

# Geobiology 2013 Lecture 11

## Oxygenation of Earth's Atmosphere

# Need to know

- How C and S- isotopic data in rocks are informative about the advent and antiquity of biogeochemical cycles
- Geologic indicators of changes in atmospheric  $pO_2$
- A general overview of the course of oxygenation of the atm-ocean system
- Reading: Anbar & Knoll, 2002. Science 297, 1137.

# Biogeochemical Redox Couples



oxygenic photosynthesis

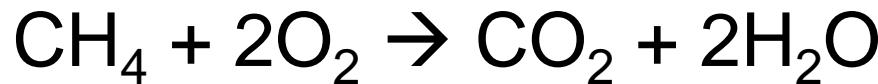


Interdependency?

aerobic respiration



methanogenesis



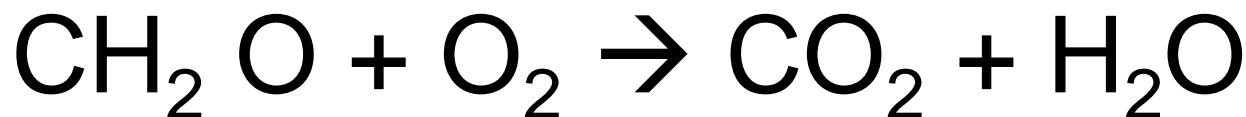
oxidative methanotrophy



anoxygenic photosynthesis

# Biogeochemical Redox Couples

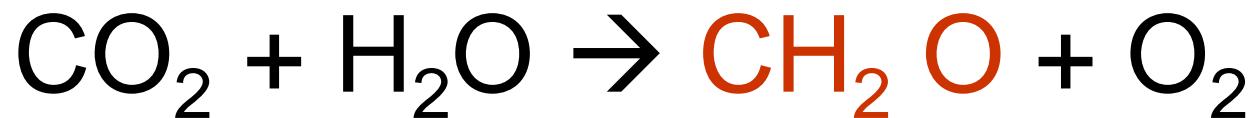
aerobic respiration



Biosynthesis requires approx. 1mole ATP per 4g of cell carbon

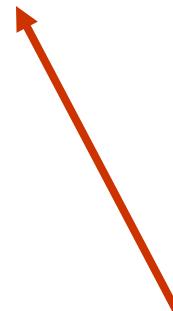
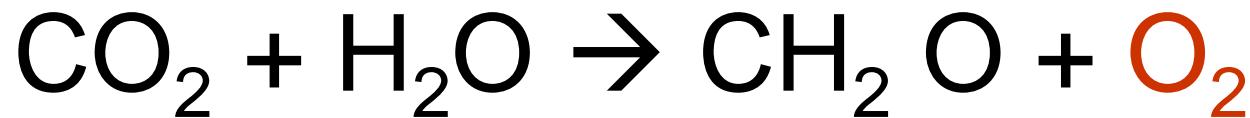
# Biogeochemical Redox Couples

oxygenic photosynthesis



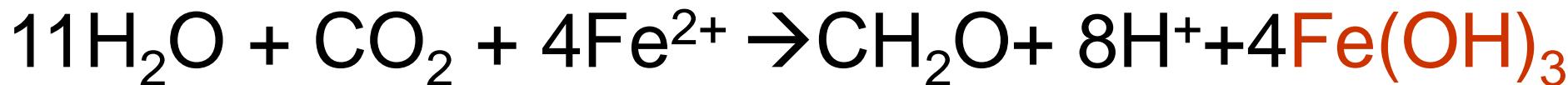
# Biogeochemical Redox Couples

oxygenic photosynthesis



# Biogeochemical Redox Couples

anoxygenic photosynthesis









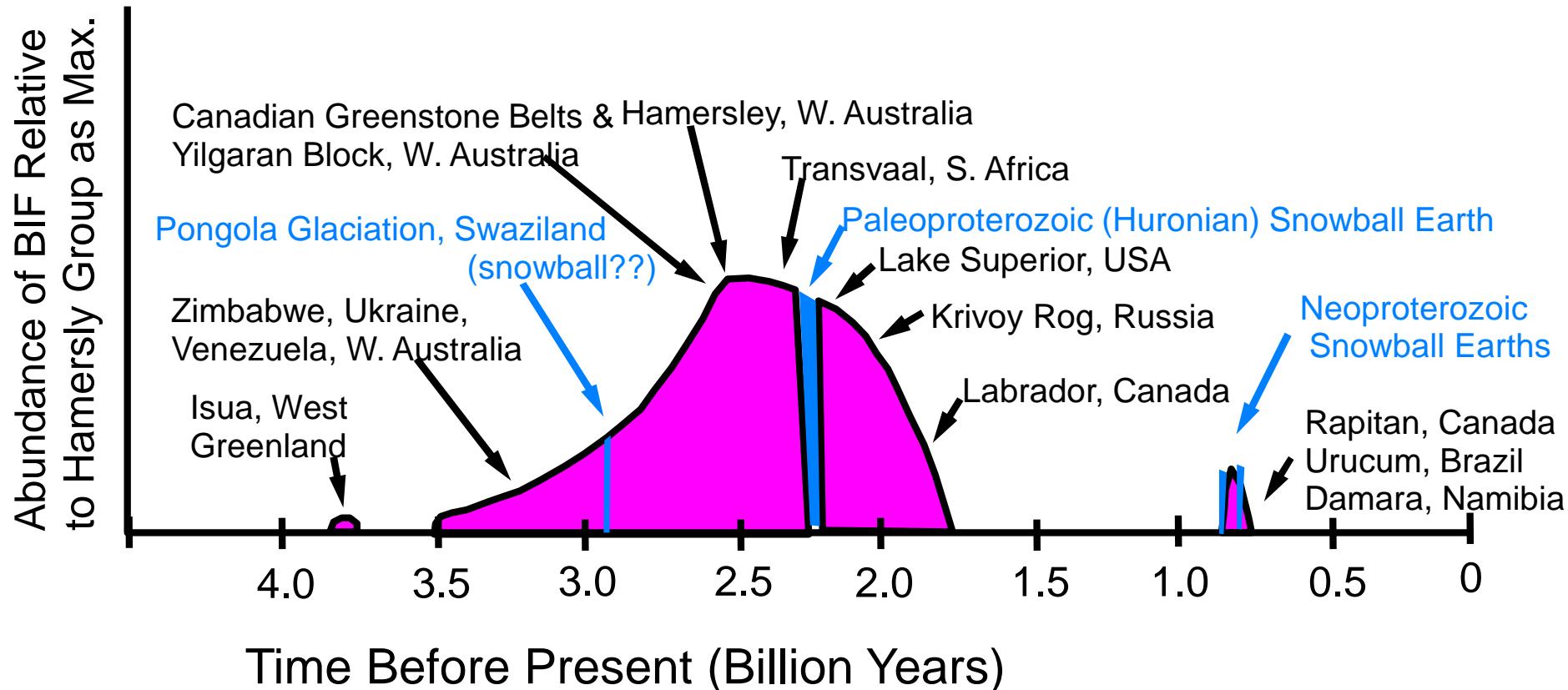






# Precambrian Banded Iron Formations (BIFs)

(Adapted from Klein & Beukes, 1992)

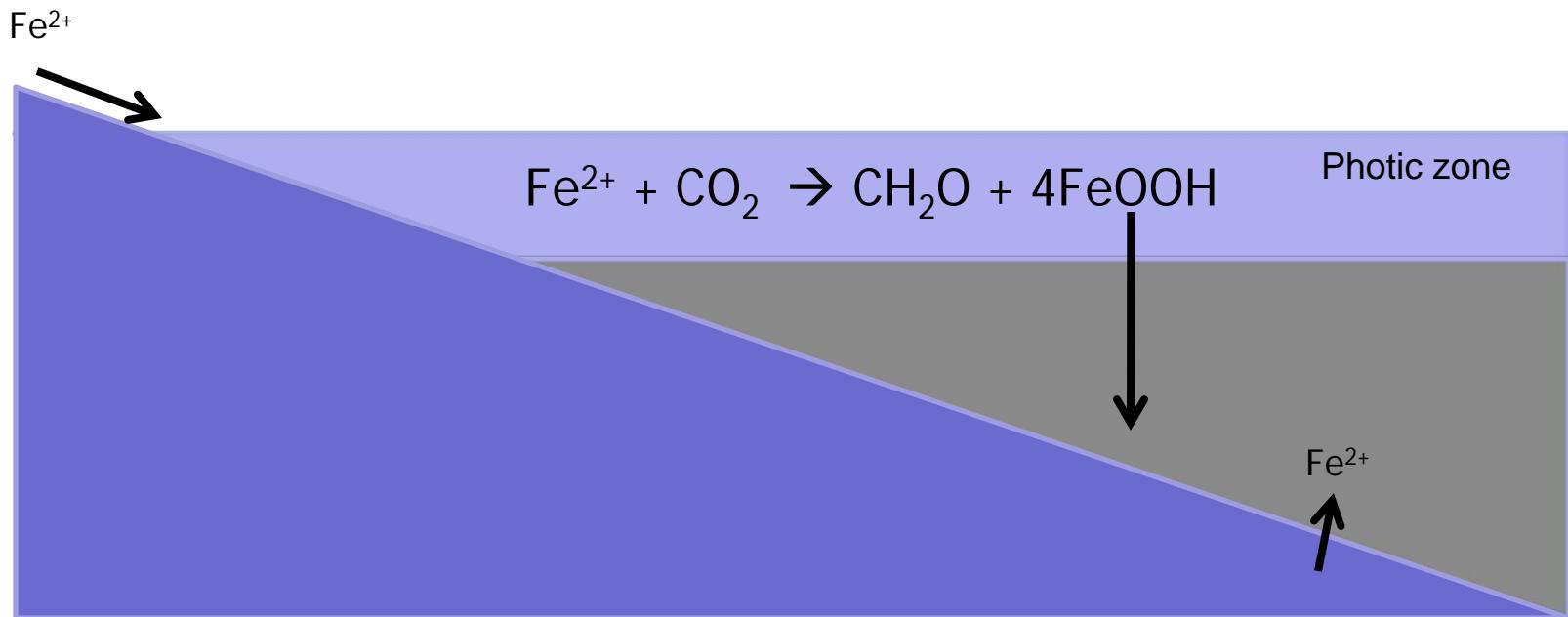


Courtesy Joe Kirschvink, CalTech

Courtesy of Joe Kirschvink. Used with permission.



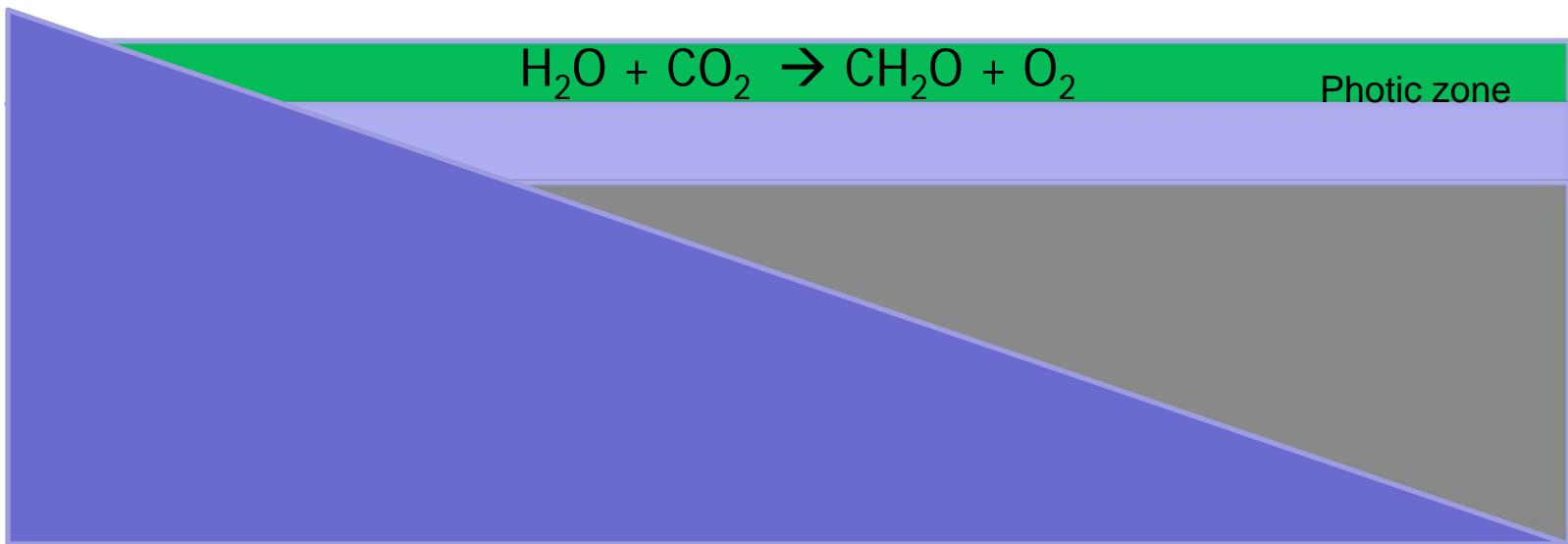
Image by MIT OpenCourseWare.



(Canfield et al. 2006, Kharecha et al. 2005, Kappler et al. 2005)



Image by MIT OpenCourseWare.



# STROMATOLITE RECORD OF MICROBIAL INTERACTIONS WITH SEDIMENTS

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<http://www.annualreviews.org/doi/full/10.1146/annurev-earth-042711-105327>.





'Classic' picture of stromatolites, Telegraph Station, Hamelin Pool WA. These are effectively stranded above high water and 'dead'.



Small (0.5) club-shaped subtidal stromatolites, Telegraph Station



1m domal subtidal stromatolites, Carbla Point, Hamelin Pool



'Reef' of 1m stromatolites, Carbla Point

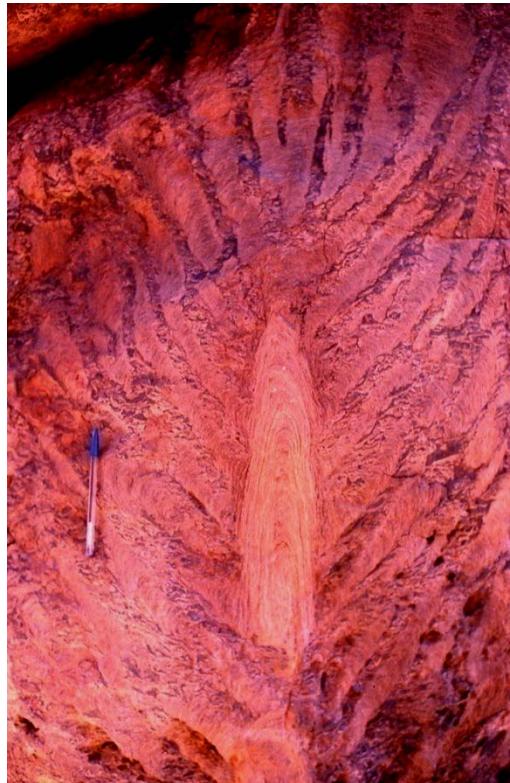
# STROMATOLITES AS INDICATORS OF MICROBIAL PROCESSES

3.4 Ga



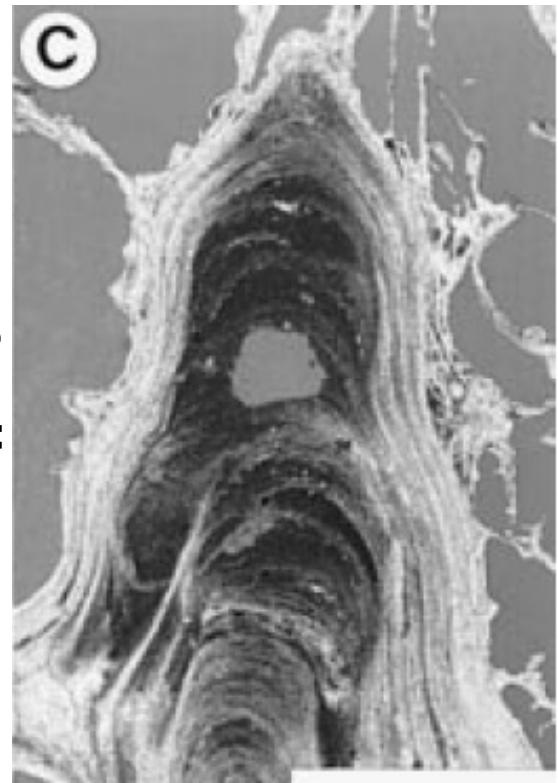
? =

1.2 Ga



? =

modern



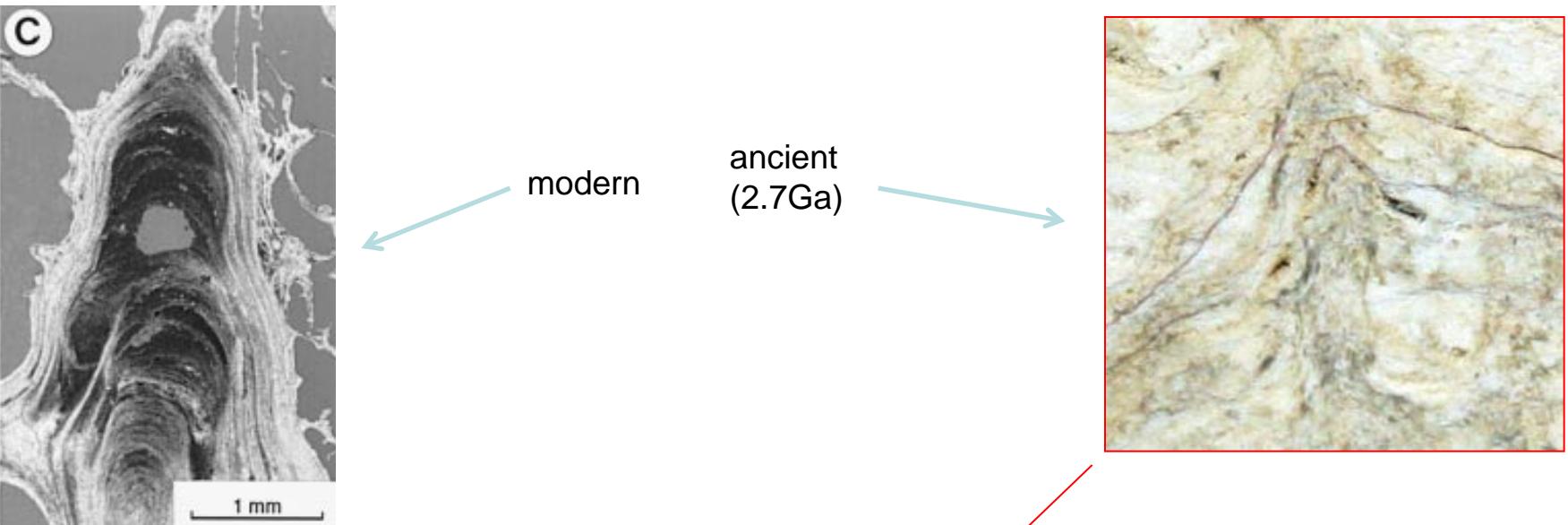
Allwood et al. 2007

Photo: P. Hoffman

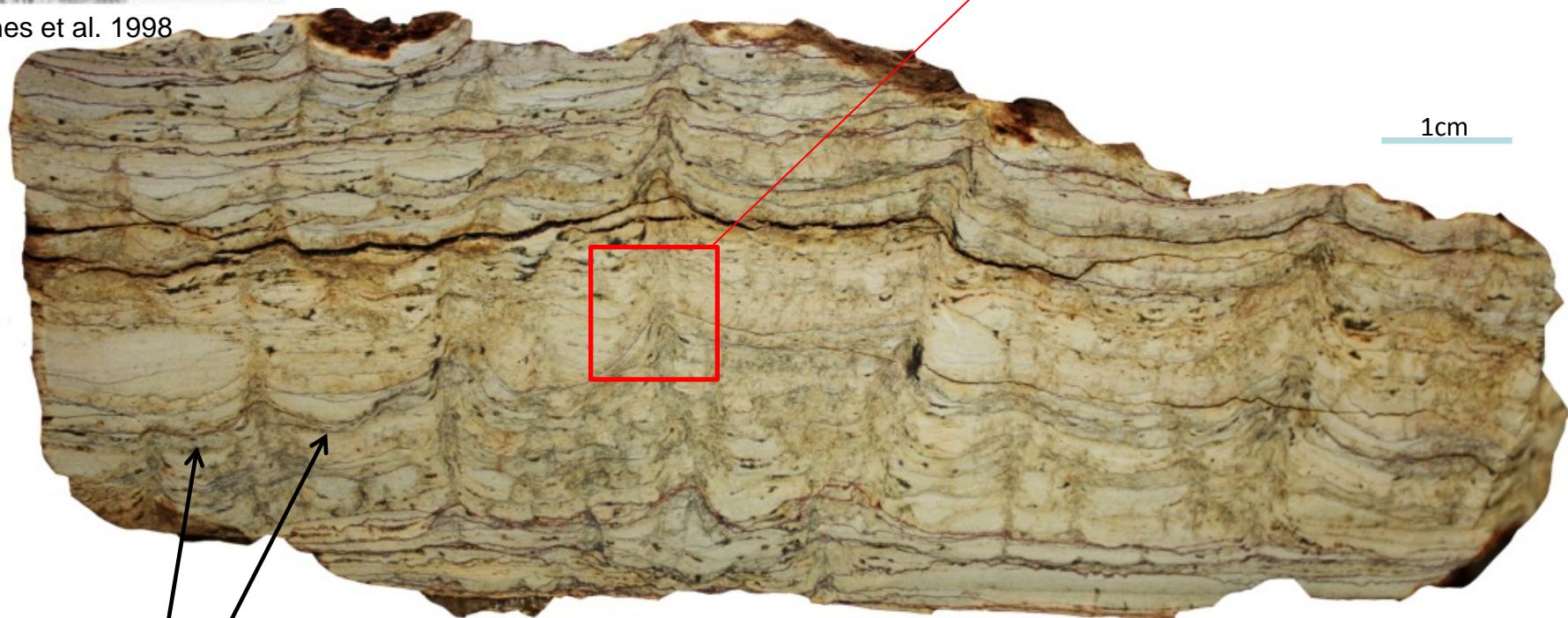
Jones et al. 1998

1 mm

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Jones et al. 1998



regularly occurring inter-column laminae

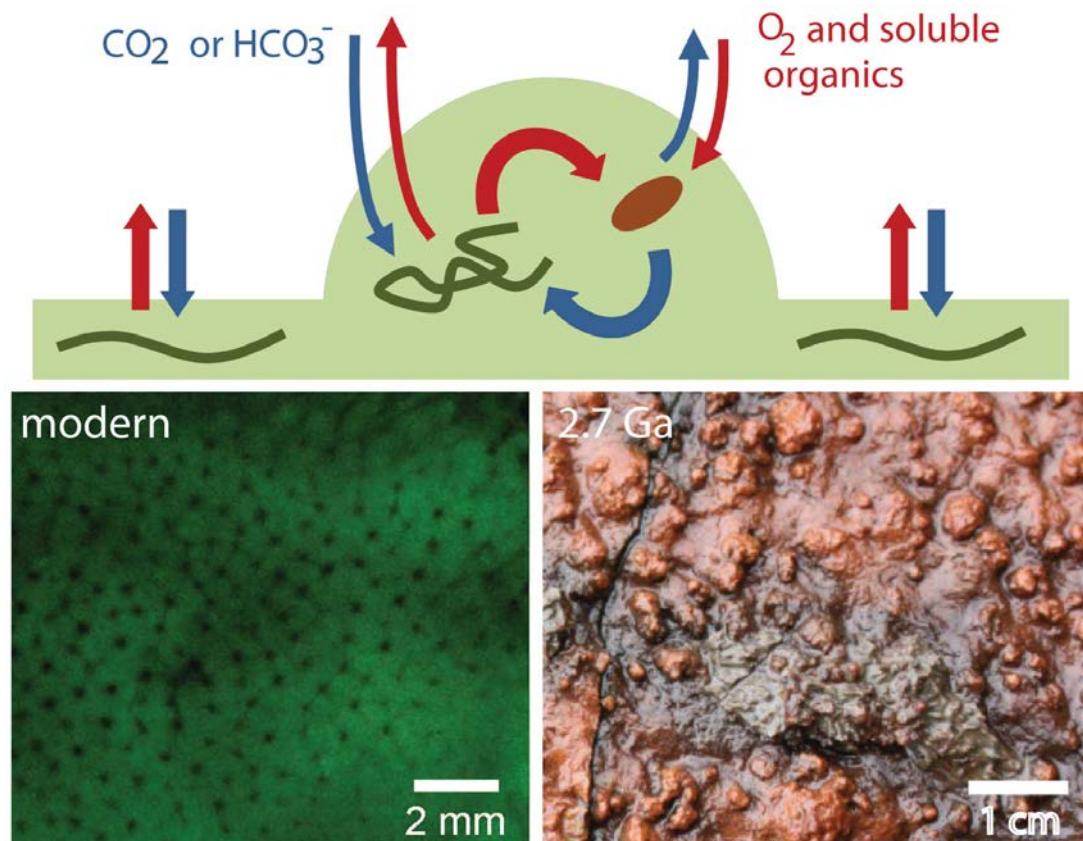
Flannery et al., 2012

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# STROMATOLITE MORPHOLOGY AND OXYGENIC PHOTOSYNTHESIS AT 2.7 GA?

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# STROMATOLITE MORPHOLOGY AND OXYGENIC PHOTOSYNTHESIS AT 2.7 GA?

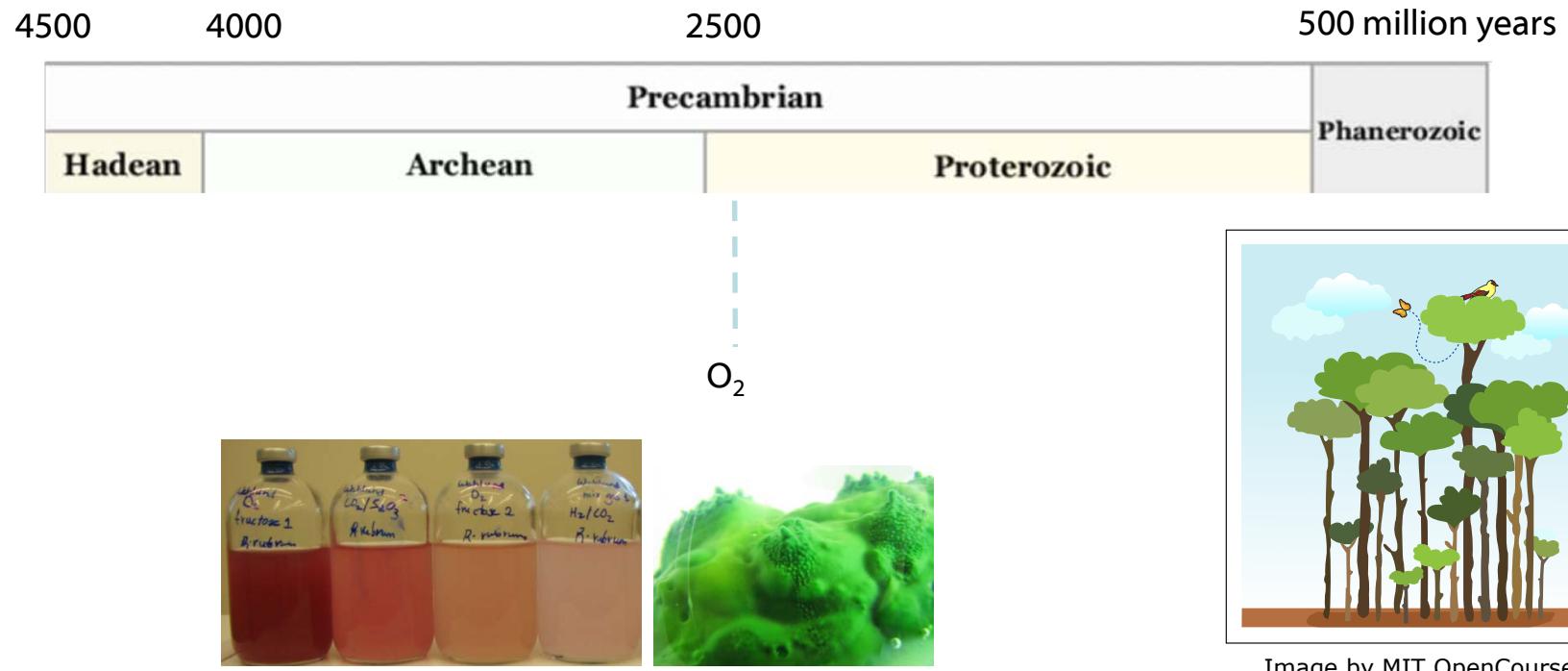


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Sim et al. 2012

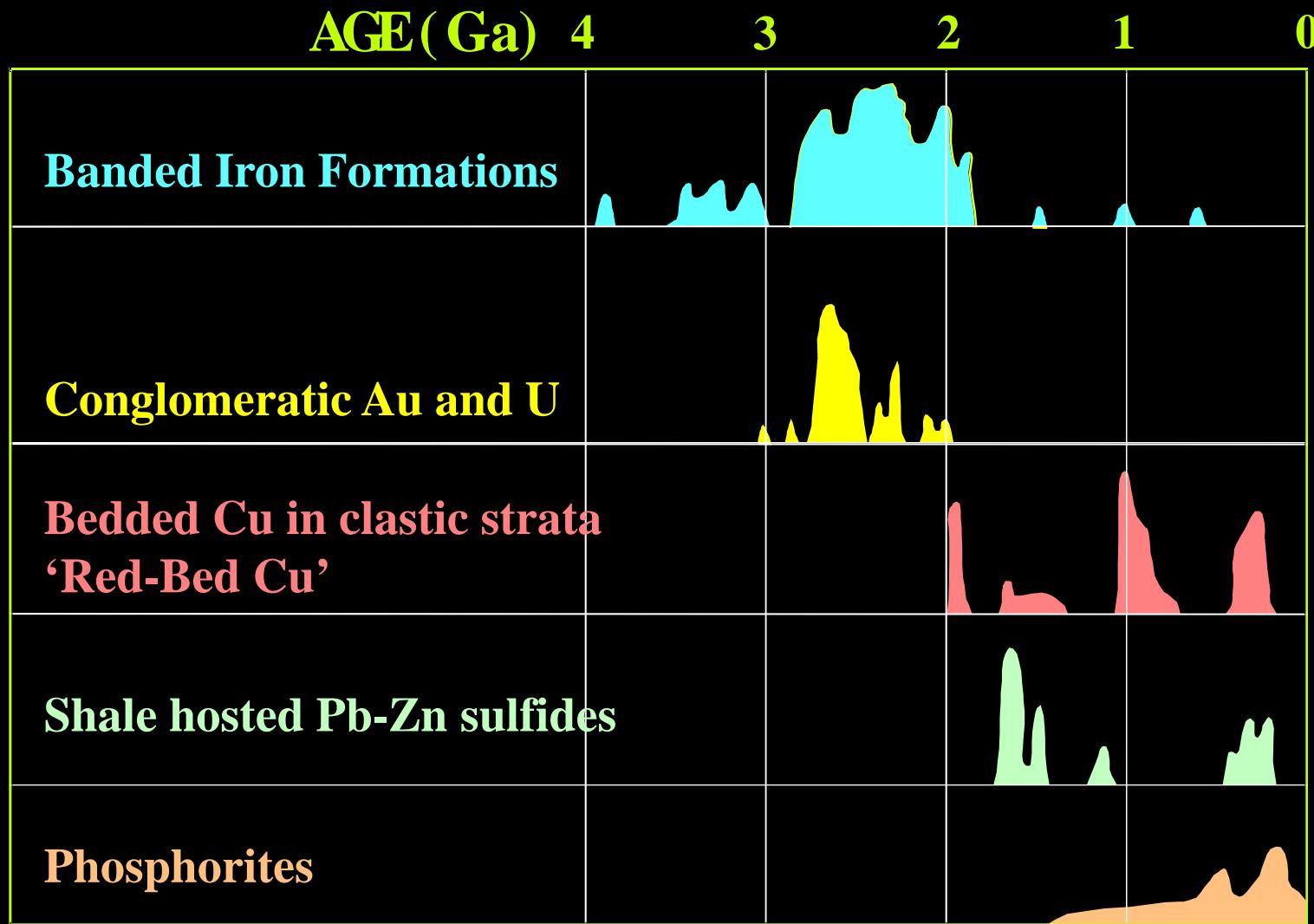
# STROMATOLITE MORPHOLOGY AND OXYGENIC PHOTOSYNTHESIS AT 2.7 GA?

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<http://www.annualreviews.org/doi/full/10.1146/annurev-earth-042711-105327>.



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# MINERALIZATION THROUGH GEOLOGIC TIME



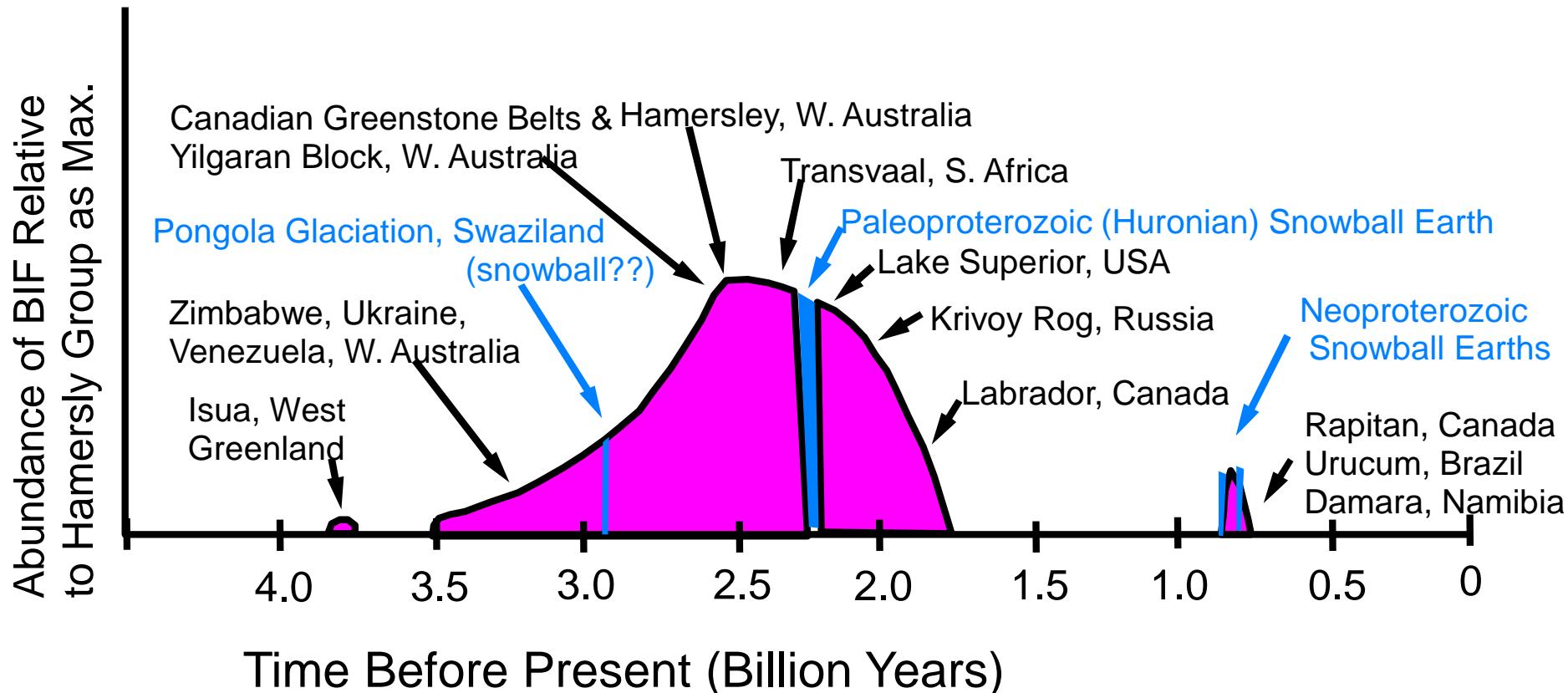
( adapted from Lambert & Groves ,1981 )

# An Atypical Banded Iron Stone (BIF)



BIF — NEGAUNEE IRON FORMATION, MICHIGAN — 2.2 Ga

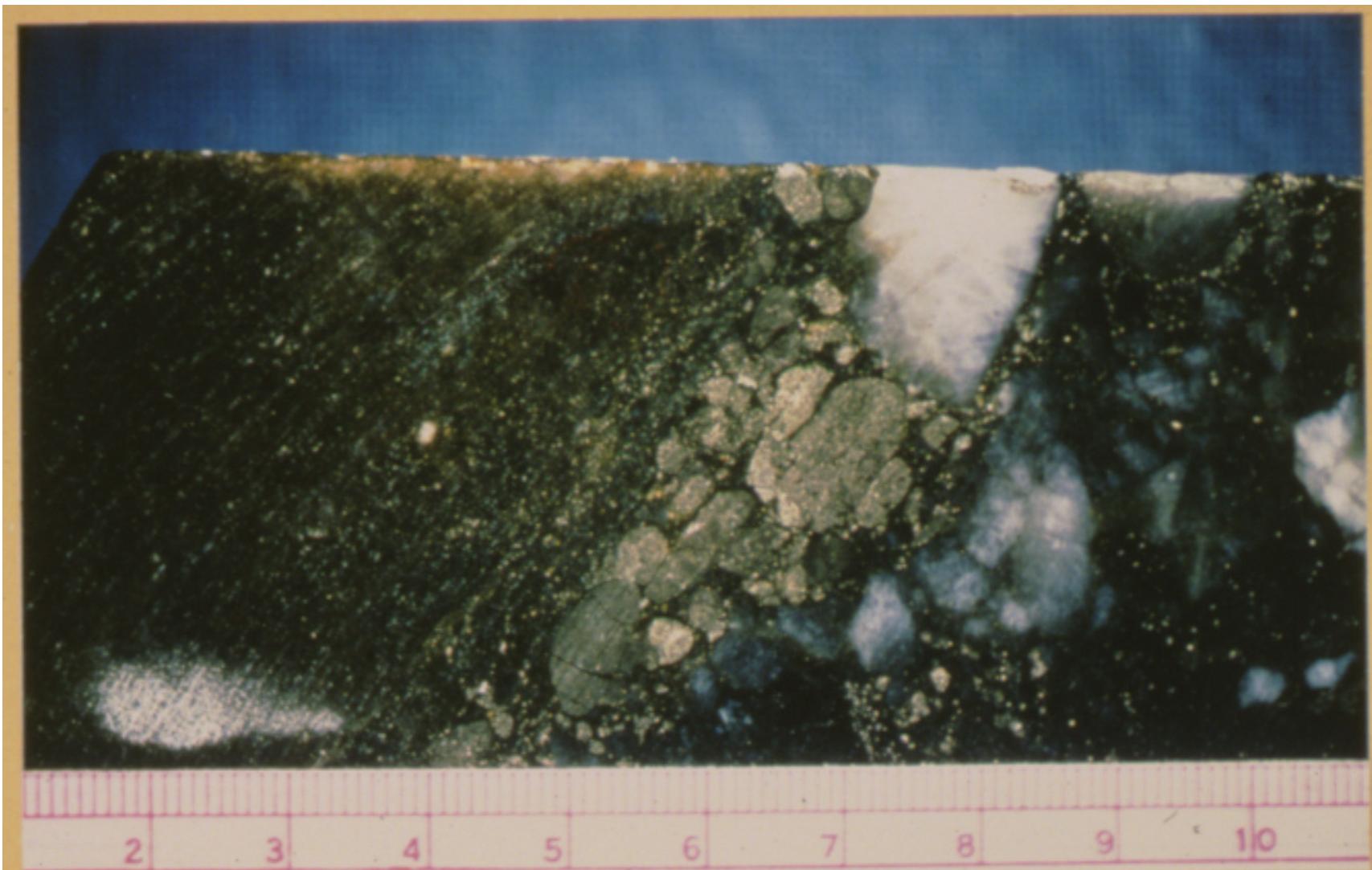
# Precambrian Banded Iron Formations (BIFs) (Adapted from Klein & Beukes, 1992)



Courtesy Joe Kirschvink, CalTech

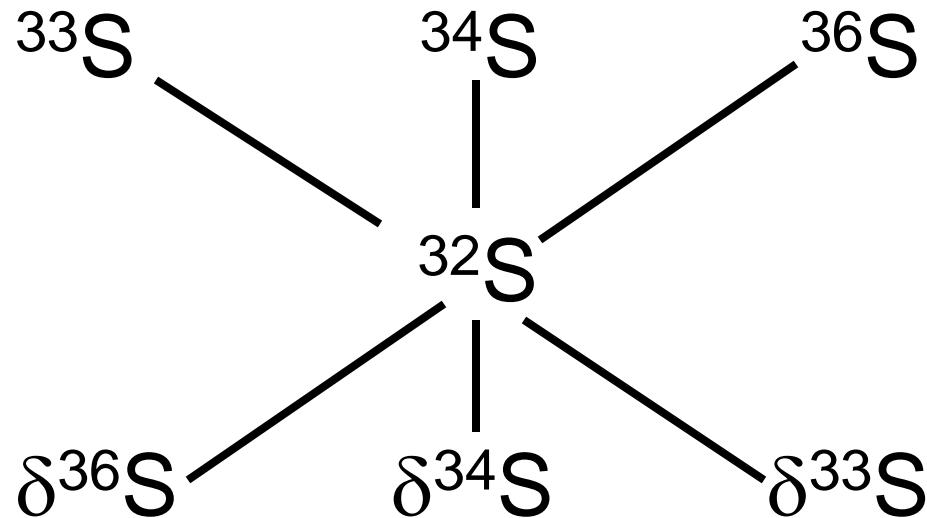
Courtesy of Joe Kirschvink. Used with permission.

# Pyrite ( $\text{FeS}_2$ ) is Unstable in $\text{O}_2$ -Rich Environments



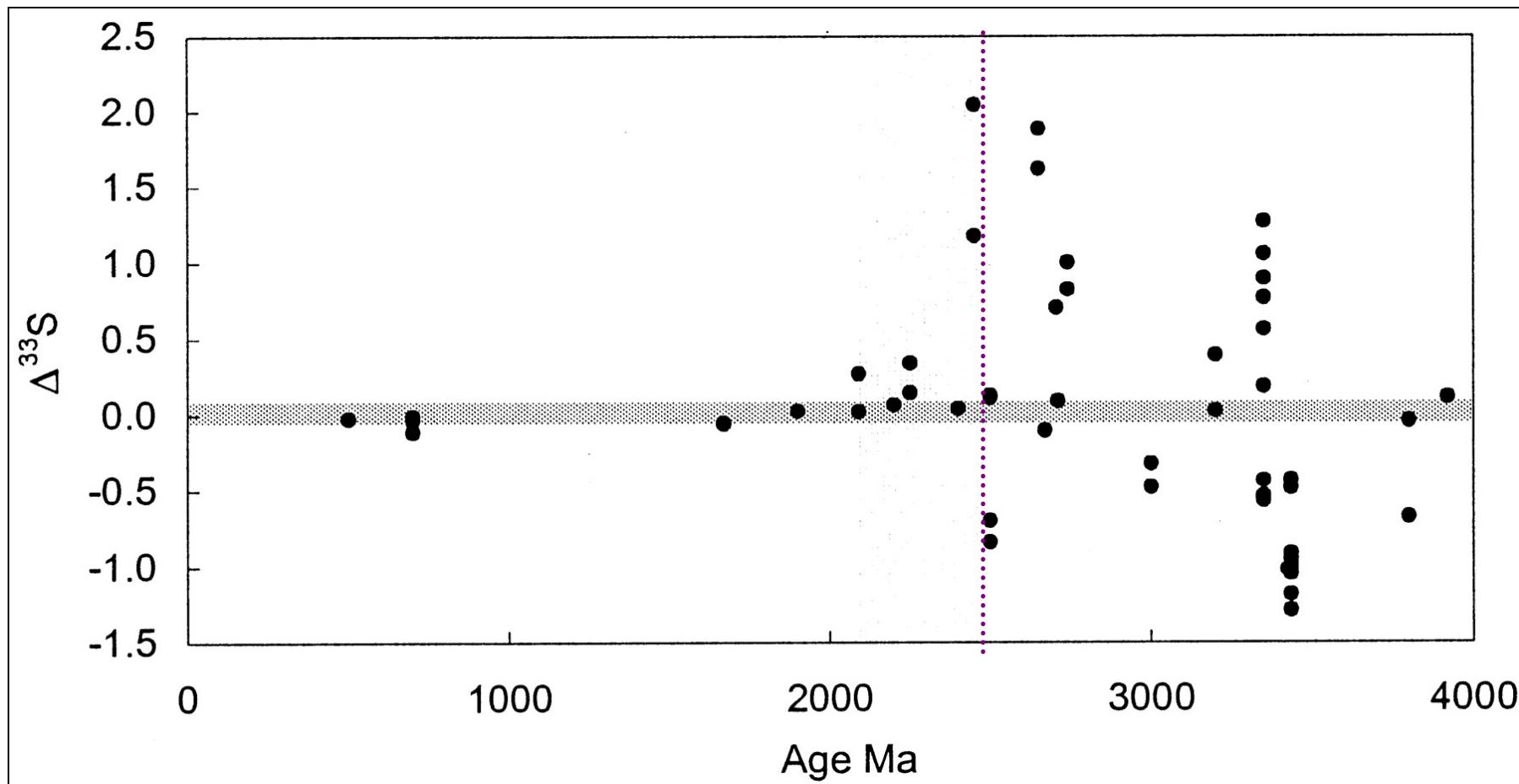
DETTRITAL PYRITE — V.C.R., SOUTH AFRICA — 2.5 Ga

# Multiple sulfur isotopes



Mass-dependent Fractionation:  
 $\delta^{33}\text{S}=0.515\delta^{34}\text{S}$ ,  $\delta^{36}\text{S}=1.91\delta^{34}\text{S}$

# A quantitative O<sub>2</sub> barometer?? Sulfur Isotopic Evidence for pO<sub>2</sub> > 10<sup>-5</sup> PAL



J. Farquhar, H. Bao, M. Thiemens (2000) *Science* **289**:756-758.

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Conundrum: If oxygen-producing photosynthesis was occurring by 3.5-2.7 Ga, why doesn't free O<sub>2</sub> appear until 2.3 Ga, a 1200-400 Myr delay?

The BIG question in geobiology today!!

Conundrum: If oxygen-producing photosynthesis was occurring by 3.5-2.7 Ga, why doesn't free O<sub>2</sub> appear until 2.3 Ga, a 1200-400 Myr delay?

## Sources

- Photosynthesis
- Hydrogen escape

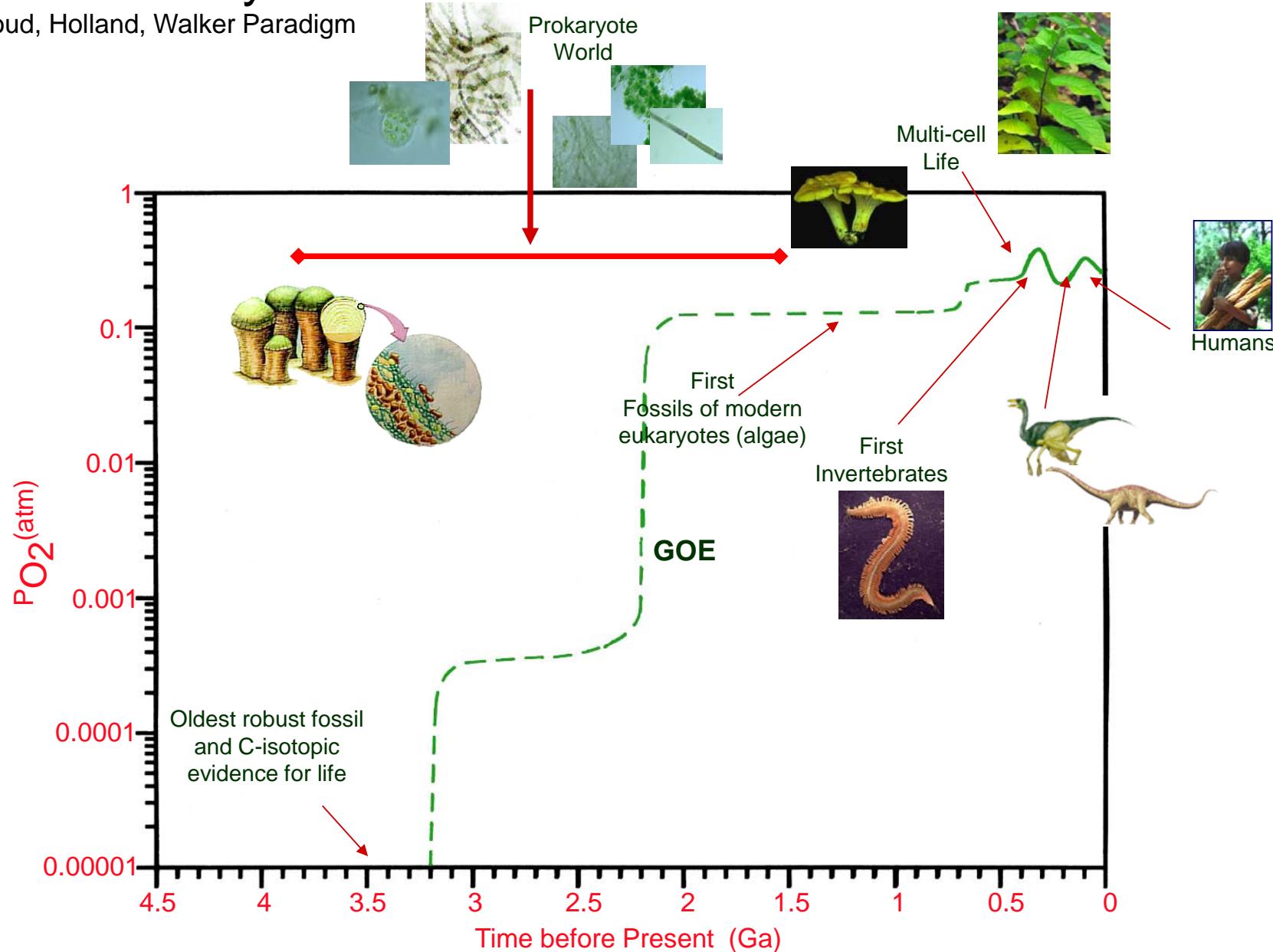
Vs.

## Sinks

- Respiration
- Reduced minerals in rocks
  - Reduced volcanic gases
- Reduced hydrothermal vent fluids

# Life's History on Earth

Cloud, Holland, Walker Paradigm



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## Anbar & Knoll: Fig. 1. Biological and geochemical changes during the Proterozoic Eon.

Color gradations denote postulated changes in deep sea redox. **(A)** Periods of deposition of banded iron formations. **(B) Range of values of  $\delta^{34}\text{S}$** , the difference in  $\delta^{34}\text{S}$  between coeval marine sulfides and sulfates. Dashed line:  $\delta^{34}\text{S} = 20\text{\textperthousand}$ , the maximum Archean value. Dotted line:  $\delta^{34}\text{S} = 45\text{\textperthousand}$ , the maximum fractionation associated with single-step BSR. Asterisk:  $\delta^{34}\text{S}$  determined from a single sample, and thus not well constrained. **(C) Range of values of  $\delta^{13}\text{C}_{\text{carb}}$  (after a compilation by A. J. Kaufman)**. The frequency and magnitude of variations in the Paleoproterozoic are somewhat uncertain. **(D) Eukaryotic evolution, as indicated** by the first appearances of body fossils (solid lines) and molecular biomarkers (dotted lines), including chlorophytes (1), ciliates (2), dinoflagellates (3), rhodophytes (4), eukaryotes of unknown affinities, possibly stem groups (5), stramenopiles (6), and testate amoebae (7). See text for geochemical references. Fossil distributions from (147).

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This image has been removed due to copyright restrictions. Please see Figure 2 in paper online at <http://www.sciencemag.org/content/297/5584/1137.full>.

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**Fig. 2. Schematic depiction of effects of changing ocean redox conditions on the depth distributions of Mo (dashed lines) and Fe (solid lines).** Influences of nutrient-type depletion and aeolian inputs on surface seawater concentrations are omitted for simplicity. Color gradations are the same as in Fig. 1. During the Archean, oceans are anoxic but not sulfidic. Significant O<sub>2</sub> is only associated with cyanobacterial “blooms.” Mo is scarce because it is not readily mobilized from crustal rocks during weathering under low P<sub>O2</sub>. *Fe is abundant in the absence of O<sub>2</sub> and H<sub>2</sub>S.* From 1850 to 1250 Ma, moderate P<sub>O2</sub> oxygenates surface waters but sulfidic deep waters develop. Mo is scarce because of rapid removal in sulfidic waters. Mo is somewhat elevated at the surface because of upper ocean oxygenation and enhanced oxidative weathering. Fe, as in the modern Black Sea, is depleted in sulfidic deep waters, severely depleted in oxic surface waters, and enriched near the redoxcline where both O<sub>2</sub> and H<sub>2</sub>S are scarce. During the Phanerozoic, O<sub>2</sub> penetrates to the sediment-water interface. Mo and Fe distributions are similar to today’s. See text for details and references.

# Evidence for O<sub>2</sub> pulses during the Phanerozoic

Pulse of atmospheric oxygen during the late  
Cambrian

Matthew R. Saltzman, Seth A. Young, Lee R.  
Kump, Benjamin C. Gilld, Timothy W. Lyons,  
and Bruce Runnegar

PNAS 108, 3876–3881

## Abstract

A rise in atmospheric O<sub>2</sub> has been linked to the Cambrian explosion of life. For the plankton and animal radiation that began some 40 million yr later and continued through much of the Ordovician (Great Ordovician Biodiversification Event), the search for an environmental trigger(s) has remained elusive. Here we present a carbon and sulfur isotope mass balance model for the latest Cambrian time interval spanning the globally recognized Steptoean Positive Carbon Isotope Excursion (SPICE) that indicates a major increase in atmospheric O<sub>2</sub>. We estimate that this organic carbon and pyrite burial event added approximately  $19 \times 10^{18}$  moles of O<sub>2</sub> to the atmosphere (i.e., equal to change from an initial starting point for O<sub>2</sub> between 10–18% to a peak of 20–28% O<sub>2</sub>) beginning at approximately 500 million years. We further report on new paired carbon isotope results from carbonate and organic matter through the SPICE in North America, Australia, and China that reveal an approximately 2‰ increase in biological fractionation, also consistent with a major increase in atmospheric O<sub>2</sub>. The SPICE is followed by an increase in plankton diversity that may relate to changes in macro- and micronutrient abundances in increasingly oxic marine environments, representing a critical initial step in the trophic chain. Ecologically diverse plankton groups could provide new food sources for an animal biota expanding into progressively more ventilated marine habitats during the Ordovician, ultimately establishing complex ecosystems that are a hallmark of the Great Ordovician Biodiversification Event.

**Plot of (14) and (17) data from Mt. Whelan core in Australia that were used in the isotope mass balance model (see Table S1) to calculate changes in atmospheric O<sub>2</sub>.**

This image has been removed due to copyright restrictions. Please see the figure in the paper:  
Saltzman, Matthew R., Seth A. Young, et al. "Pulse of Atmospheric Oxygen During the Late Cambrian." *DfcWYXjb[gcZh\YBUh]cbU'5WXYa mcZGVYbWg* 108, no. 10 (2011): 3876-81.

## Arial D. Anbar, Yun Duan, et al.

High-resolution chemostratigraphy reveals an episode of enrichment of the redox-sensitive transition metals molybdenum and rhenium in the late Archean Mount McRae Shale in Western Australia. Correlations with organic carbon indicate that these metals were derived from contemporaneous seawater. Rhenium/osmium geochronology demonstrates that the enrichment is a primary sedimentary feature dating to  $2501 \pm 8$  million years ago (Ma). Molybdenum and rhenium were probably supplied to Archean oceans by oxidative weathering of crustal sulfide minerals. These findings point to the presence of small amounts of O<sub>2</sub> in the environment more than 50 million years before the start of the Great Oxidation Events.

<http://www.sciencemag.org/content/317/5846/1903.full>

Image by MIT OpenCourseWare.

# Geochemical data from Mt McRae Shale ABDP-9

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Anbar, Ariel D., Yun Duan, et al. "A Whiff of Oxygen Before the Great Oxidation Event?." *Glycobiology* 317, no. 5846 (2007): 1903-6.

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**12.007 Geobiology**

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