12.007 Geobiology
Spring 2009

Geobiology 2009 Lecture 9

Biogeochemical Tracers #2
leading into Early Life

Common tracers for biogeochemical cycling:

- Elemental abundances
  - Redfield ratio
- Isotopes
- Microfossils
- Stromatolites

Terminology

α **= is the kinetic fractionation factor =** $\dfrac{dX_{h,p}/X_{h,s}}{dX_{l,p}/X_{l,s}}$

Where p is product, s is substrate, h is heavy and l is light.

Written precisely this is

$$\alpha = [(\delta_R + 1000) / (\delta_P + 1000)]$$

$$\varepsilon = 10^3 (\alpha\text{-}1)$$

A general approximation is

~~$\varepsilon = \delta_P - \delta_R$~~ **or** $\delta_P = \delta_R - \varepsilon$

ε is also called the isotope effect or epsilon !!

Equilibrium isotope effects are simply related to kinetic effects by

α **= k2/k1**

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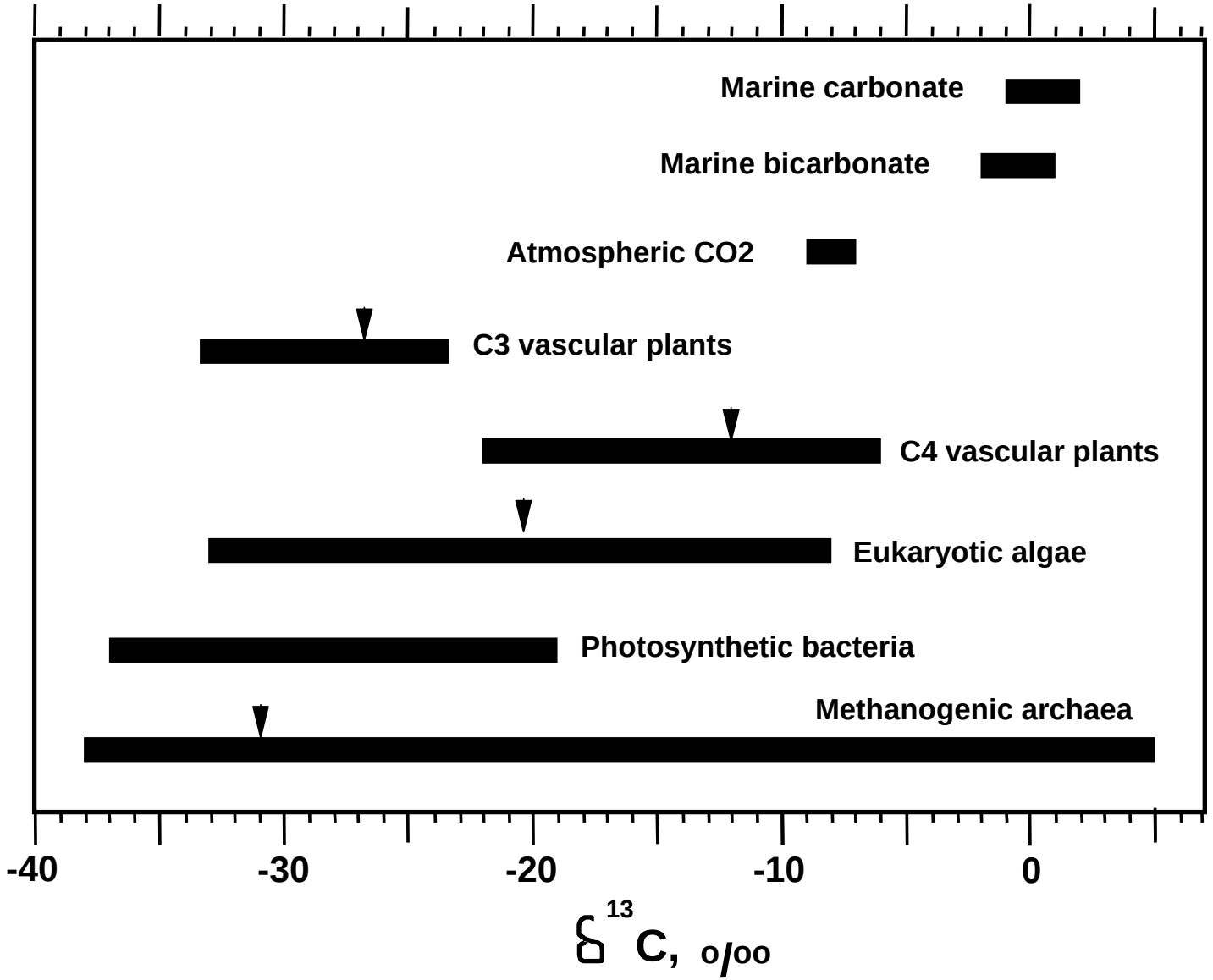
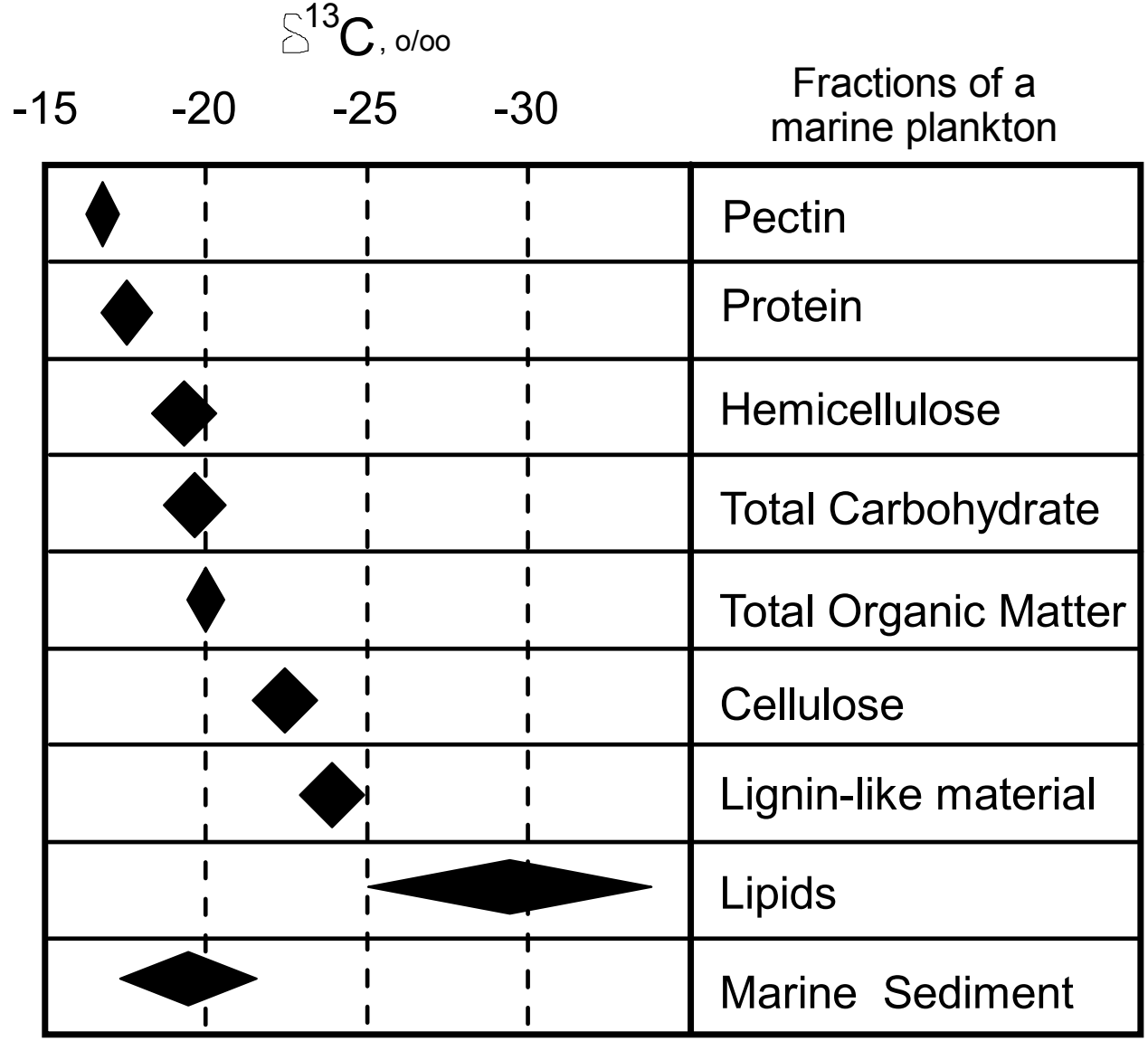
Natural variability in bulk C-isotopes



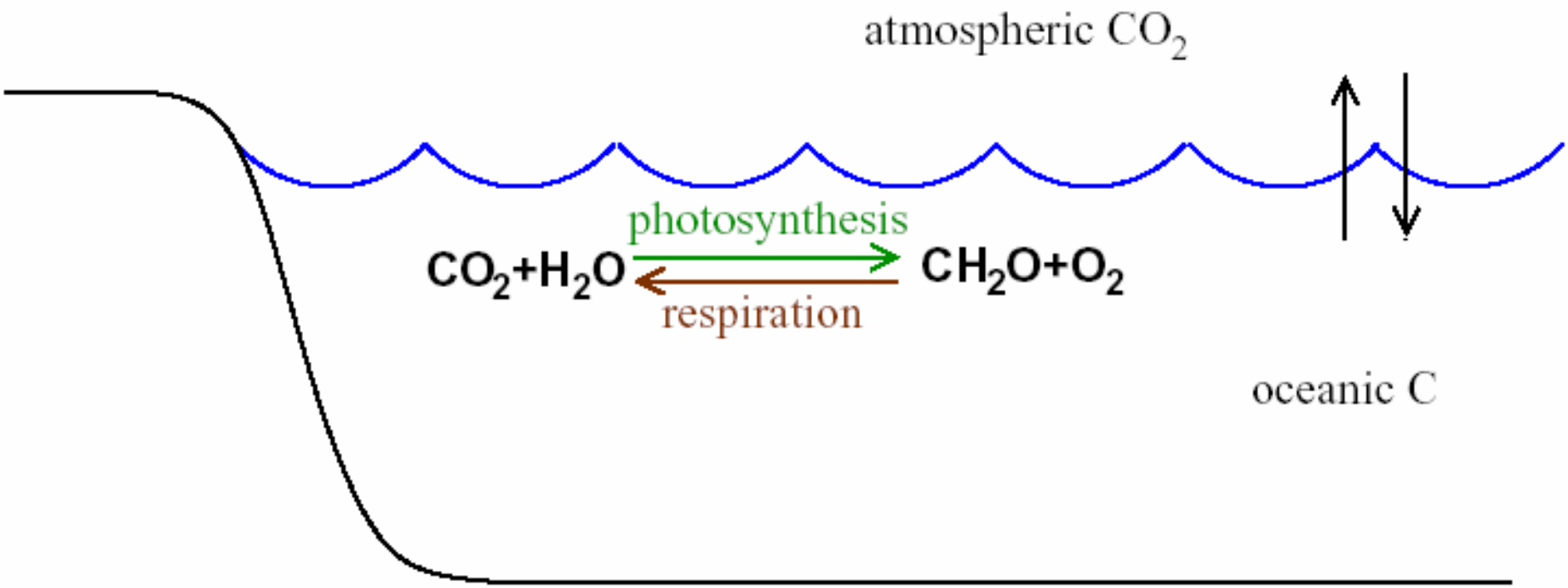
Organismal variability in bulk C-isotopes



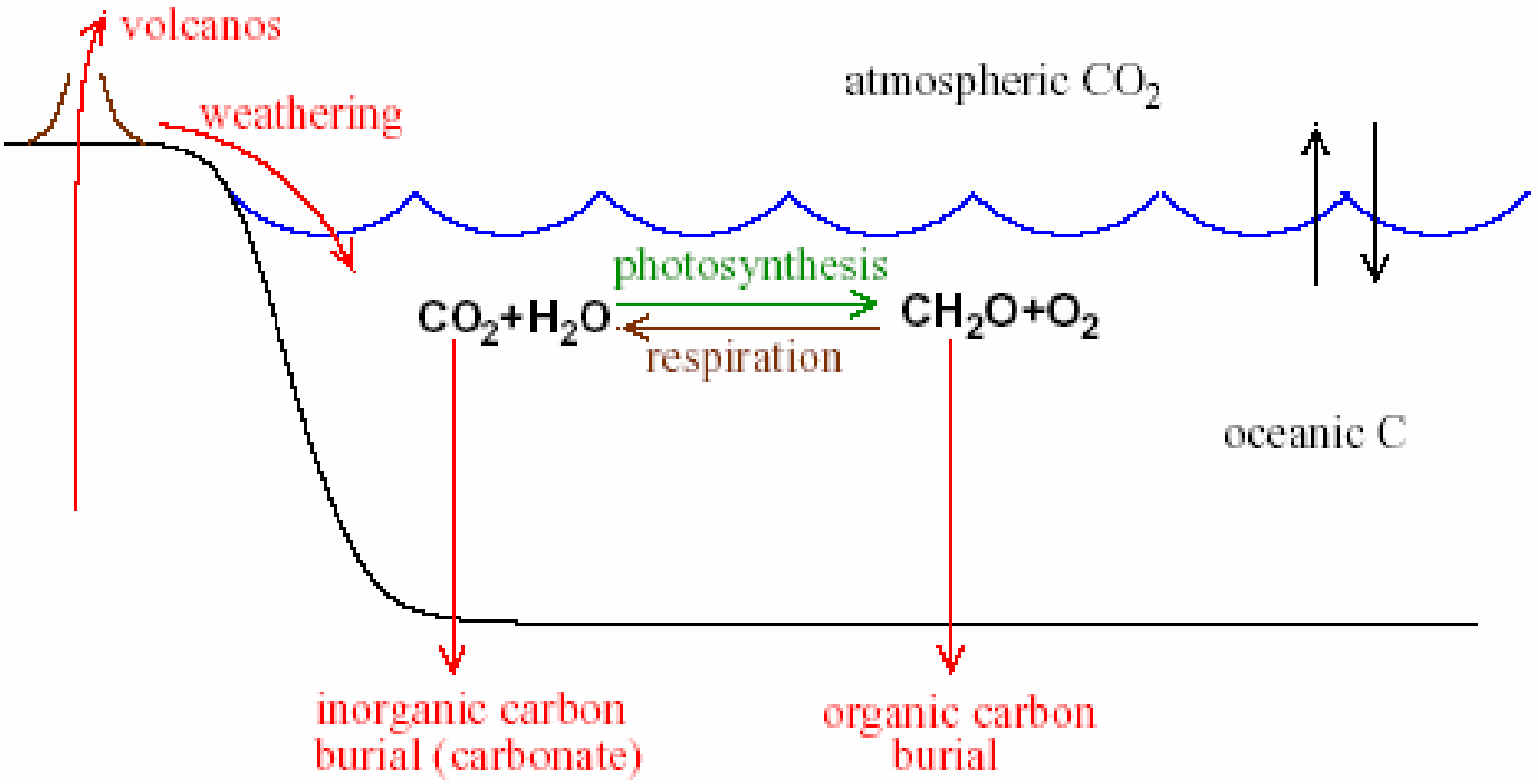
Degens, 1969

Reprise to Evidence of Early Life

Carbon cycle



Carbon cycle



Geologic time scales: $\frac{d[O_2]}{dt} \simeq$ photosynthesis – respiration

$\simeq$ organic carbon burial.

Isotopic Mass Balance of Crustal Carbon Reservoirs

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(Des Marais, 2002)

^{13}C Evidence for Antiquity of Earthly Life

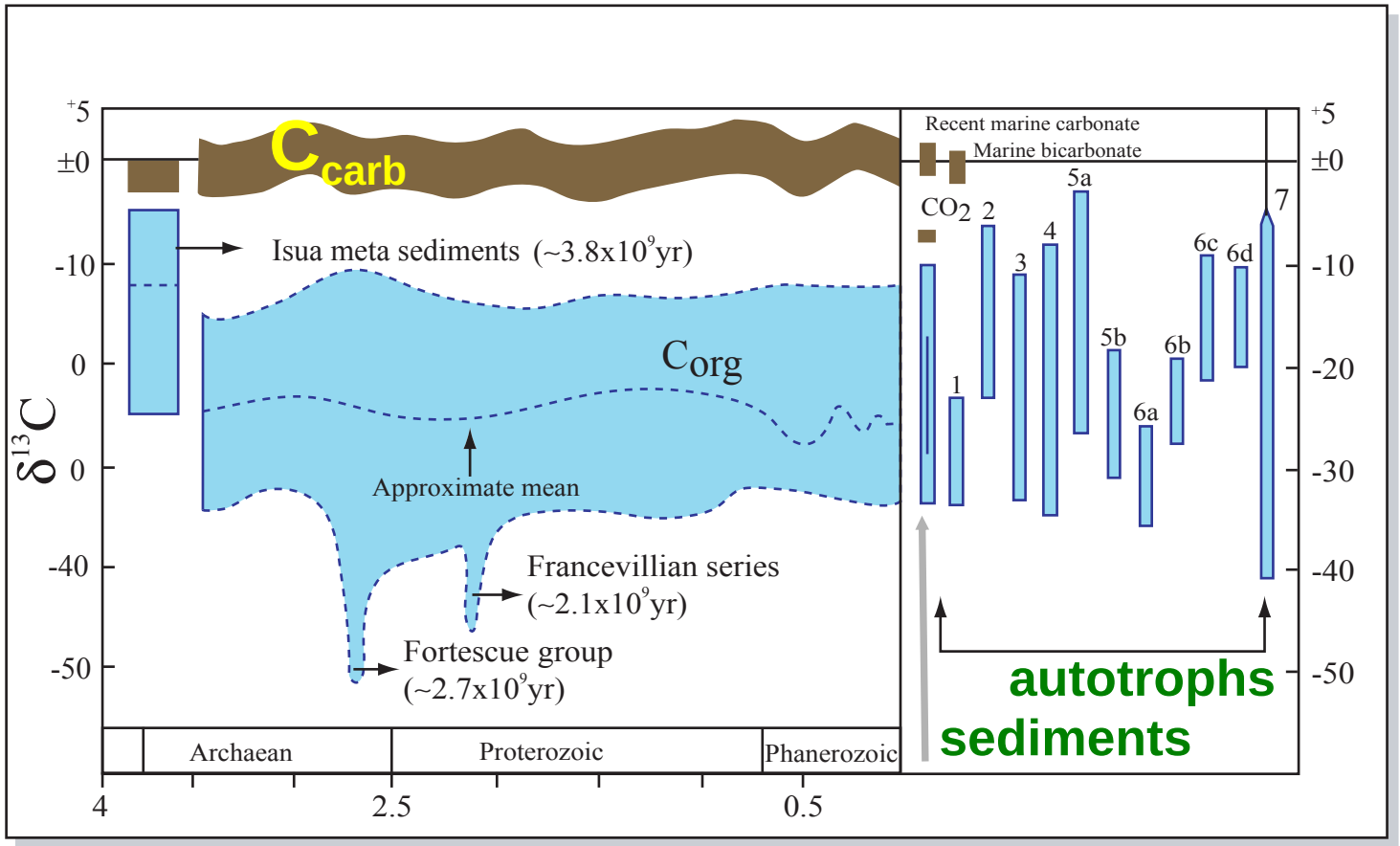


Figure by MIT OpenCourseWare.

Time Ga

Span of modern values

S.J.Mojzsis et al., “Evidence for life on Earth before 3,800 million years ago” …based on isotopically light carbon in graphite in apatite ..

Image removed due to copyright restrictions.

Cover of *Nature*, Volume 384, Issue 6604, November 1996.

But …..

Sano et al. ’99 report the apatite had U/Pb and Pb/Pb ages of only ~ 1.5 Ga.

And……

Tracing Life in the Earliest Terrestrial Rock Record, *Eos Trans. AGU, 82*(47),
Fall Meet. Suppl., Abstract P22B-0545 , 2001
Lepland, A., van Zuilen, M., Arrhenius, G

References: Mojzsis,S.J, .Arrhenius,G., McKeegan, K.D.,.Harrison, T.M.,.Nutman, A.P \& C.R.L.Friend.,1996. Nature 384: 55 Schidlowski, M., Appel, P.W.U., Eichmann, R. \& Junge, C.E., 1979. Geochim. Cosmochim. Acta 43: 189-190.

^{13}C Evidence for Antiquity of Earthly Life

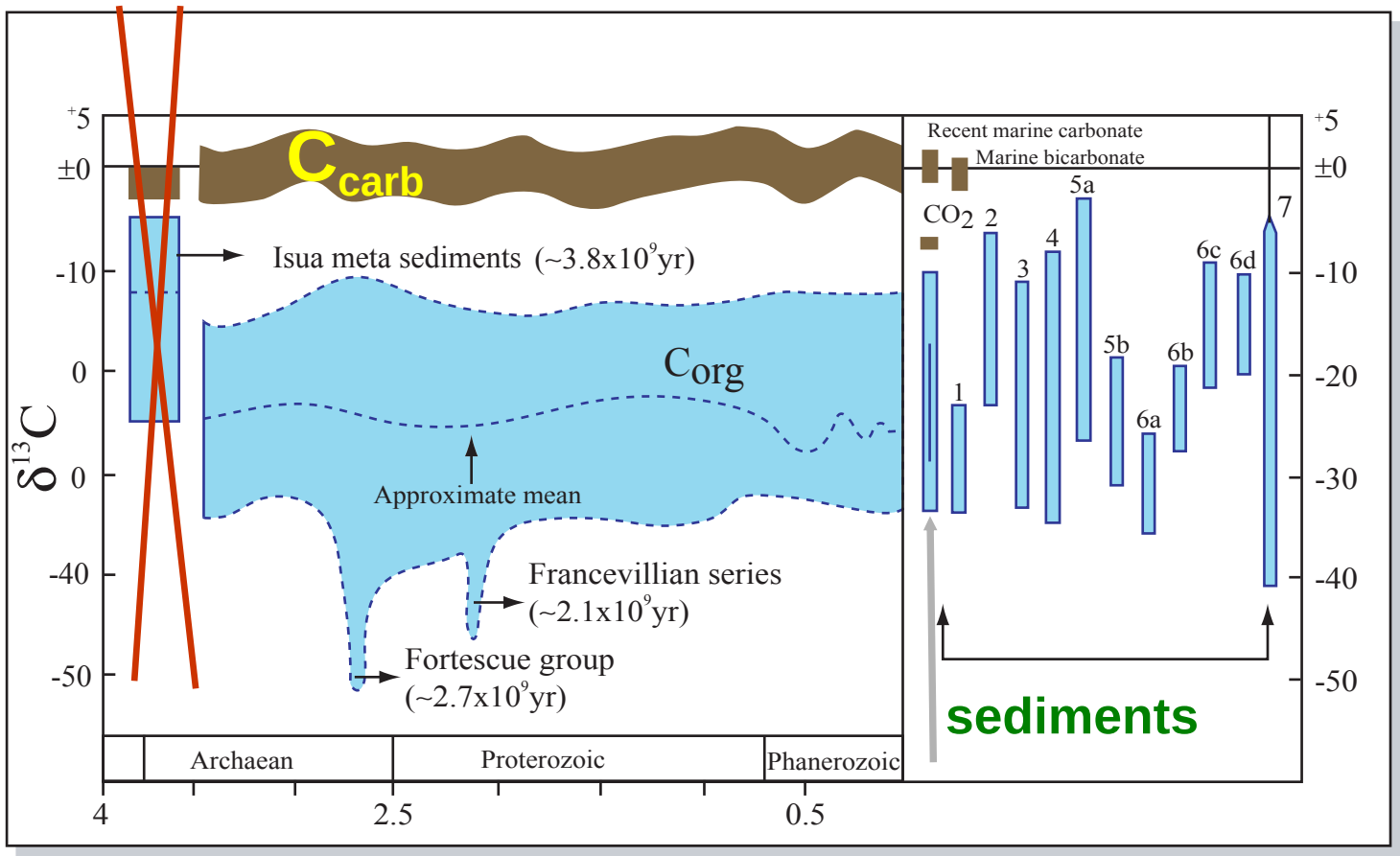


Figure by MIT OpenCourseWare.

Time Ga

Span of modern values

Sulfur forms and their oxidation state

Compound	Formula	Oxidation state
Sulfide	S^{2-}	-2
Polysulfide	S_n^{2-}	-2, 0
Sulfur	S_8	0
Hyposulfite (dithionite)	$S_2O_4^{2-}$	+3
Sulfite	SO_3^{2-}	+4
Thiosulfate	$S_2O_3^{2-}$	-2, +6

Sulfur forms and their oxidation state

Compound	Formula	Oxidation state
Dithionate	$S_2O_6^{2-}$	+5
Trithionate	$S_3O_6^{2-}$	-2, +6
Tetrathionate	$S_4O_6^{2-}$	-2, +6
Pentathionate	$S_5O_6^{2-}$	-2, +6
Sulfate	SO_4^{2-}	+6

Abundances of stable sulfur isotopes

(MacNamara & Thode, 1950. *Phys. Rev.*)

^{32}S:	95.02%
^{33}S:	0.75%
^{34}S:	4.21%
^{36}S:	0.02%

However, the abundances of stable isotopes may vary from their average values as a result of **biological** and **inorganic** reactions, Involving the chemical transformation of sulfur compounds.

δ notation

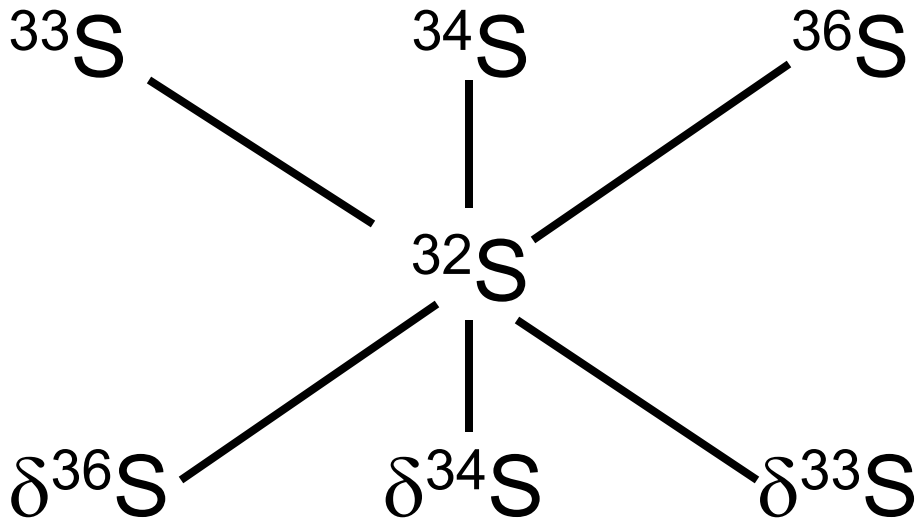
$$\delta^{34}S = \left(\frac{(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{standard}}{(^{34}S/^{32}S)_{standard}} \right) X\ 1000‰$$

Standard:

I: troilite (FeS) from the Cañon Diablo meteorite, CDT

II: IAEA-S-1 (Ag_2S), V-CDT

Multiple sulfur isotopes



Mass-dependent Fractionation:

$\delta^{33}S=0.515\delta^{34}S$, $\delta^{36}S=1.91\delta^{34}S$

Dissimilatory sulfate reduction

$$SO_4^{2-} + CH_2O \longrightarrow H_2S + HCO_3^-$$

$$SO_4^{2-} + H_2 \longrightarrow H_2S + H_2O$$

^{32}S-O bond easier to break than ^{34}S-O

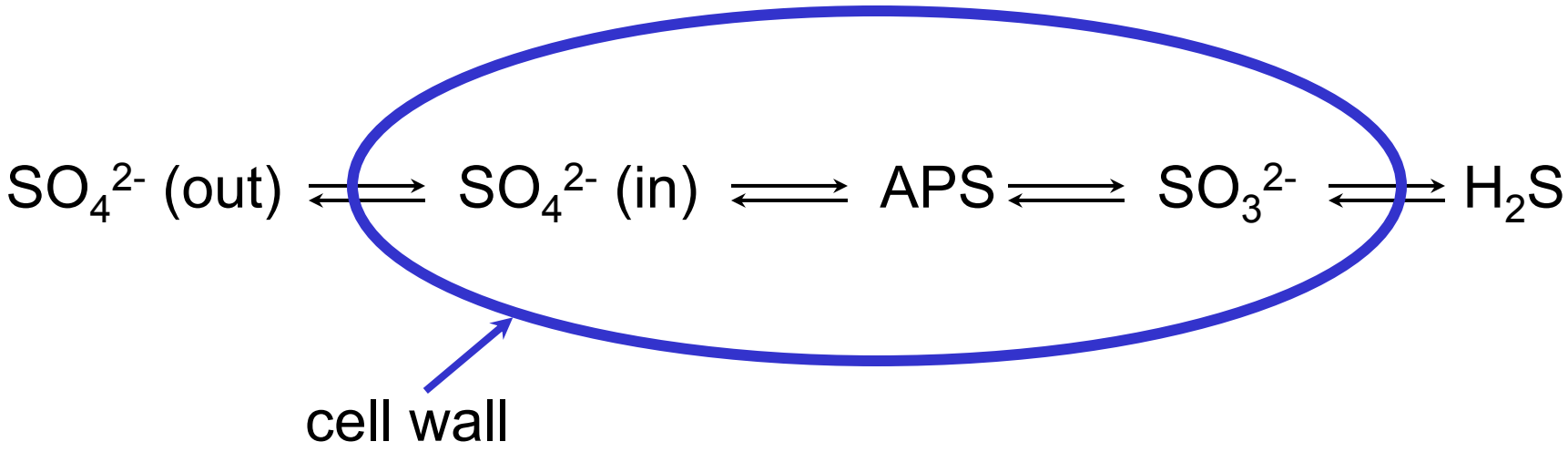
Sulfides become enriched in ^{32}S and depleted in ^{34}S

Sulfur isotope fractionation

The partitioning of isotopes between two substances (H_2S and SO_4) with different isotope ratios

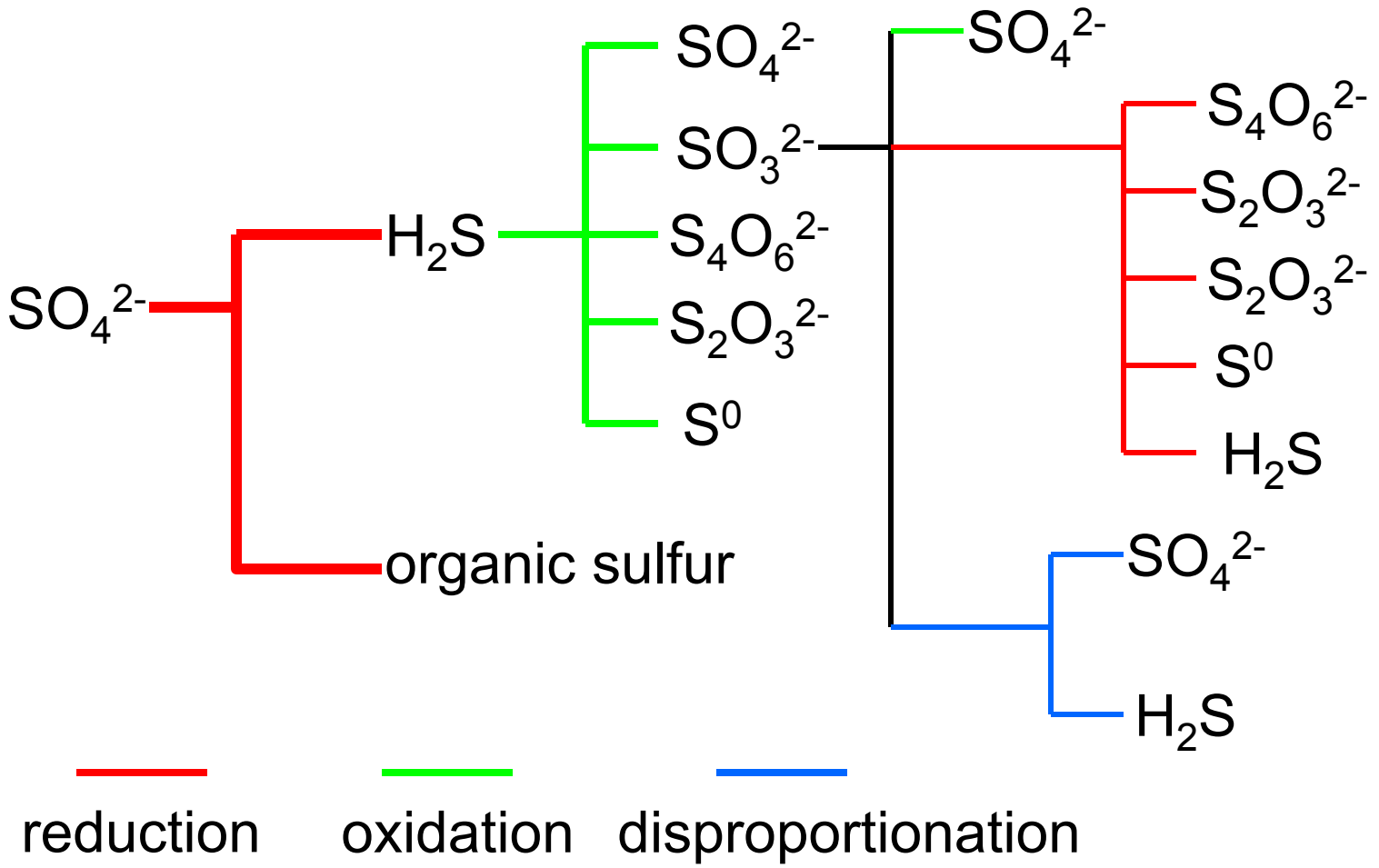
$$\text{Fractionation } (\varepsilon_{SR}) = \delta^{34}S_{SO4} - \delta^{34}S_{H2S}$$

Biochemical pathway of dissimilatory SR



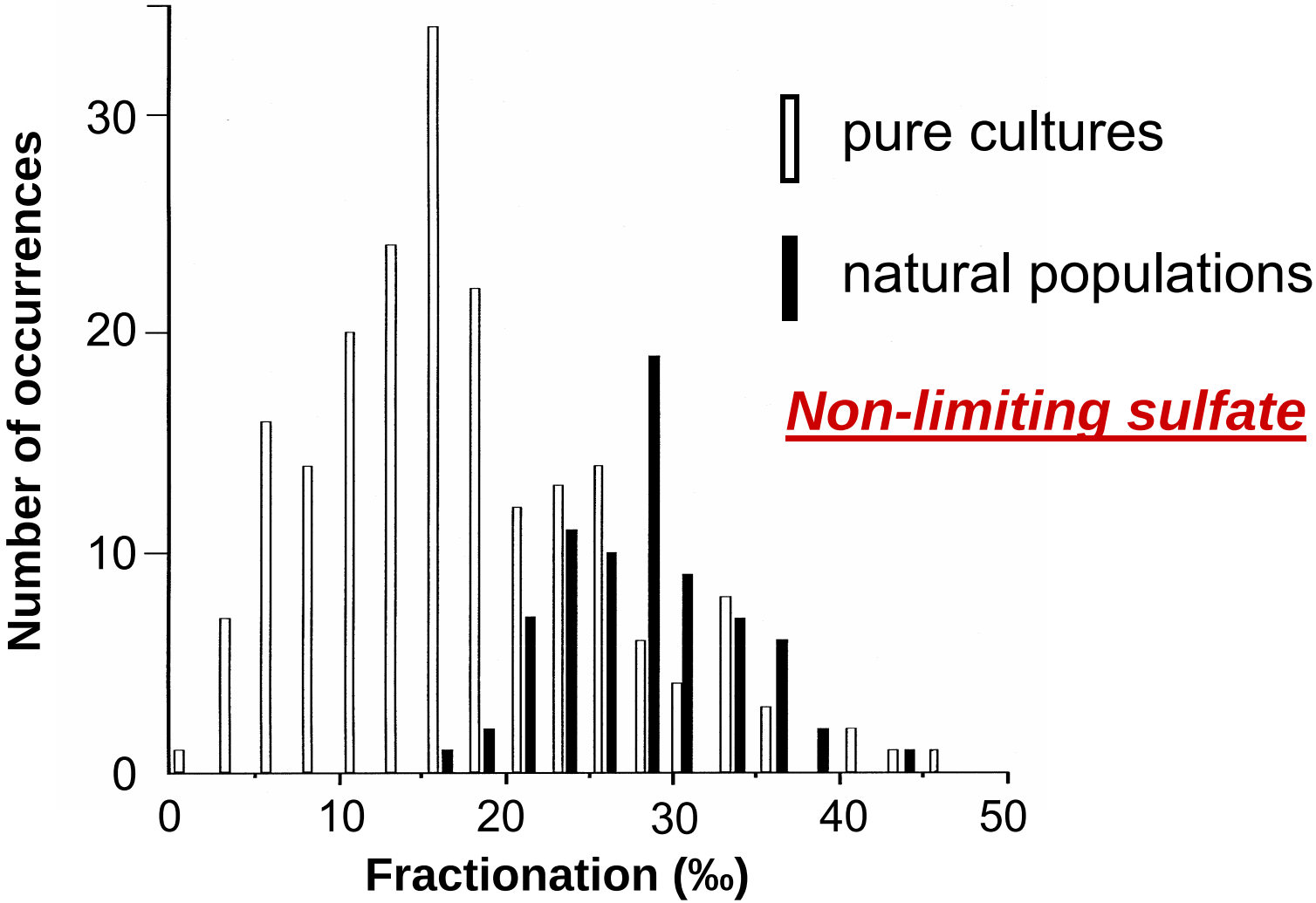
Fractionation	-3‰	0‰	15‰	25‰

Tree of Biological Sulfur Cycle

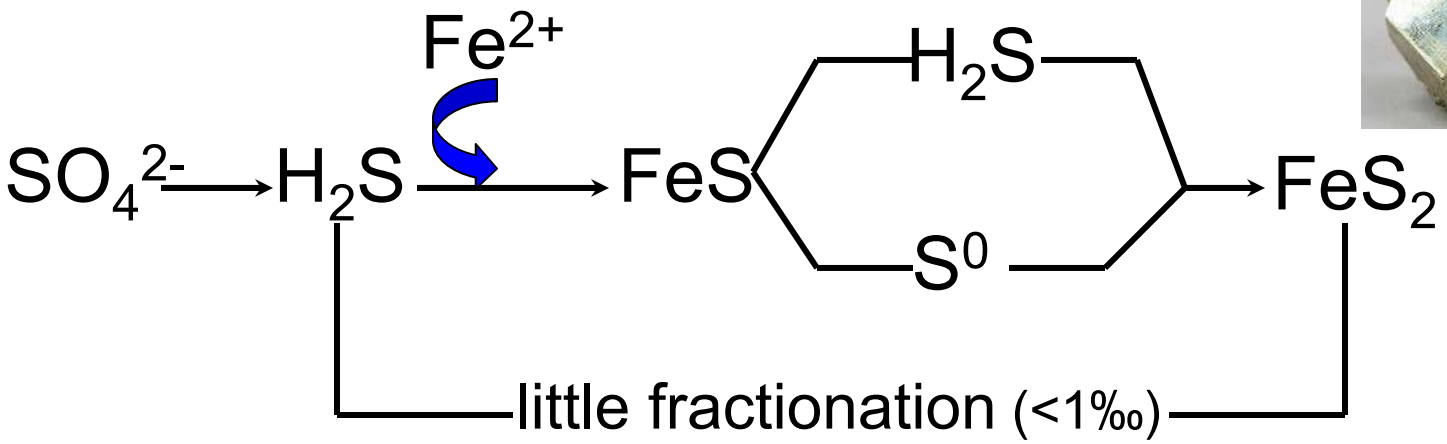


Empirical Measurements of S-isotopic fractionation during sulfate reduction

(Shen and Buick, 2004. *Earth-Sci. Rev.*)



Pyrite formation and S-isotope preservation

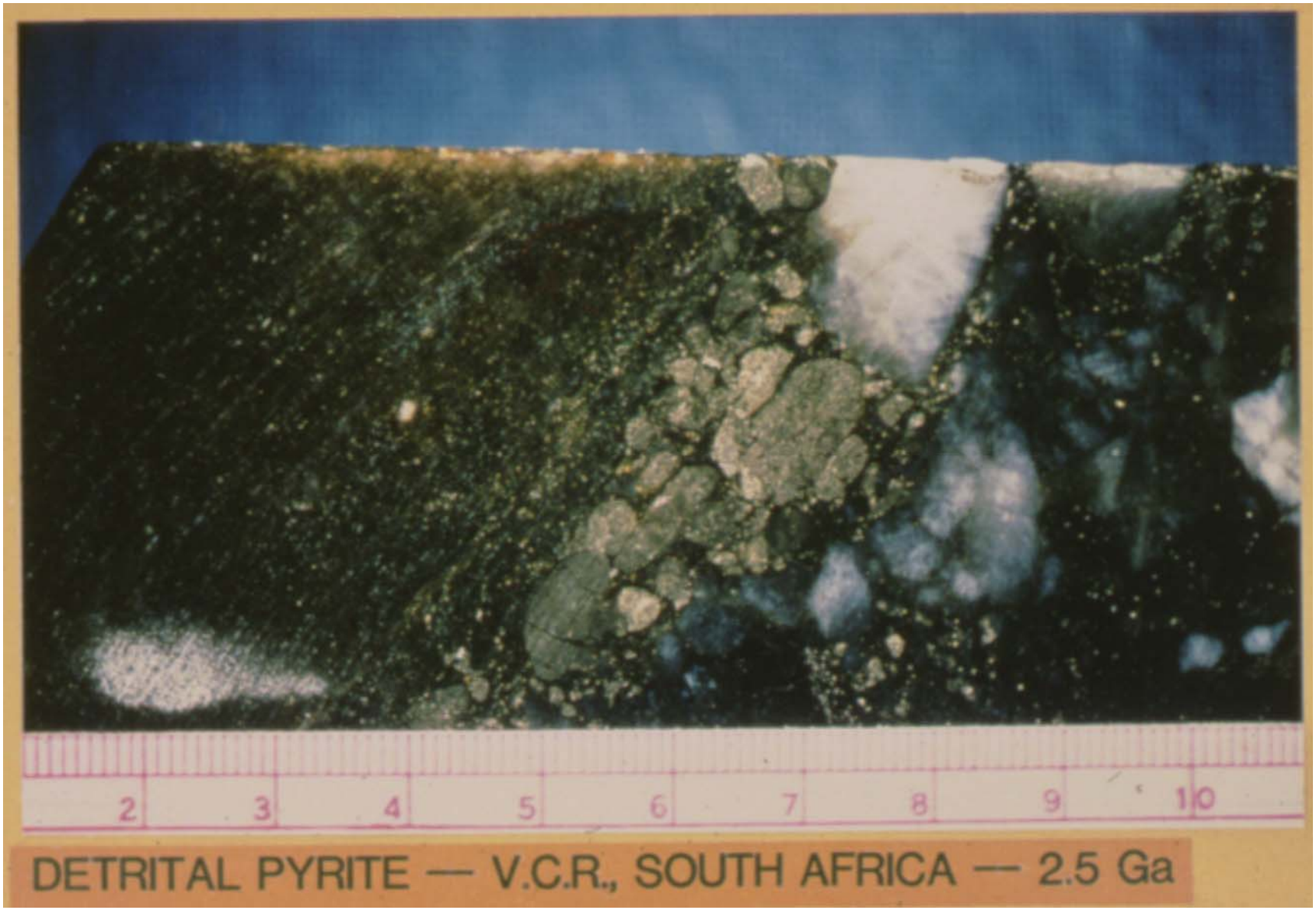


Therefore, $\delta^{34}S$ of pyrite in sedimentary rocks provide indication:

I: activity of SRB (***Life***)

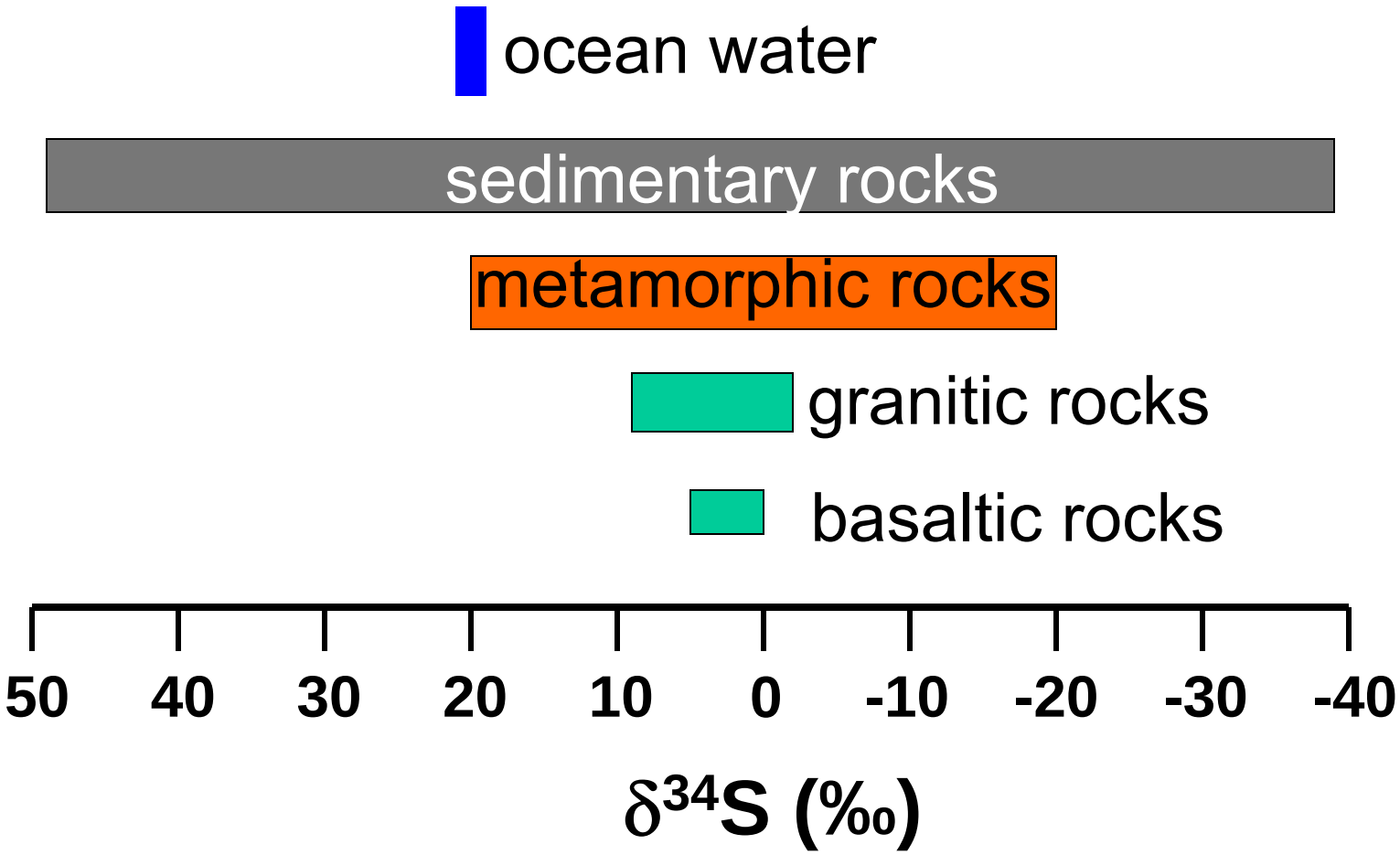
II: conditions of sulfide formation (***Environment***)

Pyrite (FeS_2) is Unstable in O_2-Rich Environments



Typical $\delta^{34}S$ values of some geological material

(relative to CDT)



Isotopic evidence for microbial sulfate reduction

1. Isotope signature is primary from sedimentary rocks

2. $\delta^{34}S$ values are distinctly shifted to the negative values.

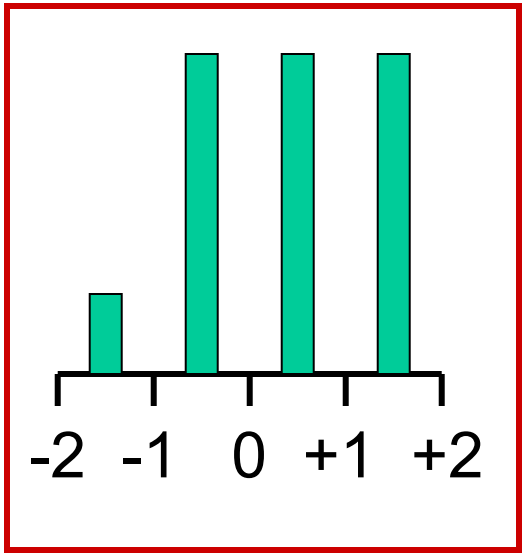
3. Fairly large spread of $\delta^{34}S$ values for sulfides, and thus large fractionations.

The oldest terrestrial S-isotopic records (~3.8 Ga) from the Isua Superacrustal Belt, Greenland

(Monster et al., 1979. *GCA*)

* Narrow range $\delta^{34}S$ (ave. 0.5±0.9‰)

* Similar to those of magmatic sulfides



Models for low fractionation of 0±5‰

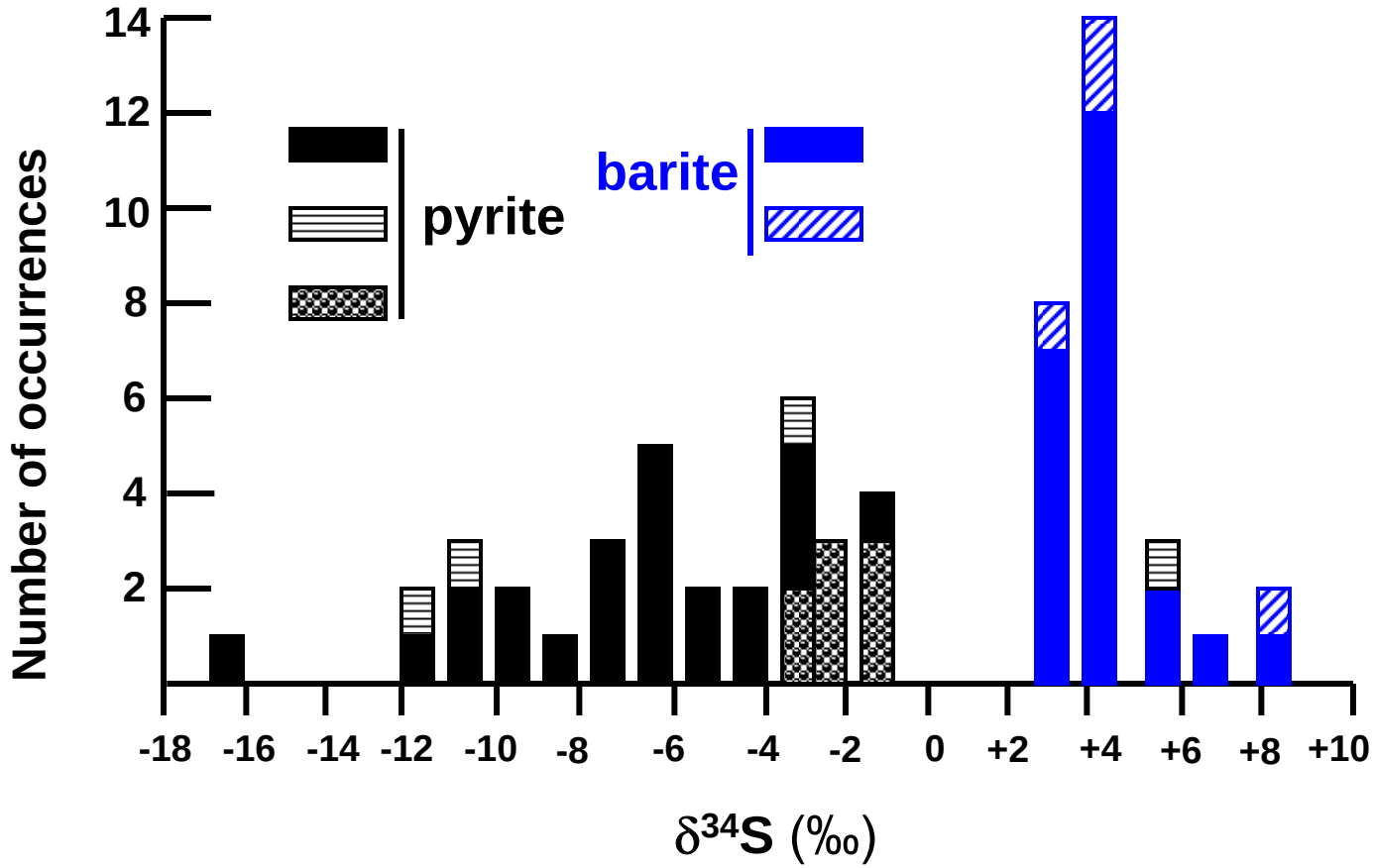
(~3.8 Ga – 2.7 Ga)

(Paytan, 2000. *Science*)

Non-biological fractionation	Low sulphate concentration	High SRR	Closed system effect
Low pO_2 Low SO_4^{2-} SRB not active	$pO_2=10^{-12}$atm SO_4^{2-} <1mM SRB active	$pO_2=10^{-2.5}$ atm SO_4^{2-} >10mM SRB active T ~ 40^0C	$pO_2=10^{-2.5}$ atm SO_4^{2-} >10mM SRB active SR Rates> diffusion rates

The $\delta^{34}S$ of sulfur species from the North Pole barite, northwestern Australia

(Shen et al., 2001. *Nature* 410: 77-81)



Isotopic evidence for microbial sulphate reduction in the early Archaean era

Yanan Shen*, Roger Buick² & Donald E. Canfield* NATURE |VOL 410 | 1 MARCH 2000p79-81

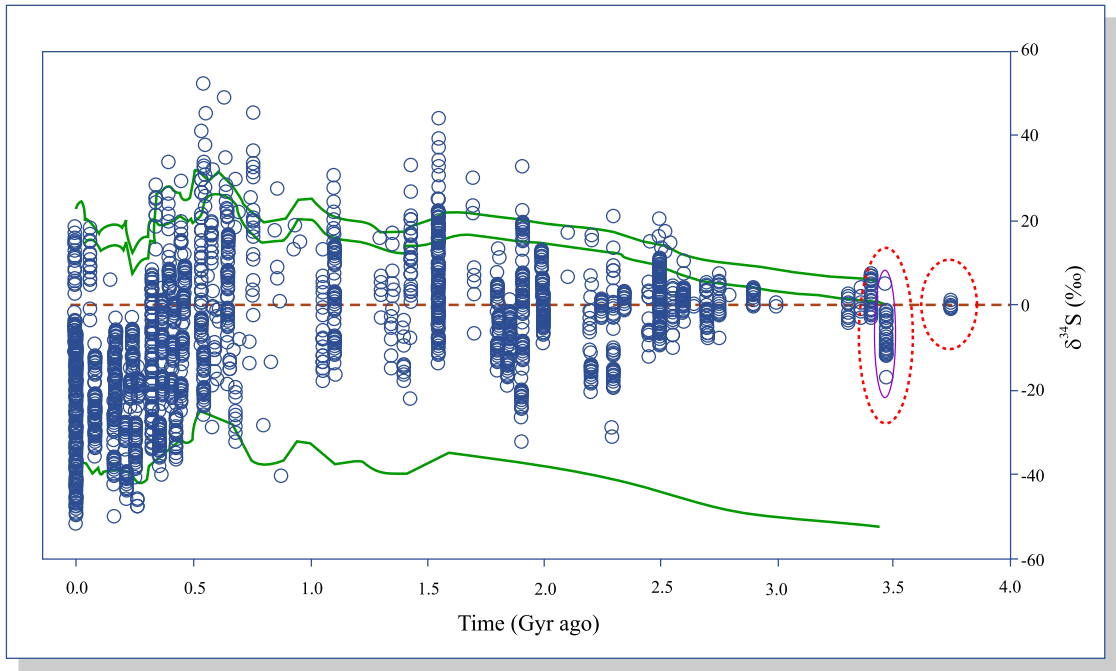


Figure by MIT OpenCourseWare. After Shen, Buick and Canfield, 2000.

Figure 3 The secular trends in the isotopic composition of seawater sulphate and sulphide over geological time. Data within the oval are from this work, the other data are from refs 2, 29. The band (double line) in the upper part of the figure represents the isotopic composition of seawater sulphate through time. The single line in the lower part of the figure is displaced from the seawater sulphate trend by 55per mil, representing themaximum fractionation between sulphate and sulphide through the past 600 million years. Before 1.7 Gyr ago, constraints on the isotopic composition of seawater sulphateare sparse.

Mass Independent Fractionation

- Detectable when there are >2 isotopes fractionated by different mechanisms
- Seems to apply to gas phase chemistry (eg atmospheric processes in Nature)
- Examples occur in O_3, O_2, CO_2, CO, N_2O, H_2O_2 and sulfate aerosols. The isotopic anomalies are apparently linked to photochemical reactions
- A well-known example is the transfer, in the stratosphere, of ^{17}O and ^{18}O from molecular oxygen to CO_2 via ozone.
- Oxygenated sulfur species undergo gas phase reactions leading to MIF in the absence of O_2
- This is the 'origin' of MIF in Archean sulfur species (eg Farquhar et al) although the precise mechanisms are still to be elucidated

Mass Independent Fractionation

Available online at www.sciencedirect.com
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Earth and Planetary Science Letters 213 (2003) 15–30
www.elsevier.com/locate/epsl

New insights into Archean sulfur cycle from mass-independent sulfur isotope records from the Hamersley Basin, Australia

Shuhei Ono[a,*], Jennifer L. Eigenbrode[b], Alexander A. Pavlov[c], Pushker Kharecha[b], Douglas Rumble III[a], James F. Kasting[b], Katherine H. Freeman[b]

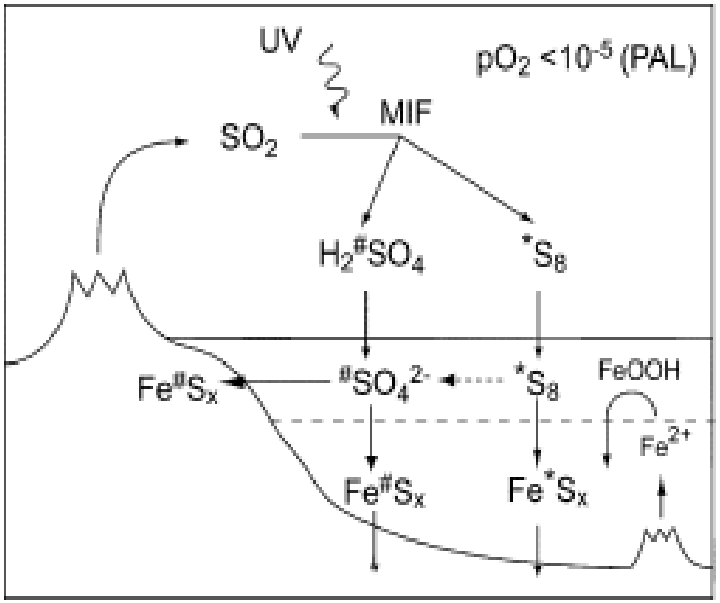
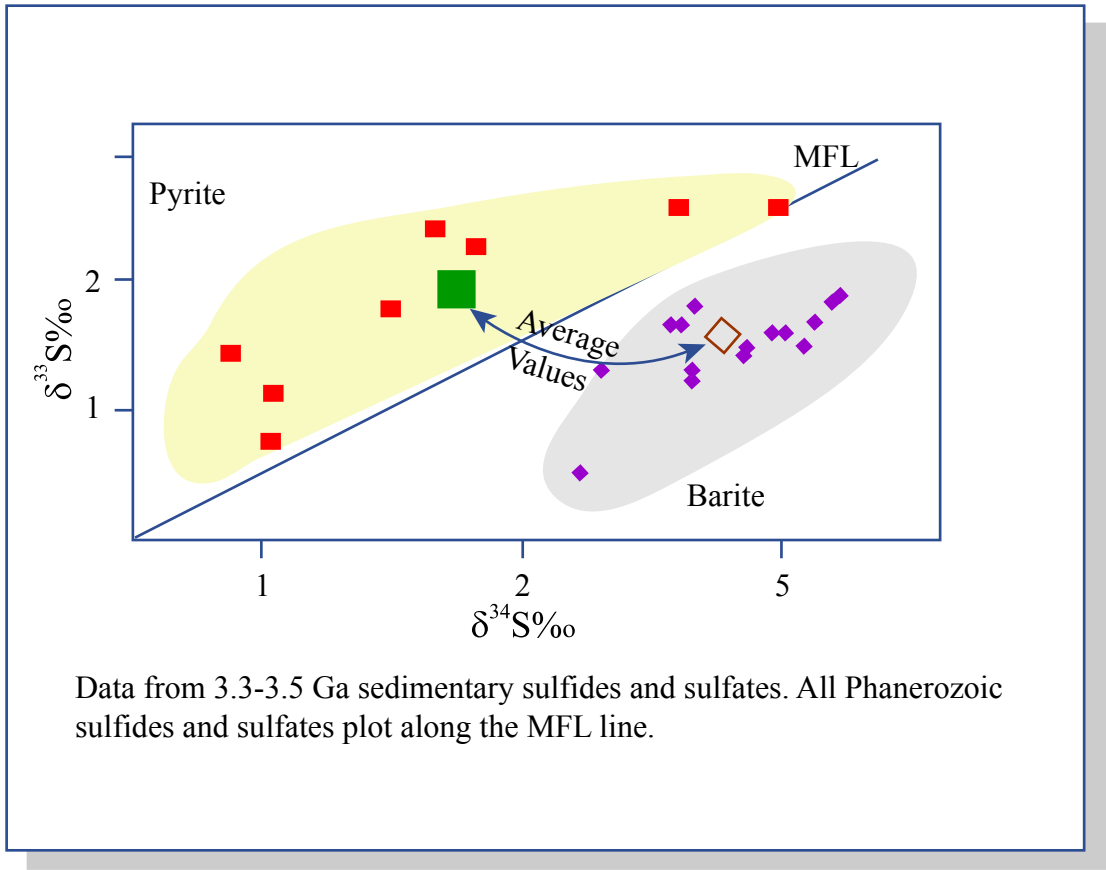


Fig. 3. A conceptual model of Archean sulfur cycle. Photochemistry in the atmosphere causes MIF in sulfur isotopes, and aerosols of S_8 and H_2SO_4 carry sulfur with positive (*S) and negative (#S) v33S signatures, respectively. The preservation of MIF signatures in the sediments implies incomplete oxidation of S8 in the ocean (dashed arrow).

Mass Independent Fractionation

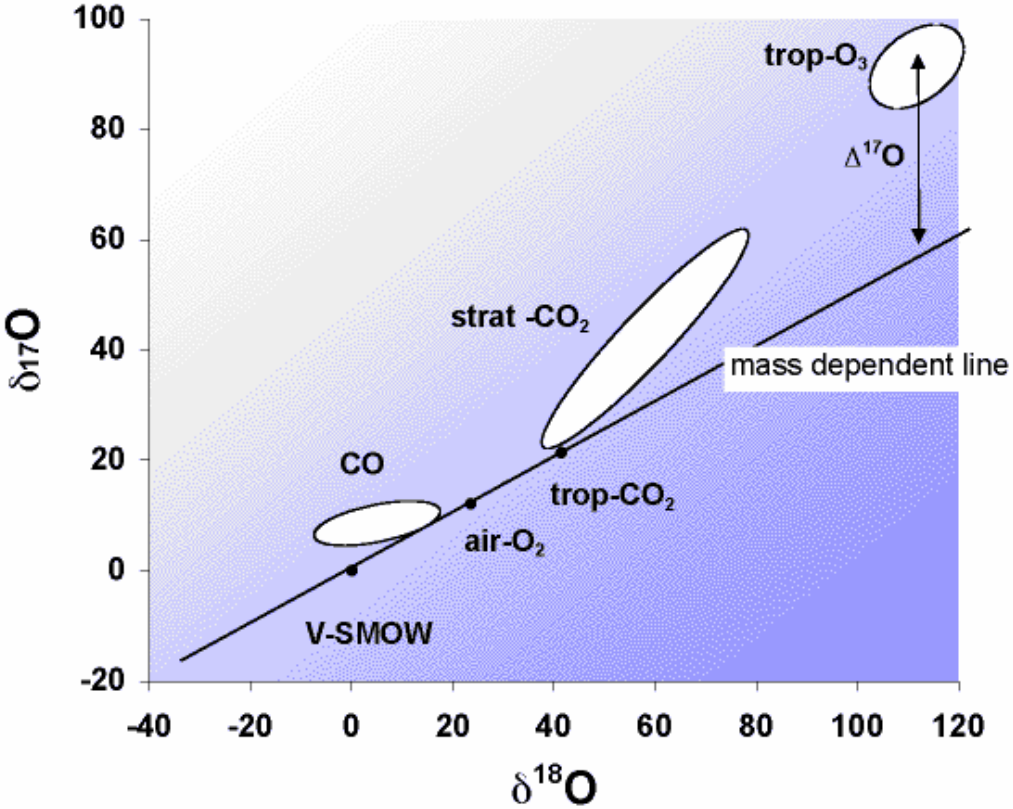


Data from 3.3-3.5 Ga sedimentary sulfides and sulfates. All Phanerozoic sulfides and sulfates plot along the MFL line.

Figure by MIT OpenCourseWare. After Farquhar et al., 2001.

Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere
A.A. PAVLOV and J.F. KASTING **ASTROBIOLOGY Volume 2, Number 1, 2002**

Mass Independent (Anomalous) Fractionation of O-isotopes in Atmospheric Gases



http://www.igac.noaa.gov/newsletter/16/mass-new.php

Figure 3. A three-isotope plot showing the mass dependent line and the most important deviations for CO_2, CO, and tropospheric O3. Stratospheric ozone (not shown here) is further enriched.

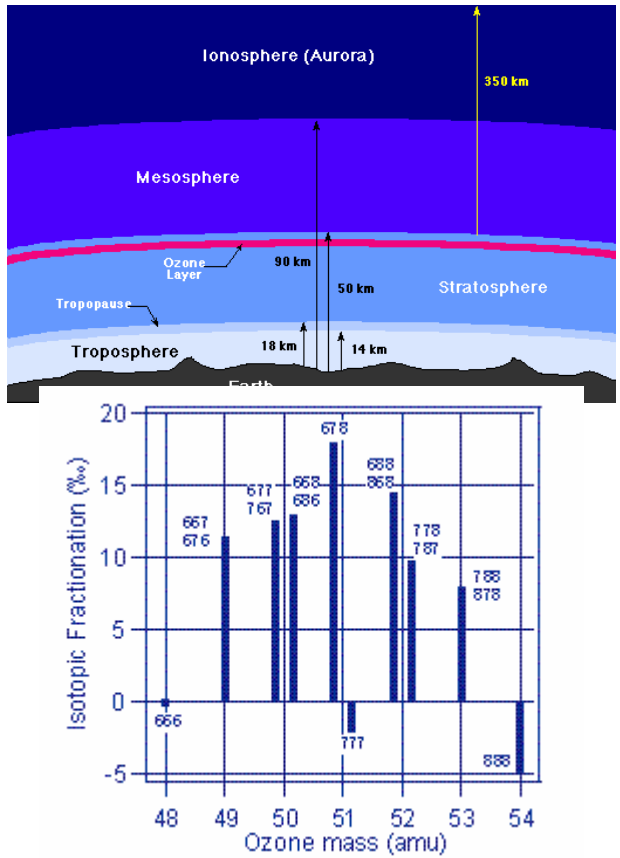


Figure 1. The distribution of ozone isotopomers measured by using enriched mixtures. The asymmetric molecules are formed preferentially. Numbers next to bars indicate molecular composition, e.g., "667" = 16O16O17O.

Figures courtesy of IGAC.

Summary

The wide spread of $\delta^{34}S$ values of microscopic pyrites aligned along growth faces of former gypsum crystals in the North Pole barite deposit demonstrate that sulfate-reducing prokaryotes had evolved by 3.47 Ga.

The large S-isotopic fractionations in this localized and sulfate-rich environment imply that Archean ocean was low in sulfate, and, by implication, low oxygen in the atmosphere.