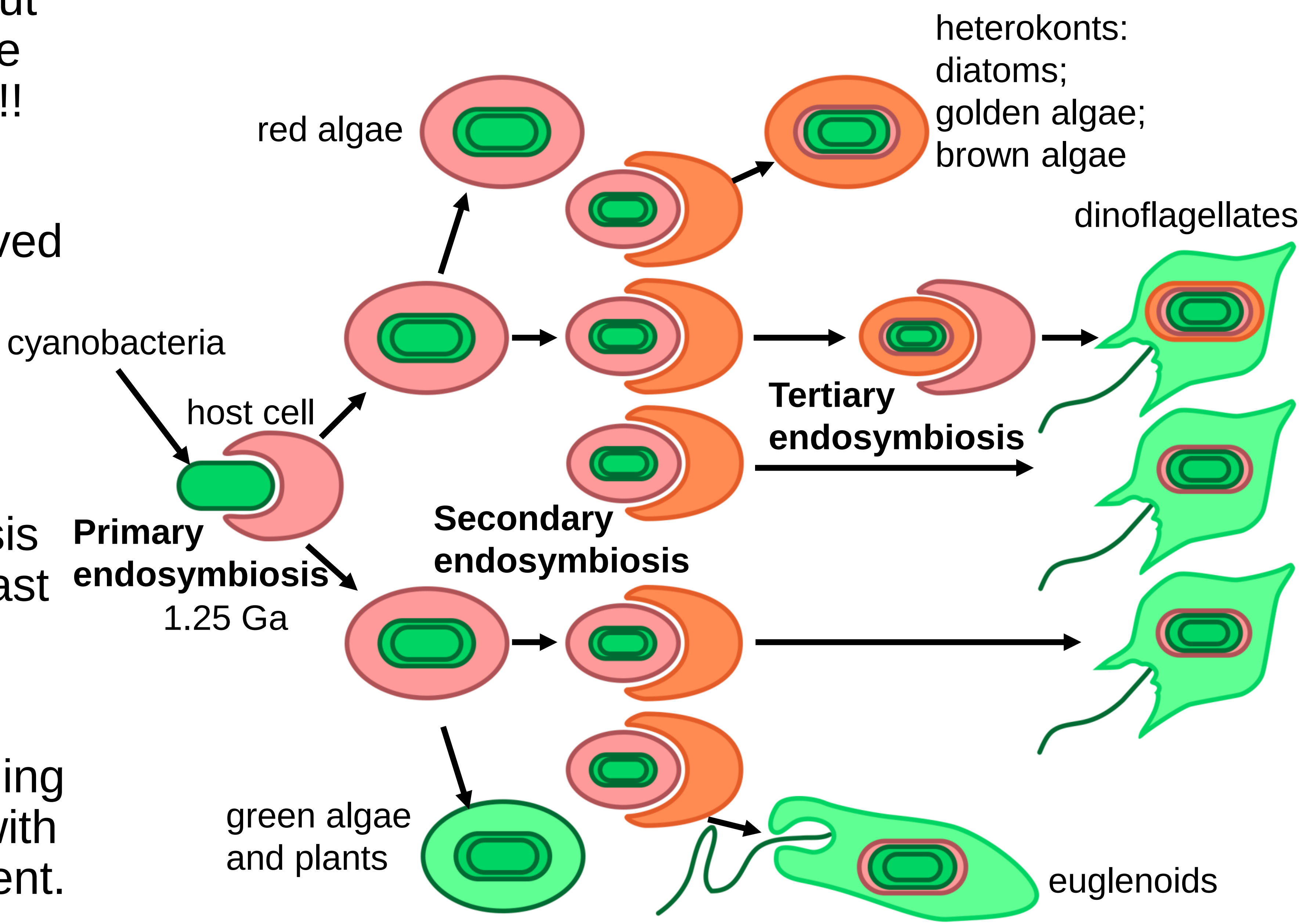


Oyxgenic Photosynthesis: How Cyanobacteria Make O_2



Importance of cyanobacteria

- Cyanobacteria figured out how to make oxygen; the only ones ever to do so!!!
- All chloroplasts are derived from cyanobacteria
- Multiple sequential episodes of primary and secondary endosymbiosis account for the chloroplast diversity we see today.
- The number of surrounding membranes increases with each endosymbiosis event.



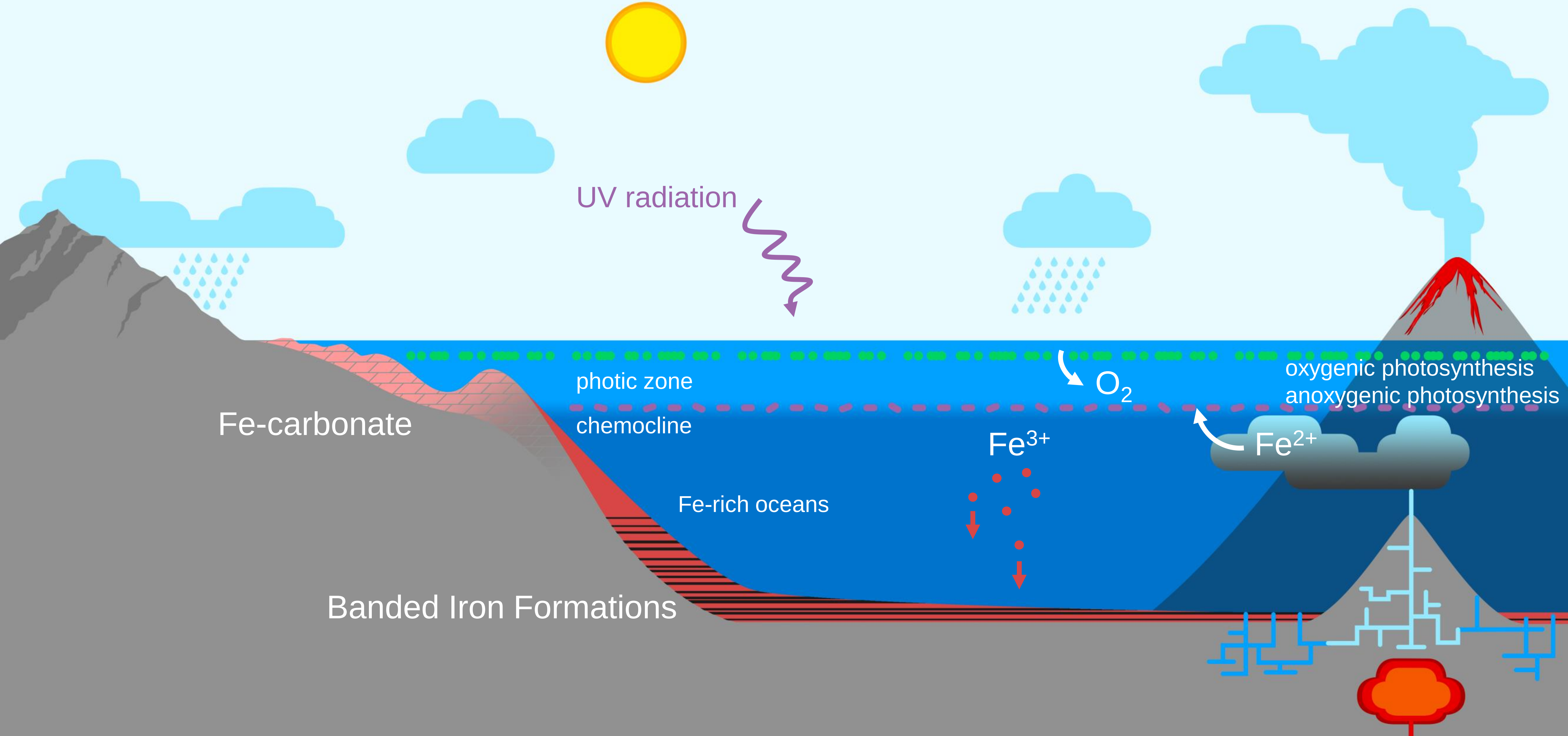
Evidence for rise of O_2 from the rock record

Red Beds – hematite coated detrital sediments

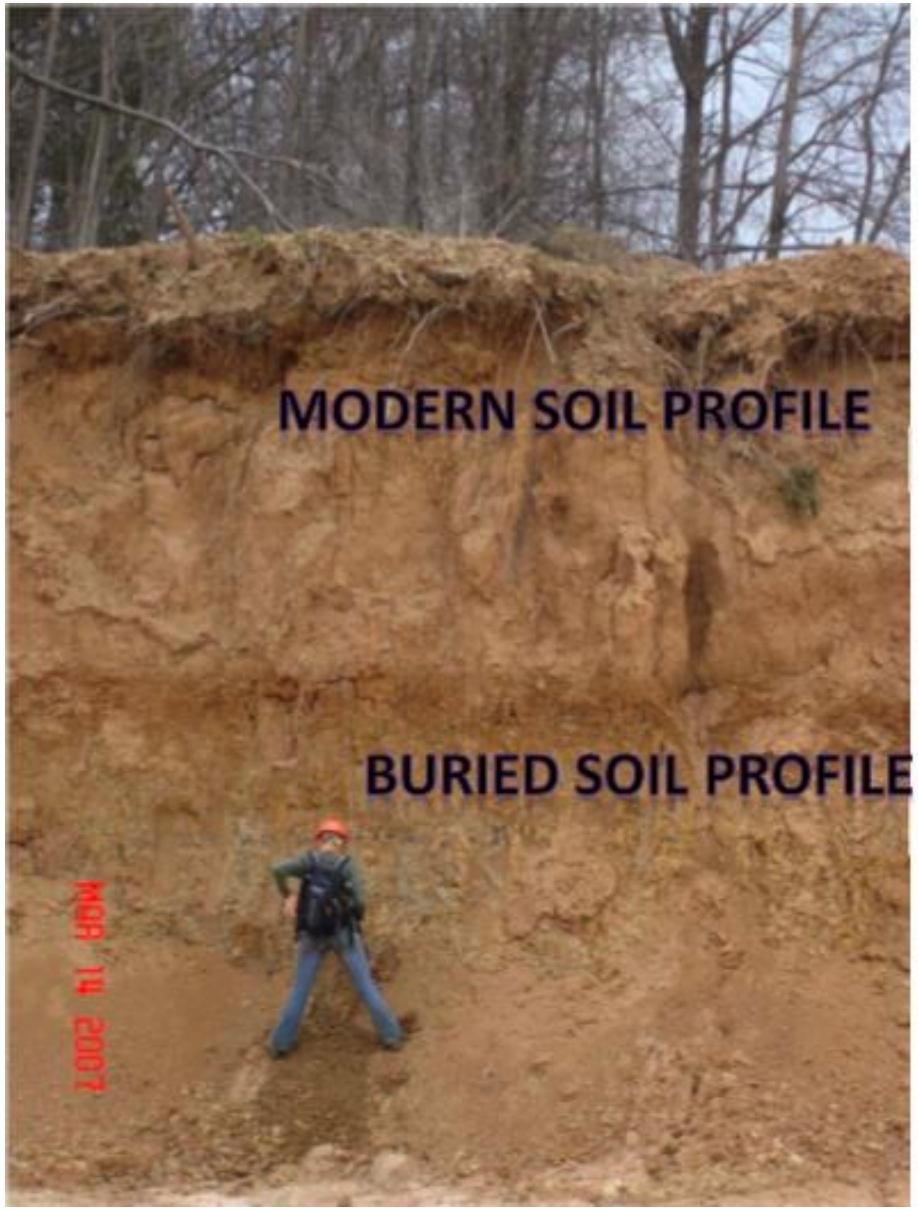
2.0 Ga red beds at Lake Segozero, Russian Karelia

Banded Iron Formation

Formation of Iron Formations

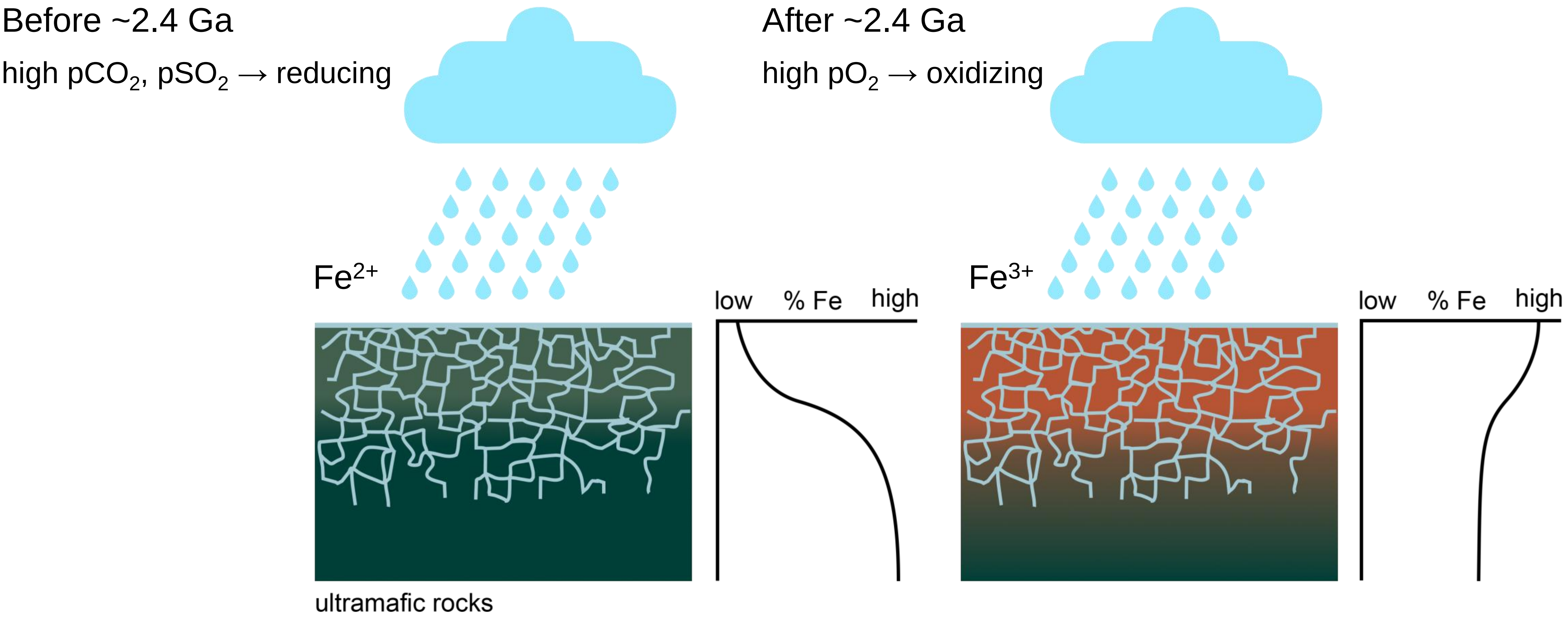


Paleosols: Ancient Soil Horizons



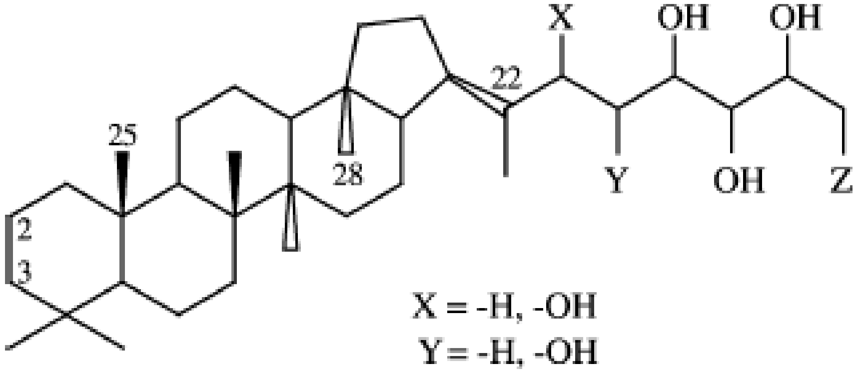
Paleosols – indicators of weathering regimes

- Ancient soil horizon
- Immobile elements (Al, Ti, Zr) and mobile elements (Ca, Mg, Na, K).
- Redox sensitive elements (Fe, Mn).



Organic biomarkers relevant for pO_2

Hopanes (cyanobacteria)

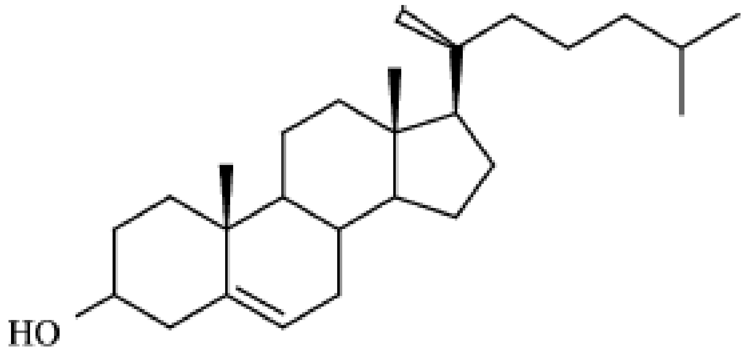


X = -H, -OH
Y = -H, -OH
Z = -OH, various -OR, and -NHR substituents

(56) Bacteriohopanepolyols (BHP)

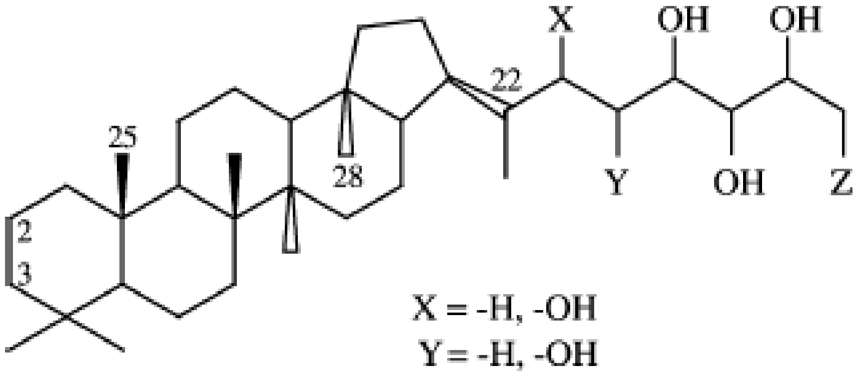
Organic biomarkers relevant for pO_2

Steranes (eukaryotes)



(65) Cholesterol

Hopanes (cyanobacteria)



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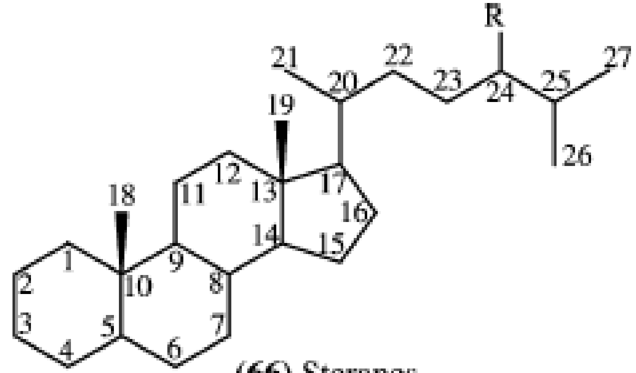
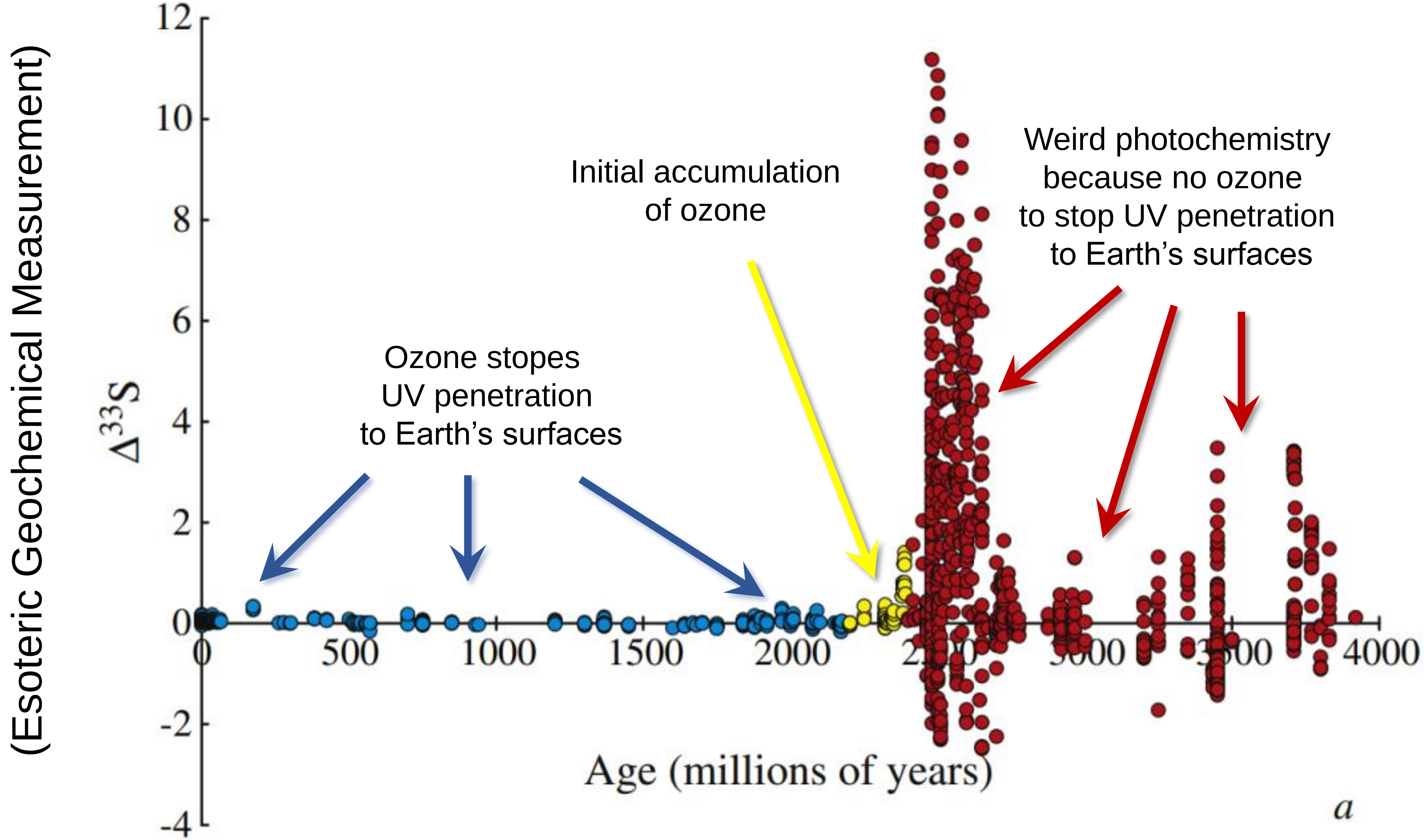


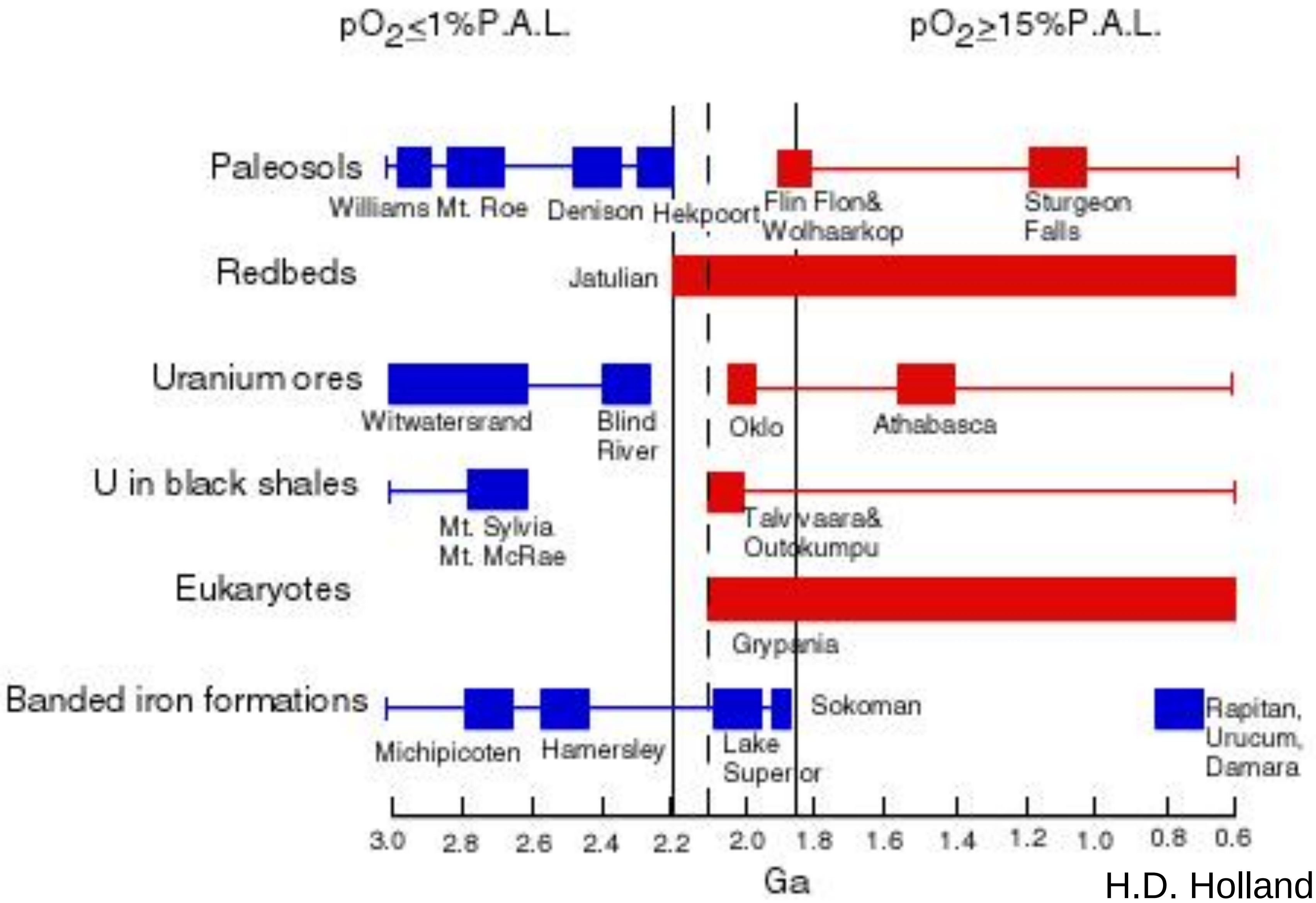
(66) Steranes

(a) R = H (cholestane); **(b)** R = Me (ergostane);
(c) R = Et (stigmastane); **(d)** R = *n*-Pr (24-*n*-proplycholestane);
(e) R = i-Pr (24-isopropylcholestane).

Sulfur-bearing Minerals Record Initial Appearance of Ozone

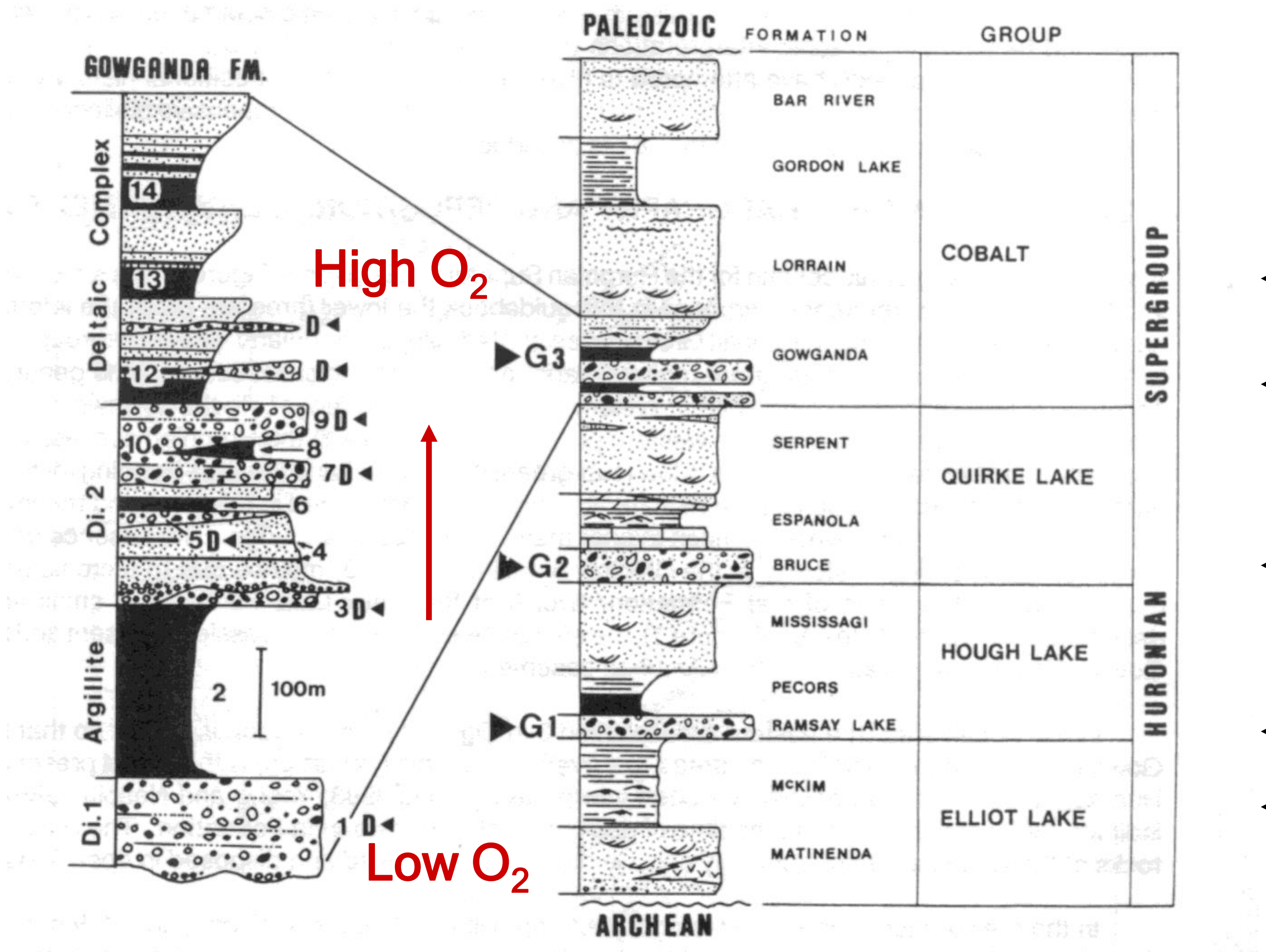


Geologic indicators show atmospheric O_2 was low prior to ~2.2 Ga



H.D. Holland (1994)

Huronian Supergroup (2.45-2.2 Ga)



S. Roscoe, 1969

Redbeds

Glaciations

Detrital uraninite and pyrite

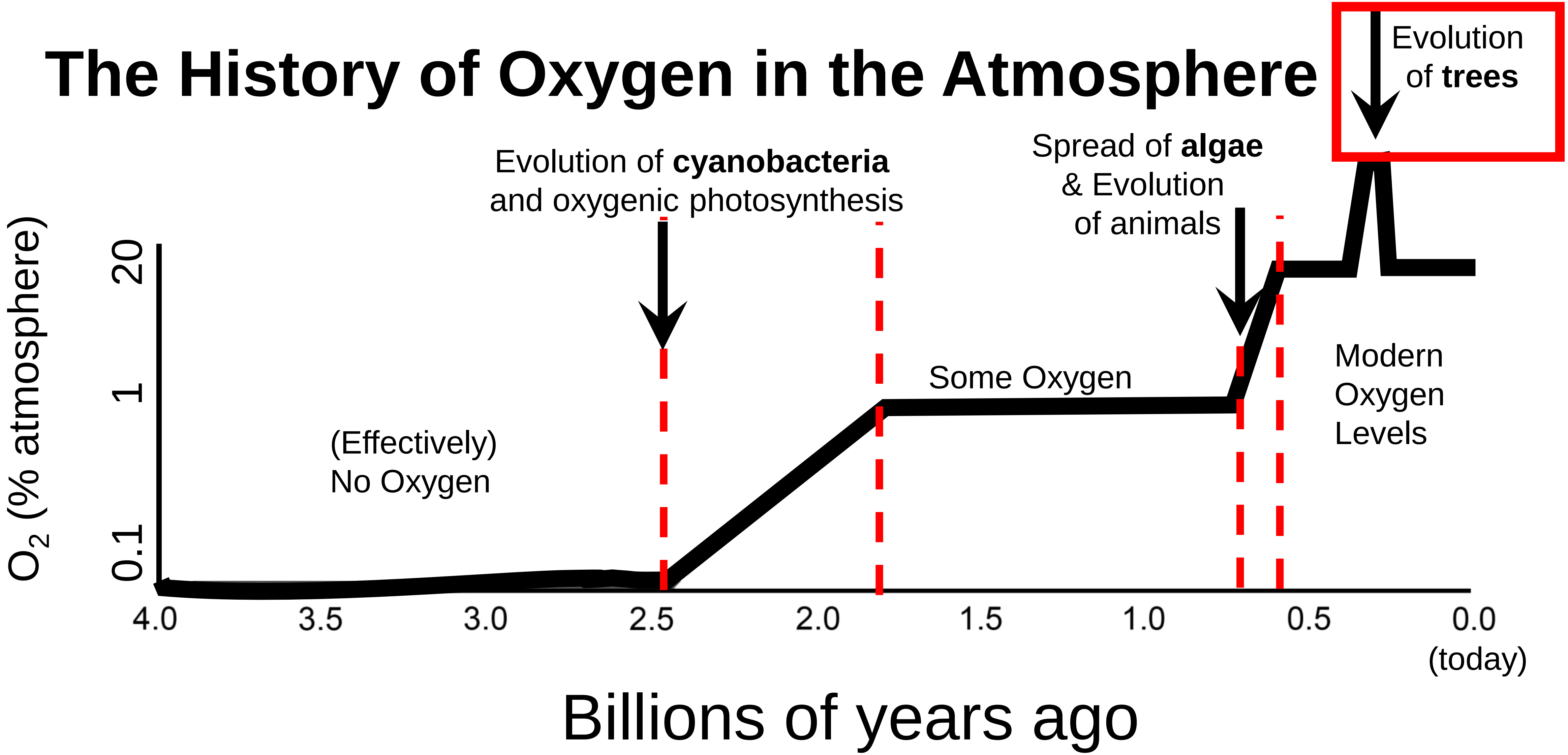
What's the connection between glaciation and appearance of O_2 in the atmosphere?

- Methane (CH_4) is a very potent greenhouse gas and was thought to be abundant on the early Earth

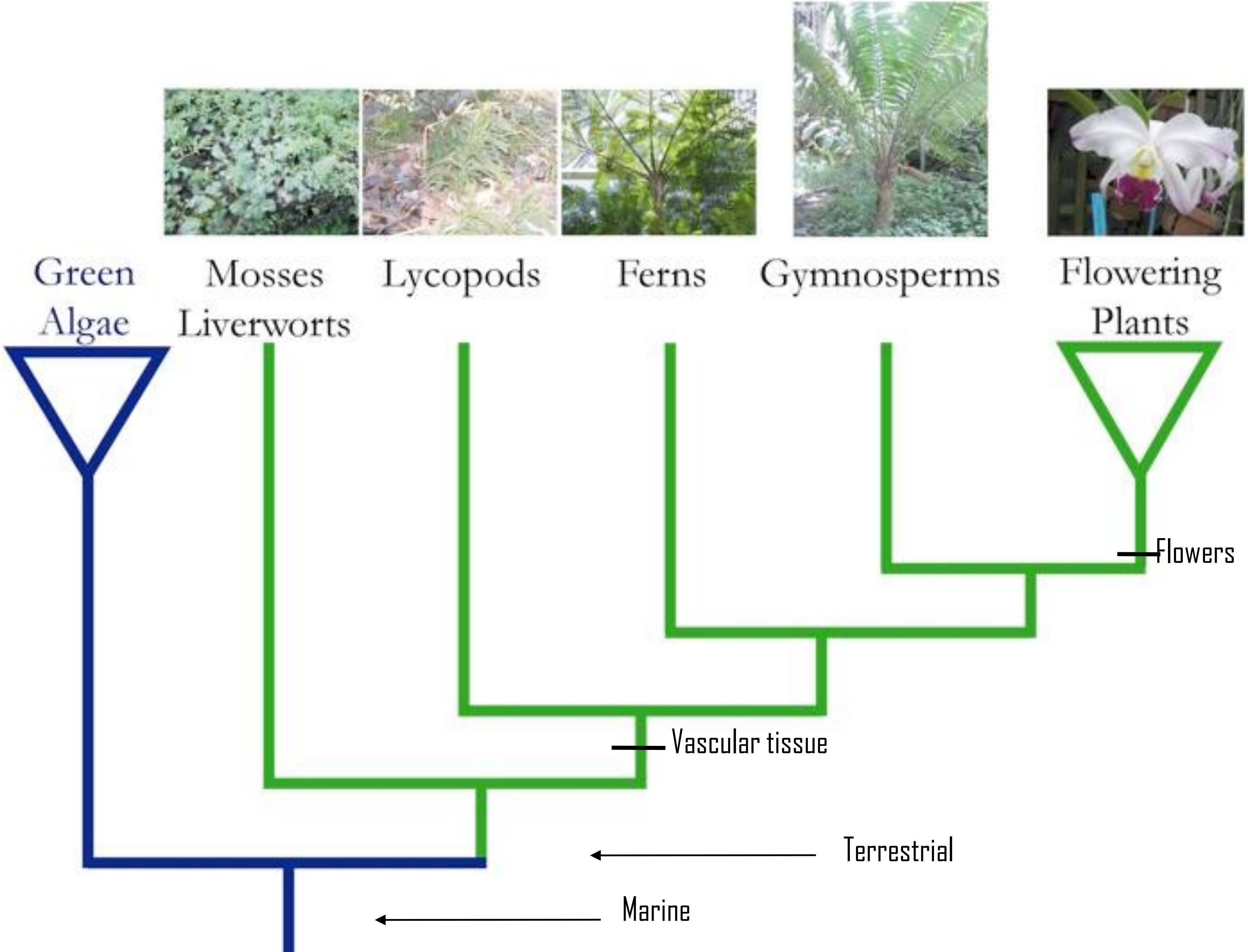
- Oxygen destroys methane by oxidizing it to CO_2
  - CO_2 is also a greenhouse gas but much less potent

- Loss of methane results in a drop of global temperatures

The History of Oxygen in the Atmosphere



Colonization of the Land by Plants


Green Algae
Mosses Liverworts
Lycopods
Ferns
Gymnosperms
Flowering Plants
Flowers
Vascular tissue
Terrestrial
Marine

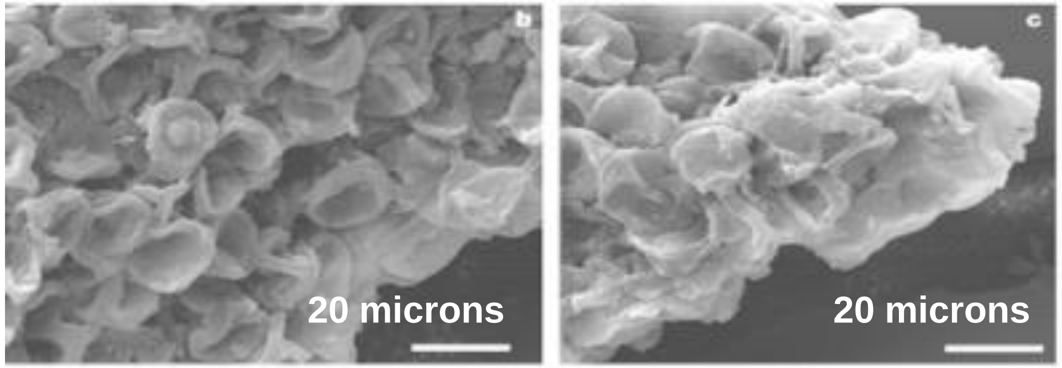
Plants Invade the Land

- First unambiguous spores: 475Ma, Libya

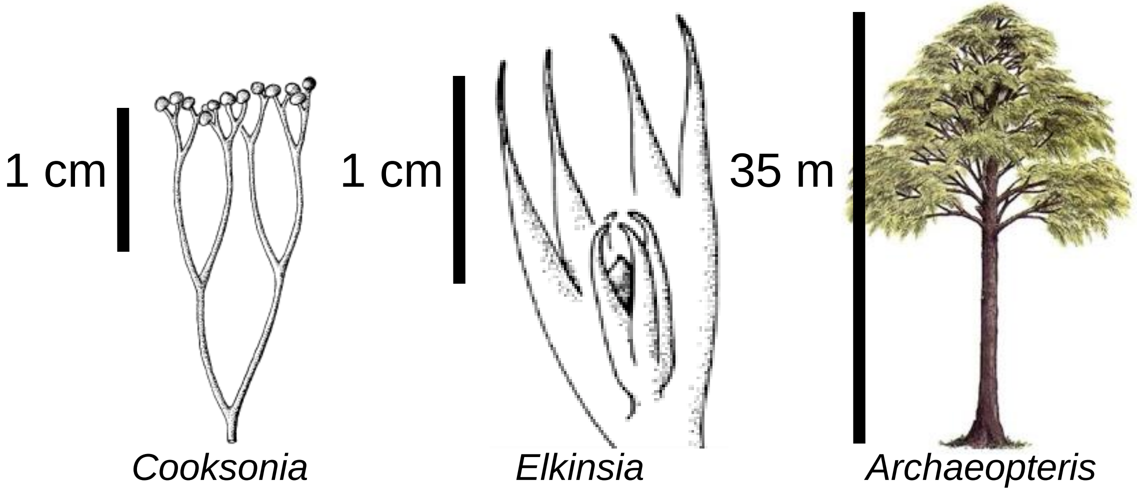
- First unambiguous sporophytes: ~430Ma, Cooksonia

- First seeds: ~390Ma, West Virginia, Elkinsia

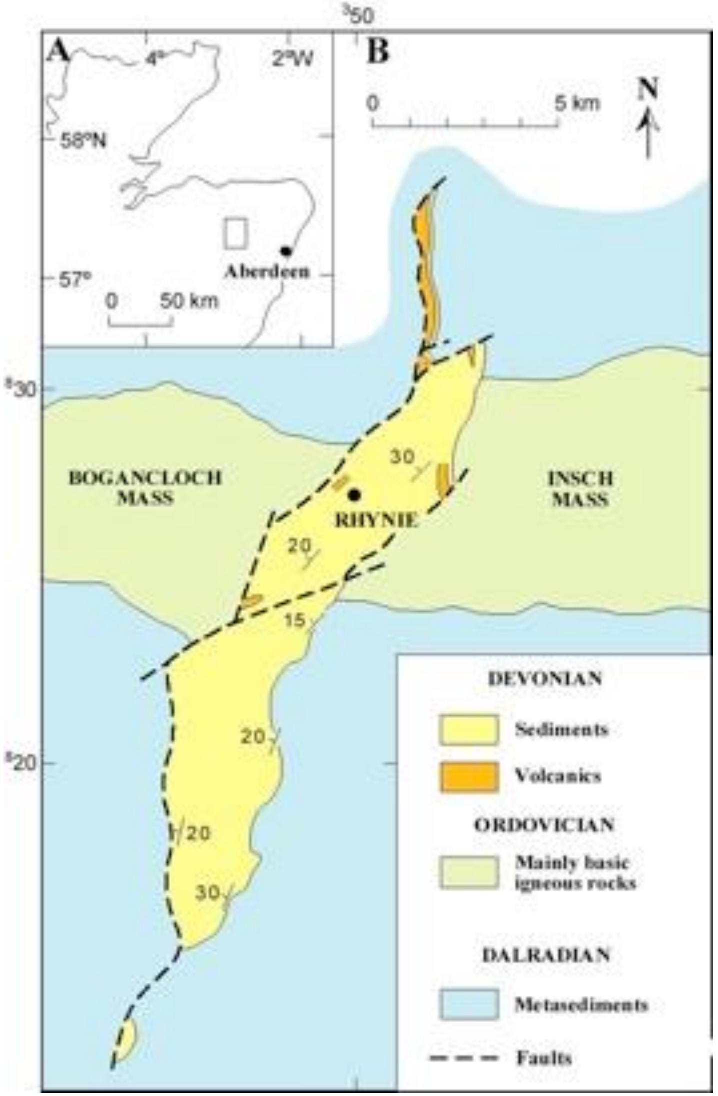
- First trees: ~380Ma, Archaeopteris



From Wellman et al., *Nature* 2003:
“Fragments of the Earliest Land Plants”



The Rhynie Chert

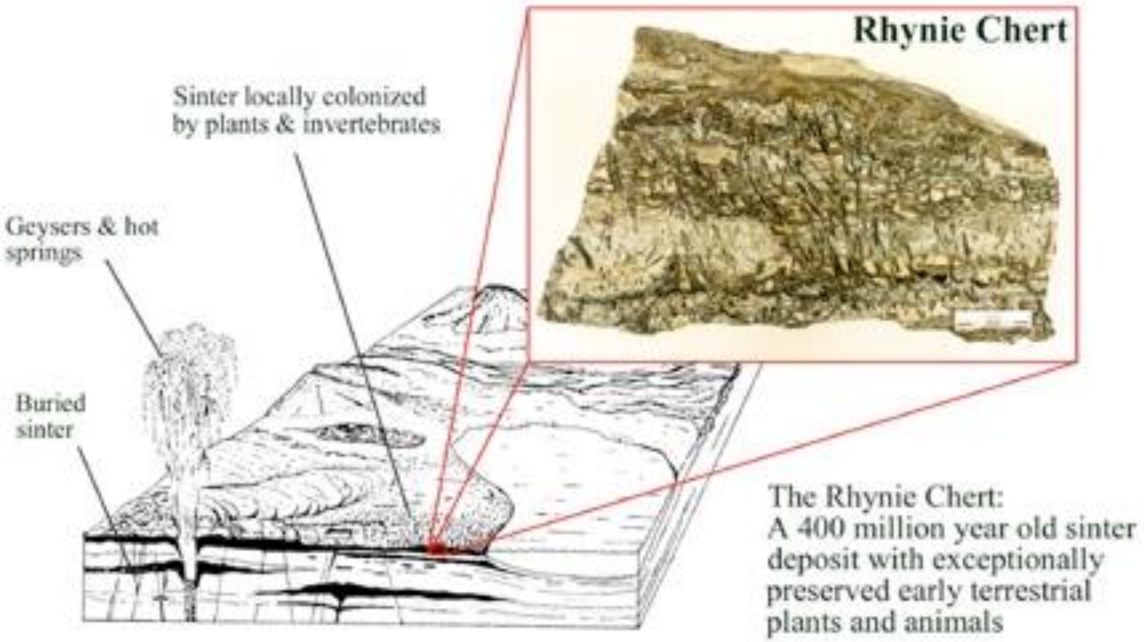


Discovered in 1912, described in 1917-1921 by Kidston and Lang

Age: 396 ± 12 Ma

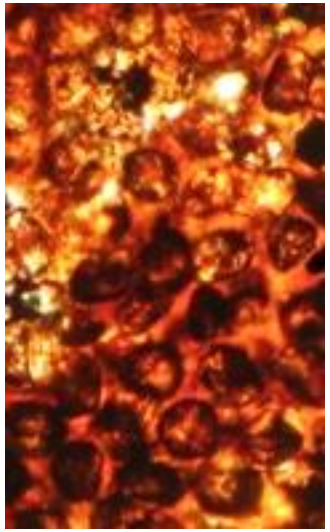
Volcanic sinter/geyser complex
(like Yellowstone)

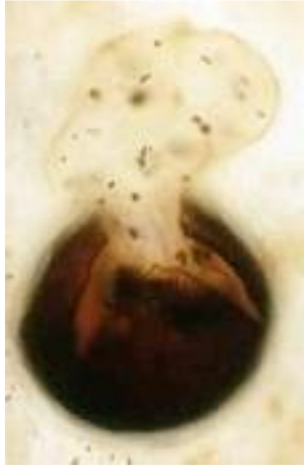
William Mackie

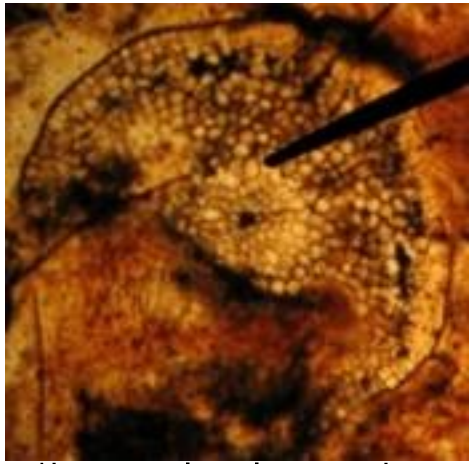


The Rhynie Chert

Unpolished hand sample

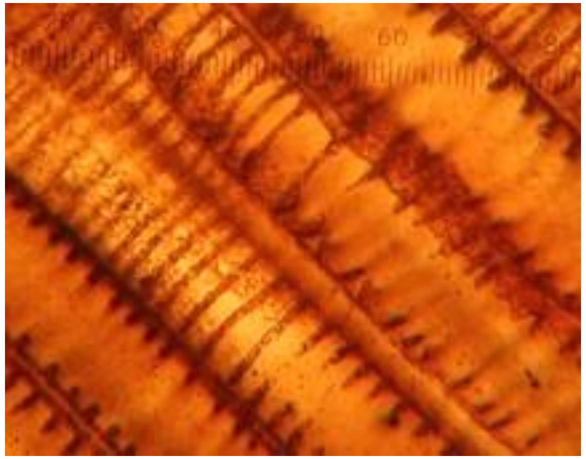


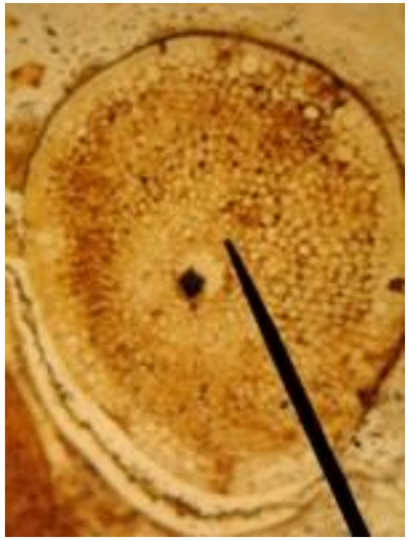




Nonvascular plants and their spores

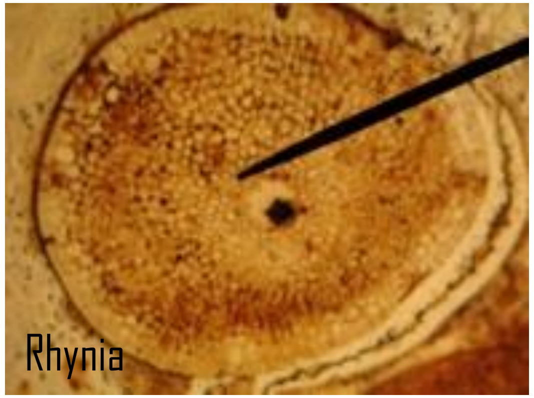
Vascular plants, preserved in place, with small leaves!





Early plant fossils

Stems



Rhynia

Medullosa

Leaves and branches

Alethopteris

Sawdonia

Neuropteris

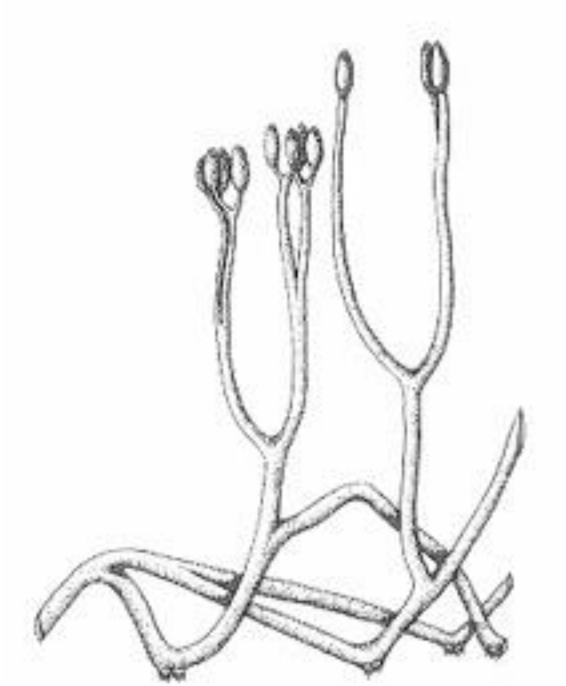
Spores and cones

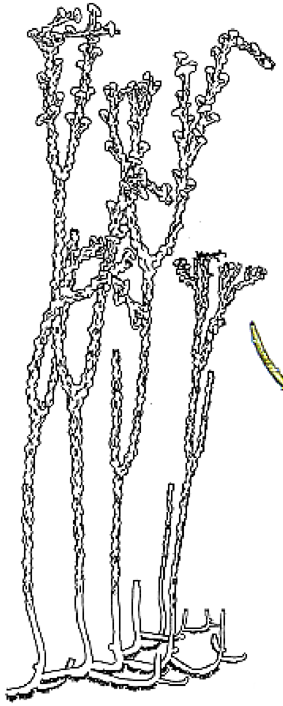
Horneophyton spores

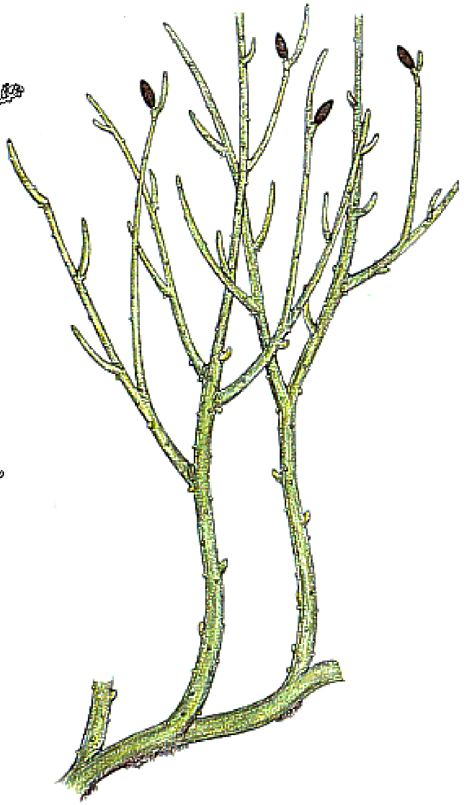
Conifer cone

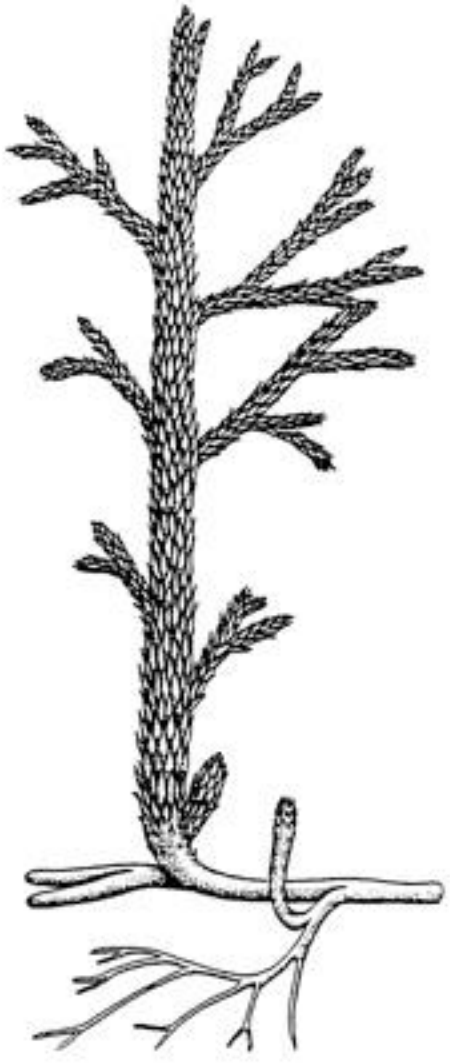
Conifer cone

Rhynie Chert Flora

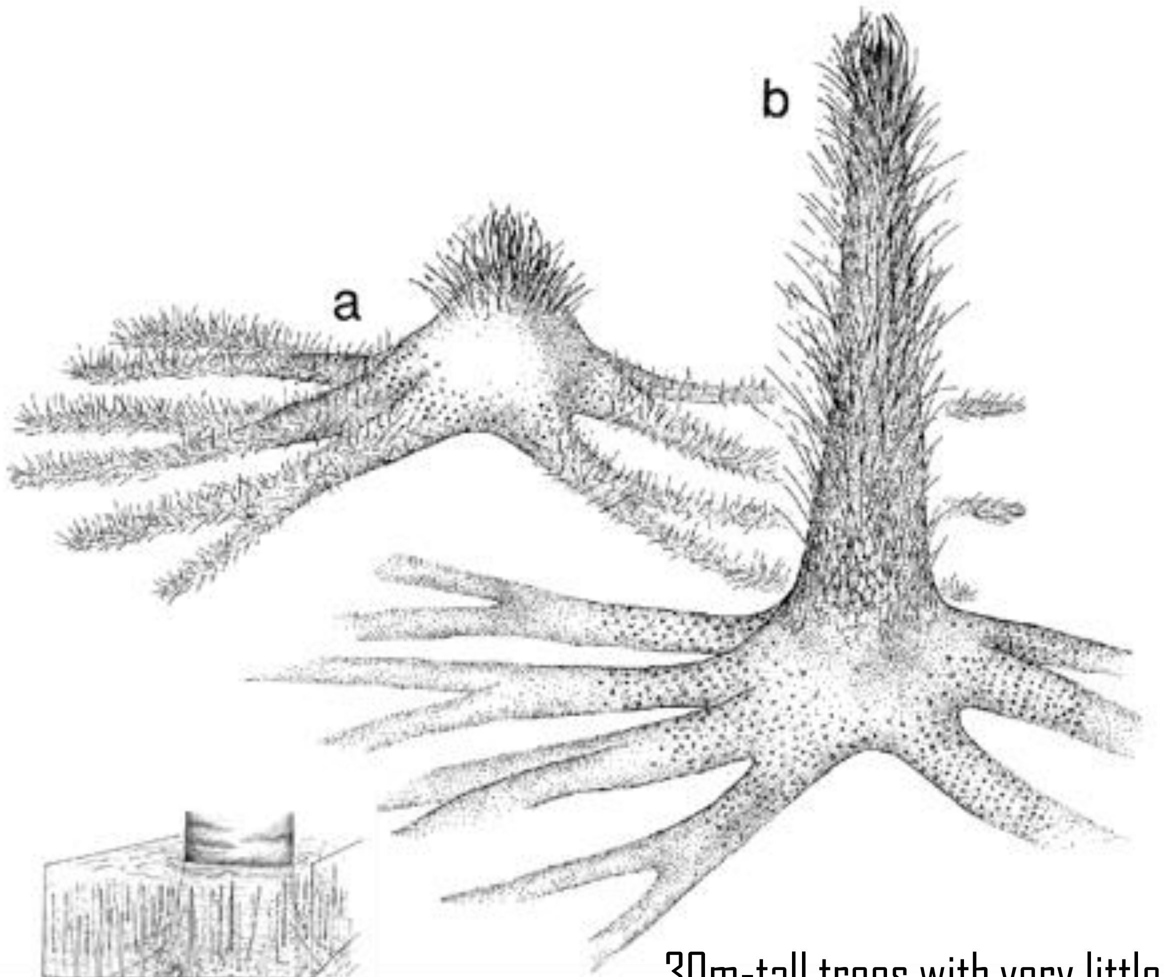


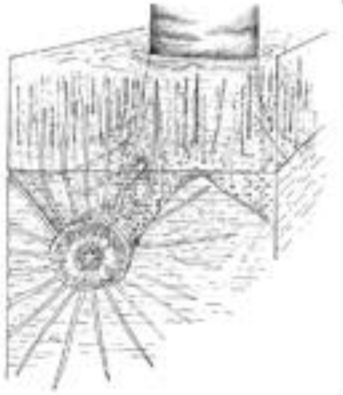


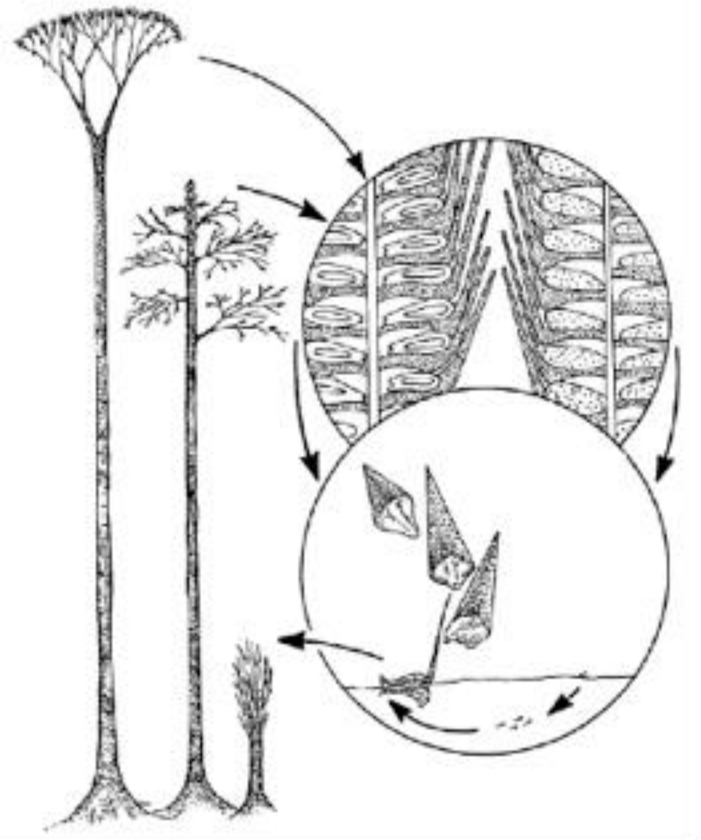




Arborescent Lycopods



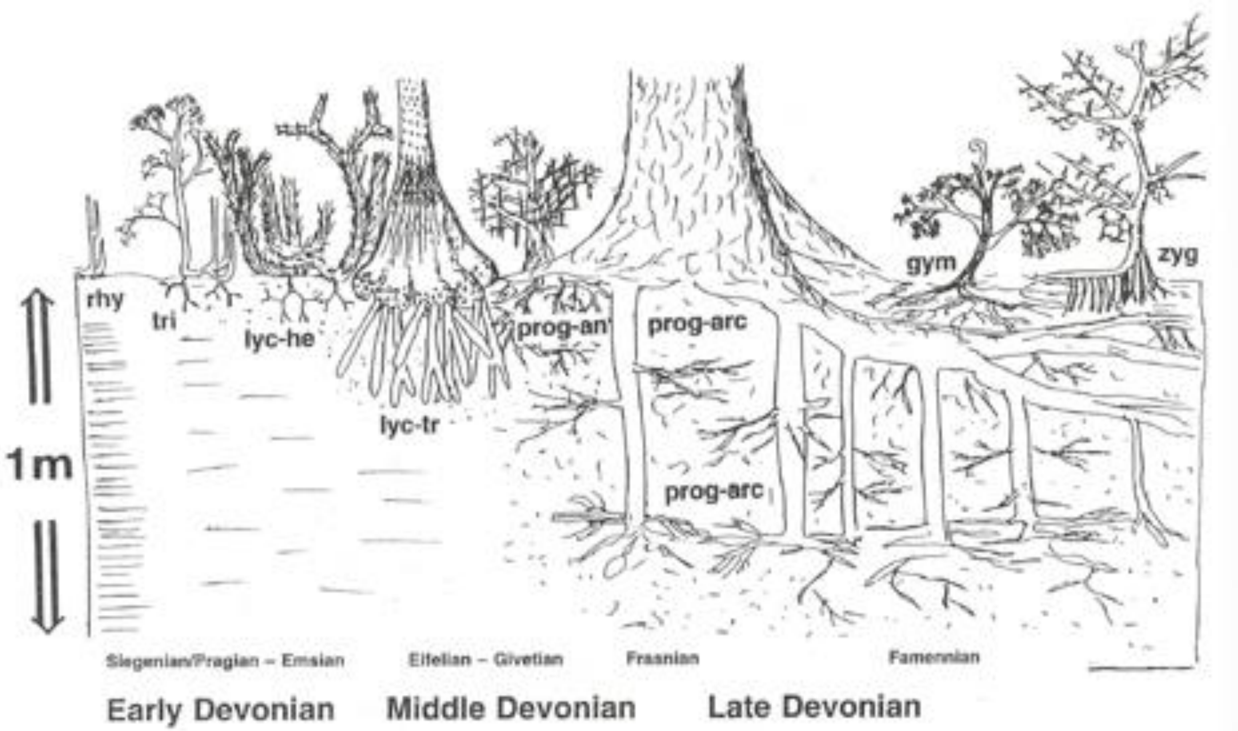




30m-tall trees with very little wood and branching!
"Tree-sized herbs": grew fast, didn't live long.

Dominated swampy, black-water environments.

Rise of Devonian Forests

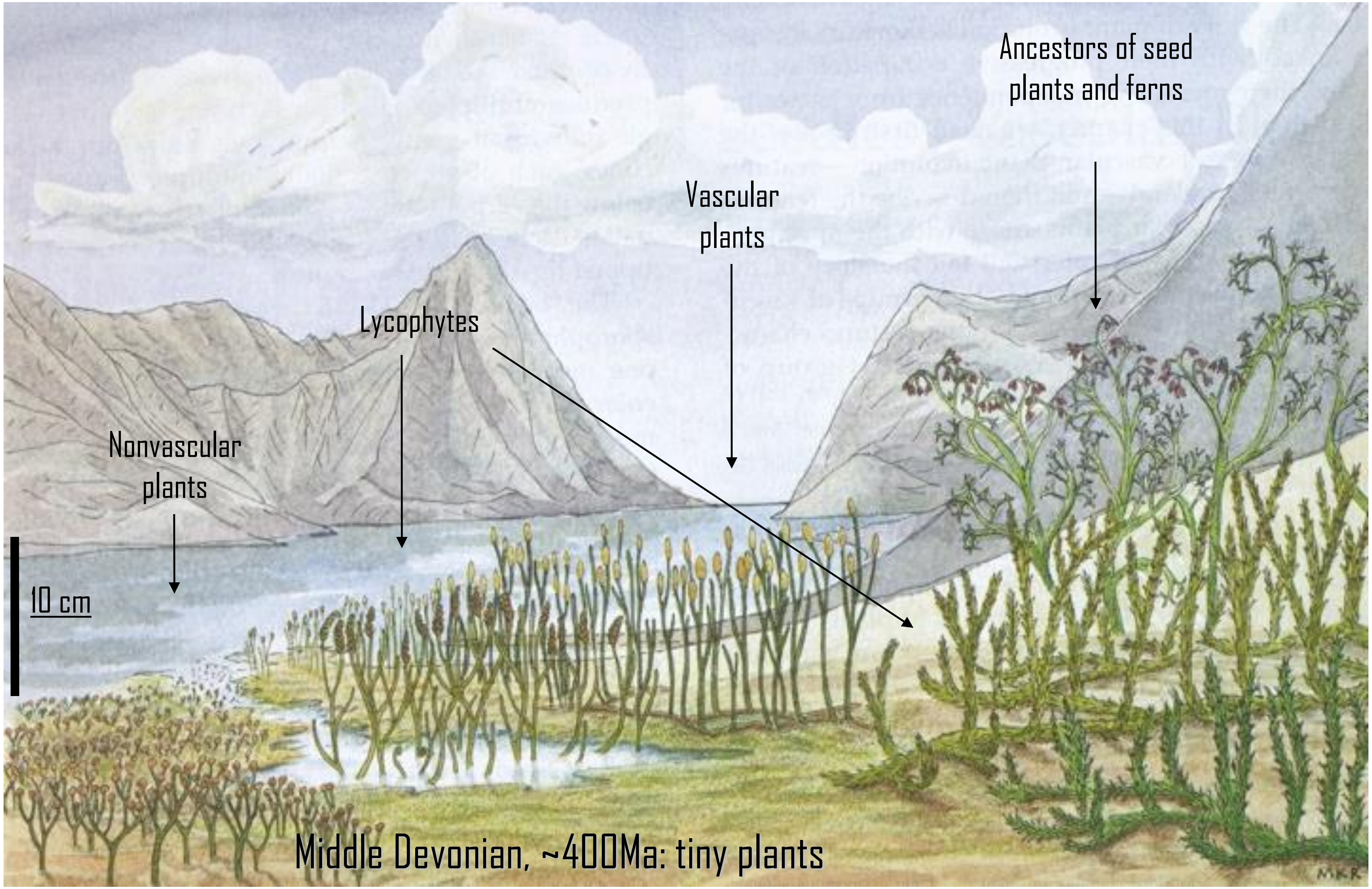


Increase in ecosystem complexity and rooting depth through the Devonian.

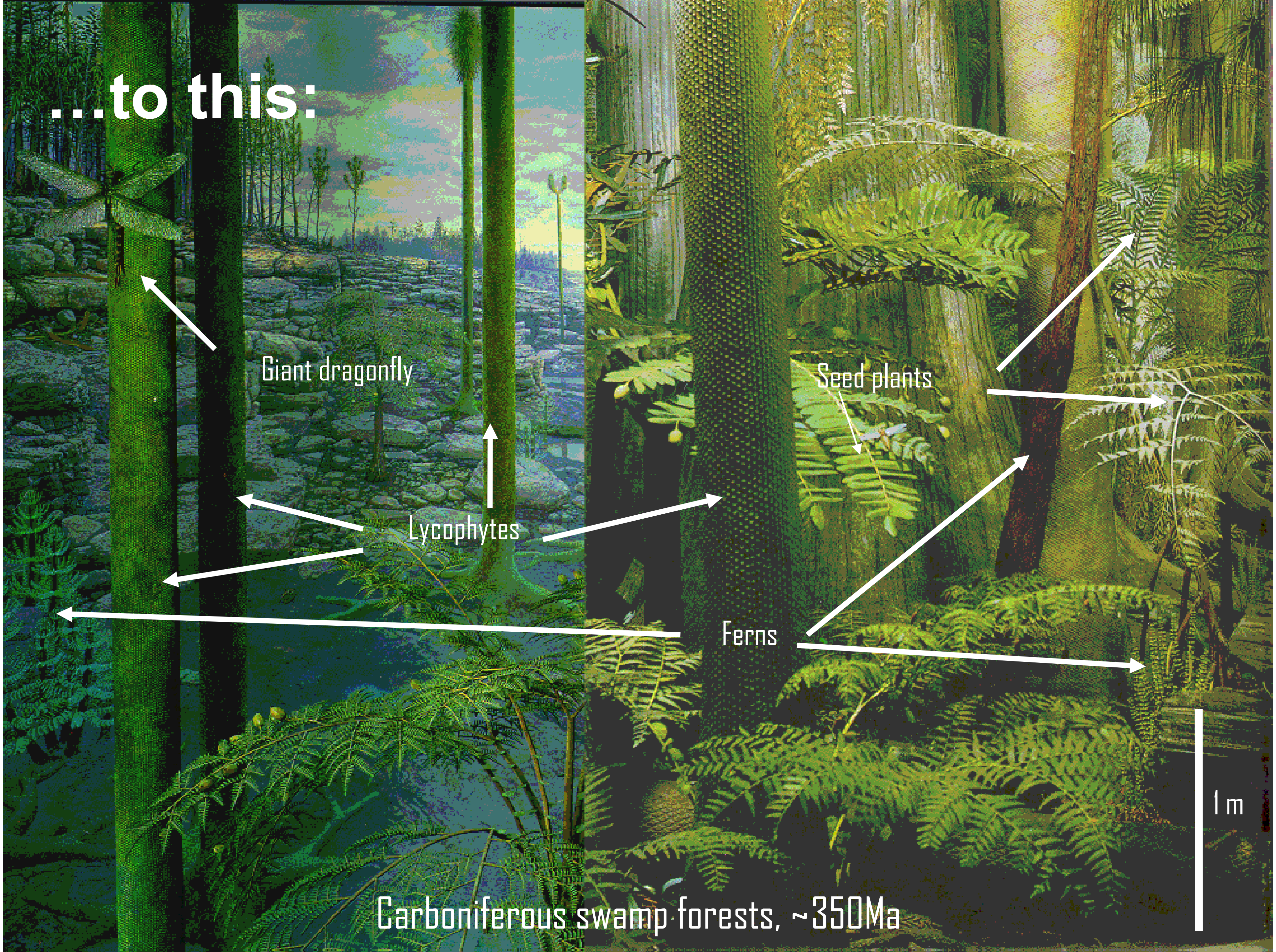
Effects on biogeochemical cycles

Archaeopteris, the first tree

In 50 million years, from this:



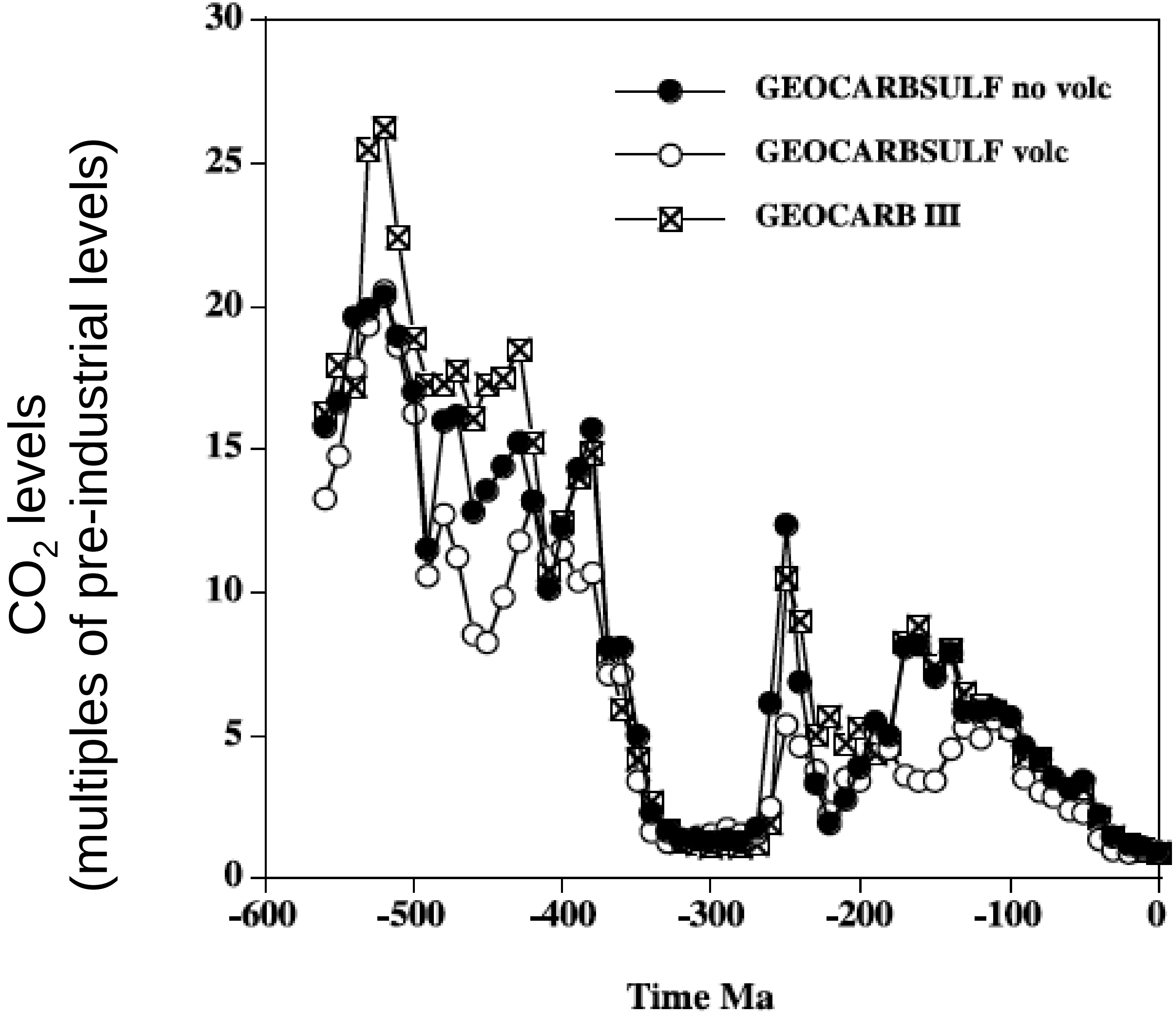
...to this:



Carboniferous swamp forests, ~350Ma

The "Age of Coal"

Evolution of Trees Draws Down CO_2 levels

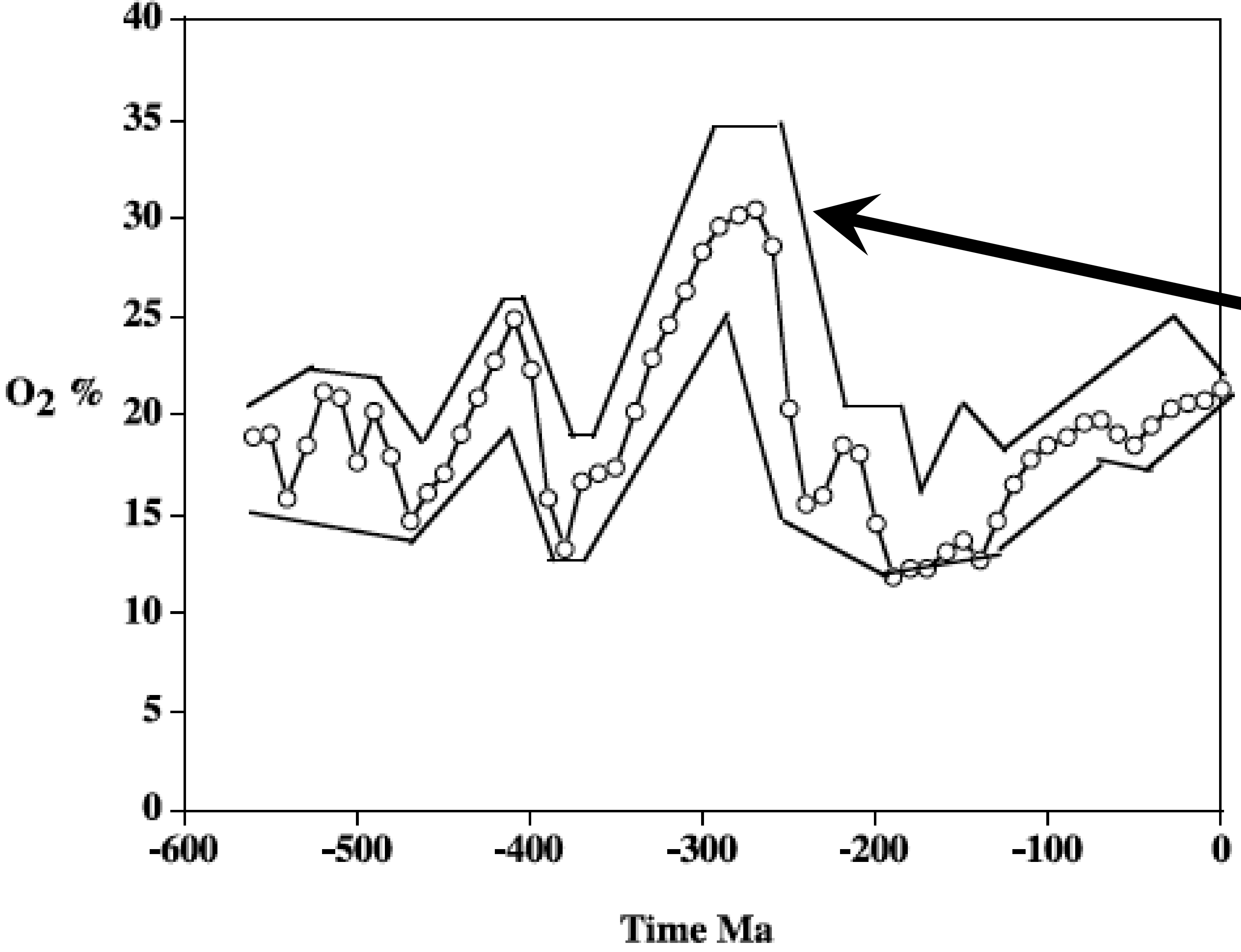


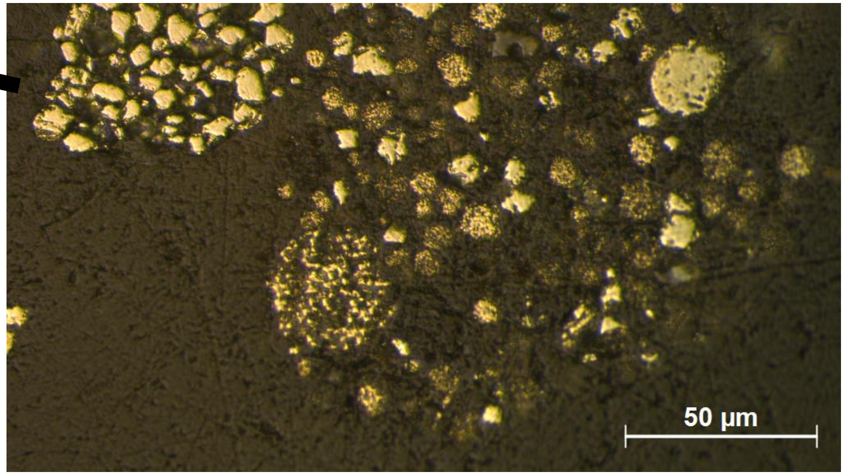
And leads to glaciation

Berner 2006

Evolution of Trees Increases Atmospheric O_2 levels

And leads to widespread fires and evolution of giant flying insects



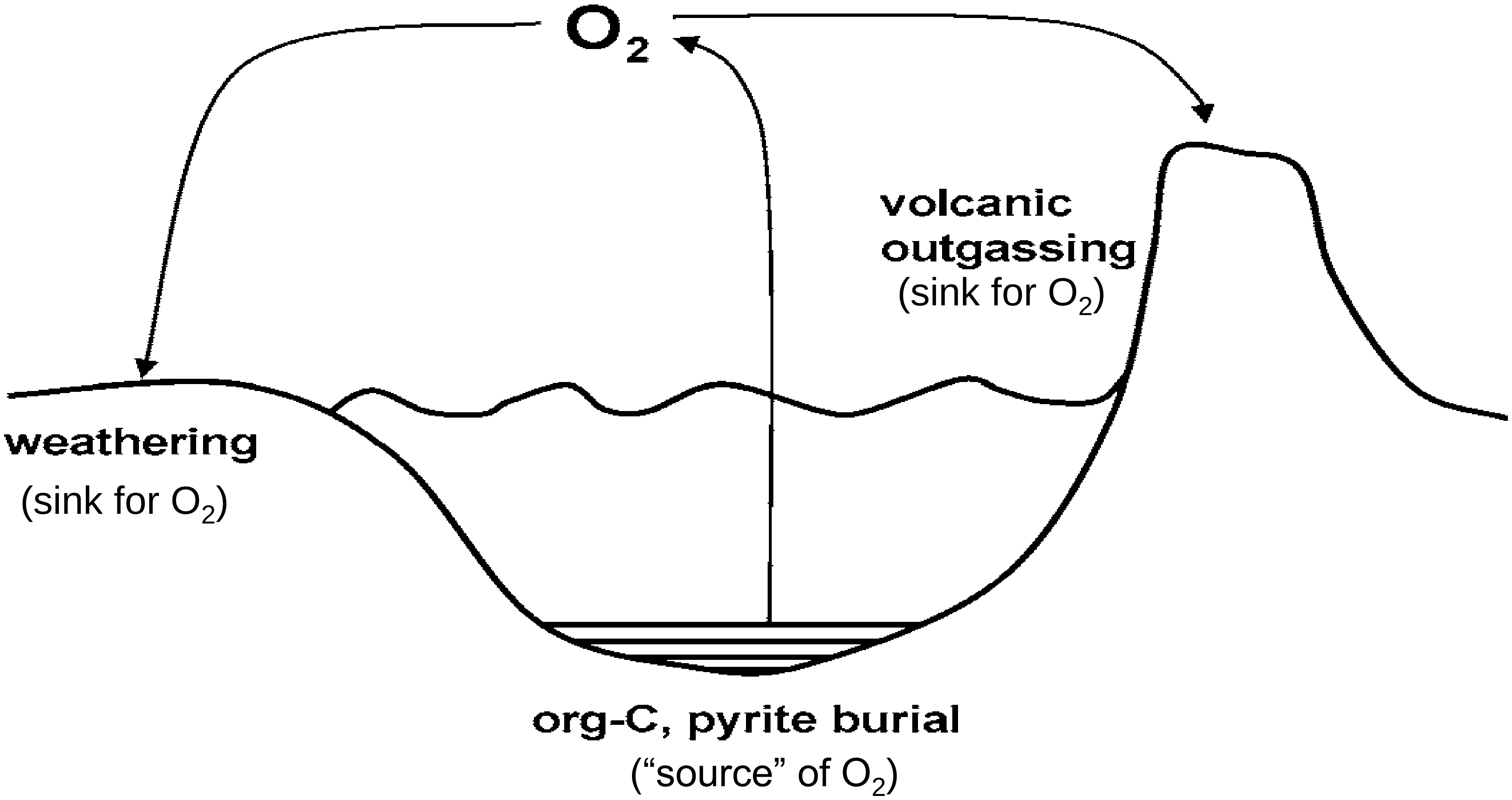


The formation of pyrite (FeS_2), with reduced Fe^{2+} and S^{2-}, is a key factor controlling atmospheric oxygen levels

Berner 2006

Controls on long-term pO_2: balancing production/consumption

Photosynthesis produces oxygen; aerobic respiration consumes it. Oxygen only accumulates in the atmosphere when organic carbon (and other chemically reducing phases like pyrite (FeS_2)) are buried in marine sediments, swamps, and lakes



Stable Isotope Analysis

Stable isotopes are non-radioactive versions of elements with different weights due to differing numbers of neutrons.

1) metabolic activity generates large isotopic differences between products and reactants

- which depend upon environmental & ecological conditions

2) isotopic composition of sedimentary phases are the best record of ancient conditions over Earth history.

C isotopes:

^{12}C: 98.9%; ^{13}C: 1.1%; ^{14}C: < 0.0000000001%

Canonically measure $^{13}C/^{12}C$ ratio:

$\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{std}-1]*10^3$, ‰ (V-PDB)

Stable Isotope Analysis

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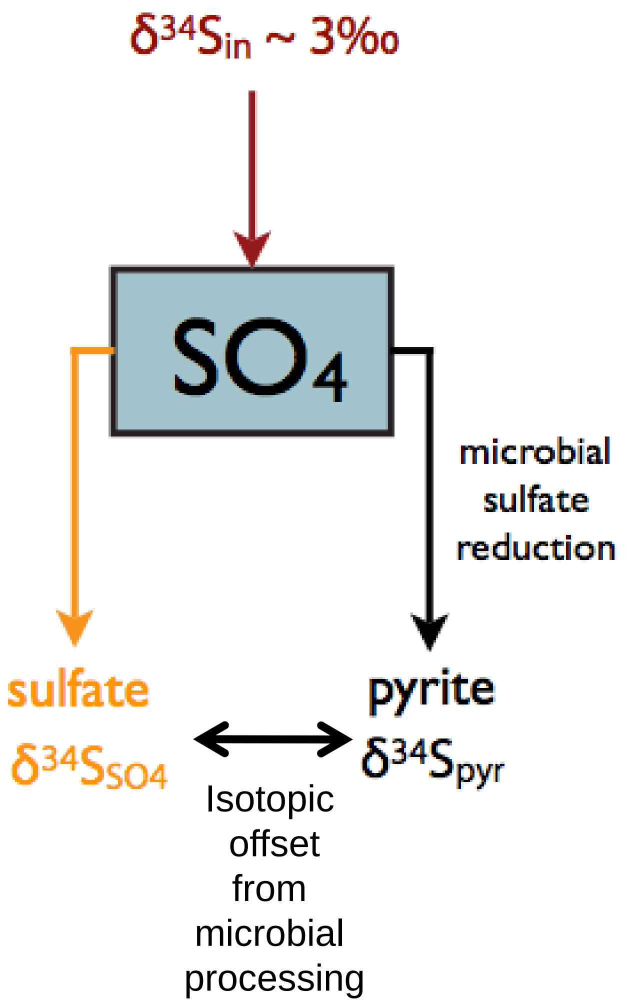
S isotopes:

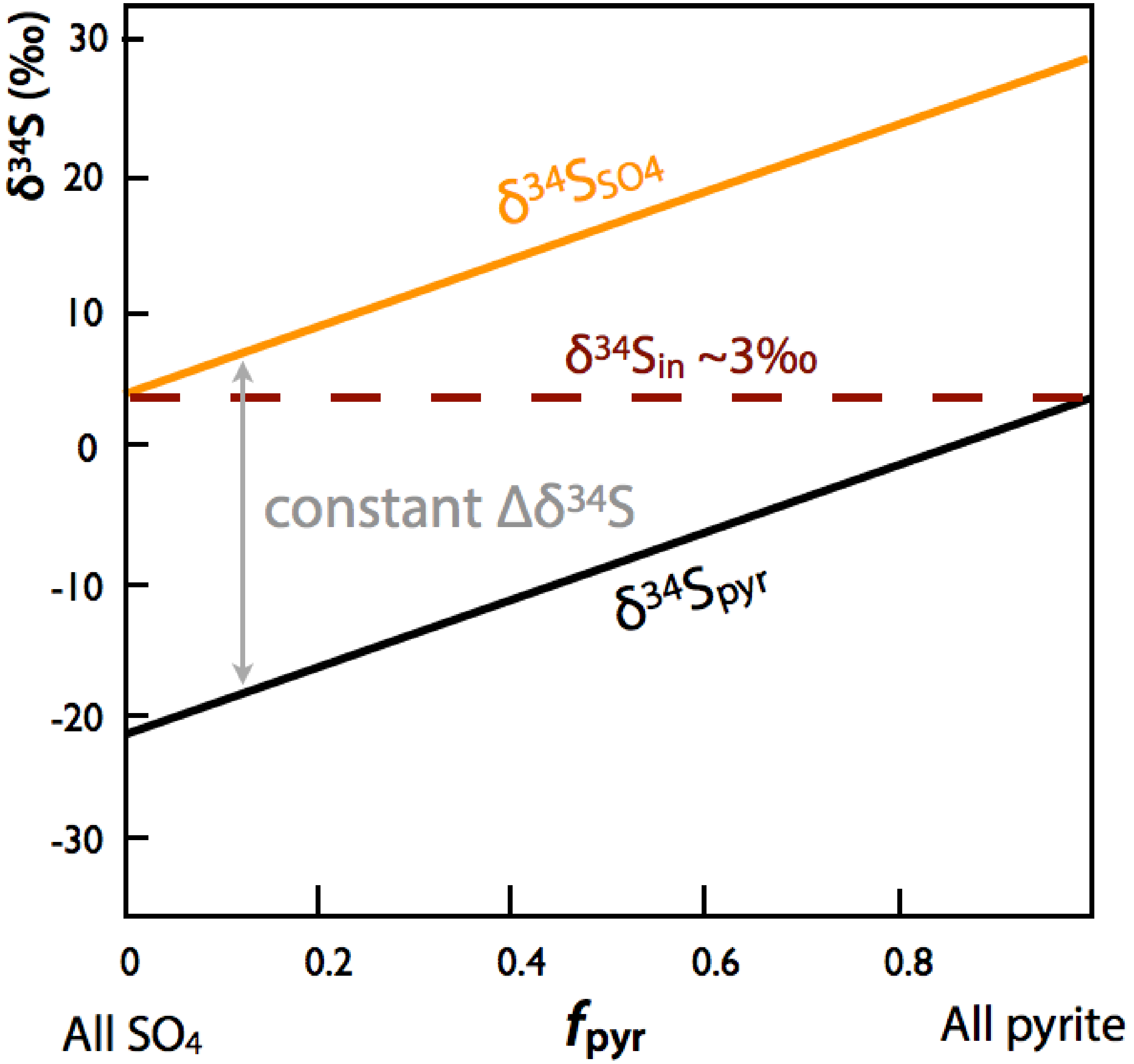
^{32}S: 95.02%; ^{33}S: 0.76%; ^{34}S: 4.20%; ^{36}S: 0.02%

Canonically measure $^{34}S/^{32}S$ ratio:

$$\delta^{34}S = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{std}-1]*10^3\text{ , ‰ (V-CDT)}$$

Overview of the S cycle



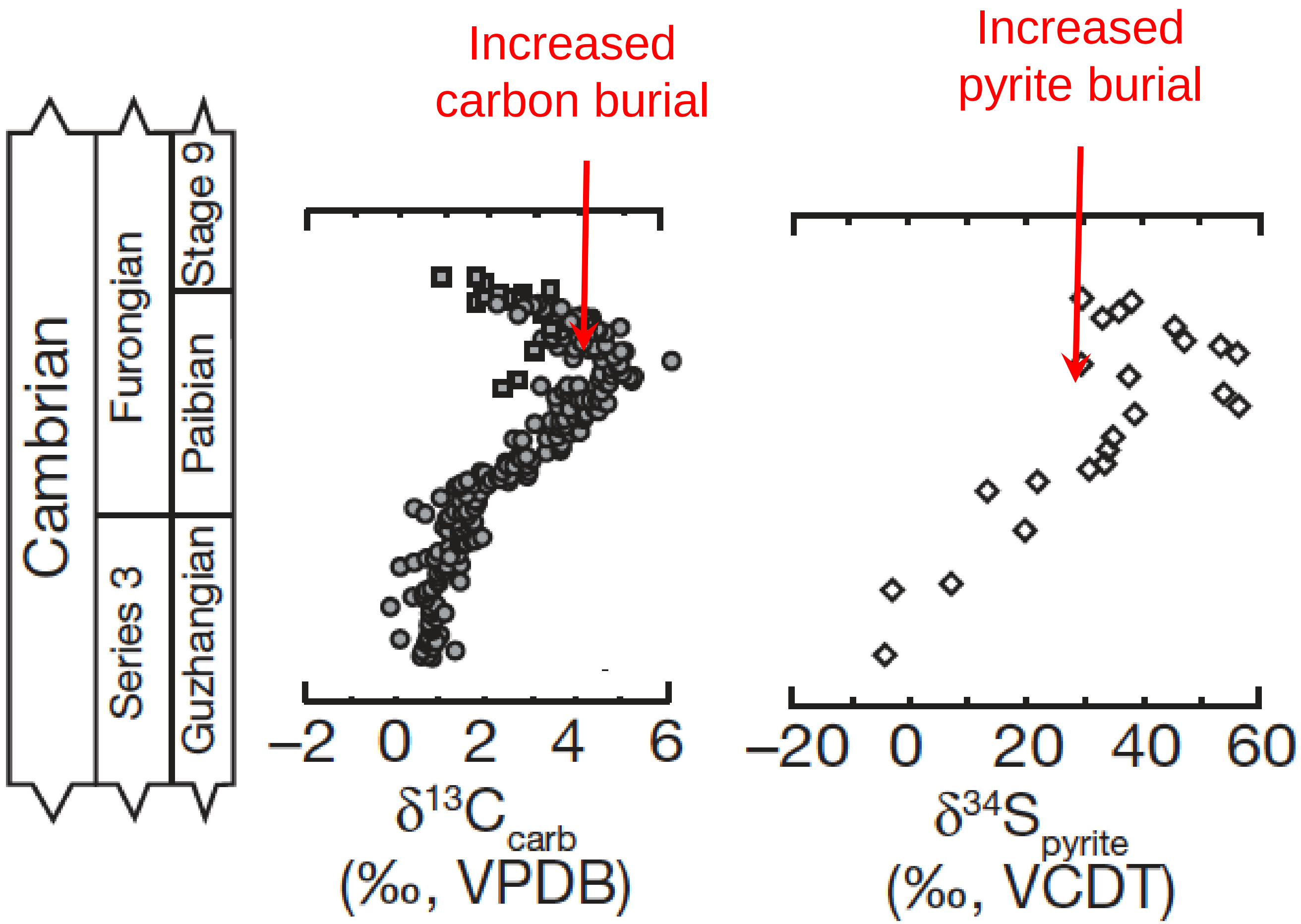


Take away: higher $\delta^{34}S$ → more pyrite burial → more oxygen release to the atmosphere

Changes in Burial and Inferred Oxygenation

Late Cambrian (510 million years ago)

- Pulse of increased sedimentary burial of organic carbon and pyrite
- Interpreted to reflect pulse of oxygen release to the atmosphere



Gill et al. 2011

Palaeogeography, Palaeoclimatology, Palaeoecology (Global and Planetary Change Section), 75 (1989) : 97–122 97
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LETTER

doi:10.1038/nature09700

Geochemical evidence for widespread euxinia in the Later Cambrian ocean

Benjamin C. Gill[1]†, Timothy W. Lyons[1], Seth A. Young[2], Lee R. Kump[3], Andrew H. Knoll[4] & Matthew R. Saltzman[5]

A global perturbation to the sulfur cycle during the Toarcian Oceanic Anoxic Event

Benjamin C. Gill [a,b,*], Timothy W. Lyons [b], Hugh C. Jenkyns [c]

nature Vol 444|7 December 2006|**doi:10.1038/nature05345**

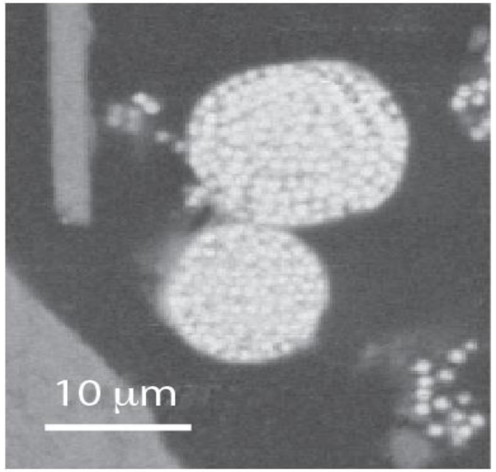
LETTERS

Oxidation of the Ediacaran Ocean

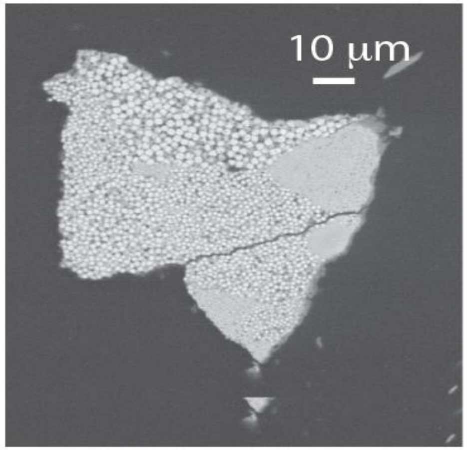
D. A. Fike[1], J. P. Grotzinger[1]†, L. M. Pratt[2] & R. E. Summons[1]

However, Observations Identify Multiple Distinct Populations of Pyrite Crystals

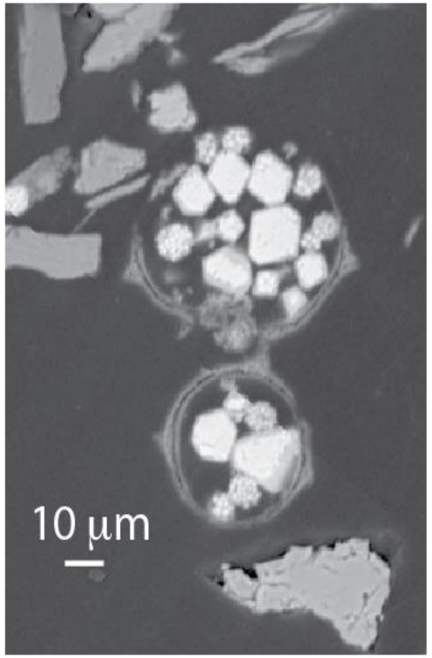
What if they have equally distinct geochemical signatures???



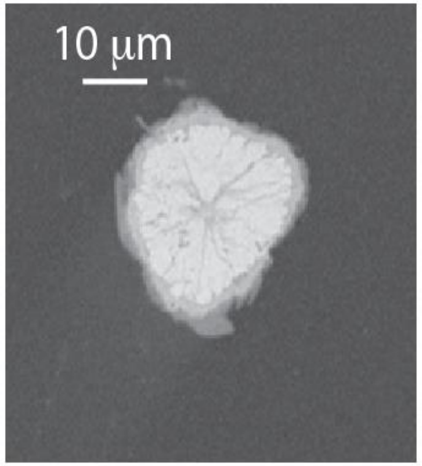
framboids



masses of nanocrystals

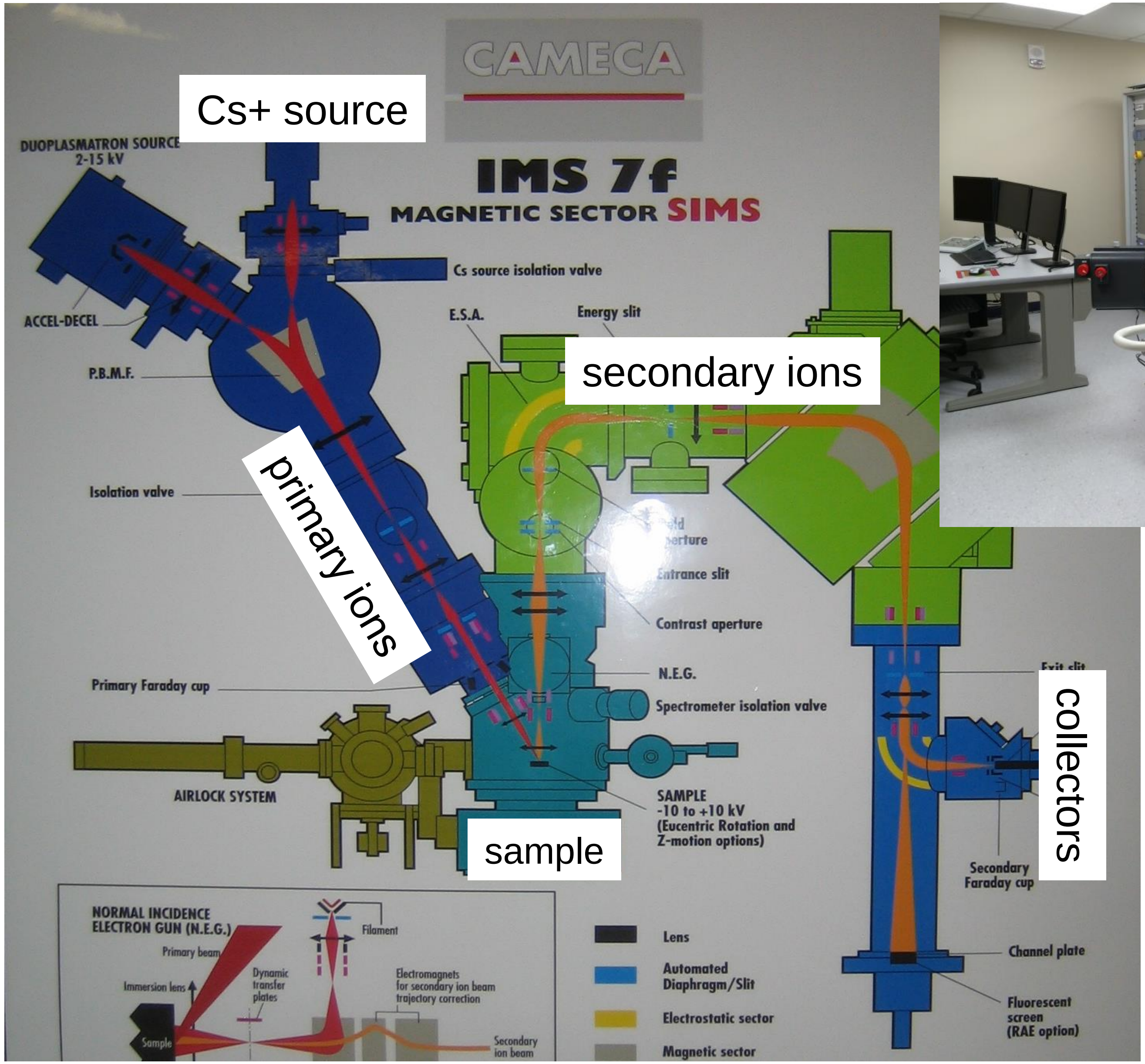


euhedral



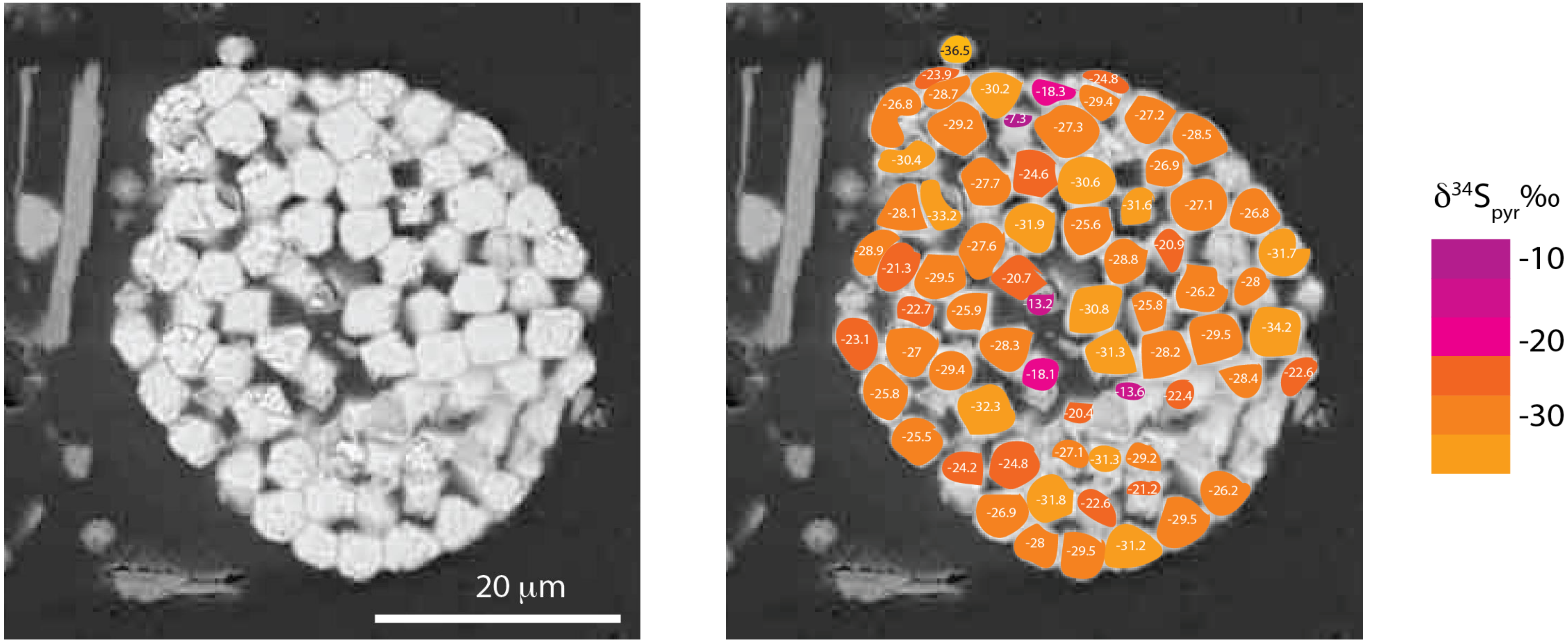
recrystallization

Secondary Ion Mass Spectrometry (SIMS)



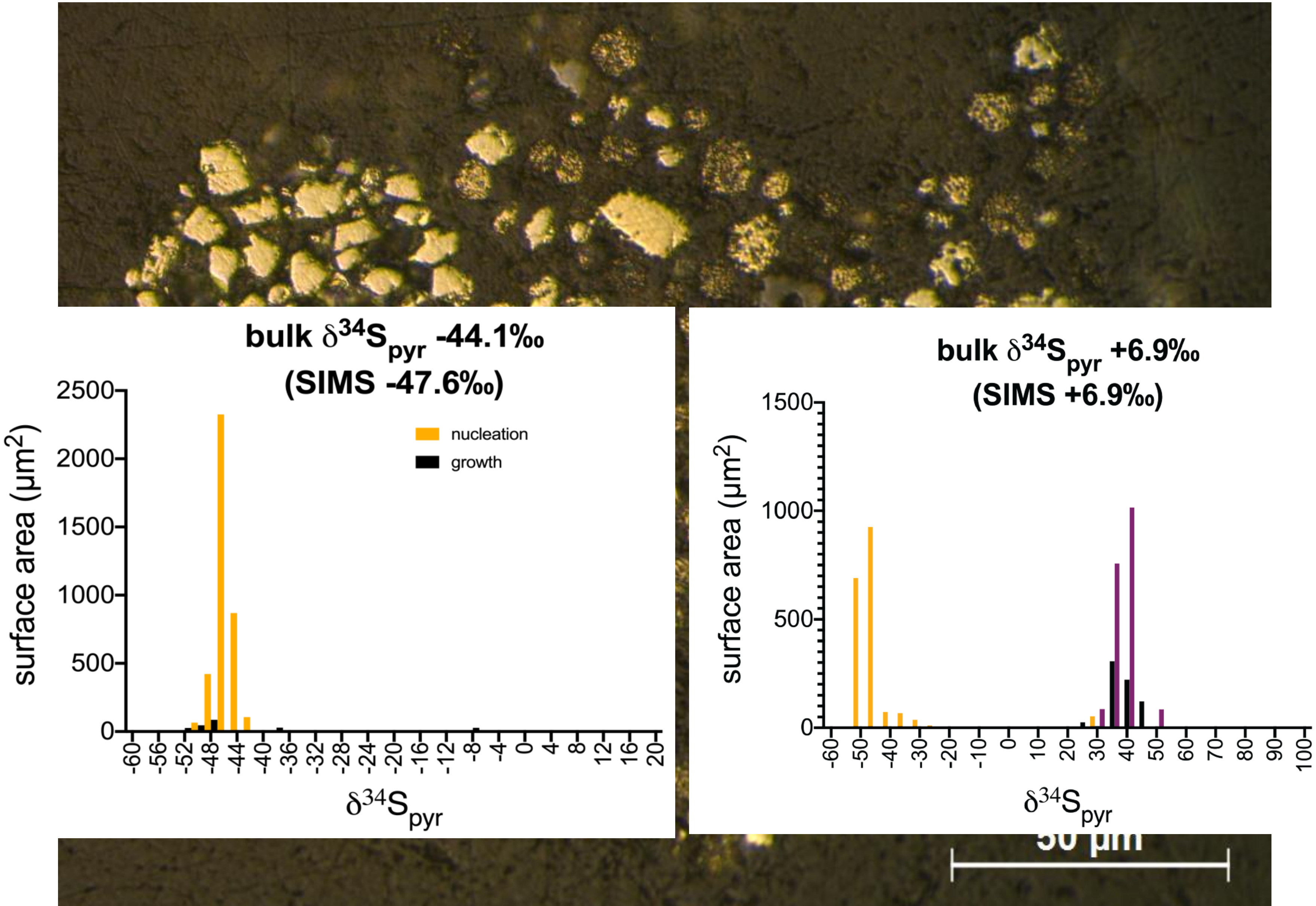
7f-GEO instrument (basement of Rudolph Hall)

SIMS Measurements: Geochemical Analysis down to the micron scale



Allows for the smaller-scale inter- and intra-grain isotopic variability to be more easily assessed….

Need to investigate geochemical signatures across spatial scales



With novel micron-scale analytical techniques:

1. Access environmental information previously beyond our abilities

2. Document enormous geochemical variability between different populations in a single sample
   - Each of population encodes meaningful biological, and environmental information

3. Demonstrate that previous inferences about past environments drawn from ‘bulk’ analyses need to be revisited
   - Working to revise the record of atmospheric oxygen over Earth History!

From research to teaching to administration...

Environmental Studies
WASHINGTON UNIVERSITY IN ST. LOUIS

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International Center for Energy, Environment and Sustainability

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Creation of 3 new majors (and associated minors): Earth Science, Environmental Science, and Planetary Science -- and a new minor in Geospatial Science.

We are eager to help lead the Chancellor’s new vision for Environmental, Climate, and Sustainability work on campus, in the St. Louis region, and around the world.

Earth & Planetary Sept 2022

Thank you for your attention. Happy to take any questions.