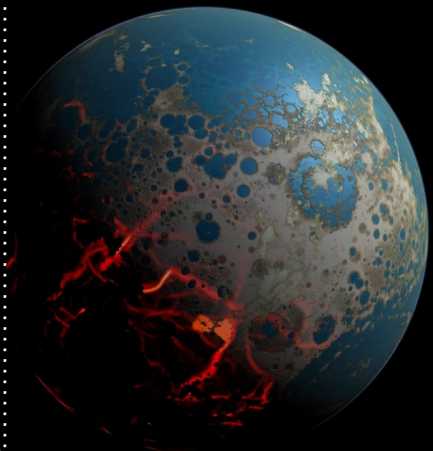


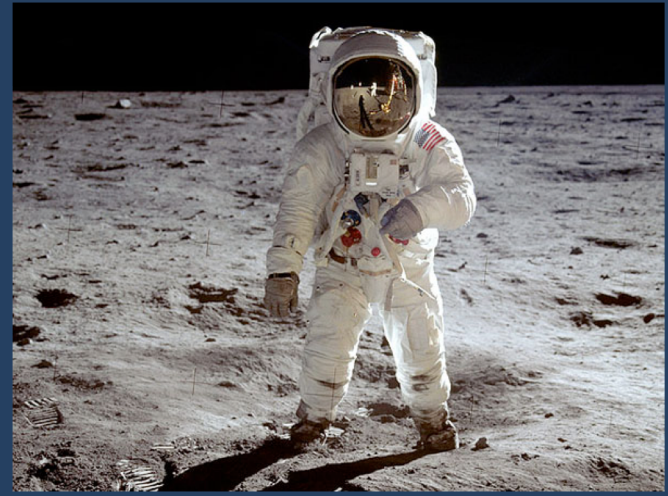


Rise of Oxygen on Earth and Detectable Biosignatures

*T.W. Lyons, Alternative Earths Team of the NASA Astrobiology Institute, Department of Earth and Planetary Sciences, University of California, Riverside and Prebiotic Chemistry and Early Earth Environments Consortium of the NASA Research Coordination Network*







# NASA ASTROBIOLOGY INSTITUTE

Understanding Life on Earth and Beyond 









$N = 1$



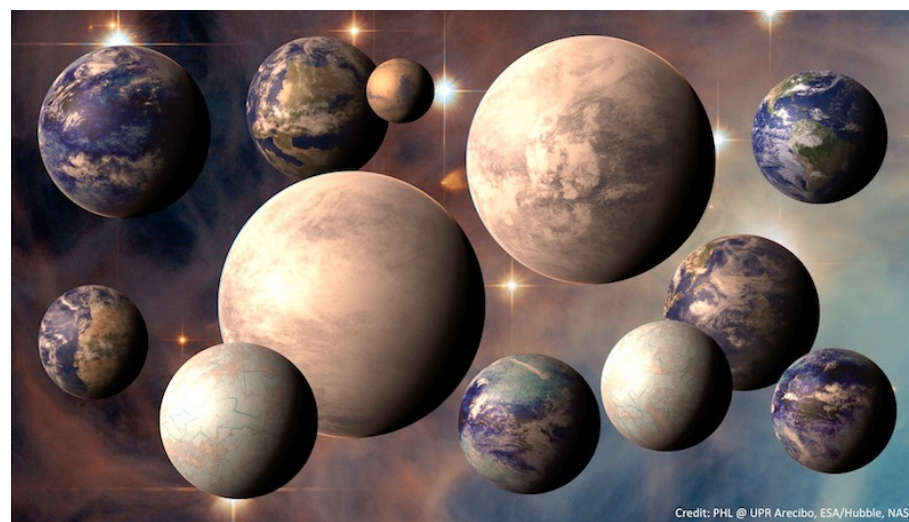


# Alternative Earths

A MEMBER OF THE NASA ASTROBIOLOGY INSTITUTE

Exploring four billion years of persistent habitability on a dynamic early Earth...

...to guide NASA's mission-specific search for life on distant worlds.







4.5 billion years ago





The Hadean

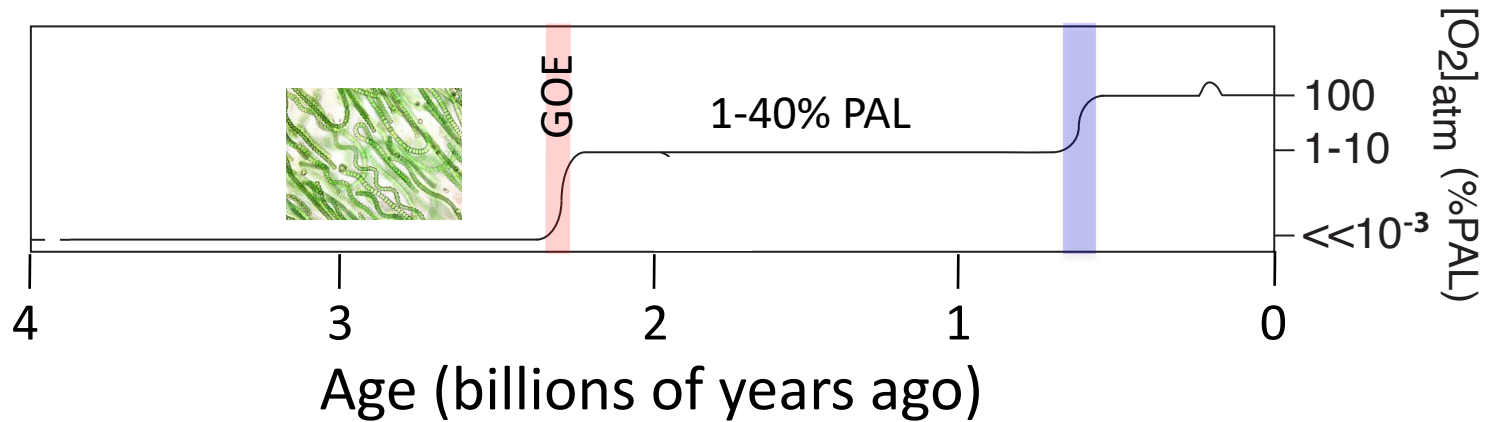






# Oxygen (O<sub>2</sub>)

Atmospheric oxygen levels



## The Classic Two Step View



# Archean Biomarkers: Chapters 1 and 2

## Archean Molecular Fossils and the Early Rise of Eukaryotes

Jochen J. Brocks,<sup>1,2\*</sup> Graham A. Logan,<sup>2</sup> Roger Buick,<sup>1</sup>  
Roger E. Summons<sup>2</sup>

(Science, 1999)

## Reappraisal of hydrocarbon biomarkers in Archean rocks

Katherine L. French<sup>a,1,2</sup>, Christian Hallmann<sup>b,c</sup>, Janet M. Hope<sup>d</sup>, Petra L. Schoon<sup>e</sup>, J. Alex Zumberge<sup>e</sup>, Yosuke Hoshino<sup>f</sup>,  
Carl A. Peters<sup>f</sup>, Simon C. George<sup>f</sup>, Gordon D. Love<sup>e</sup>, Jochen J. Brocks<sup>d</sup>, Roger Buick<sup>g</sup>, and Roger E. Summons<sup>h</sup>

(PNAS, 2015)

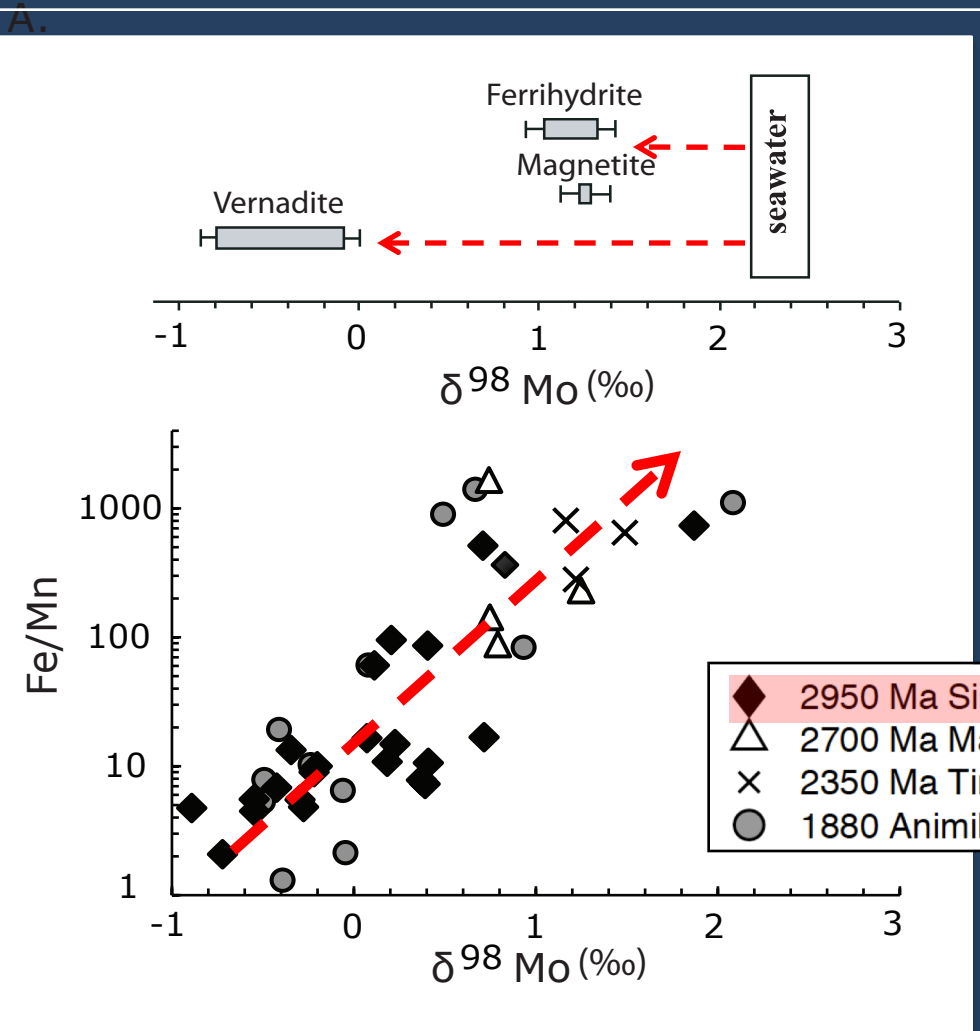
## Inorganic Perspectives



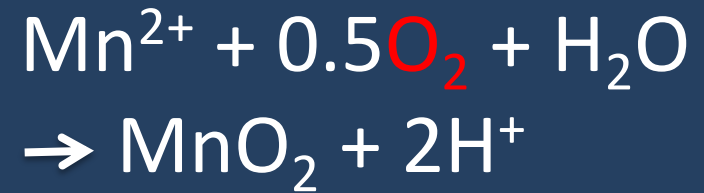




# Mo Isotope Fractionation Coupled to Mn Cycling (ca. 3.0 Ga)



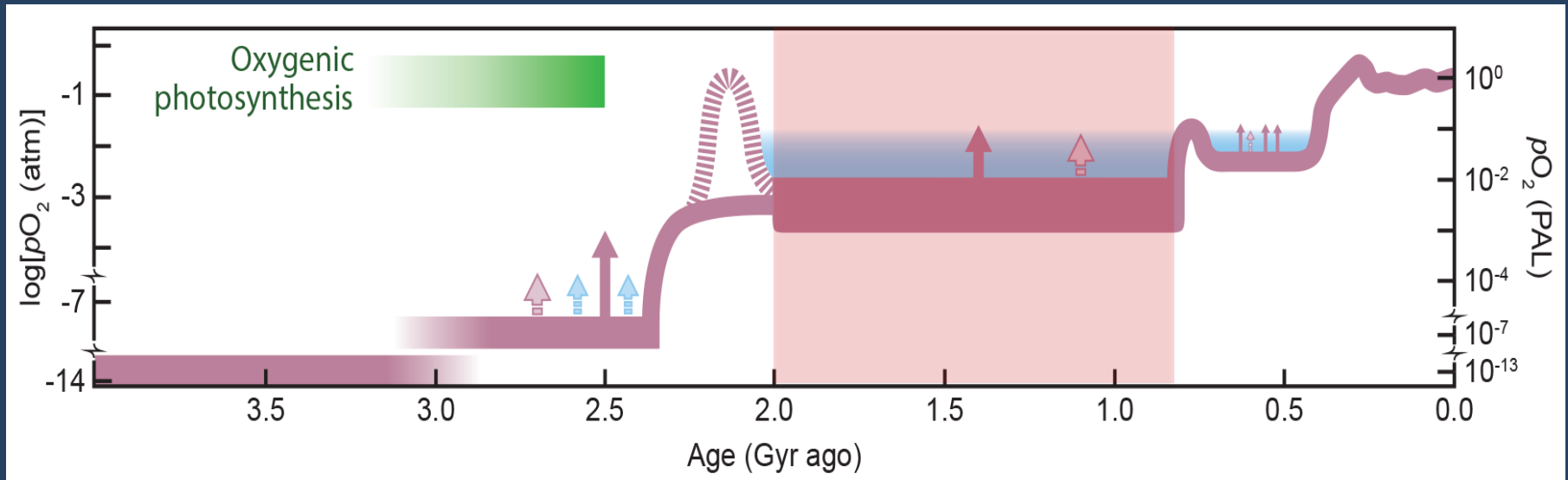
Mo isotope values in BIFs provide a signature for Mn oxidation =  $\text{O}_2$



as  $\text{MnO}_2 \uparrow$   $\delta^{98}\text{Mo} \downarrow$

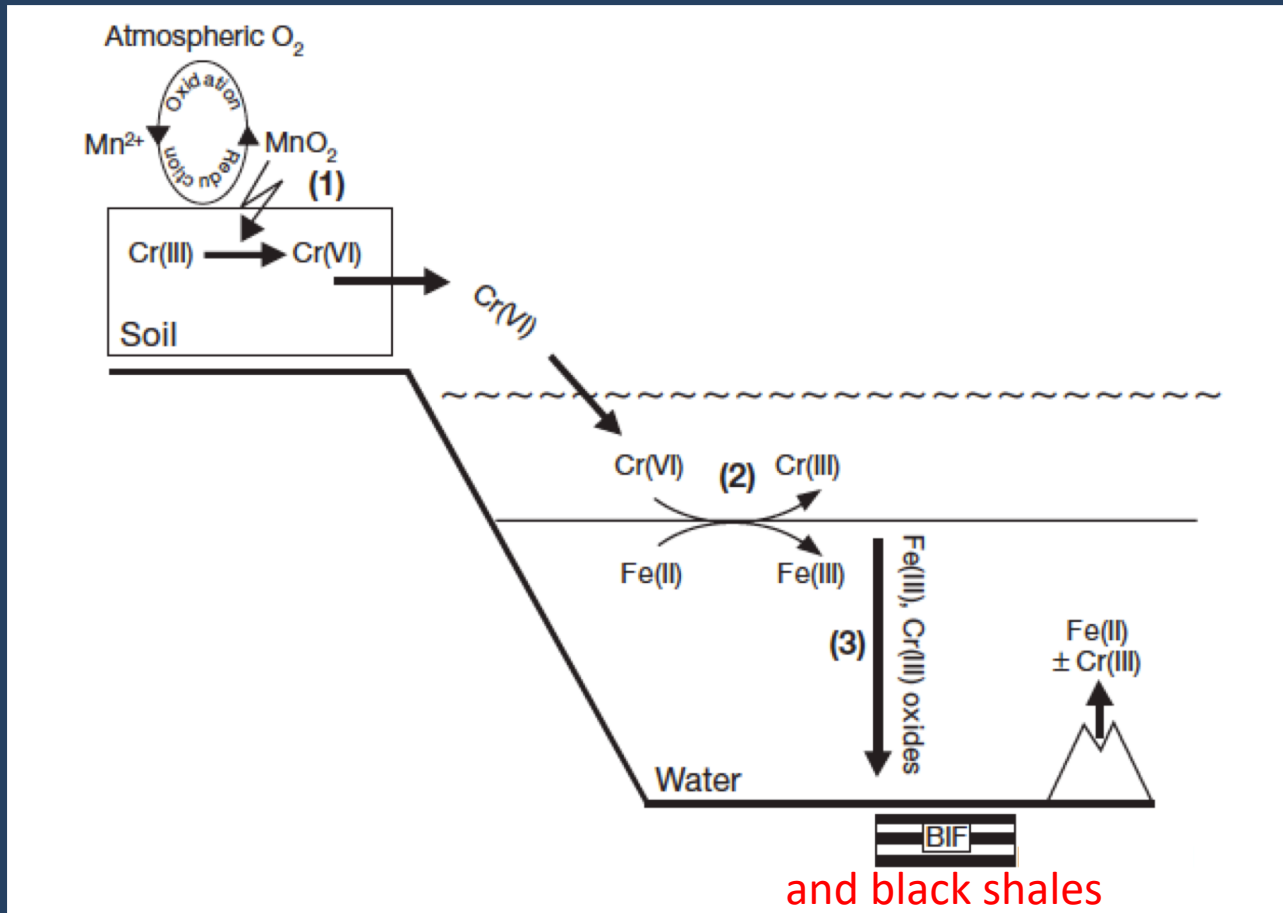


# Earth's History of Evolving O<sub>2</sub>



after Lyons et al. (2014)

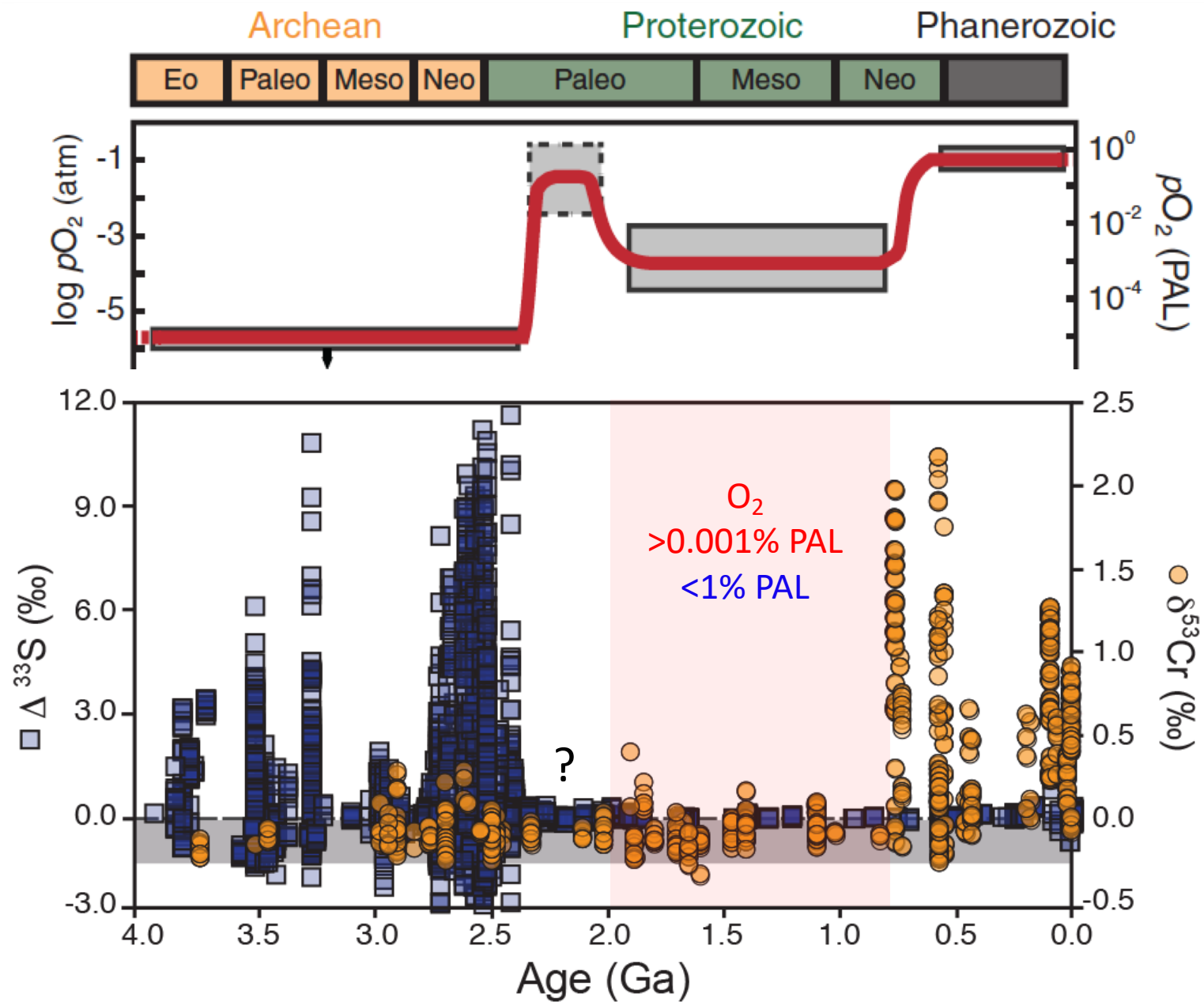
# The ancient atmosphere: Cr isotopes



and black shales

after Frei et al. (2009)





# The deep ocean: Trace metal mass balance

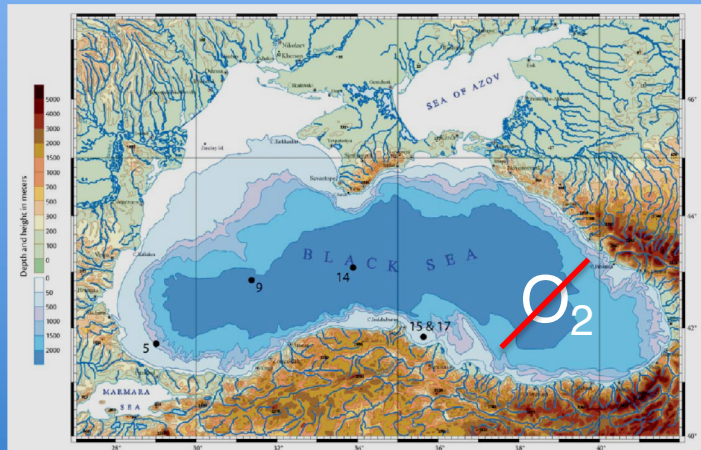


Trace metals are delivered to the ocean via oxidative weathering of the continents and scavenged in low  $O_2$  marine settings.

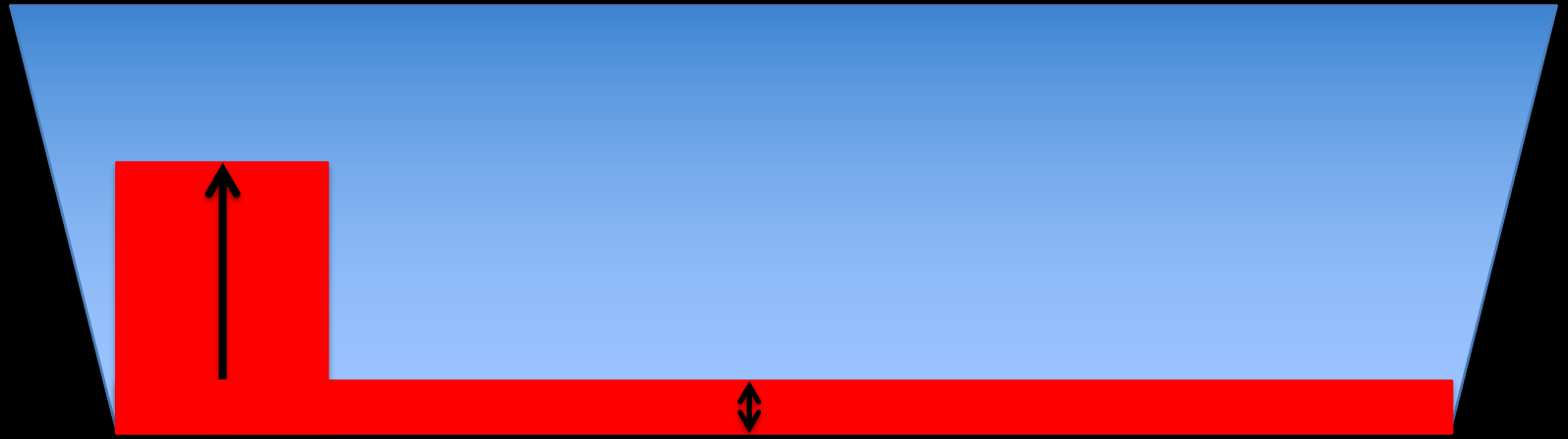
TM  
source



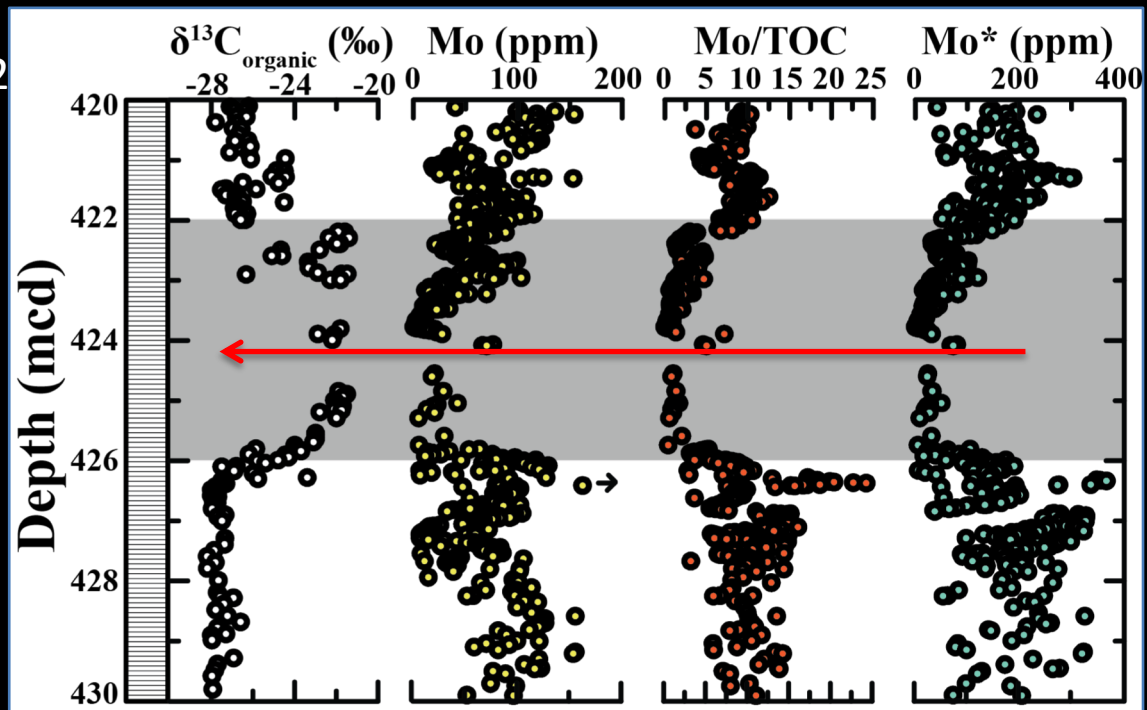
sink



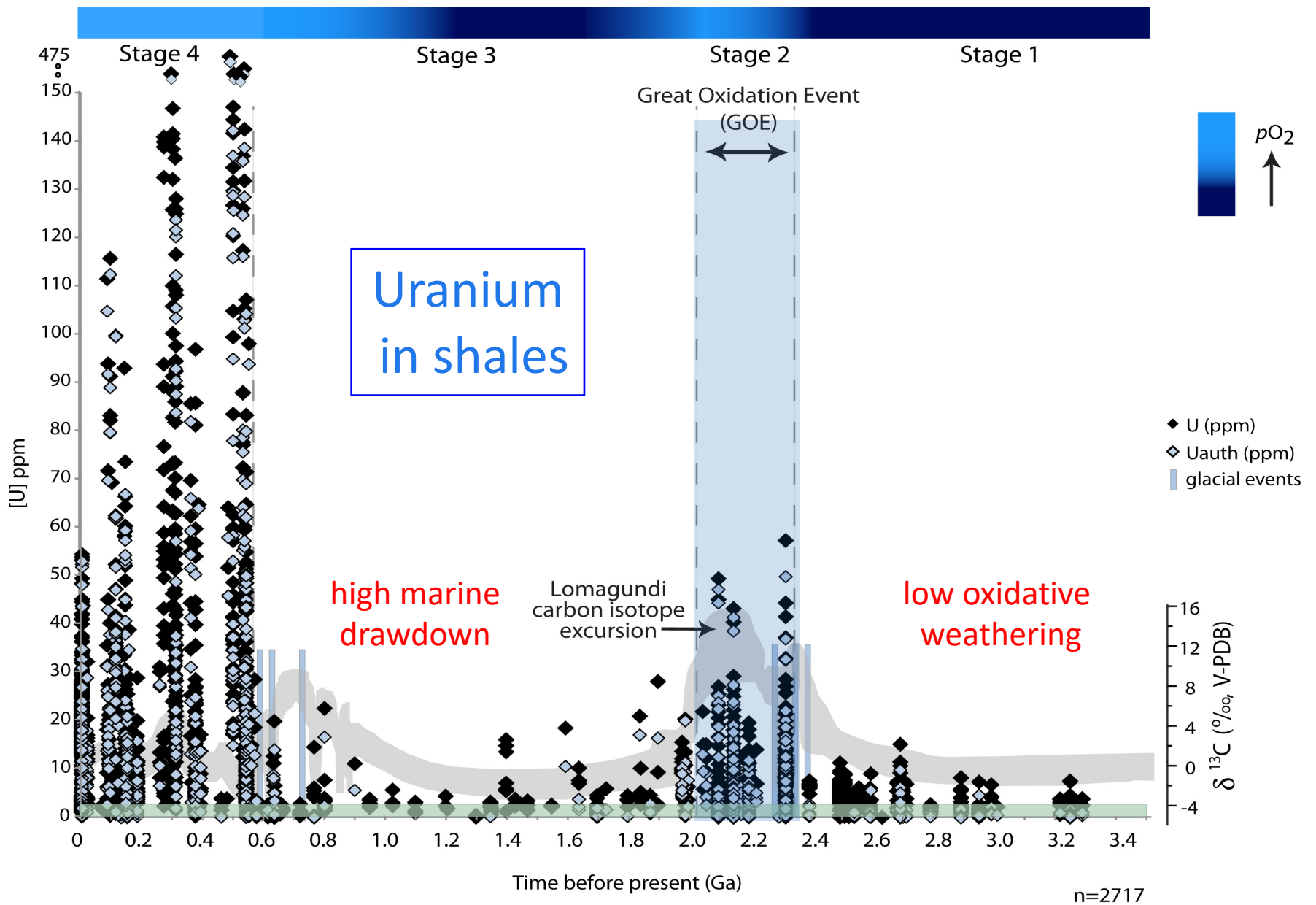




Proof of Concept:  
Cretaceous OAE 2  
Demerara Rise



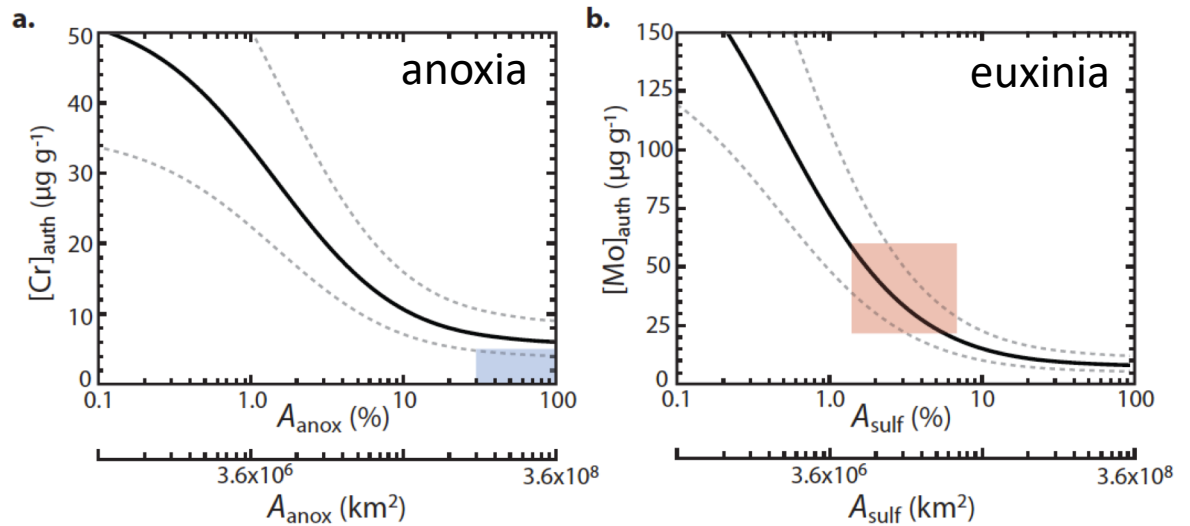
Owens et al. (2016)



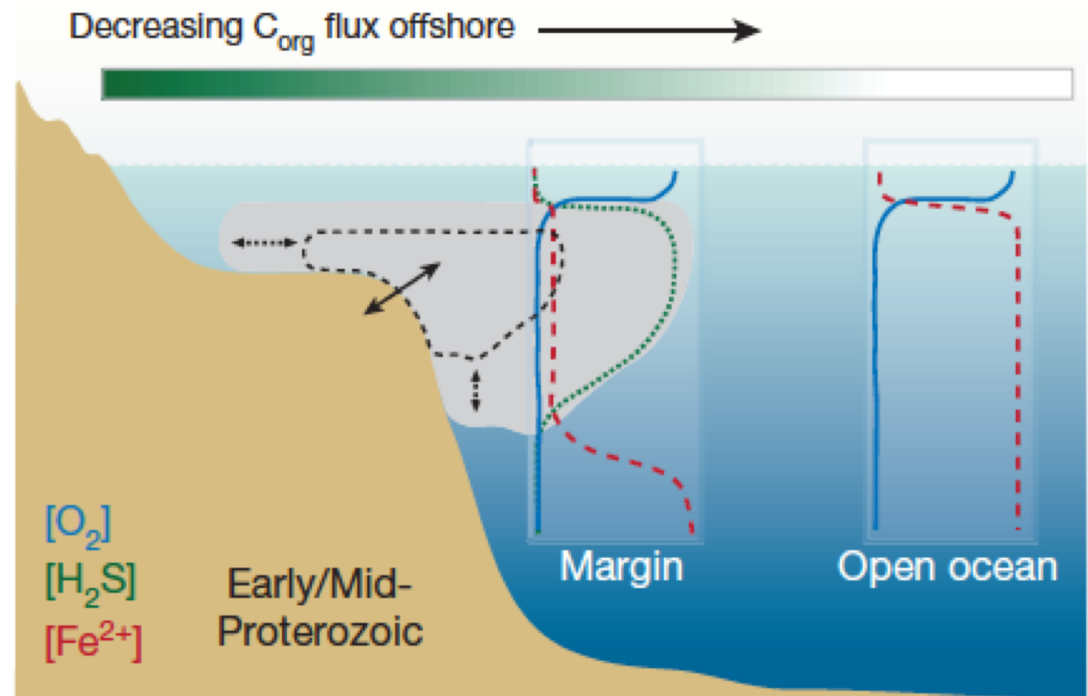


# Trace metal inventories

Reinhard et al. (2013)

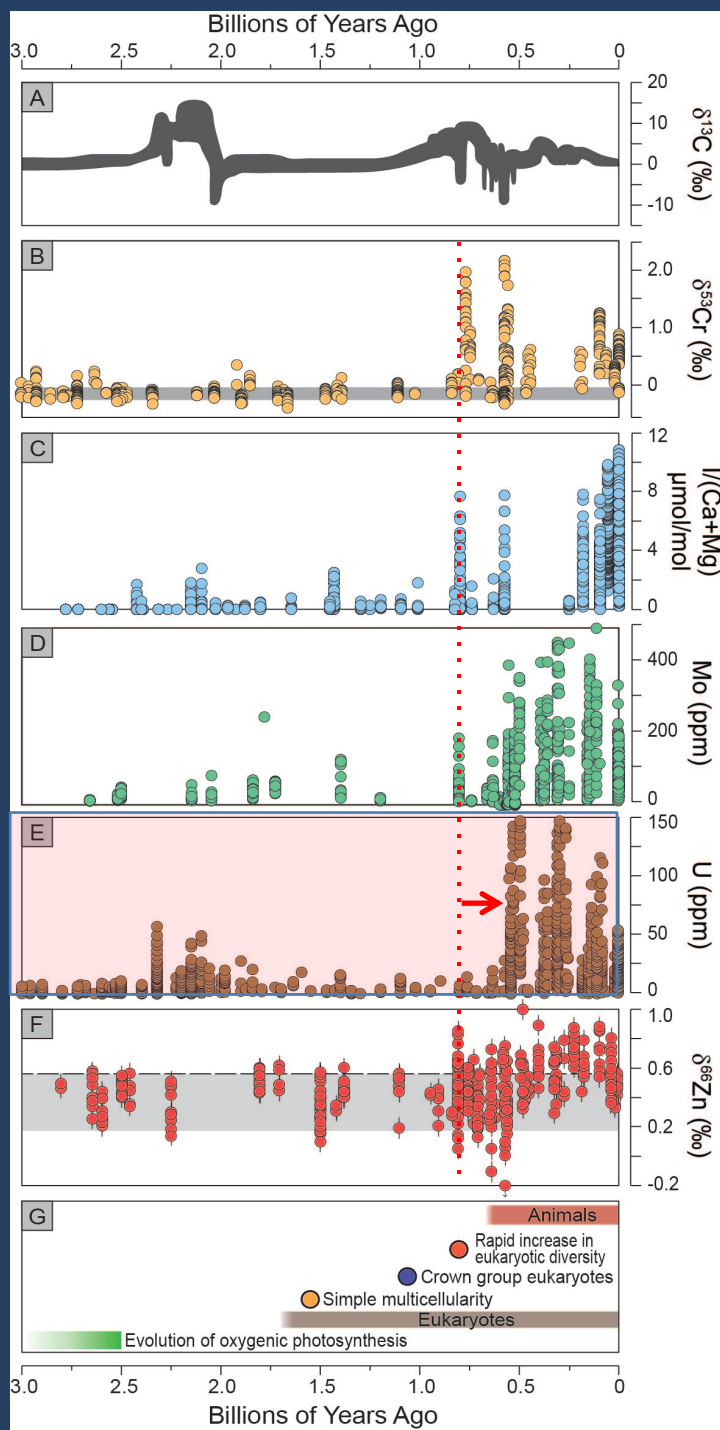
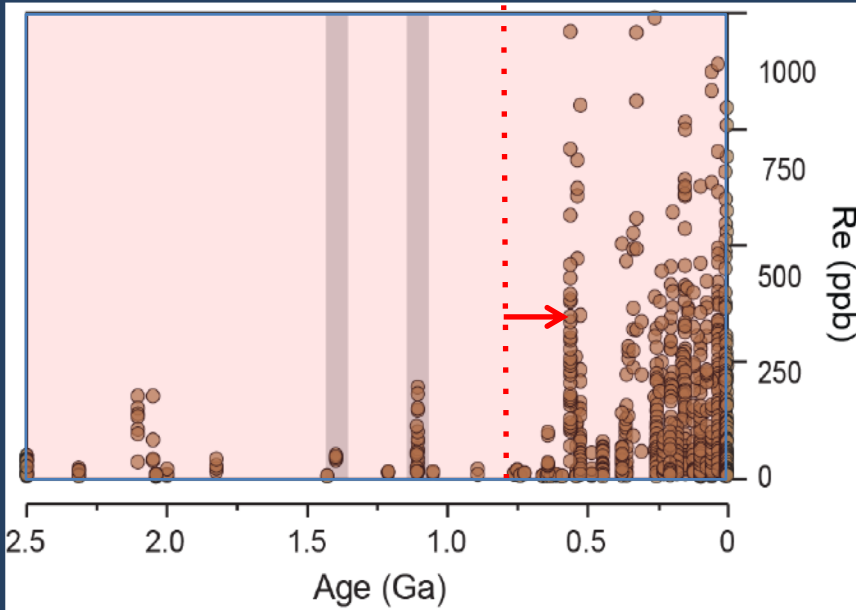
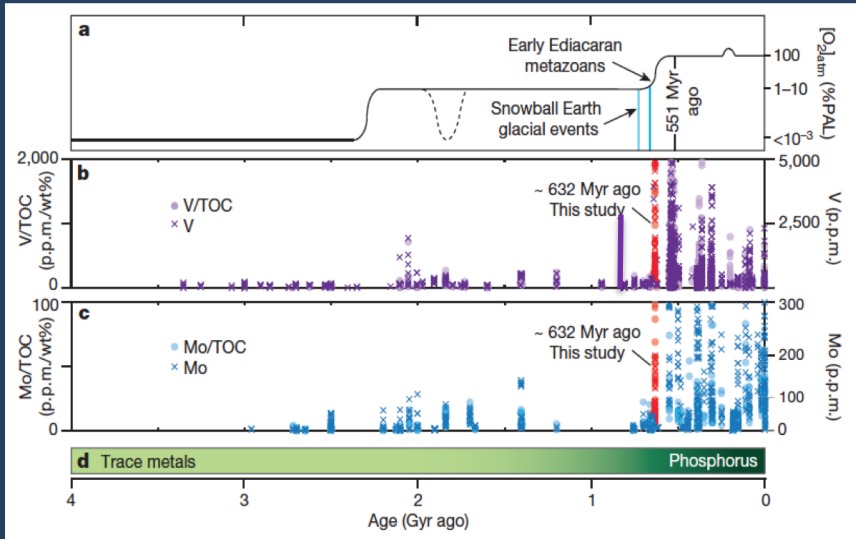


# Stratified water column (iron proxies)



Poulton and Canfield (2011), Planavsky et al. (2011), Lyons et al. (2014)

# ca. 800 Ma The second step

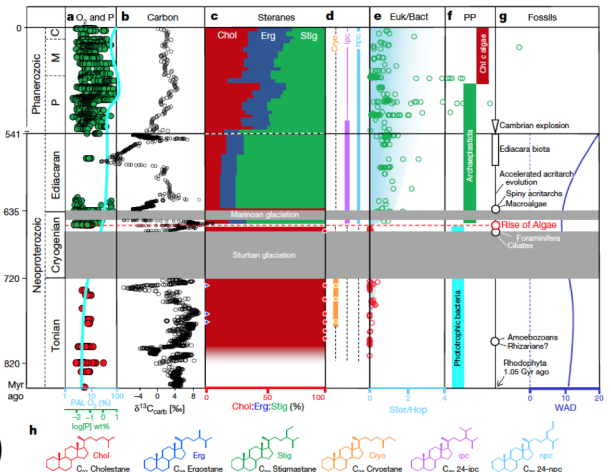
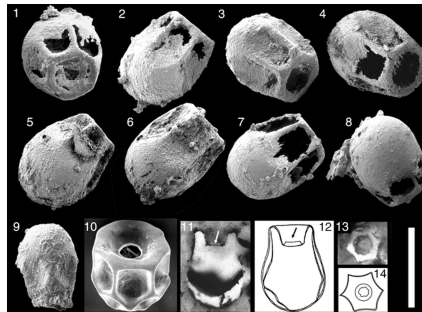
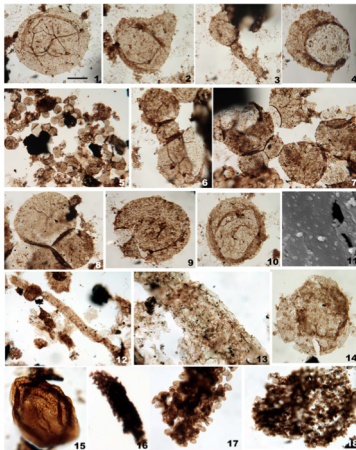
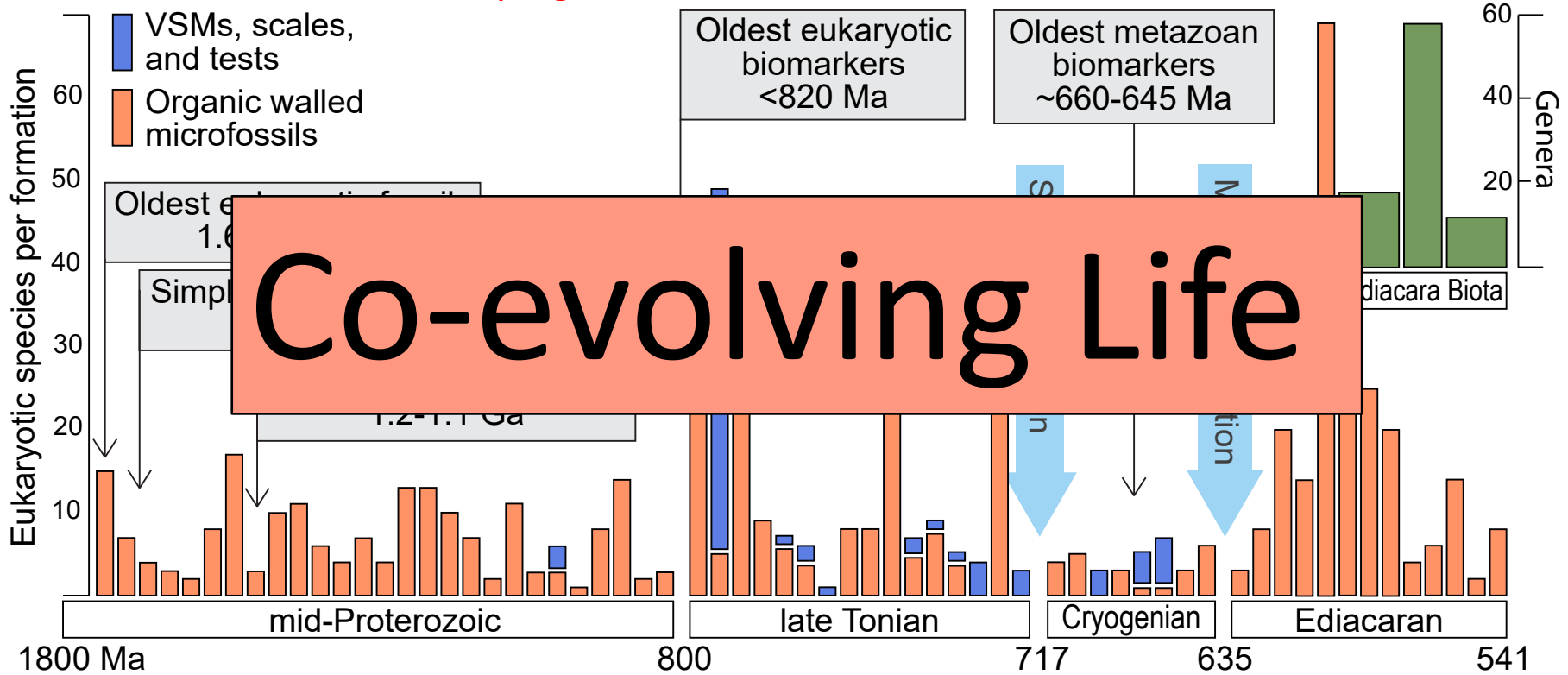


data from many sources

atmosphere to the deep ocean



— macroevolutionary lag —



Brocks et al. (2017)

Ediacaran

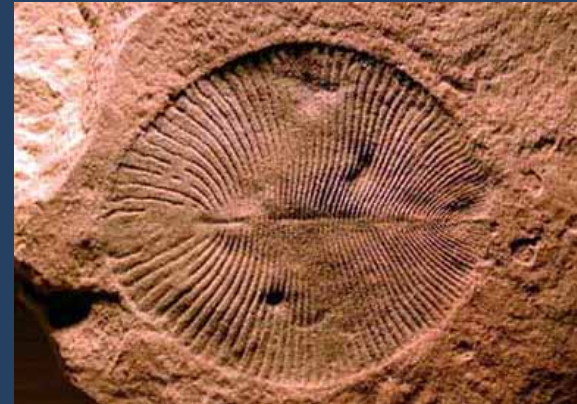
635 Ma



Cryogenian



720 Ma



nature

Vol 457|5 February 2009|doi:10.1038/nature07673

LETTERS

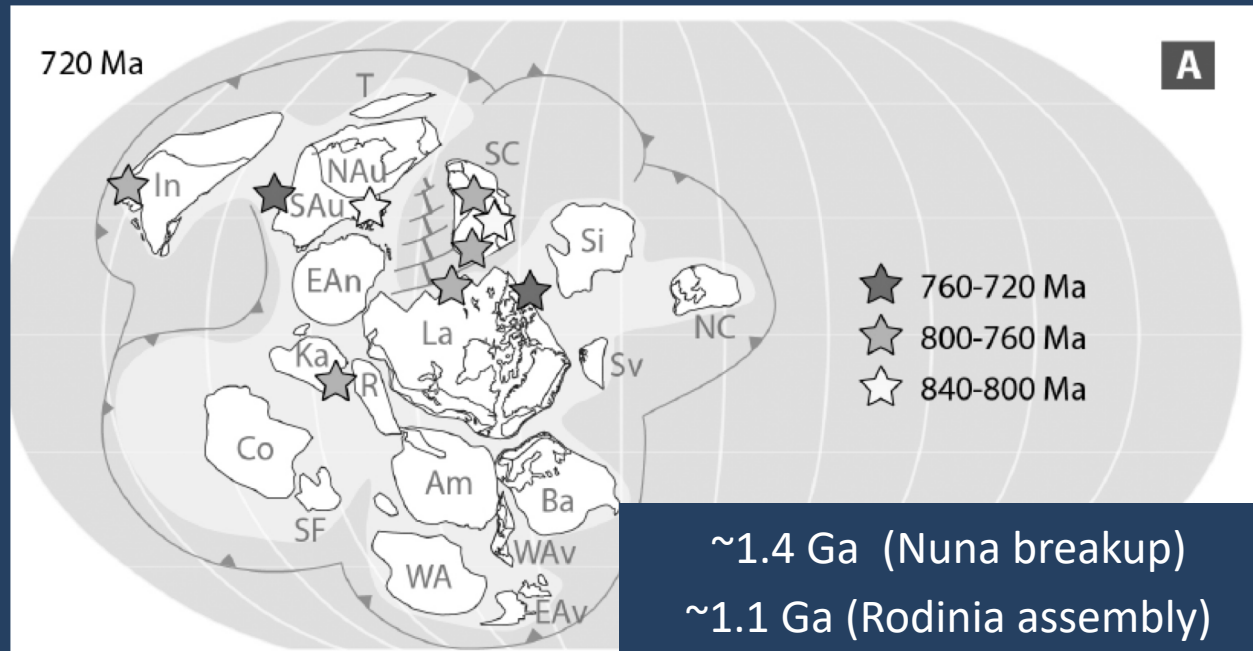
## Fossil steroids record the appearance of Demospongiae during the Cryogenian period

Gordon D. Love<sup>1,2</sup>, Emmanuelle Grosjean<sup>3</sup>, Charlotte Stalvies<sup>4</sup>, David A. Fike<sup>5</sup>, John P. Grotzinger<sup>5</sup>, Alexander S. Bradley<sup>2</sup>, Amy E. Kelly<sup>2</sup>, Maya Bhatia<sup>2</sup>, William Meredith<sup>6</sup>, Colin E. Snape<sup>6</sup>, Samuel A. Bowring<sup>2</sup>, Daniel J. Condon<sup>2†</sup> & Roger E. Summons<sup>2</sup>



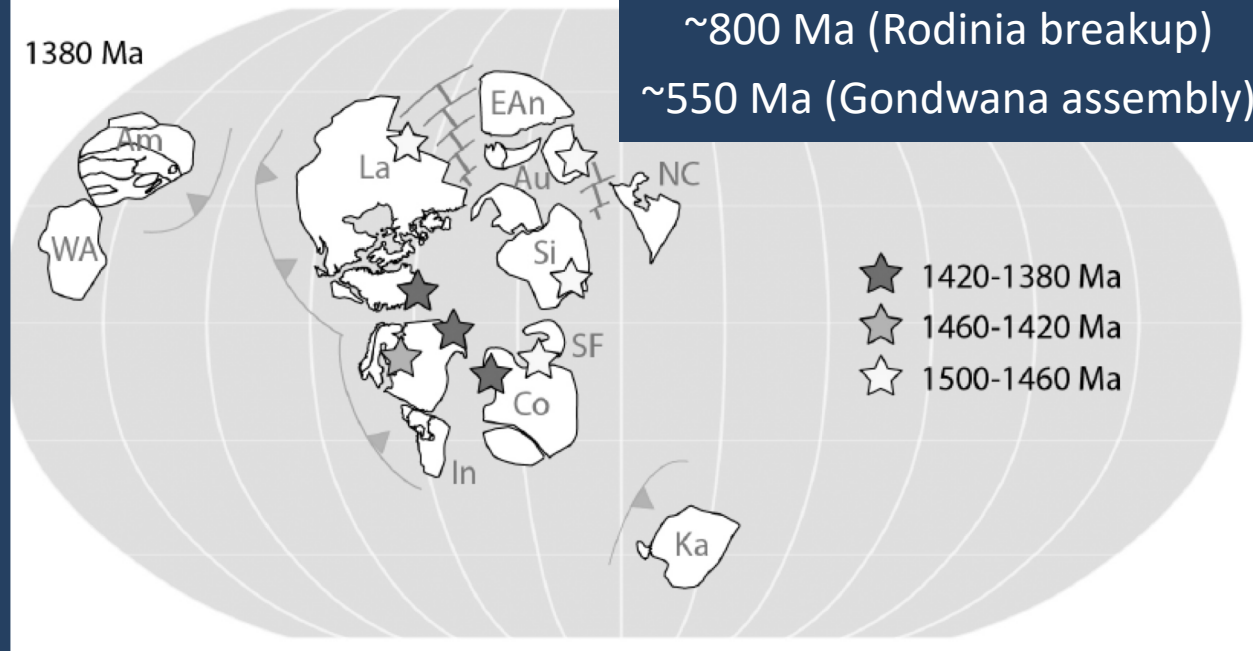
# Tectonic Drivers

Rodinia  
(Neoprot.)



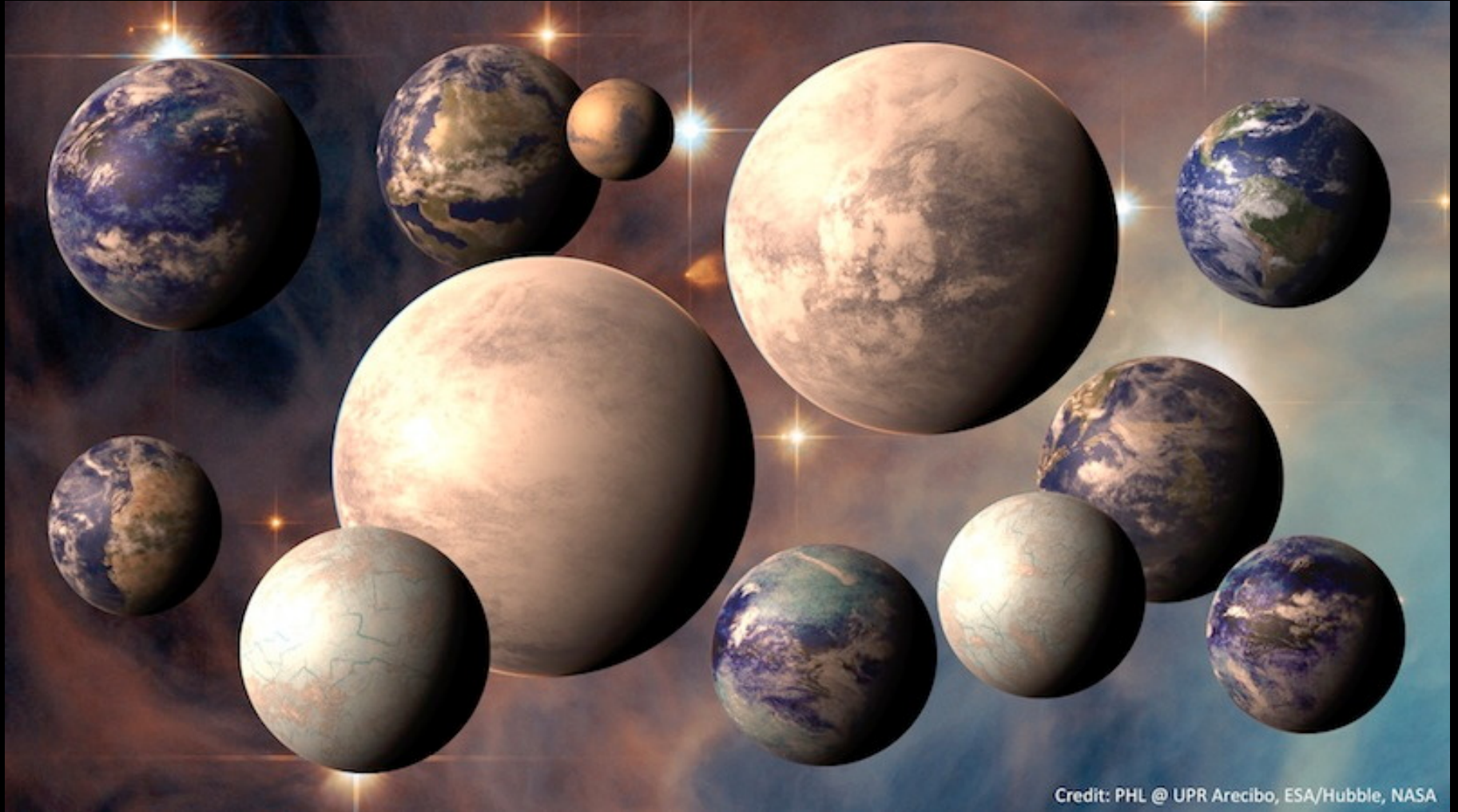
~1.4 Ga (Nuna breakup)  
~1.1 Ga (Rodinia assembly)  
~800 Ma (Rodinia breakup)  
~550 Ma (Gondwana assembly)

Nuna  
(mid-Prot.)  
“boring billion”



Dave Evans in Planavsky et al. (2015)

# The Extrapolation



Credit: PHL @ UPR Arcibo, ESA/Hubble, NASA



# *Vertical Integration*

Detectability informed by present and future telescopes using instrument simulators.

Synthetic spectra via atmosphere radiative transfer models.

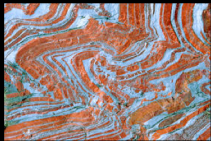
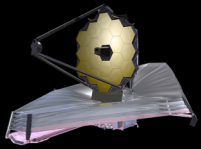
1- and 3-D photochemical climate models.

---

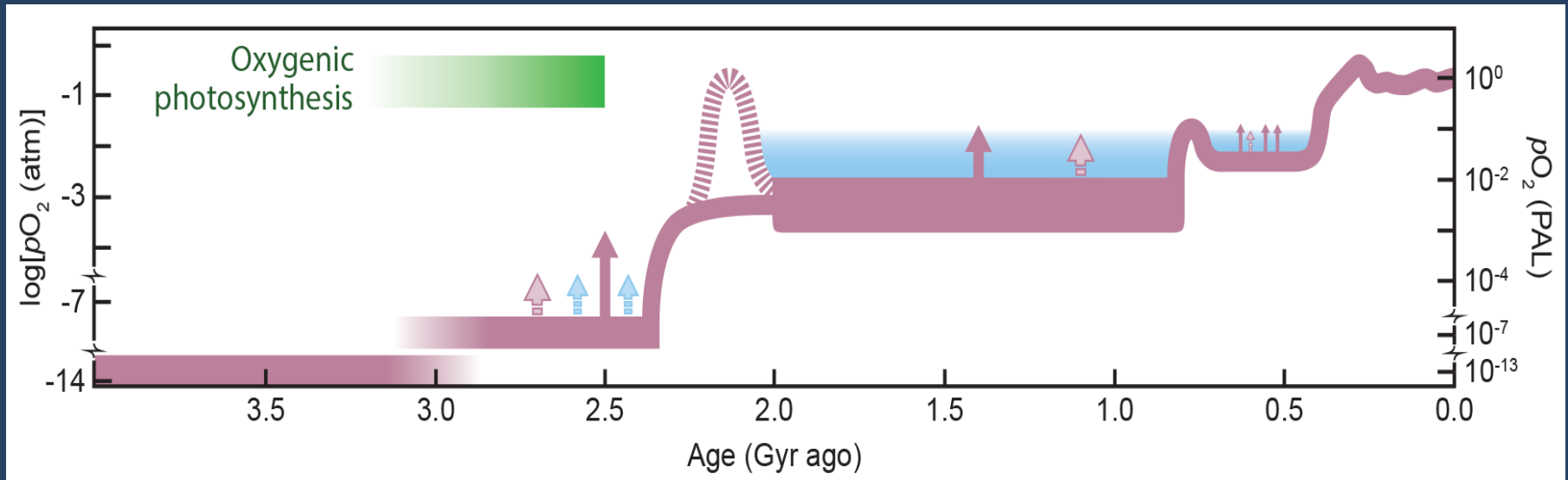
3-D models define ocean properties and fluxes to atmos.

Proxies developed by us and applied to early Earth to constrain ocean/atmosphere compositions.

Diverse planetary scenarios — in terms of habitability and biosignatures (guided by early 'alternative' Earths).



# Earth's History of Evolving O<sub>2</sub>

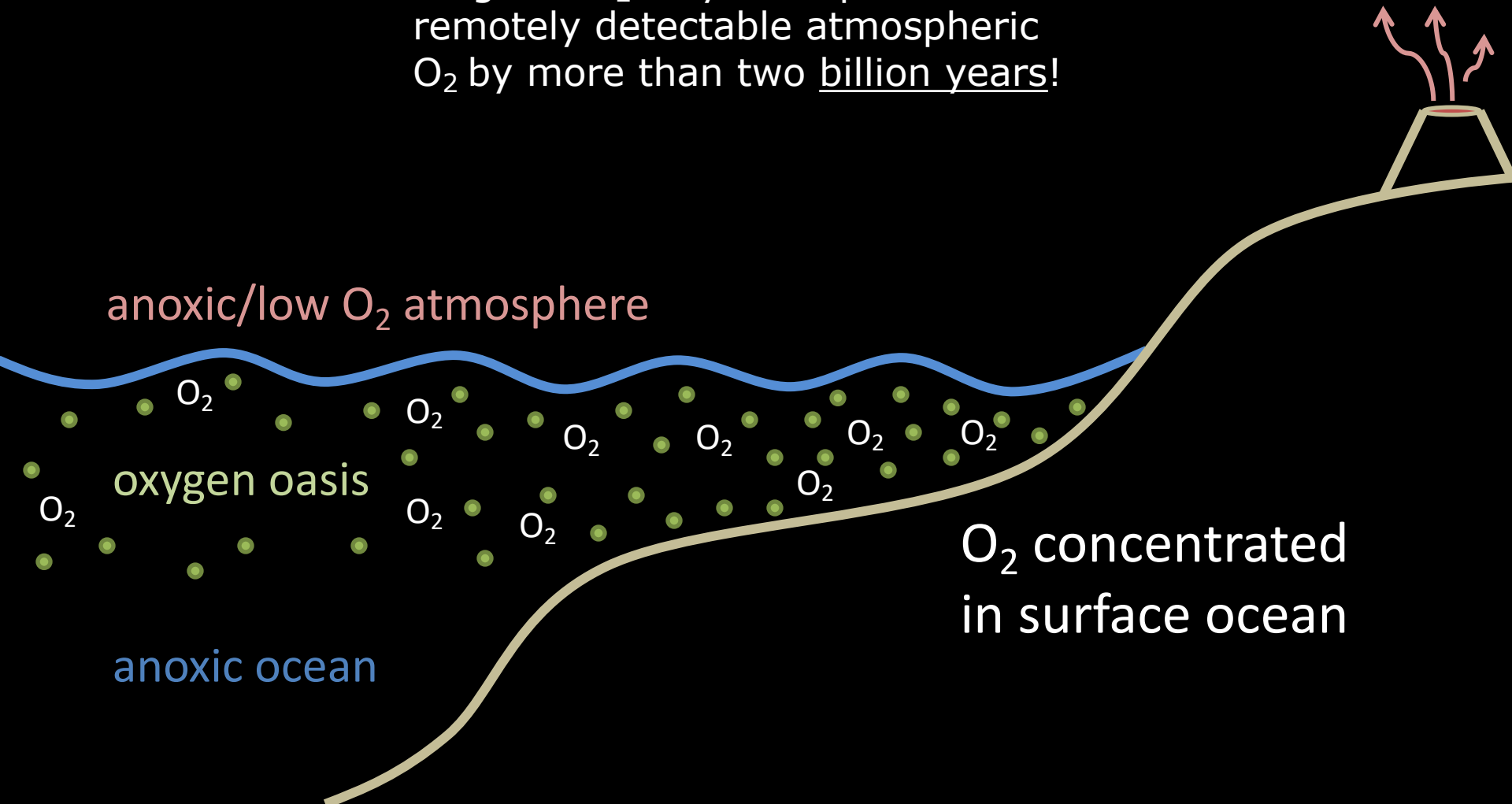


after Lyons et al. (2014)



# Earth's atmosphere may have been an unfaithful reflection of surface chemistry and biology

- ✧ Biogenic  $O_2$  may have predated remotely detectable atmospheric  $O_2$  by more than two billion years!



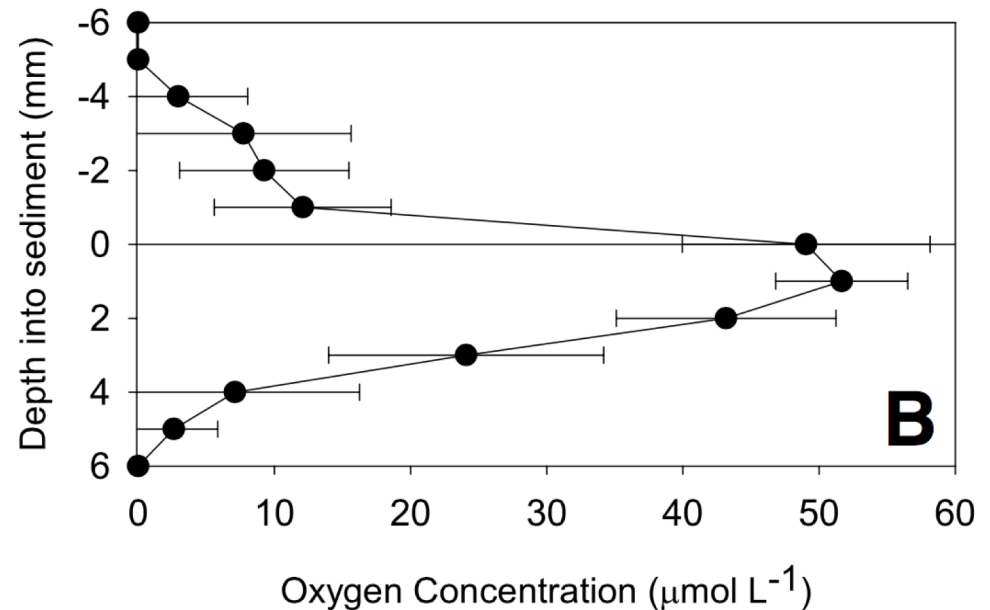
# mat-hosted micro-oases

- Chemical conditions that strongly differ from the surrounding environment
- High but extremely localized dissolved O<sub>2</sub> concentrations (mm scale)



Photo: T. Bosak

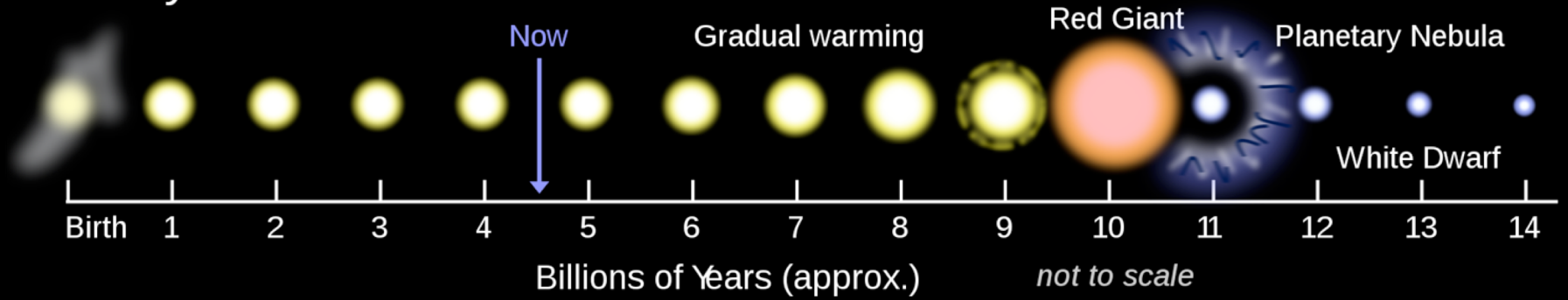
Data: Sumner et al. (2015)





# Warming Sun

## Life Cycle of the Sun

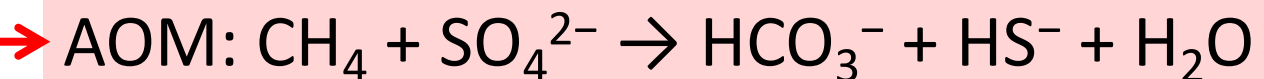


high  
 $\text{CH}_4$



# Pathways of respiration (redox)

<p>Aerobic respiration</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + xO_2 + yH^+ \rightarrow xCO_2 + yNH_4^+ + HPO_4^{2-} + 2H^+ + xH_2O$	$O_2$
<p>Denitrification</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + \frac{4}{5}xNO_3^- + (\frac{4}{5}x + y)H^+ \rightarrow xCO_2 + yNH_4^+ + \frac{2}{5}xN_2 + HPO_4^{2-} + \frac{7}{5}xH_2O$	$NO_3^-$
<p>Dissimilatory manganese reduction</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + 2xMnO_2 + (4x + y)H^+ \rightarrow xCO_2 + 2xMn^{2+} + yNH_4^+ + HPO_4^{2-} + 2H^+ + 3xH_2O$	$Mn(IV)$
<p>Dissimilatory iron reduction</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + 4xFe(OH)_3 + (8x + y)H^+ \rightarrow xCO_2 + 4xFe^{2+} + yNH_4^+ + HPO_4^{2-} + 2H^+ + 11xH_2O$	$Fe(III)$
<p>Sulfate reduction</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + \frac{1}{2}xSO_4^{2-} + (\frac{1}{2}x + y)H^+ \rightarrow xCO_2 + \frac{1}{2}x\Sigma H_2S + yNH_4^+ + HPO_4^{2-} + H^+ + xH_2O$	$SO_4^{2-}$
<p>Methanogenesis</p> $(CH_2O)_x(NH_3)_y(H_3PO_4) + yH^+ \rightarrow \frac{1}{2}xCO_2 + \frac{1}{2}xCH_4 + yNH_4^+ + HPO_4^{2-} + 2H^+$	





# METHANE MUTED

## How Did Early Earth Stay Warm?



For at least a billion years of its early history, planet Earth should have been frozen over but wasn't. The sun was up to 20% dimmer than it is today—too weak to warm the planet on its own. Atmospheric models hype methane, a potent greenhouse gas, as the primary climate warming agent for the first 3.5 billion years of Earth history, because oxygen was absent initially and little more than a whiff later on. (Newer oxygen is one fifth of the air we breathe, and it destroys methane in a matter of years.)

# Low methane flux plus weak ozone shielding

PNAS, Sept. 26, 2011

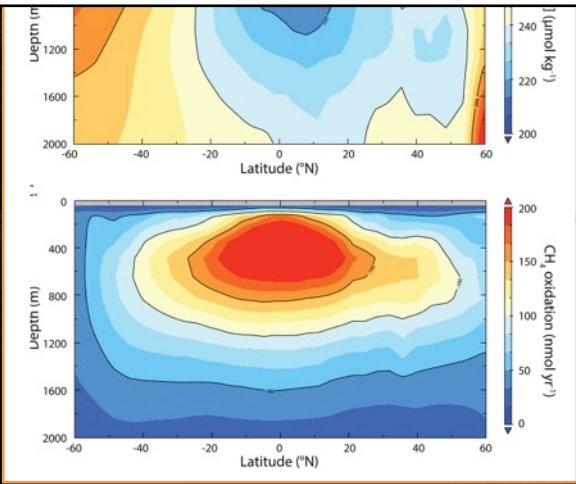
Stephanie Olson  
UC Riverside



Chris Reinhard  
Georgia Tech



Tim Lyons  
UC Riverside



The Alternative Earths Team of the NASA Astrobiology Institute finds that, contrary to popular climate models for the distant past, methane could not be the gas that kept the oceans liquid and livable.

biogeochemical cycles in which is produced in the ferment organic matter, oxygen: sulfate. Between, seawater sulfate limited

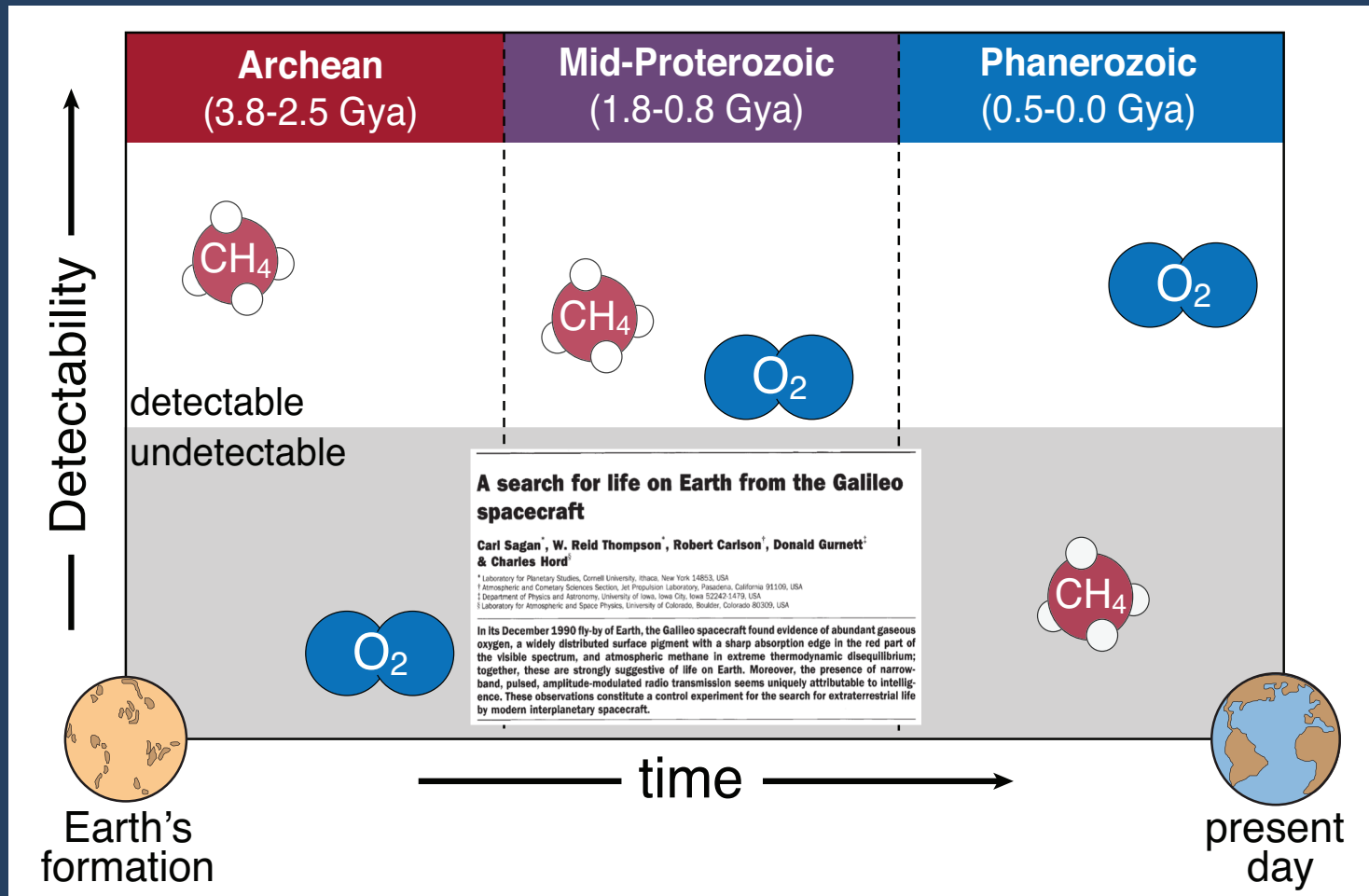
both the production and accumulation of methane to only 1 to 10 parts per million (ppm) in the atmosphere. That's a fraction of the 300 ppm touted by some previous models—*and well below remote detection limits of current technology*

**INNOVATION** | The numerical model used in this study, which calculated sulfate reduction (*top*), methane oxidation (*bottom*), and an array of other biogeochemical cycles for nearly 15,000 three-dimensional regions of the ocean, is by far the highest resolution biogeochemical model ever applied to the ancient Earth. Previous models used no more than five regions.

**IMPACT** | Astrobiologists now face a serious challenge to explain our planet's early habitability. Identifying early Earth's precise greenhouse cocktail, probably including water vapor, nitrous oxide, and carbon dioxide, is essential for spectroscopic efforts to assess the habitability of other planets in our galaxy.

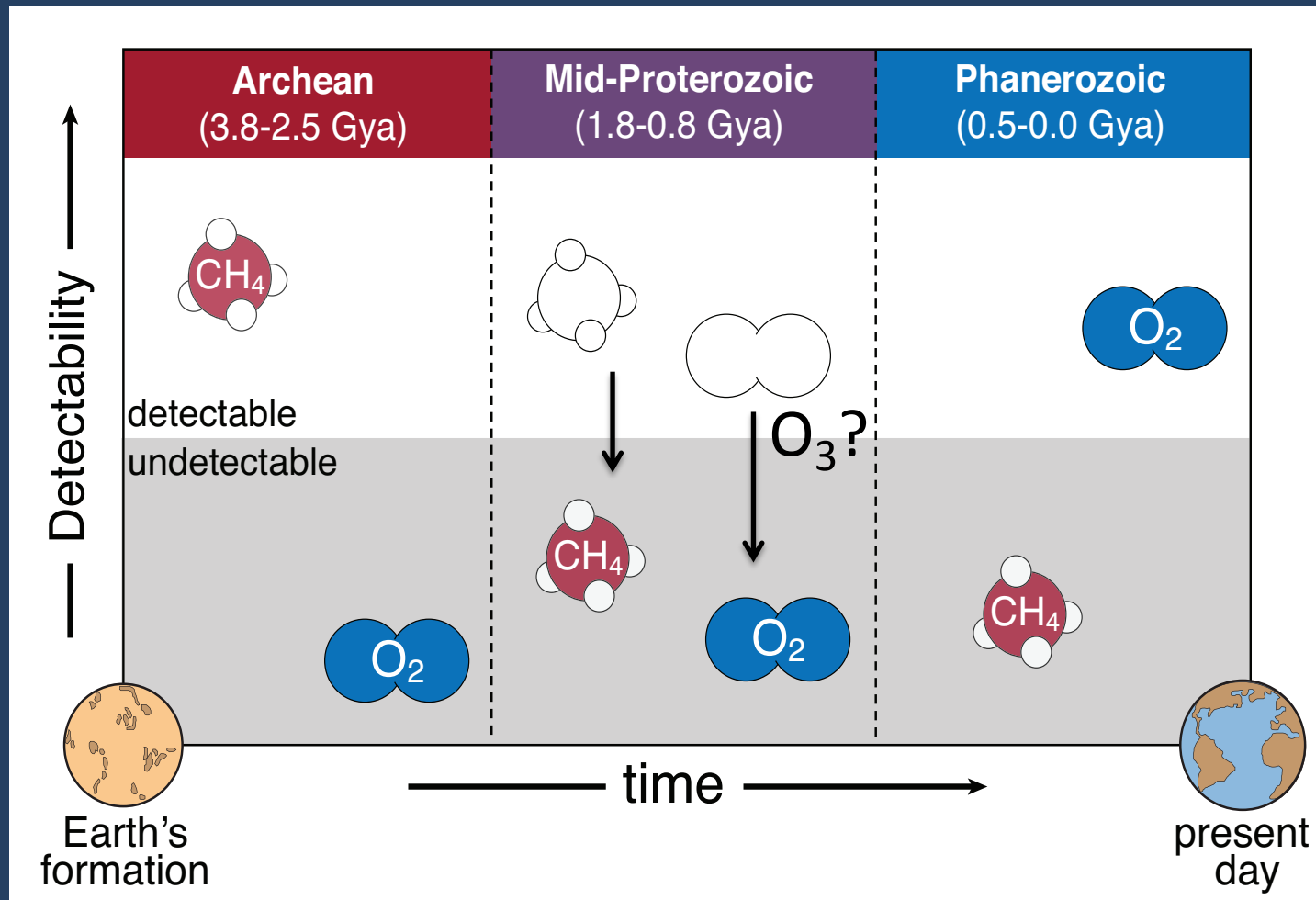
BACKGROUND IMAGE This artist's depiction of an ice-covered planet in a distant solar system resembles what early Earth might have looked like if a mysterious mix of greenhouse gases had not warmed the climate. CREDIT: EUROPEAN SOUTHERN OBSERVATORY (ESO) VIA WIKIMEDIA COMMONS

# Alternative Earth Biosignatures: The Paradigm



after Des Marais et al. (2002)

# Alternative Earth Biosignatures: An Updated View and False Negatives

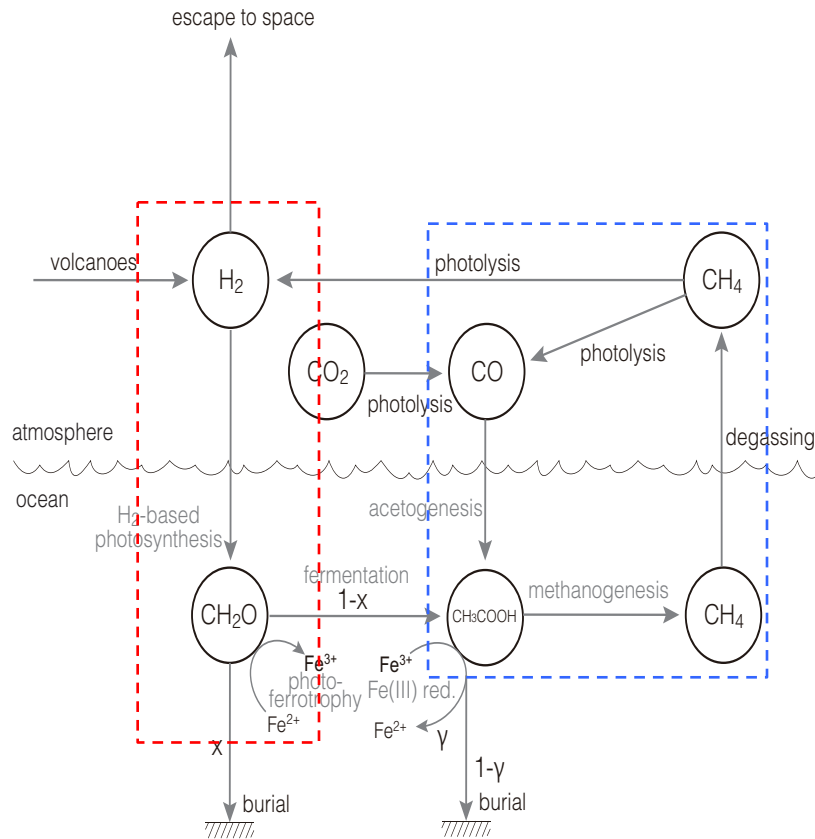


modified from Schwieterman et al. (Astrobiology, 2018)



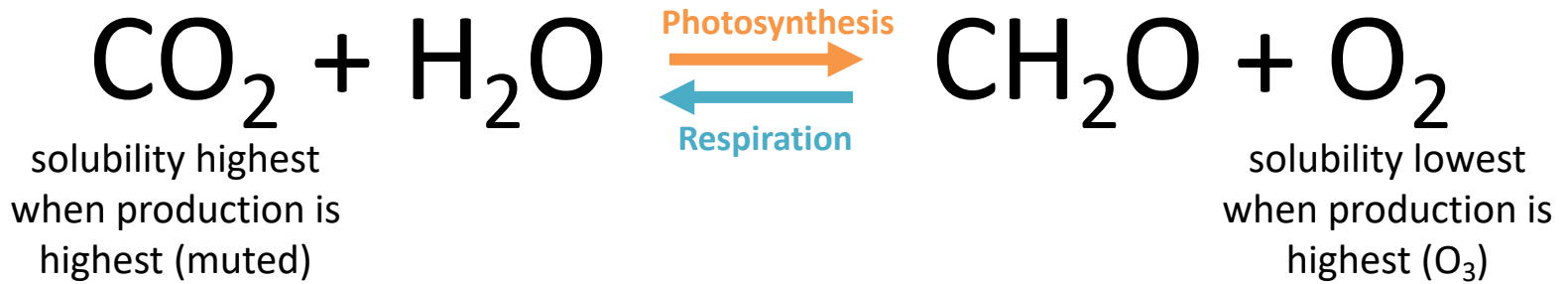
# Rethinking CO 'Anti-Biosignatures' in the Search For Life Beyond Earth

Schwieterman et al. (2019)



We demonstrate using a 1-D ecosphere-atmosphere model that anoxic biospheres can easily sustain CO levels exceeding 100 ppmv even at low H<sub>2</sub> fluxes, due to the impact of hybrid photosynthetic ecosystems.

For some exoplanets, remotely detectable carbon monoxide may actually be diagnostic of a robust microbial biosphere.



Insolation    Temperature    Gas solubility



THE ASTROPHYSICAL JOURNAL LETTERS, 858:L14 (7pp), 2018 May 10





<https://doi.org/10.3847/2041-8213/aac171>

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CrossMark

## Atmospheric Seasonality as an Exoplanet Biosignature

Stephanie L. Olson<sup>1,2</sup> , Edward W. Schwieterman<sup>1,2,3,4</sup> , Christopher T. Reinhard<sup>1,5</sup>, Andy Ridgwell<sup>1,2</sup>,  
 Stephen R. Kane<sup>1,2</sup> , Victoria S. Meadows<sup>1,6</sup> , and Timothy W. Lyons<sup>1,2</sup>

<sup>1</sup>NASA Astrobiology Institute Alternative Earths and Virtual Planetary Laboratory Teams

<sup>2</sup>Department of Earth Science, University of California, Riverside, CA, USA

<sup>3</sup>NASA Postdoctoral Program, Universities Space Research Association, Columbia, MD, USA

<sup>4</sup>Blue Marble Space Institute of Science, Seattle, WA, USA

<sup>5</sup>School of Earth and Atmospheric Science, Georgia Institute of Technology, Atlanta, GA, USA

<sup>6</sup>Department of Astronomy, University of Washington, Seattle, WA, USA

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# Importance of direct imaging

# Thanks







Received: 6 July 2018

Accepted: 27 August 2018

DOI: 10.1111/gbi.12317

ORIGINAL ARTICLE

WILEY 

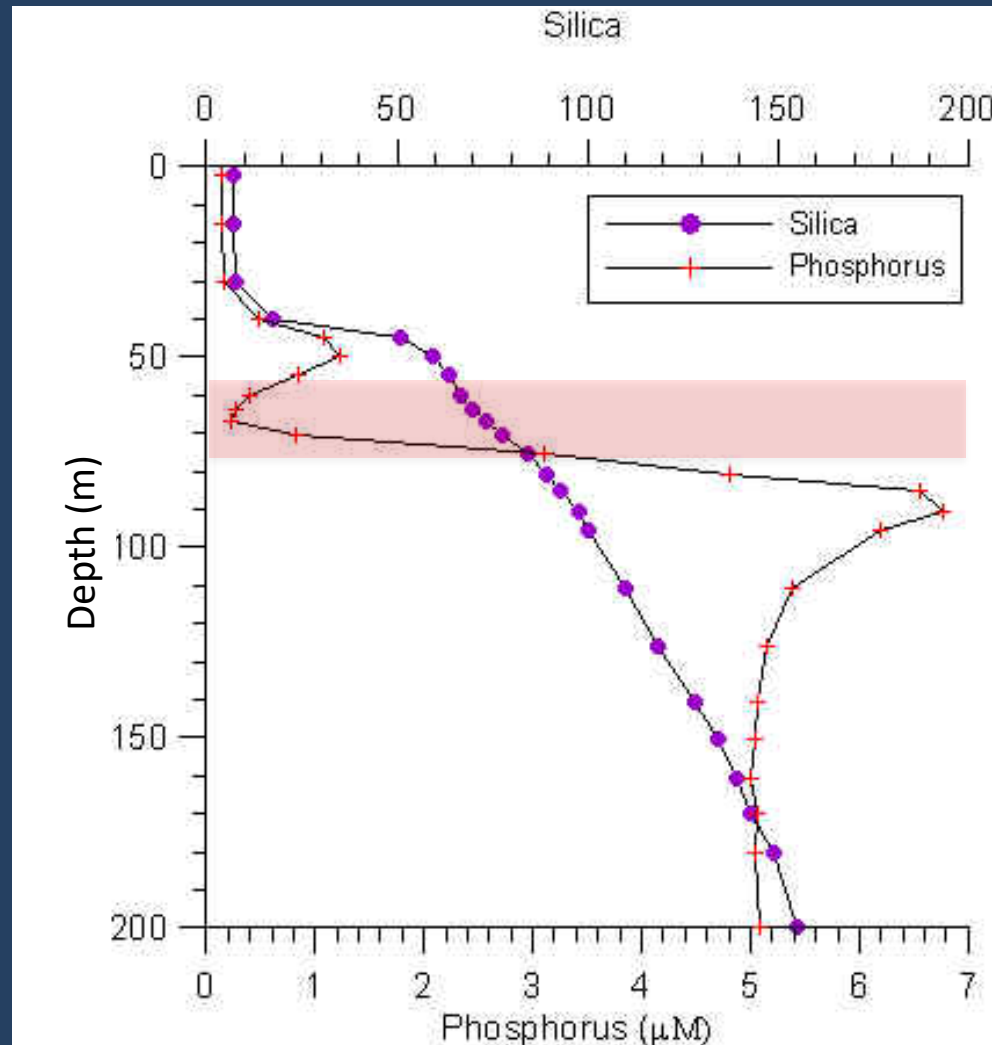
# A sluggish mid-Proterozoic biosphere and its effect on Earth's redox balance

Kazumi Ozaki<sup>1,2,3</sup>  | Christopher T. Reinhard<sup>1,2</sup> | Eiichi Tajika<sup>4</sup> 

By employing a Monte Carlo approach bounded by observations from the geologic record, we infer that the rate of net biospheric O<sub>2</sub> production was ~25% of today's value, owing largely to **phosphorus scarcity** in the ocean interior.

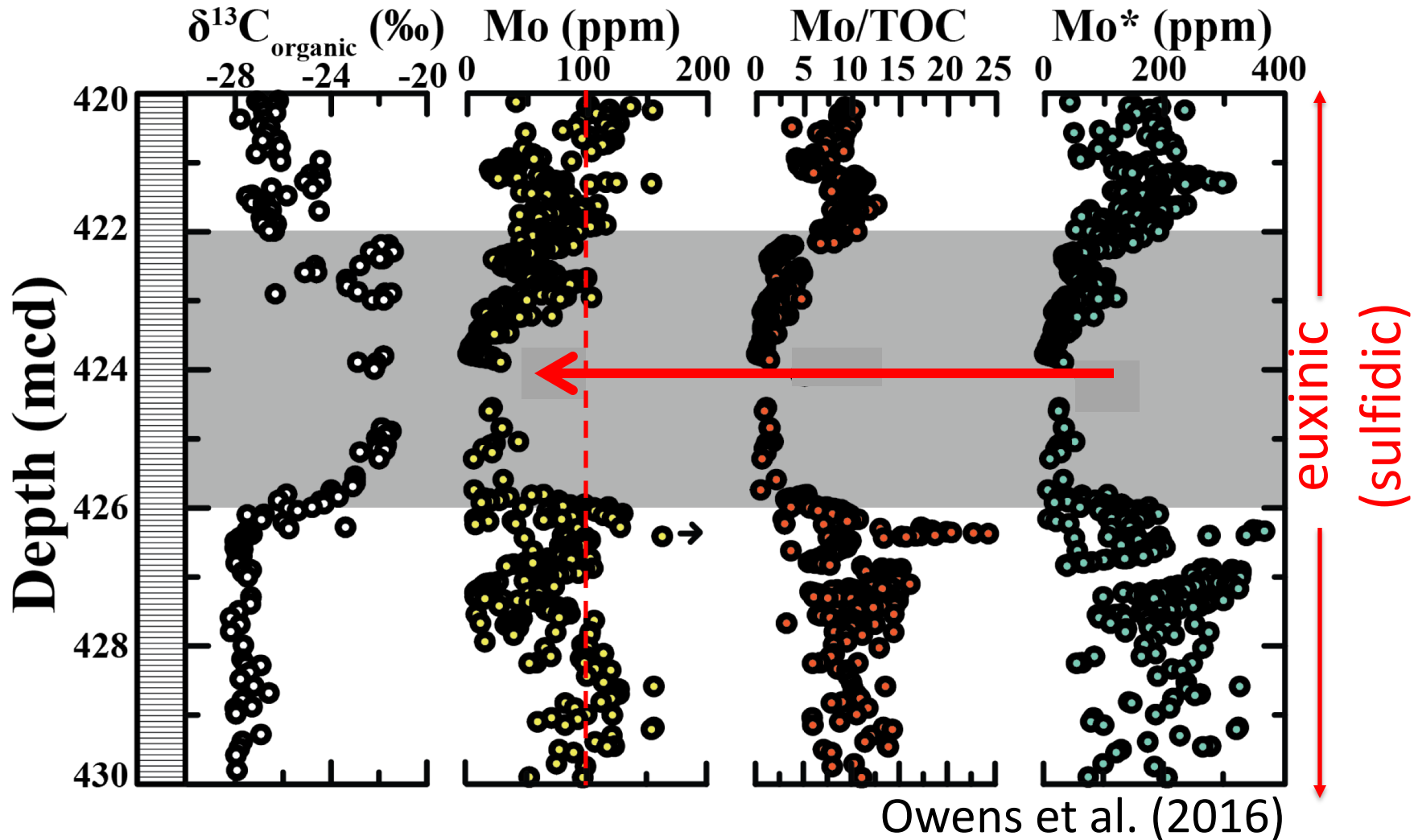
# Iron trap?

Black Sea

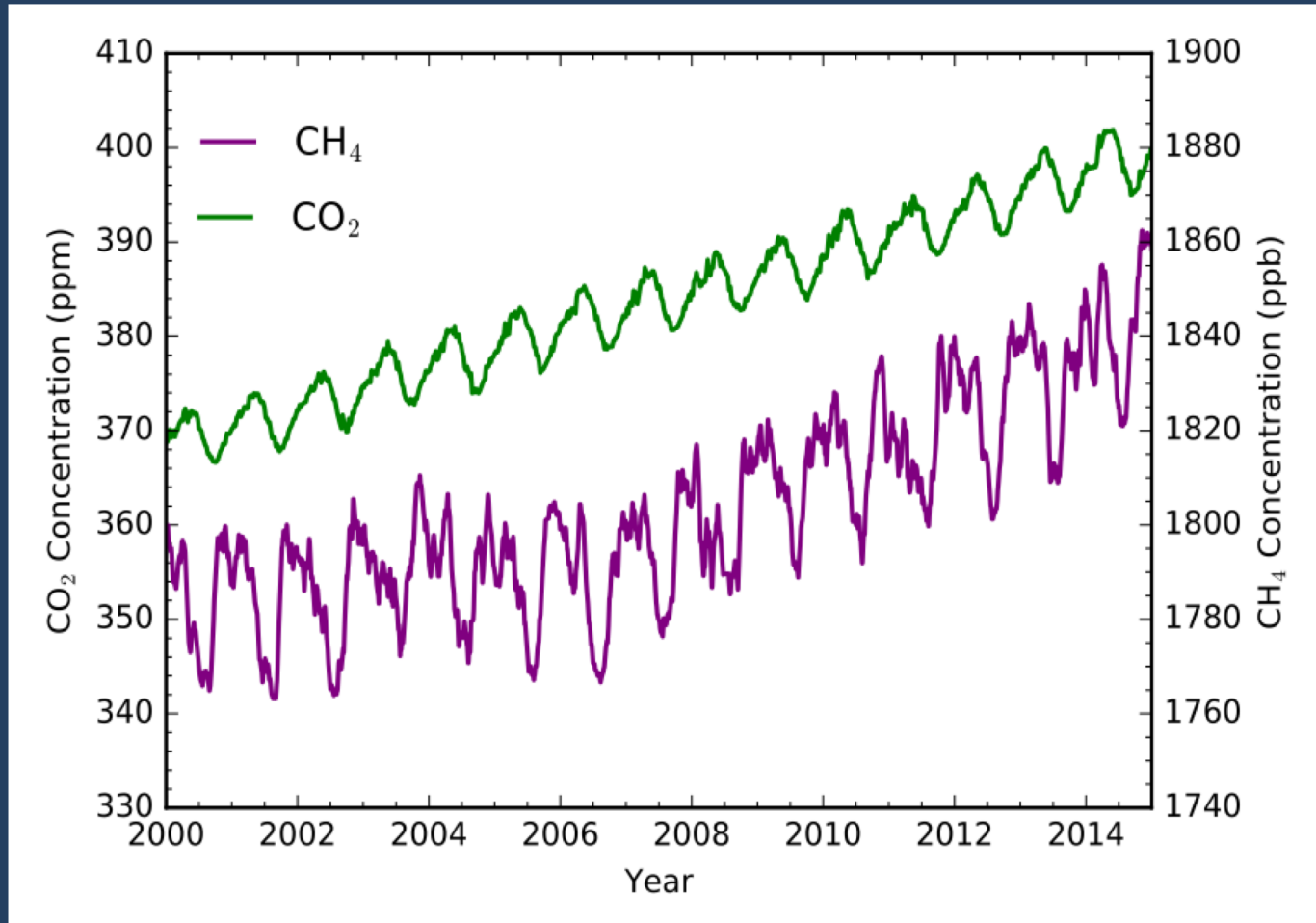




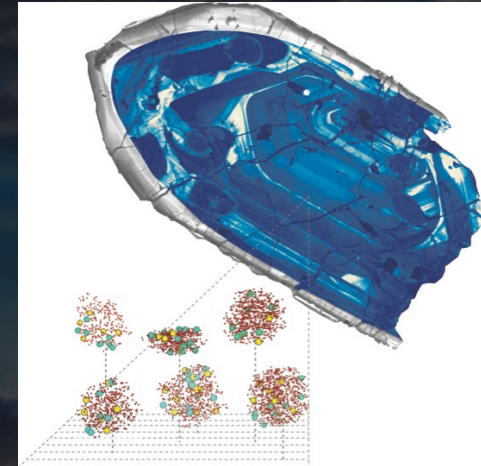
# Proof of Concept: Cretaceous OAE 2, Demerara Rise



The seasonal variations in both gases are partially reflective of the seasonal change in the productivity of the biosphere in the northern hemisphere (The secular increase in both gases is attributable to industrial emissions)



# Cooled Quickly, Early Oceans



Valley et al. (2014)

**Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago**

Simon A. Wilde\*, John W. Valley†, William H. Peck†‡ & Colin M. Graham§

(Nature, 2001)



# Got Life?

**<sup>13</sup>C-Depleted Carbon  
Microparticles in >3700-Ma  
Sea-Floor Sedimentary Rocks  
from West Greenland**

Minik T. Rosing

(Science, 1999)

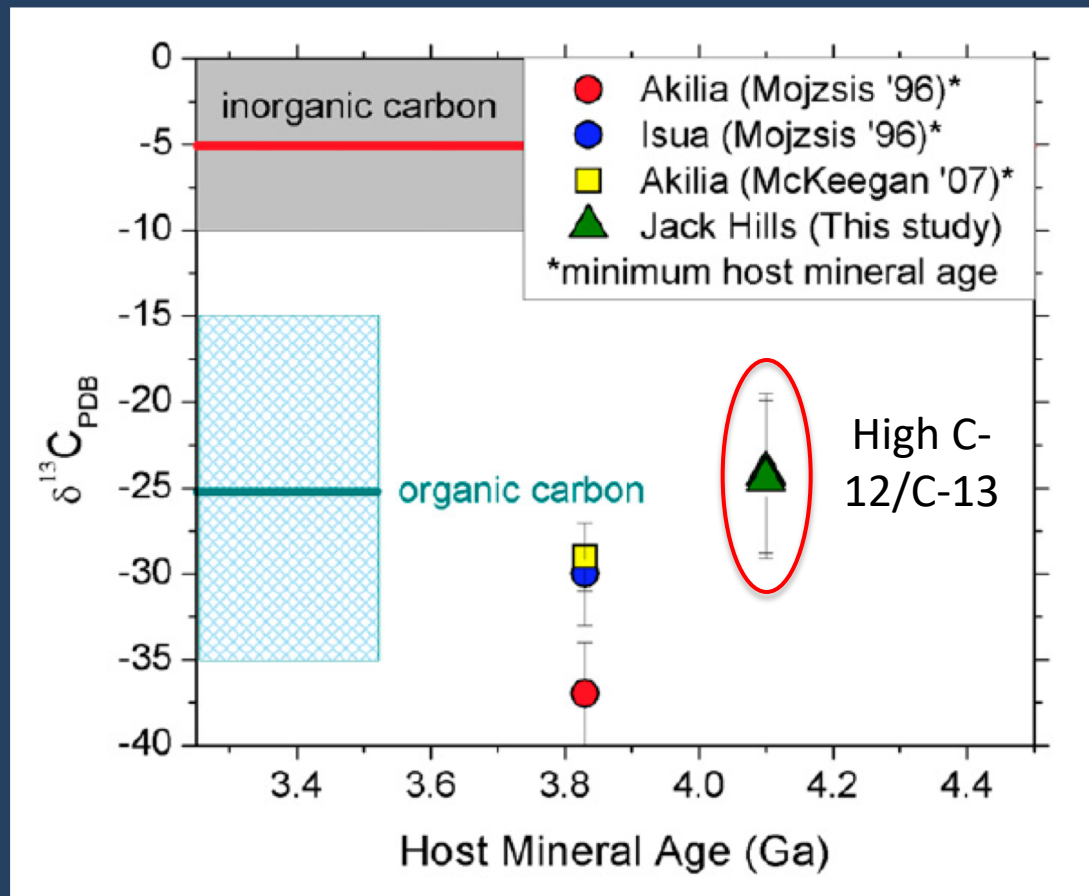


Isotopes: two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei.

# Potentially biogenic carbon preserved in a 4.1 billion-year-old zircon

Elizabeth A. Bell<sup>a,1</sup>, Patrick Boehnke<sup>a</sup>, T. Mark Harrison<sup>a,1</sup>, and Wendy L. Mao<sup>b</sup>

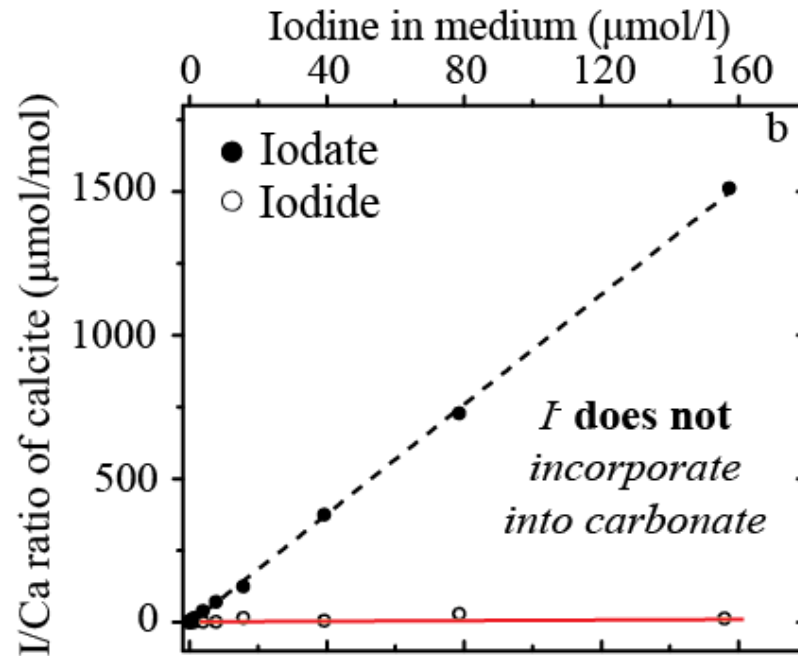
(PNAS, 2015)



# The shallow ocean: carbonate-associated iodine

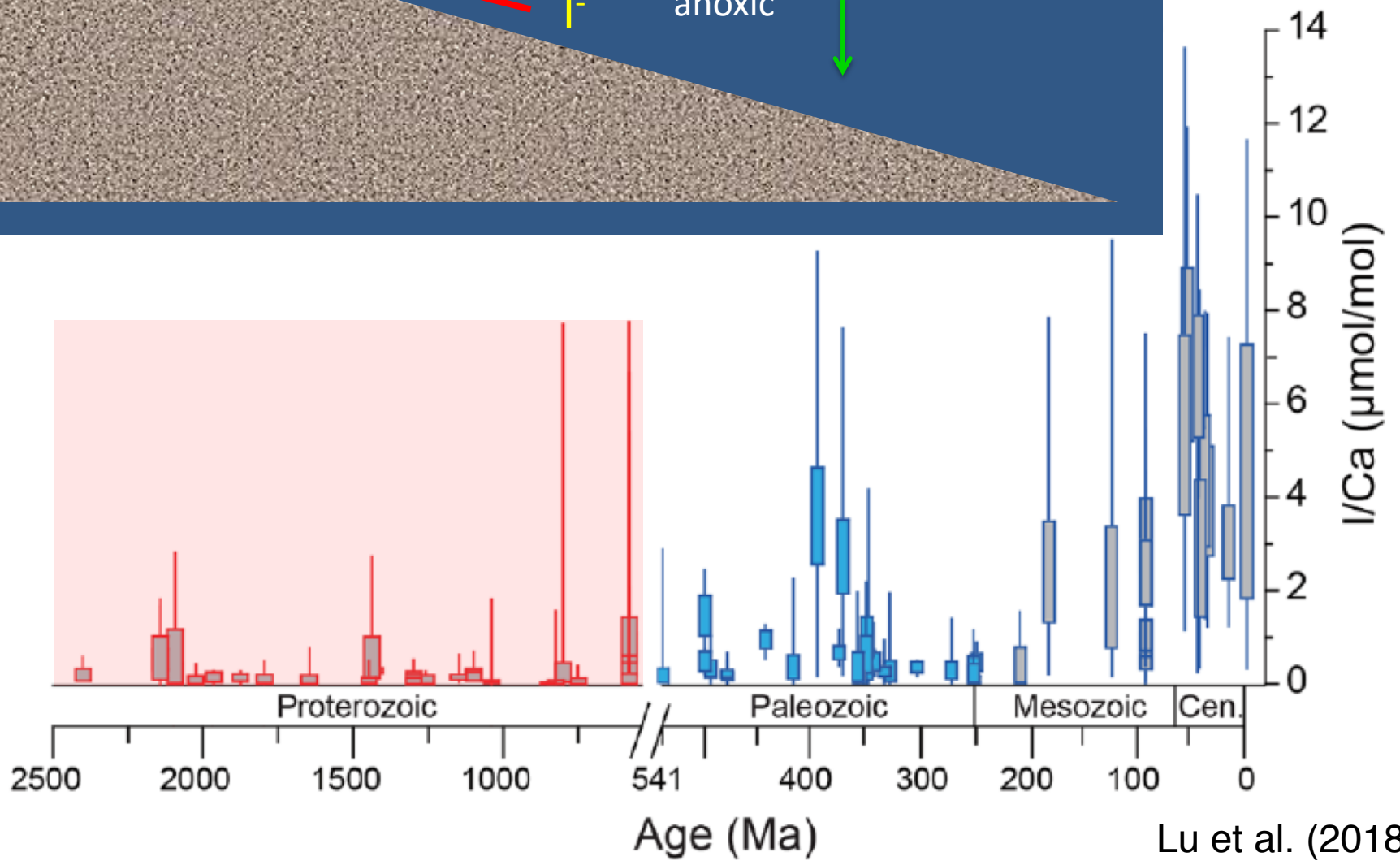
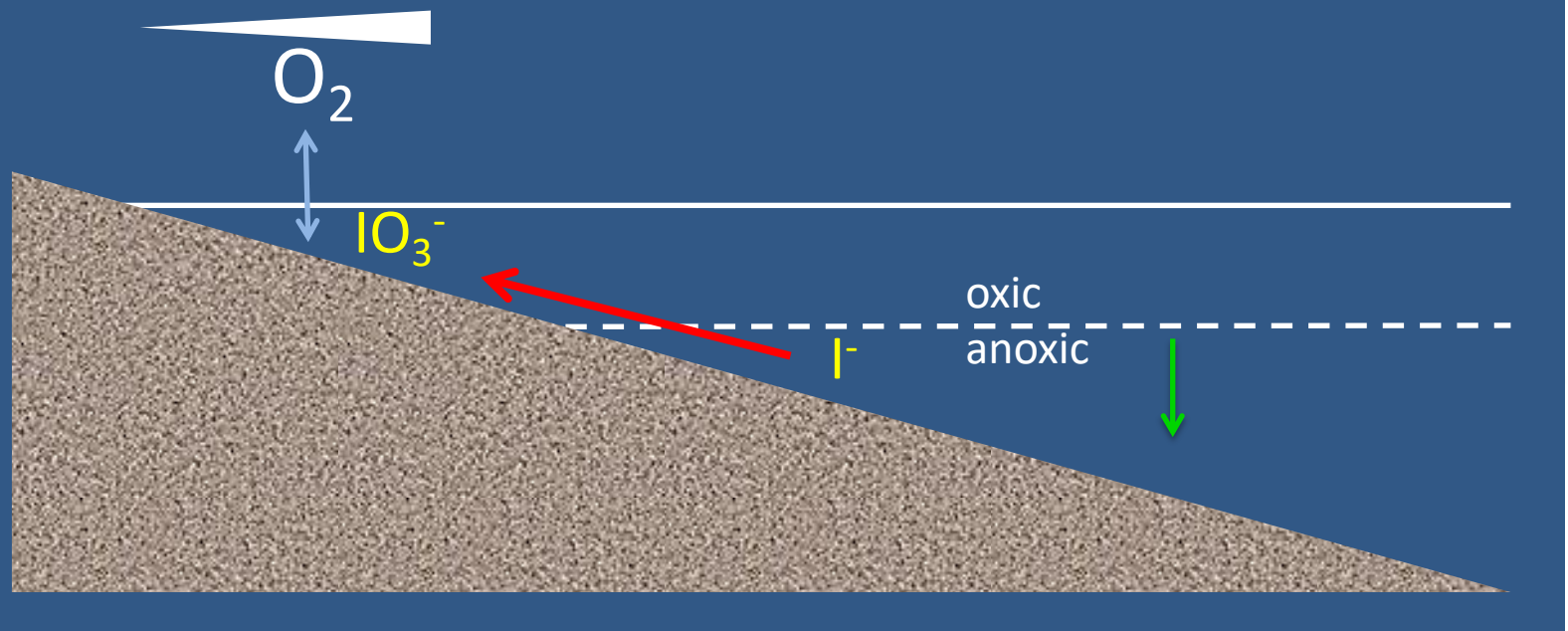


$O_2 \geq 1-3 \mu M$  ( $>200 \mu M$  in the surface mixed layer today)



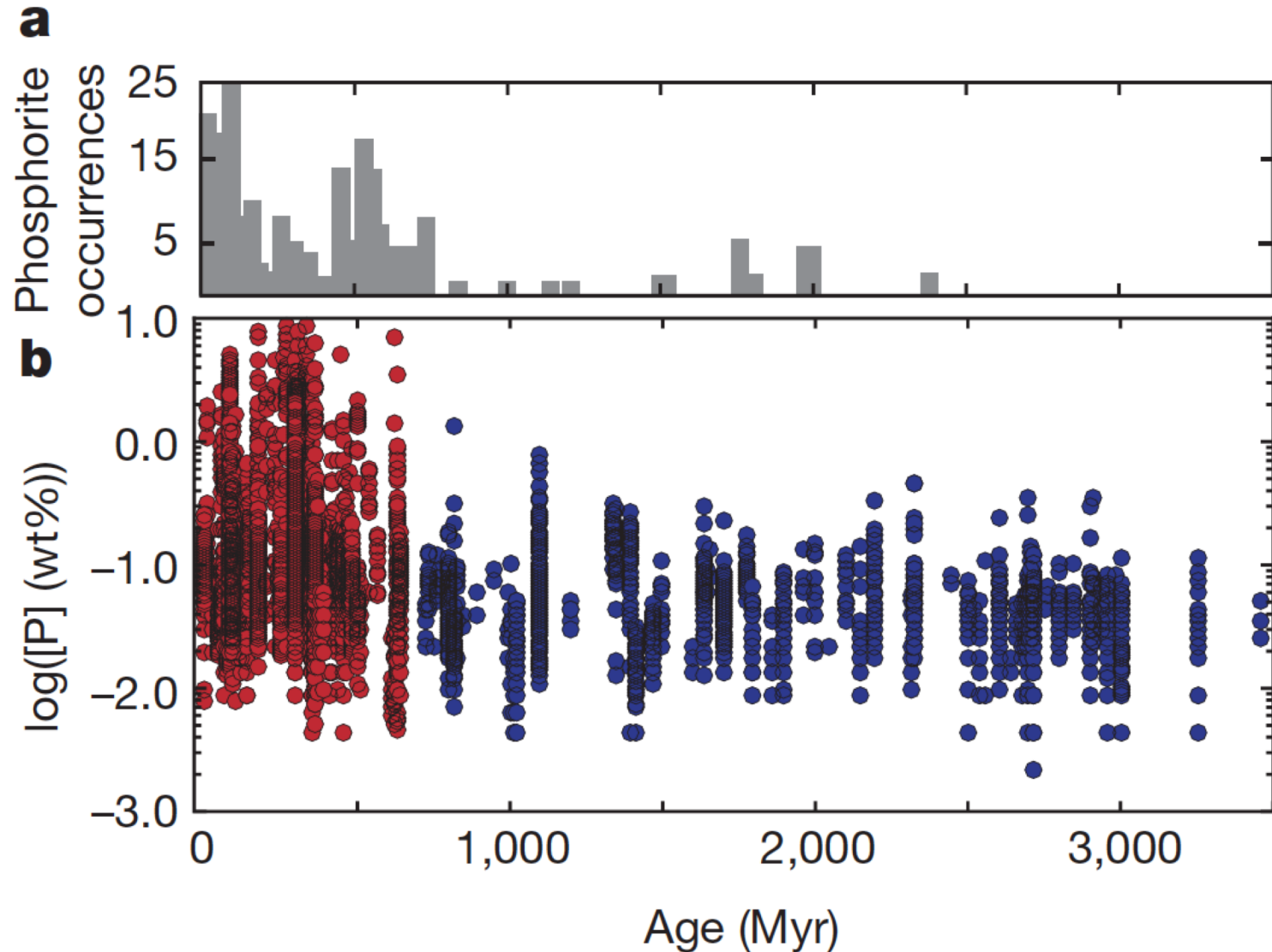
adapted from Lu et al. (2010)





# Evolution of the global phosphorus cycle

Christopher T. Reinhard<sup>1\*</sup>, Noah J. Planavsky<sup>2\*</sup>, Benjamin C. Gill<sup>3</sup>, Kazumi Ozaki<sup>1,4</sup>, Leslie J. Robbins<sup>5</sup>, Timothy W. Lyons<sup>6</sup>, Woodward W. Fischer<sup>7</sup>, Chunjiang Wang<sup>8</sup>, Devon B. Cole<sup>2</sup> & Kurt O. Konhauser<sup>5</sup>



(2017)

# P limitation?

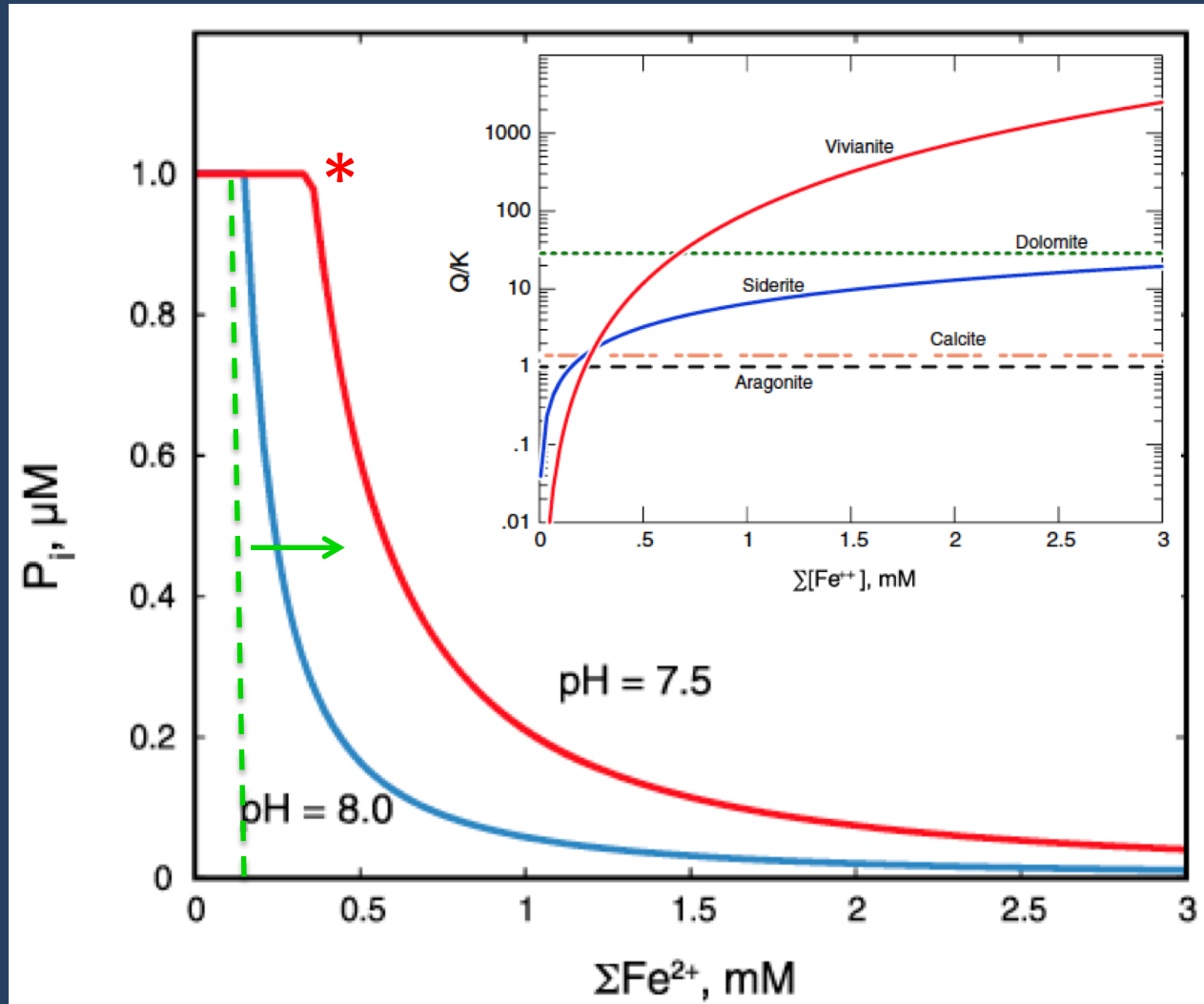
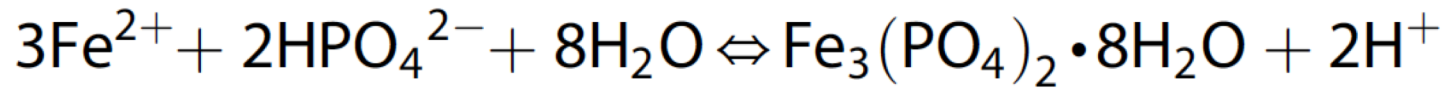
Low rates of organic remineralization  
(high burial efficiency?)

$$P_d = P_s + P_r$$

$$P_d = P_s + \frac{[O_{2s} - O_{2d}]}{r_{O_2}} + \frac{[NO_{3s} - NO_{3d}]}{r_{NO_3}} + \frac{[MnO_{2s} - MnO_{2d}]}{r_{MnO_2}} + \frac{[FeOOH_s - FeOOH_d]}{r_{FeOOH}} + \frac{[SO_{4s} - SO_{4d}]}{r_{SO_4}} + P_{CH_4}$$



# Vivianite precipitation: P buffer?



Derry (2015)

# Iron trap?

## Regulation of atmospheric oxygen during the Proterozoic

Thomas A. Laakso\*, Daniel P. Schrag

(2014)

“Low oxygen conditions are stable in our model if the flux of phosphorus to the oceans was greatly reduced during the Proterozoic. We propose a mechanism to reduce this flux through the scavenging of phosphate ions with an “iron trap” driven by greater surface mobility of ferrous iron in a low  $pO_2$  world.”

“In a low oxygen atmosphere, rivers would carry more ferrous iron because the kinetics of iron oxidation are slower. Slow oxidation of iron in solution in rivers and estuaries efficiently scavenges phosphorus.”

# soil crusts



Soil colonization places  $O_2$   
production within the  
weathering environment



Photos: USGS



