

Geobiology 2013 Lecture 4

Biogeochemical Tracers #1

Isotopics #1: C and S

COMMON TRACERS of BIOLOGY:

- Fossils
- Elemental abundances
 - Redfield ratio
- Isotopes
 - See below
- Biominerals
 - Pyrite, carbonates, silica
- Biological Marker Compounds, Biomarkers
 - See later in the course

Biogeochemical Tracers #1

Isotopics #1: C and S

Need to Know:

Isotopic nomenclature; definition of atm%, ratio, α , δ , ϵ

How to do simple isotopic calculations including mass balance

Names of the CHNOS standards, what they are and the forms that are prepared for analysis

What processes cause isotopic fractionation including C, H & N in OM and C & O in limestones; S in pyrite and sulfate

Geobiology 2012 Lecture 4

Biogeochemical Tracers #1

Isotopics #1: C and S

Assigned Reading for this week and C-cycle

- Stanley 2nd Ed Chapter 10, pp 221-240
- The Earth System, Lee R. Kump, James F. Kasting & Robert G. Crane (Prentice Hall, Upper Saddle River, NJ, 2004). Chap. 7
- Hayes, Introduction to Isotopic Calculations
- Hayes, J. M., Strauss, H. & Kaufman, A. J. (1999) The abundance of ¹³C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma *Chem. Geol.* 161, 103–125.

Other readings

- Hayes JM 2001 Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. Reviews in Mineralogy *Stable Isotopic Geochemistry*, John W. Valley and David R. Cole (eds.)
- S Ono et al. New insights into Archean sulfur cycle from mass-independent sulfur isotope records from the Hamersley Basin, Australia. *Earth and Planetary Science Letters* 213 (2003) 15-30.

Light isotope abundances

Isotope	Atom%
^1H	99.985
^2H (D)	0.015
^{12}C	98.89
^{13}C	1.11
^{14}N	99.63
^{15}N	0.37
^{16}O	99.759
^{17}O	0.037
^{18}O	0.204
^{32}S	95.00
^{33}S	0.76
^{34}S	4.22
^{36}S	0.014

Some concepts about isotope chemistry

Atom percent $^{13}\text{C} = \left(\frac{^{13}\text{C}}{^{13}\text{C} + ^{12}\text{C}} \right) \times 100$ 1.11%

Fractional abundance $^{13}\text{C} = ^{13}\text{F} = \left(\frac{^{13}\text{C}}{^{13}\text{C} + ^{12}\text{C}} \right)$ 0.0111

Carbon isotope ratio $= \frac{^{13}\text{C}}{^{12}\text{C}} = ^{13}\text{R}$ 0.0112372

The delta value δ in ‰ $= \frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}} \times 1000$ 0.00 ‰ VPDB

$^{13}\text{R} = 0.010957956 = -24.85 \text{ ‰ VPDB}$

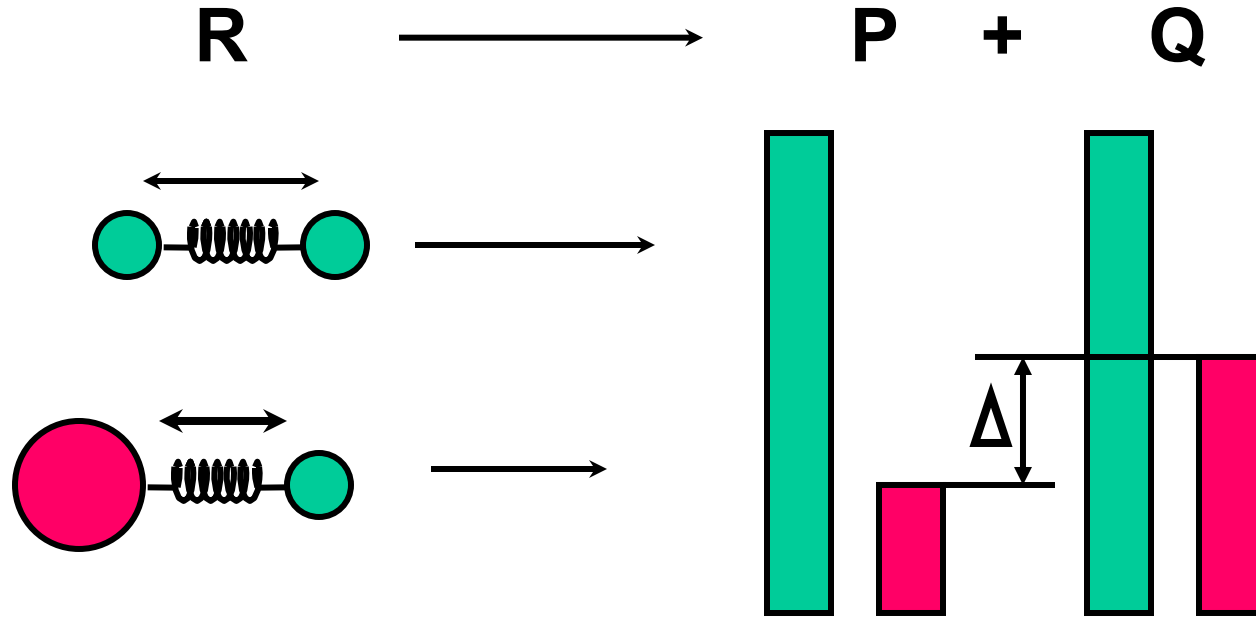
Terminology

$$R = \frac{X_{\text{heavy}}}{X_{\text{light}}} \quad \delta X_{\text{heavy}} = \frac{R_{\text{spl}} - R_{\text{std}}}{R_{\text{std}}} \times 1000$$

Primary Standards	Isotope Ratios	Ratios x 10 ⁶
Standard mean ocean water	² H/ ¹ H	155.76
“	¹⁸ O/ ¹⁶ O	2005.20
“	¹⁷ O/ ¹⁶ O	373
PeeDee belemnite (PDB)	¹³ C/ ¹² C	11237.2
Air	¹⁵ N/ ¹⁴ N	3676.5
Canyon Diablo meteorite (CDT)	³² S/ ³⁴ S	22.22

NB Standard for $\delta^{18}\text{O}/^{16}\text{O}$ in carbonates is PDB

Relationship between an isotope effect and the occurrence of isotopic fractionation

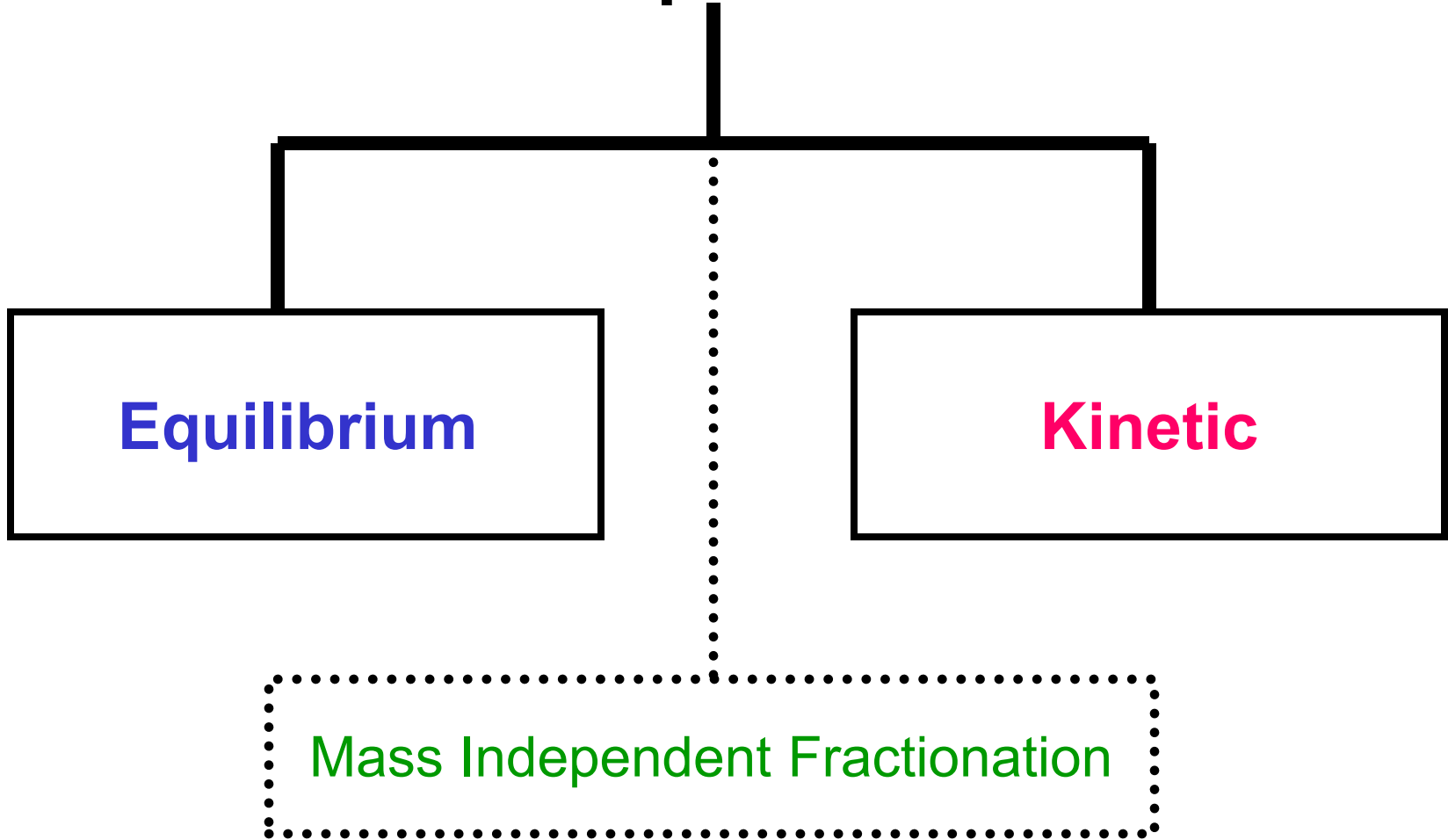


An *Isotope Effect* causes *Fractionation*

↓
a physical phenomenon arising from the mass difference between two isotopes

↓
an observable quantity

Isotope Effects



Origins of Mass Dependent Isotopic Fractionation

Equilibrium in a reversible reaction, where the heavier isotope concentrated in the more strongly bonded form:

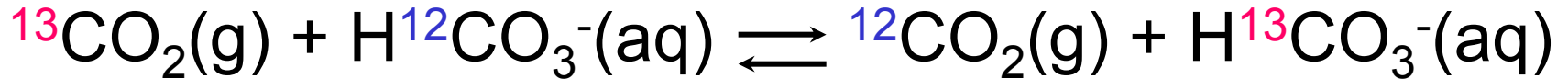


Different rates of diffusive transport where:

$^{12}\text{CO}_2$ diffuses ~1% faster than $^{13}\text{CO}_2$

**Different rates of reaction in kinetically controlled conversions - the light isotope tends to react faster:
most biochemistry**

Example of equilibrium isotope effects



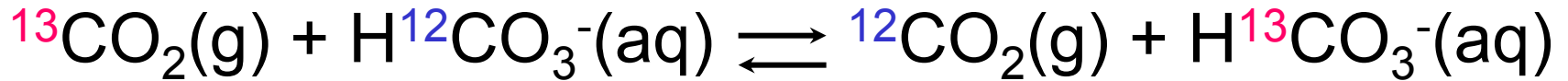
$$K = 1.0092 \text{ (0}^\circ\text{C)}$$
$$1.0068 \text{ (30}^\circ\text{C)}$$

An *equilibrium* isotope effects will cause the heavy isotope to accumulate in a particular component to a system at equilibrium

Fractionation factor $\alpha_{\text{HCO}_3^-/\text{CO}_2} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{HCO}_3^-}}{(^{13}\text{C}/^{12}\text{C})_{\text{CO}_2}}$

It is *numerically* equal to the equilibrium constant

Example of equilibrium isotope effects



The rule: the heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly

Thus, ^{13}C accumulates in the bicarbonate anion

$$\epsilon = \delta_{\text{CO}_2} - \delta_{\text{HCO}_3^-} \cong 10^3(\alpha - 1) \sim 7.9$$

Some equilibrium isotope effects

Reaction	Isotope	α equil [*]	ϵ
$\text{CO}_2 (\text{g}) \leftrightarrow \text{CO}_2 (\text{aq})$	^{13}C	0.9991	0.9
$\text{CO}_2 (\text{g}) \leftrightarrow \text{CO}_2 (\text{aq})$	^{18}O	0.9989	1.1
$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	^{13}C	0.9921	7.9
$\text{O}_2 (\text{g}) \leftrightarrow \text{O}_2 (\text{aq})$	^{18}O	1.000	0
$\text{H}_2\text{O} (\text{s}) \leftrightarrow \text{H}_2\text{O} (\text{l})$	^{18}O	1.003	-3
$\text{H}_2\text{O} (\text{s}) \leftrightarrow \text{H}_2\text{O} (\text{l})$	^2H	1.019	-19
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	^{15}N	1.020	-20
* Measured for 20-25 ° C except phase transition of water			

Kinetic Isotope Effect (KIE)

KIE occurs when the rate of a chemical reaction is sensitive to atomic mass at a particular position in one of the reacting species

The rule: A normal KIE is one which the species containing the lighter isotope tend to react **more rapidly**

Terminology

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

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

Written precisely this is

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

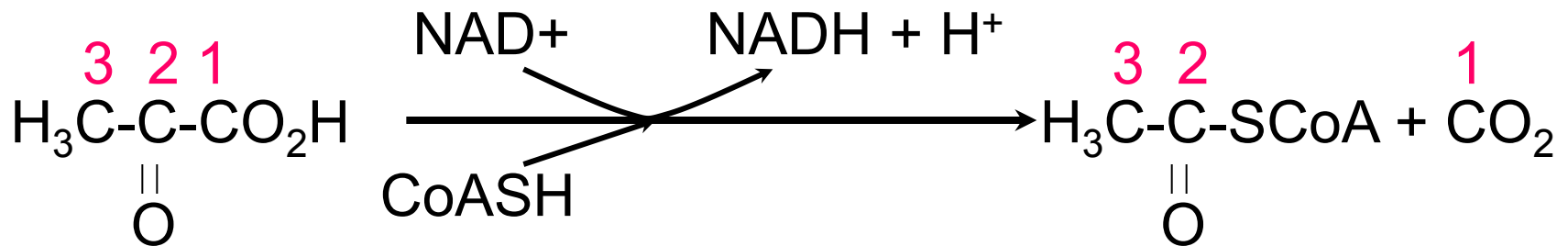
$$\varepsilon = 10^3 (\alpha - 1)$$

A general approximation is

$$\varepsilon = \delta_R - \delta_P \quad \text{or} \quad \delta_P = \delta_R - \varepsilon$$

ε is also called the isotope effect or epsilon !!

Example of Kinetic Isotope Effects (KIE)



Pyruvate Dehydrogenase

$$(^{12}\text{K}/^{13}\text{K})_{\text{C-2}} = 1.0232$$

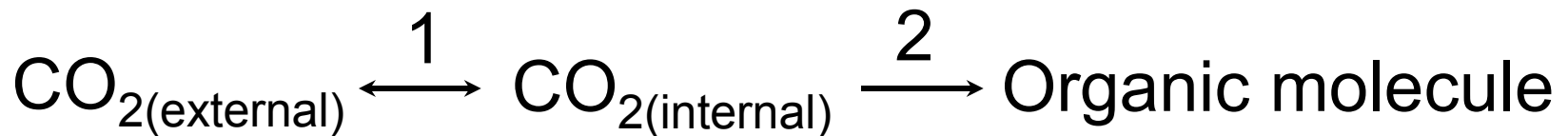
The species containing carbon-12 at position **2** reacts **1.0232 times** more rapidly than the species containing carbon-13 at that position

It is termed “**a 23‰ isotope effect**”

This could be the basis for a good exam question!

Biological carbon fixation

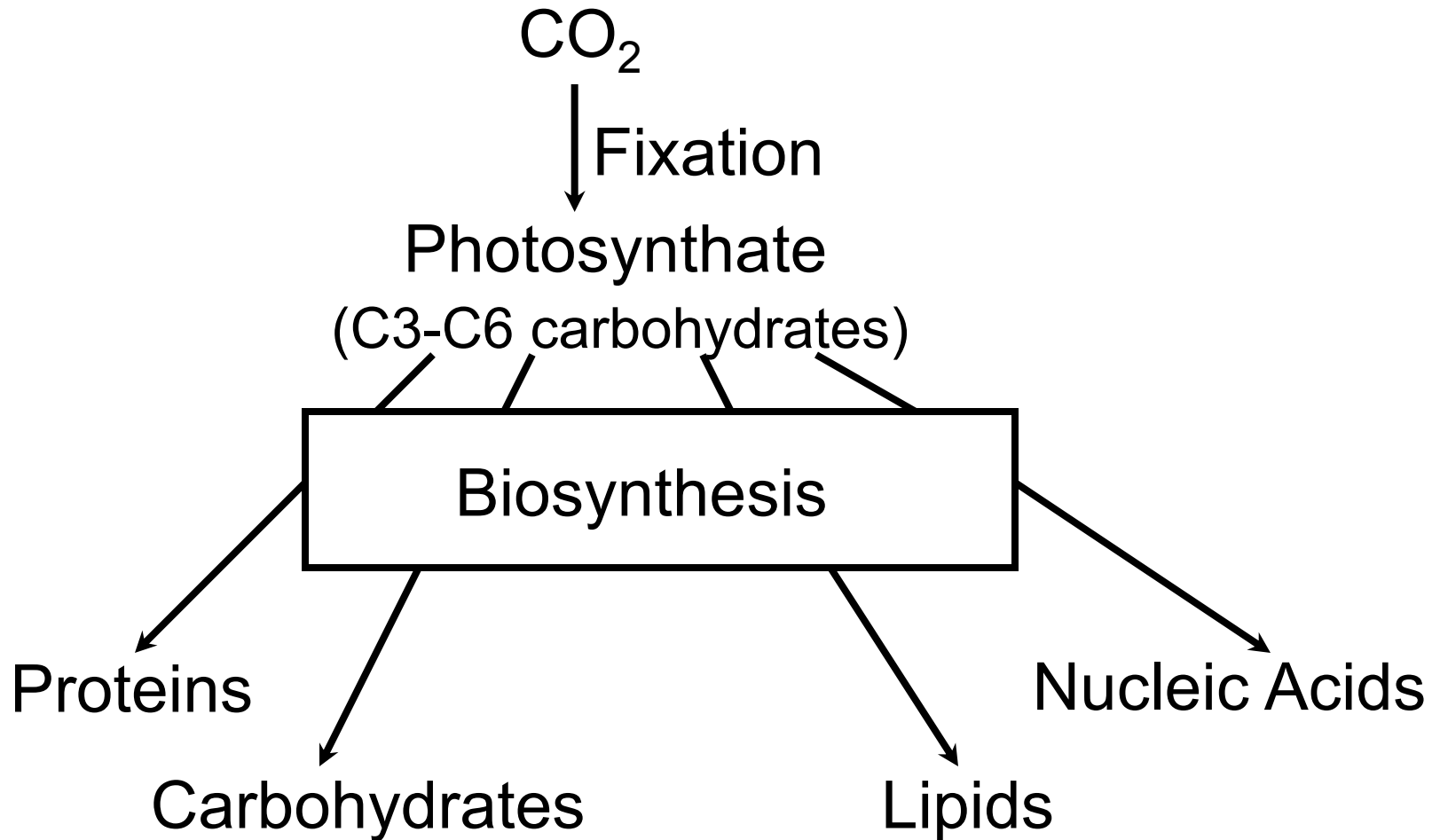
(Park & Epstein, 1960. *GCA* 21:110-126)



Step 1: the uptake and intracellular diffusion of CO₂

Step 2: the biosynthesis of cellular components

Autotrophy

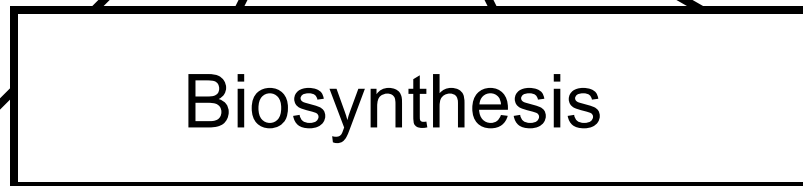


Heterotrophy

Organic material, “food”

↓ Assimilation

Metabolic intermediates
(C3-C6 acids and carbohydrates)



Biosynthesis

Proteins

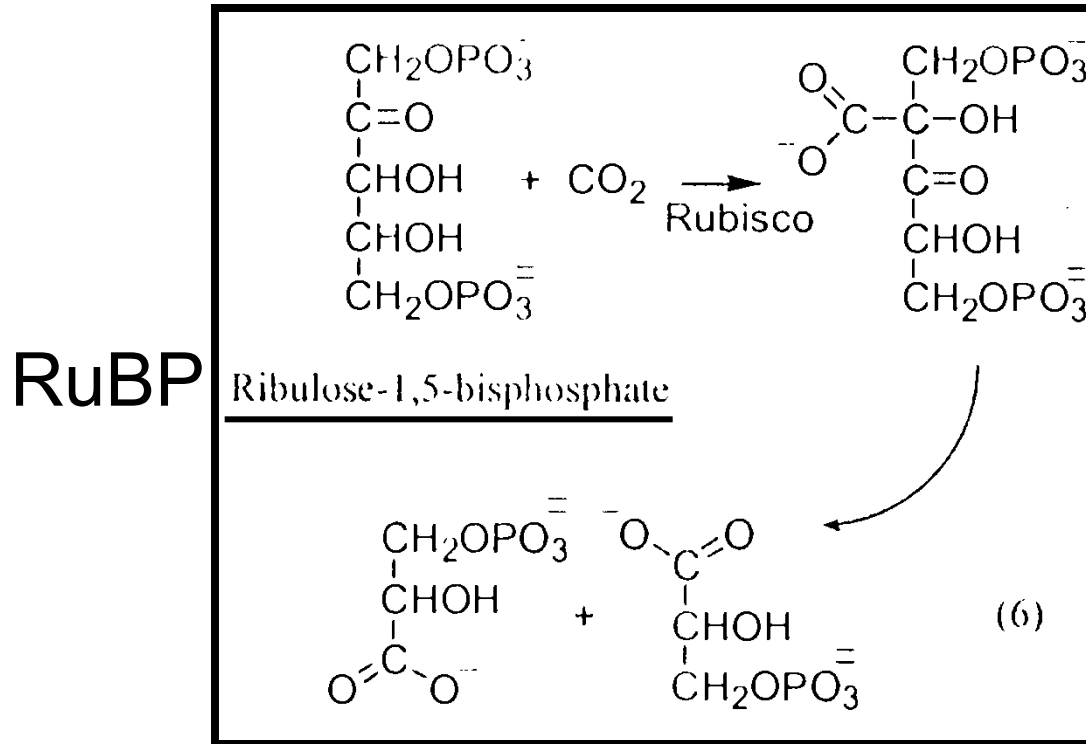
Carbohydrates

Lipids

Nucleic Acids

Carbon fixation (C3 pathway)

Calvin-Benson-Bassham or CBB pathway



Rubisco catalyzes the carboxylation of “**RuBP**”, a **5-carbon** molecule. A **6-carbon** product is formed as a transient intermediate, but the first stable products are two molecules of “**PGA**”, 3-phosphoglyceric acid, C₃H₇O₇P. The carbon

number gives its name:

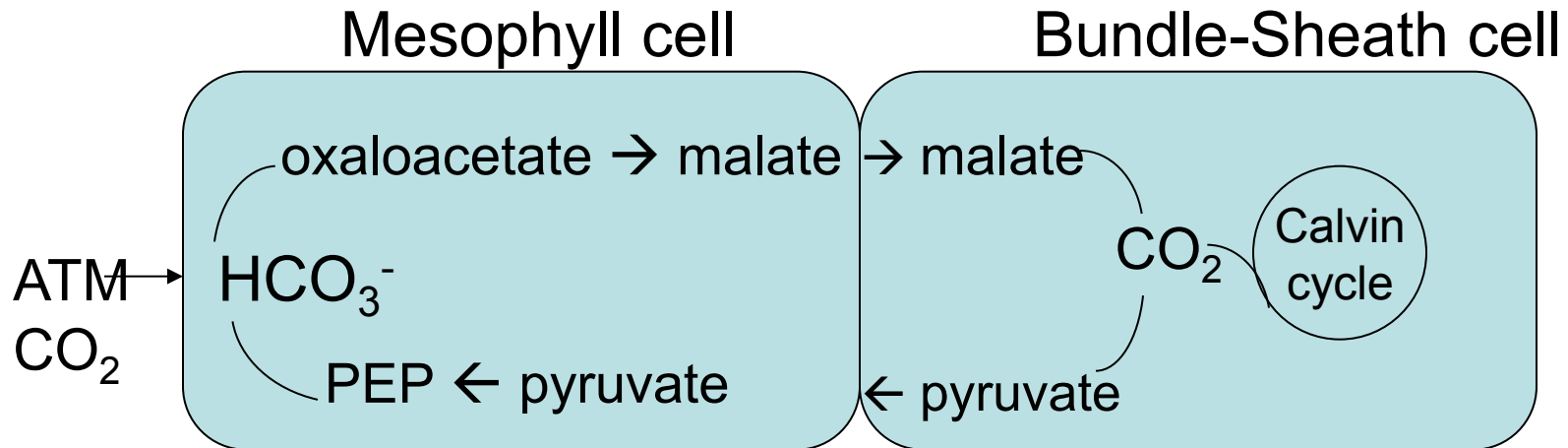
C3 photosynthesis

Rubisco: ribulose-1,5-bisphosphate
carboxylase oxygenase

$$\varepsilon = 29.4\text{‰} \text{ (O'leary, 1988; Guy, 1987)}$$

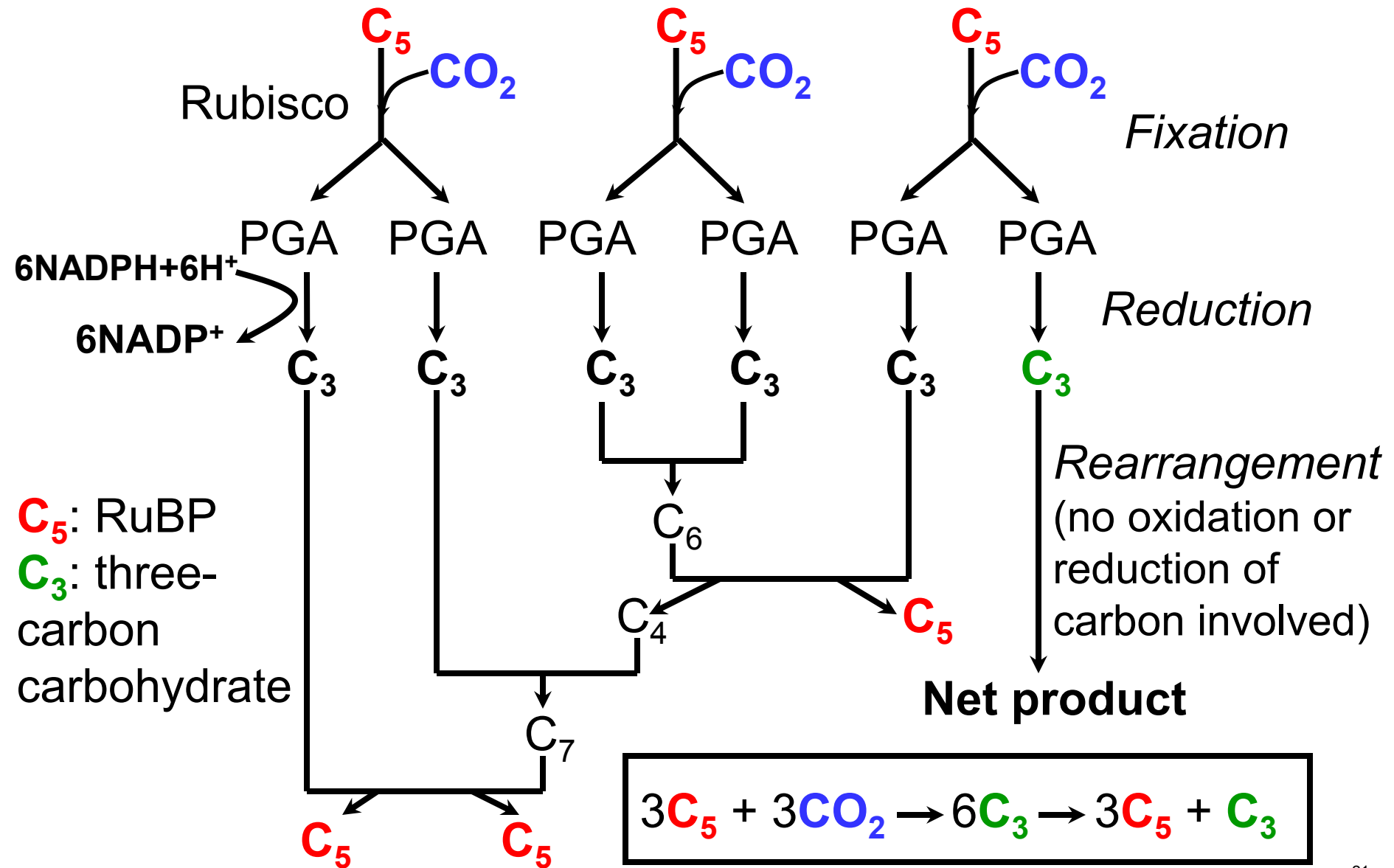
Carbon fixation (C4 & CAM pathways)

Formation of oxaloacetate from PEP (Phosphoenolpyruvate) catalysed by PEP carboxylase



CAM (Crassulacean acid metabolism): Use both C3 and C4 metabolism separated in time

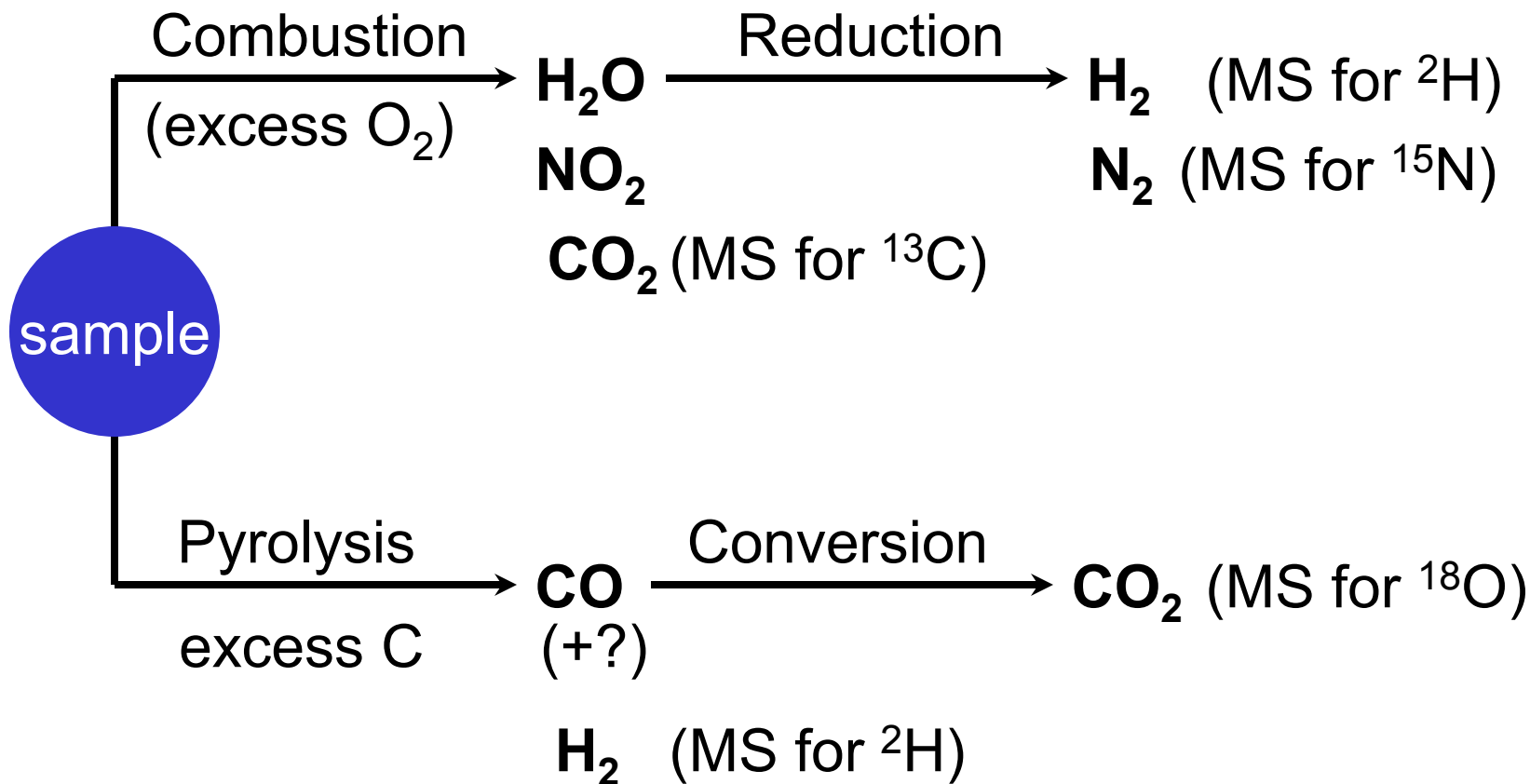
The flow of carbon in the Calvin cycle



Fractionation of C-Isotopes during Autotrophy

Pathway, enzyme	React & substr	Product	ϵ ‰	Organisms
C3			10-22	
Rubisco1	$\text{CO}_2 + \text{RUBP}$	3-PGA x 2	30	plants & algae
Rubisco2	$\text{CO}_2 + \text{RUBP}$	3-PGA x 2	22	cyanobacteria
PEP carboxylase	$\text{HCO}_3^- + \text{PEP}$	oxaloacetate	2	plants & algae
PEP carboxykinase	$\text{CO}_2 + \text{PEP}$	oxaloacetate		plants & algae
C4 and CAM	This could be the basis for a good exam question!		2-15	
PEP carboxylase	$\text{HCO}_3^- + \text{PEP}$	oxaloacetate	2	plants &
Rubisco1	$\text{CO}_2 + \text{RUBP}$	3-PGA x 2	30	algae (C4)
Acetyl-CoA			15-36	bacteria
CO dehydrog	$\text{CO}_2 + 2\text{H}^+ + \text{CoASH}$	AcSCoA	52	
Pyruvate synthase	$\text{CO}_2 + \text{Ac-CoA}$	pyruvate		
PEP carboxylase	$\text{HCO}_3^- + \text{PEP}$	oxaloacetate	2	
PEP carboxykinase	$\text{CO}_2 + \text{PEP}$	Oxaloacetate		
Reductive or reverse TCA	$\text{CO}_2 + \text{succinyl-CoA (+ others)}$	α -ketoglutarate	4-13	Bacteria esp green sulfur
3-hydroxypropionate	$\text{HCO}_3^- + \text{acetylCoA}$	Malonyl-CoA		Green non-S

Schematic representation of sample-preparation procedures



NB these processes must be complete to avoid fractionation

Standard requirements

Be used worldwide as the zero point

Be homogeneous in composition

Be available in relatively large amounts

Be easy to handle for chemical preparation
and isotope measurements

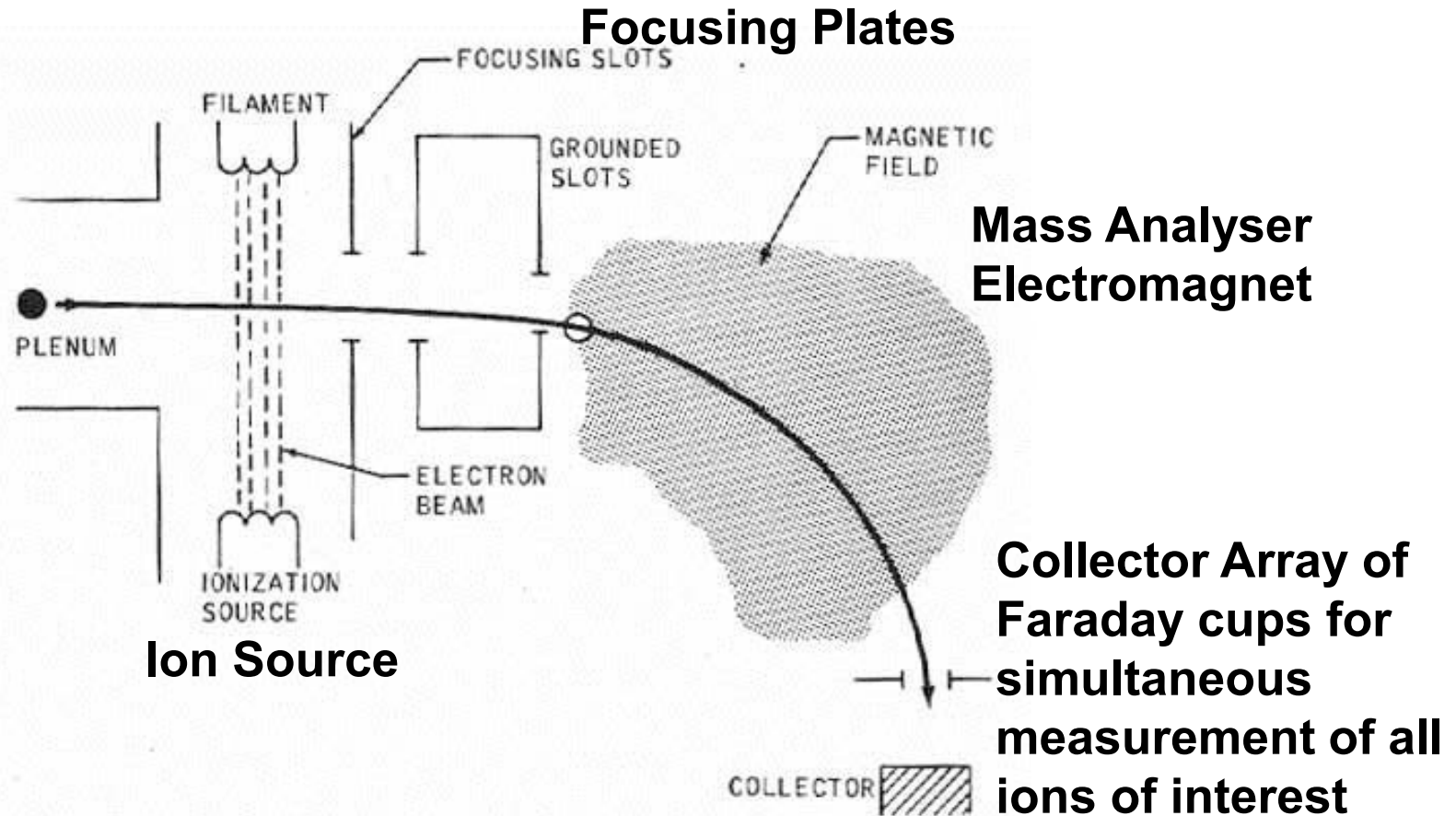
Have an isotope ratio near the middle of the
natural variation range

Isotopic compositions of primary standards

Primary Standards	Isotope Ratios	Ratios x 10⁶
Standard mean ocean water	²H/¹H	155.76
“	¹⁸O/¹⁶O	2005.20
“	¹⁷O/¹⁶O	373
PeeDee belemnite (PDB)	¹³C/¹²C	11237.2
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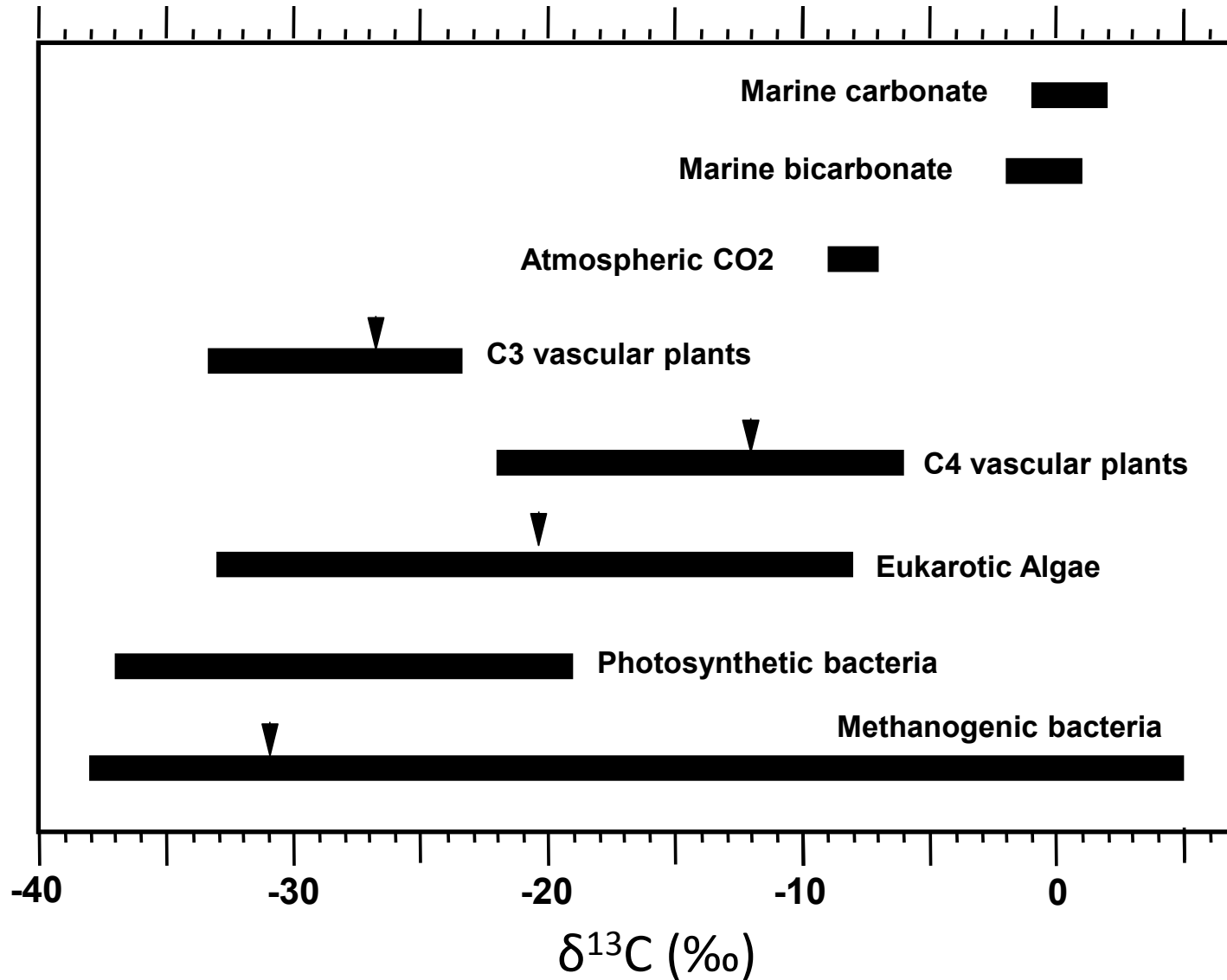
Principles of Isotopic Measurement



Inlet

Either a pure gas via a duel inlet system for sample and standard
Or a stream of gas containing sample 'slugs' interspersed with standard 'slugs'

Natural variability in bulk C-isotopes



Organismal variability in bulk C-isotopes

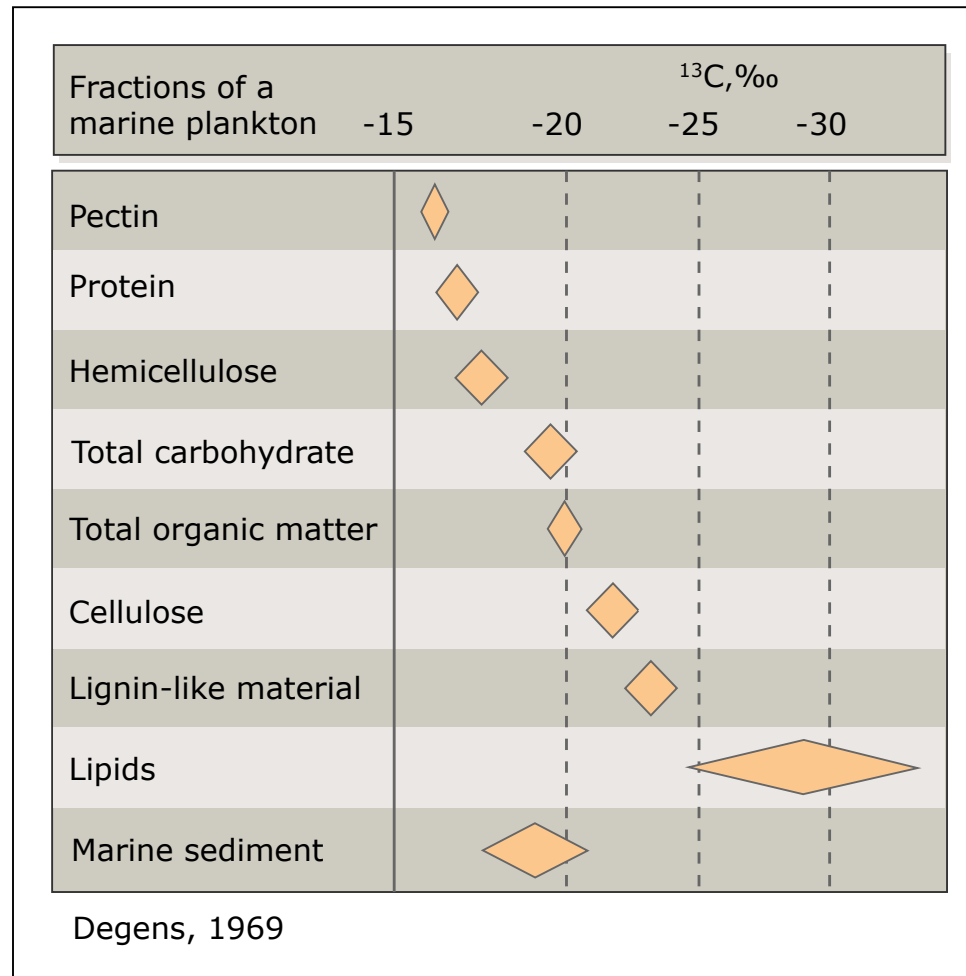
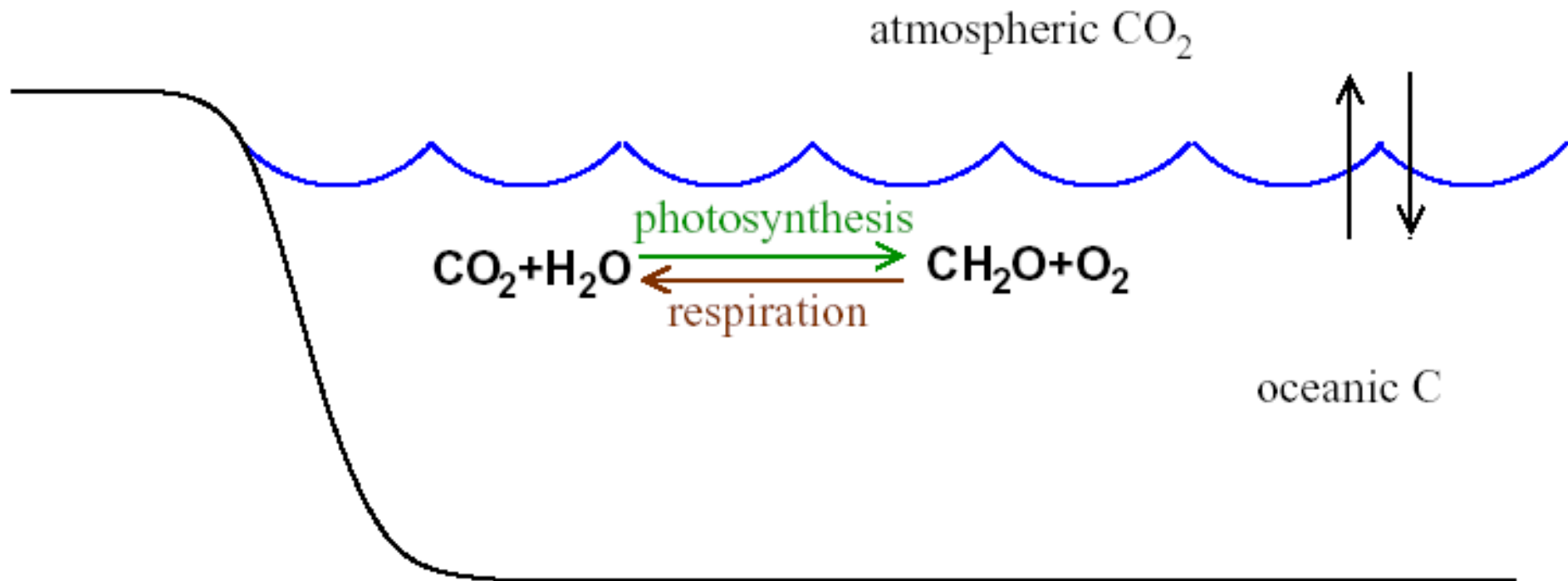
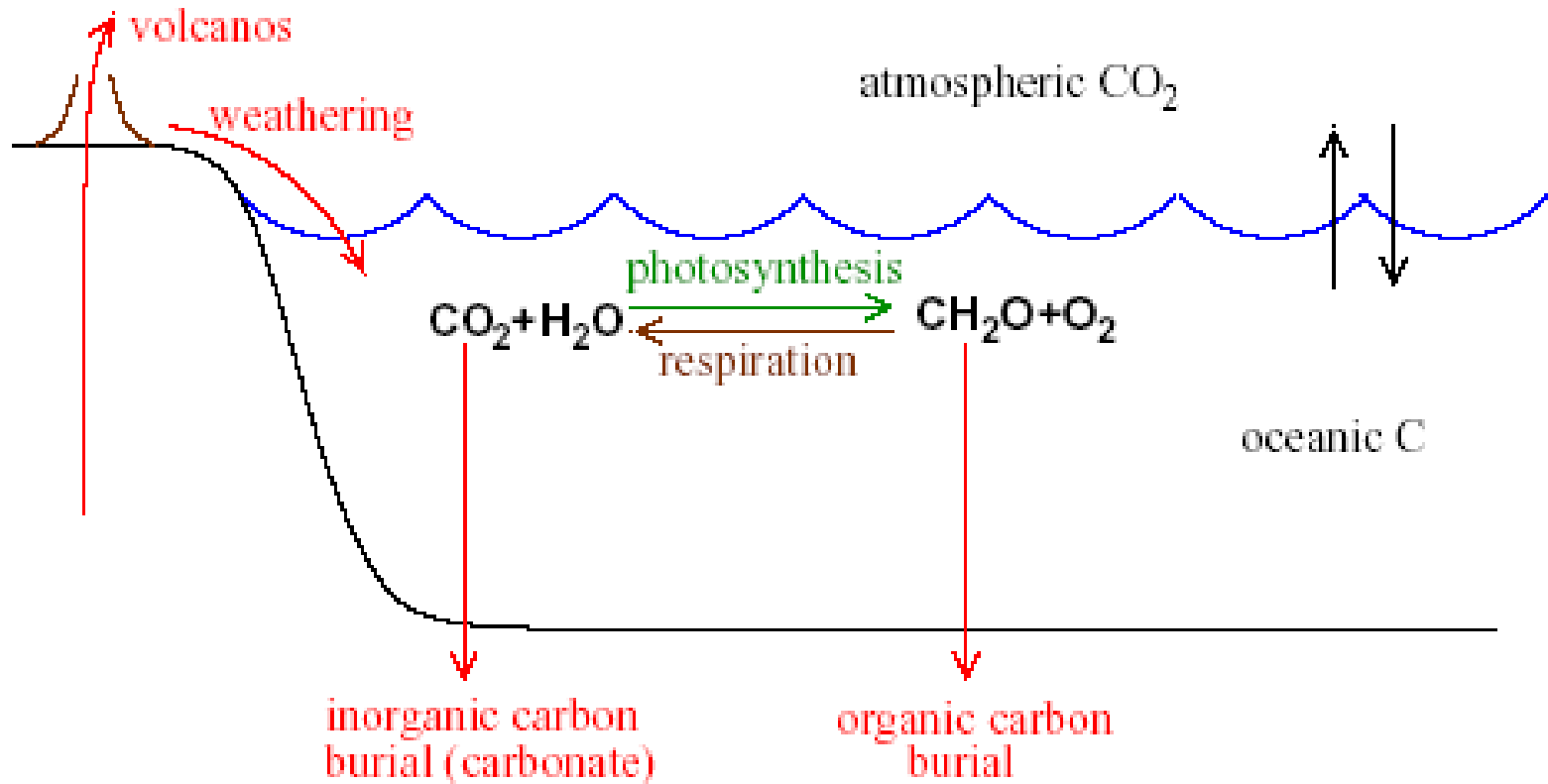


Image by MIT OpenCourseWare. After Degens, E. T. "Biogeochemistry of Stable Carbon Isotopes." *Organic Geochemistry* (1969): 304-29.

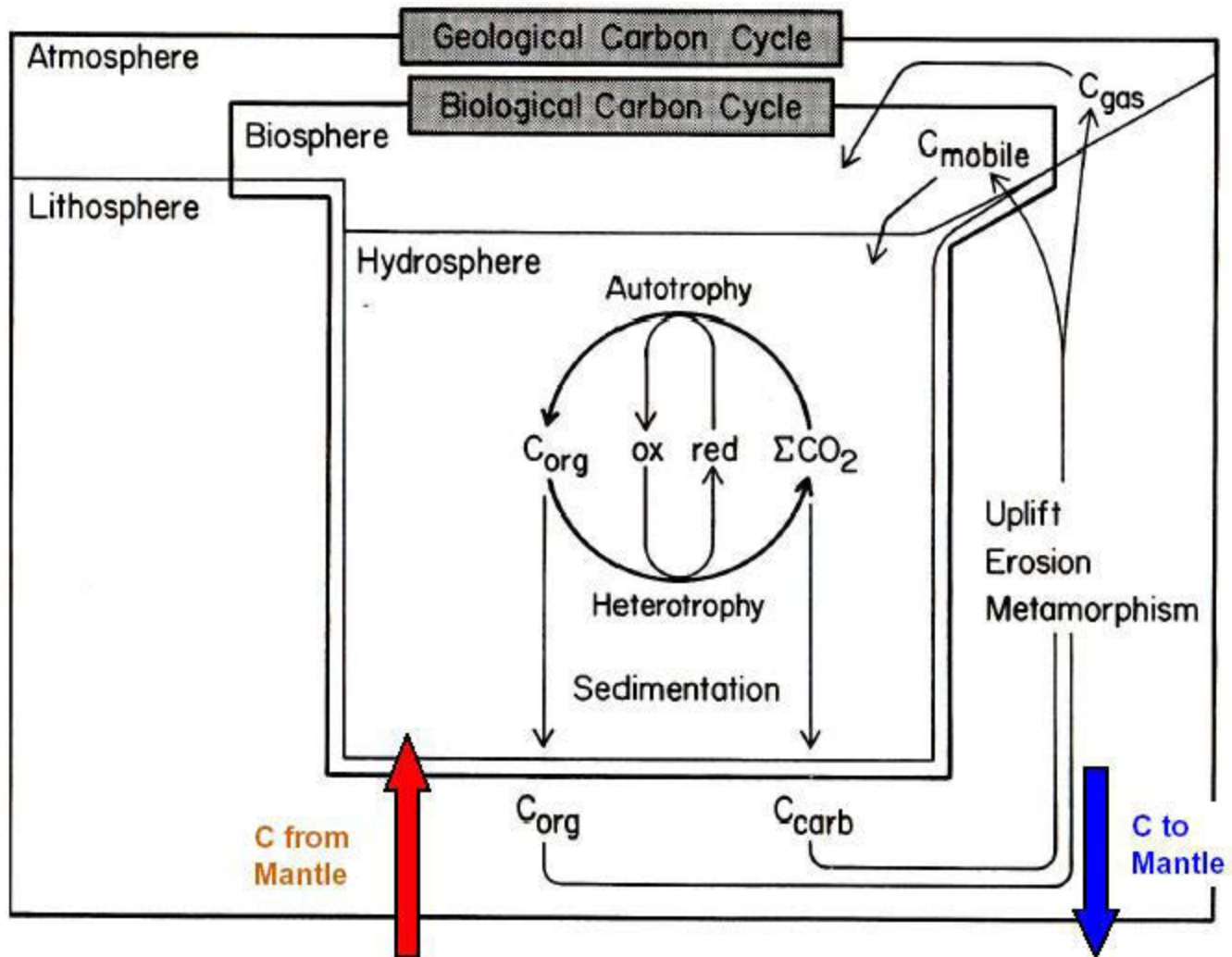
Carbon cycle



Carbon cycle

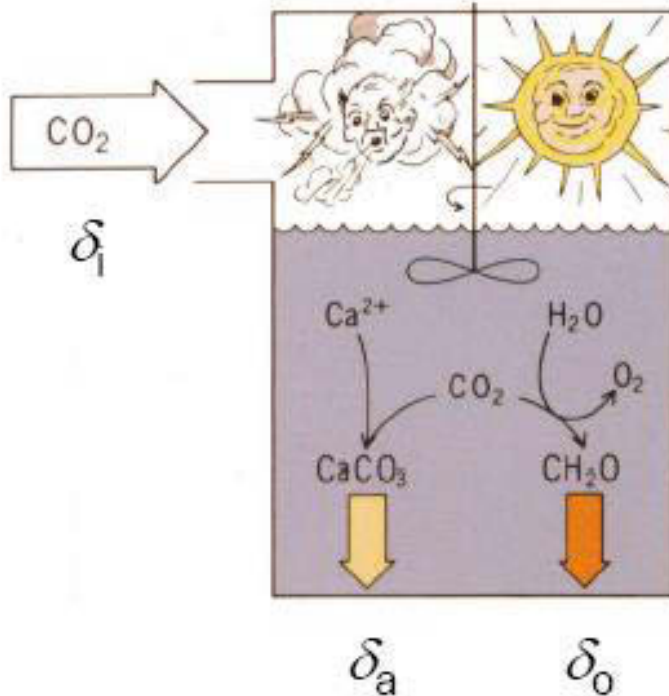


Geologic time scales: $\frac{d[\text{O}_2]}{dt} \approx$ photosynthesis – respiration
 \approx organic carbon burial.



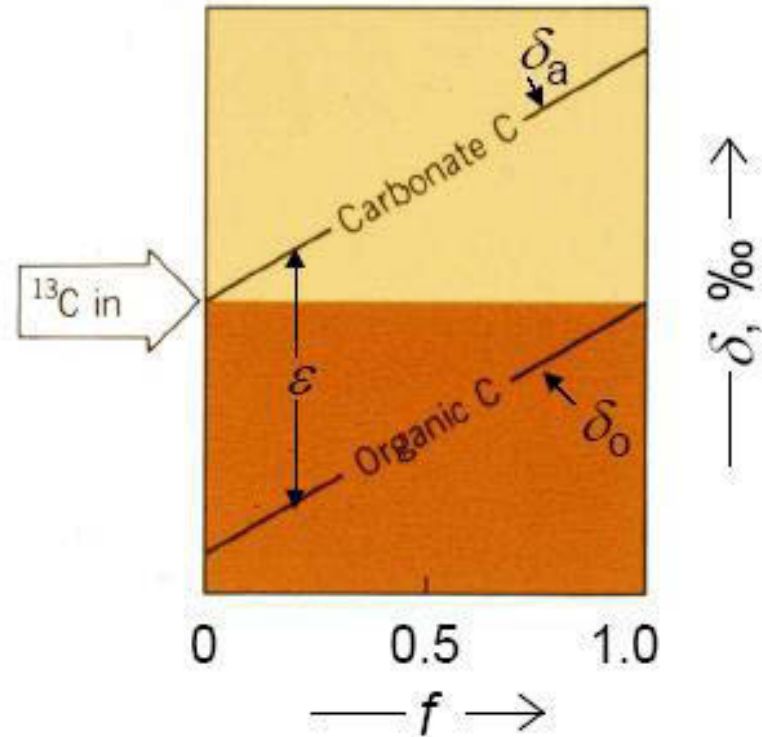
Courtesy of John Hayes. Used with permission.

Mass balance in the carbon cycle



f = fraction of carbon buried in organic form

$$\delta_1 = f\delta_o + (1 - f)\delta_a$$

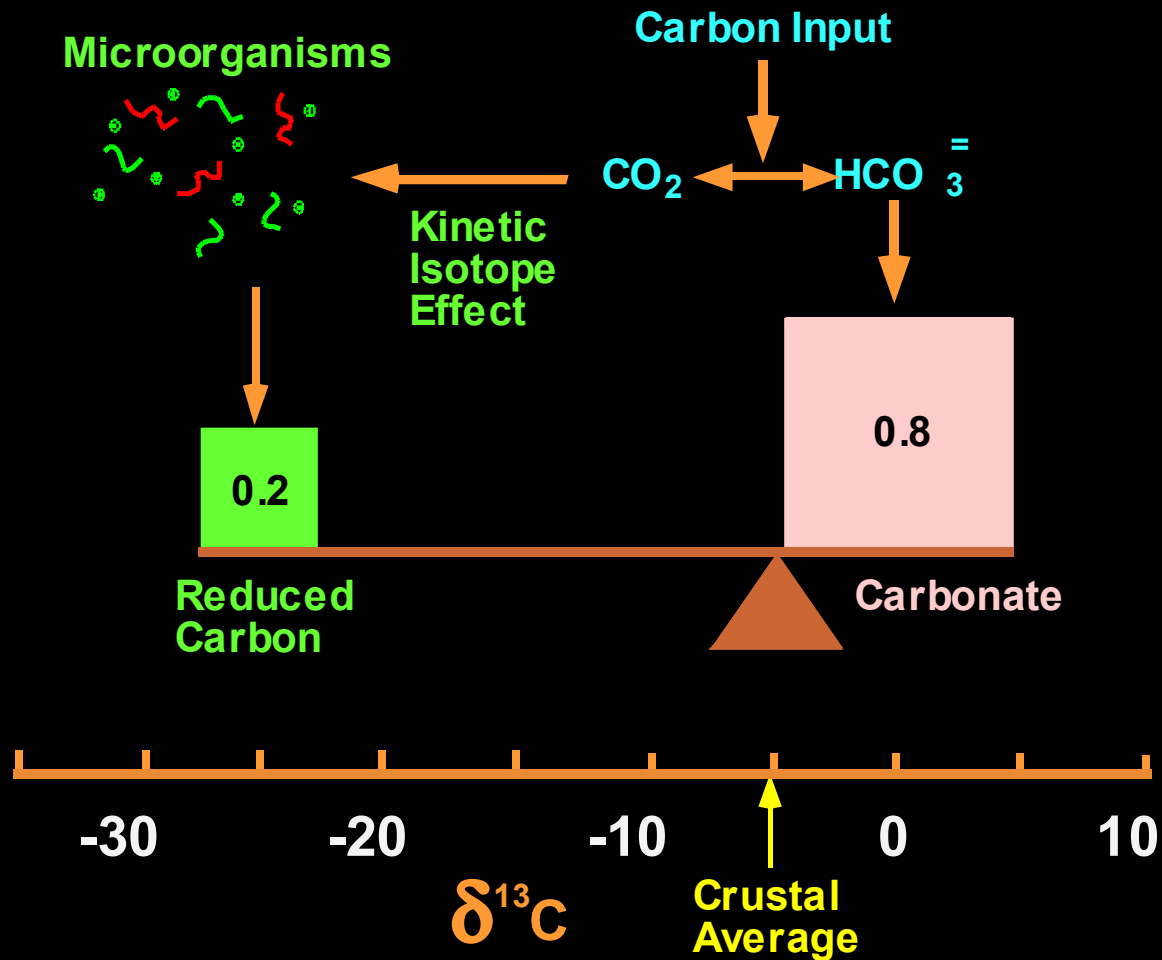


$$\delta_a = \delta_1 + f\epsilon$$

$$\delta_o = \delta_1 - (1 - f)\epsilon$$

Courtesy of John Hayes. Used with permission.

Isotopic Mass Balance of Crustal Carbon Reservoirs



Reprise to Evidence of Early Life

^{13}C Evidence for Antiquity of Earthly Life

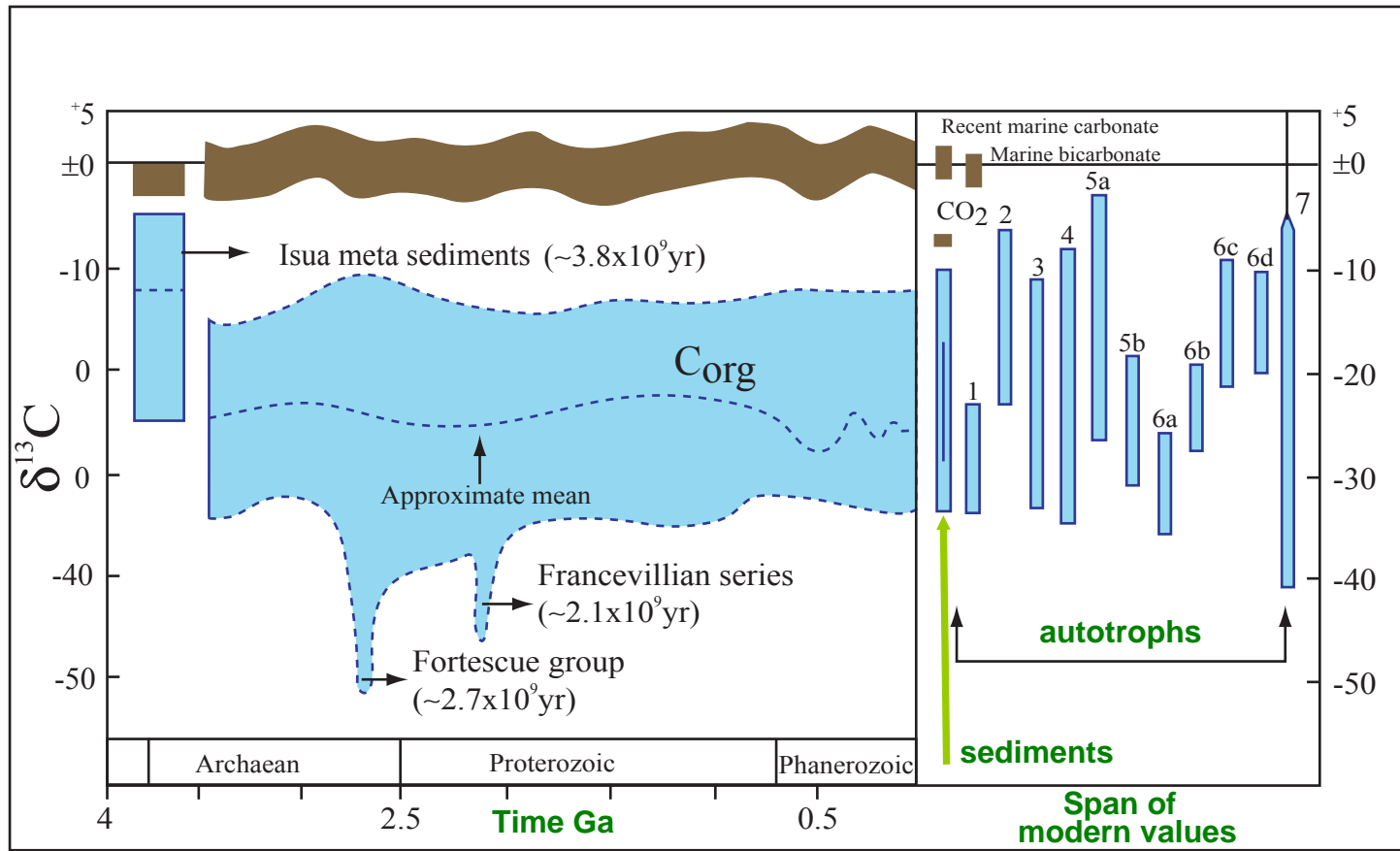


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nature

INTERNATIONAL WEEKLY JOURNAL OF SCIENCE

Volume 384 No. 6604 7 November 1996

Oldest traces of life on Earth?

How vertebrates tell left from right

Controlling inflammation

Science in South Africa

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 ..

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

The principal method for studying the earliest traces of life in the metamorphosed, oldest (> 3.5 Ga) terrestrial rocks involves determination of isotopic composition of carbon, mainly prevailing as graphite. It is generally believed that this measure can distinguish biogenic graphite from abiogenic varieties. However, the interpretation of life from carbon isotope ratios has to be assessed within the context of specific geologic circumstances requiring (i) reliable protolith interpretation (ii) control of secondary, metasomatic processes, and (iii) understanding of different graphite producing mechanisms and related carbon isotopic systematics. We have carried out a systematic study of abundance, isotopic composition and petrographic associations of graphite in rocks from the ca. 3.8 Ga Isua Supracrustal Belt (ISB) in southern West Greenland. Our study indicates that most of the graphite in ISB occurs in carbonate-rich metasomatic rocks (metacarbonates) while sedimentary units, including banded iron formations (BIFs) and metacherts, have exceedingly low graphite concentrations. Regardless of isotopic composition of graphite in metacarbonate rocks, their secondary origin disqualifies them from providing evidence for traces of life stemming from 3.8 Ga. Recognition of the secondary origin of Isua metacarbonates thus calls for reevaluation of biogenic interpretations by Schidlowski et al. (1979) and Mojzsis et al. (1996) that suggested the occurrence of 3.8 Ga biogenic graphite in these rocks. The origin of minute quantities of reduced carbon, released from sedimentary BIFs and metacherts at combustion steps > 700 C remains to be clarified. Its isotopic composition ($\delta^{13}C$ from -18 to -25%) may hint at a biogenic origin. However, such isotopically light carbon was also found in Proterozoic mafic dykes cross-cutting the metasedimentary units in the ISB. The occurrence of isotopically light, reduced carbon in biologically irrelevant dykes may indicate secondary graphite crystallization from CO₂ or CH₄-containing fluids that in turn may derive from bioorganic sources. If this were the case, trace amounts of isotopically light secondary graphite can also be expected in metasediments, complicating the usage of light graphite as primary biomarker. The possibility of recent organic contamination, particularly important in low graphite samples, needs also to be considered; it appears as a ubiquitous component released at combustion in the 400 to 500 deg range. - A potential use of the apatite-graphite association as a biomarker has been proposed in the study by Mojzsis et al. (1996). Close inspection of several hundred apatite crystals from Isua BIFs and metacherts did, however, not show an association between these two minerals, moreover graphite is practically absent in these metasediments. In contrast, apatite crystals in the non-sedimentary metacarbonate rocks were found commonly to have invaginations, coatings and inclusions of abundant graphite. Considering that such graphite inclusions in apatite are restricted to the secondary metasomatic carbonate rocks in the ISB this association can not be considered as a primary biomarker in the Isua Supracrustal Belt

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.

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Source: From Lepland, A., M. van Zuilen, and G. Arrhenius. "Tracing Life in the Earliest Terrestrial Rock Record." In *AGU Fall Meeting Abstracts 1* (2001): 0545.

^{13}C Evidence for Antiquity of Earthly Life

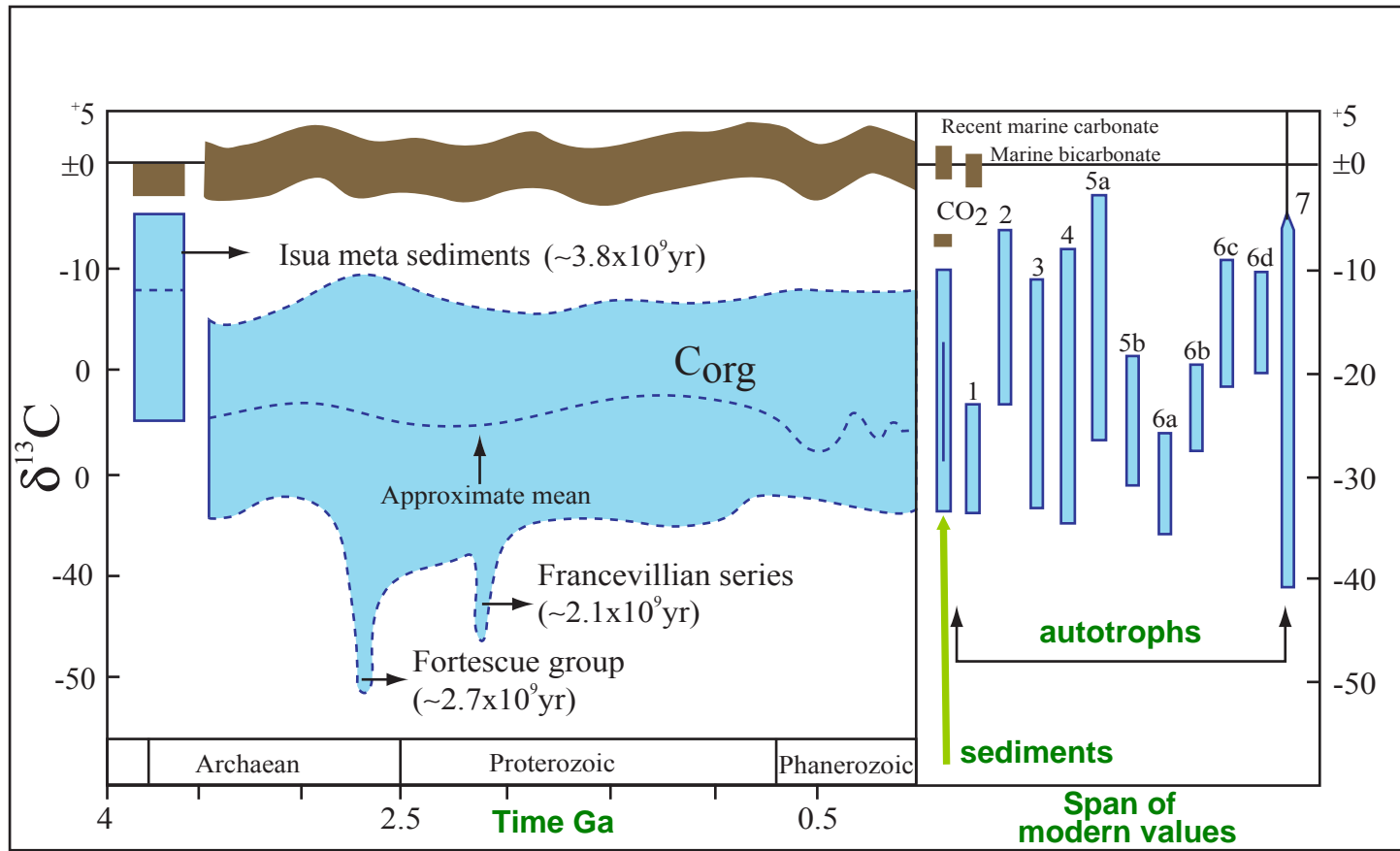


Image by MIT OpenCourseWare.

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.

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

δ notation

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

Standard:

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

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

Dissimilatory sulfate reduction



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

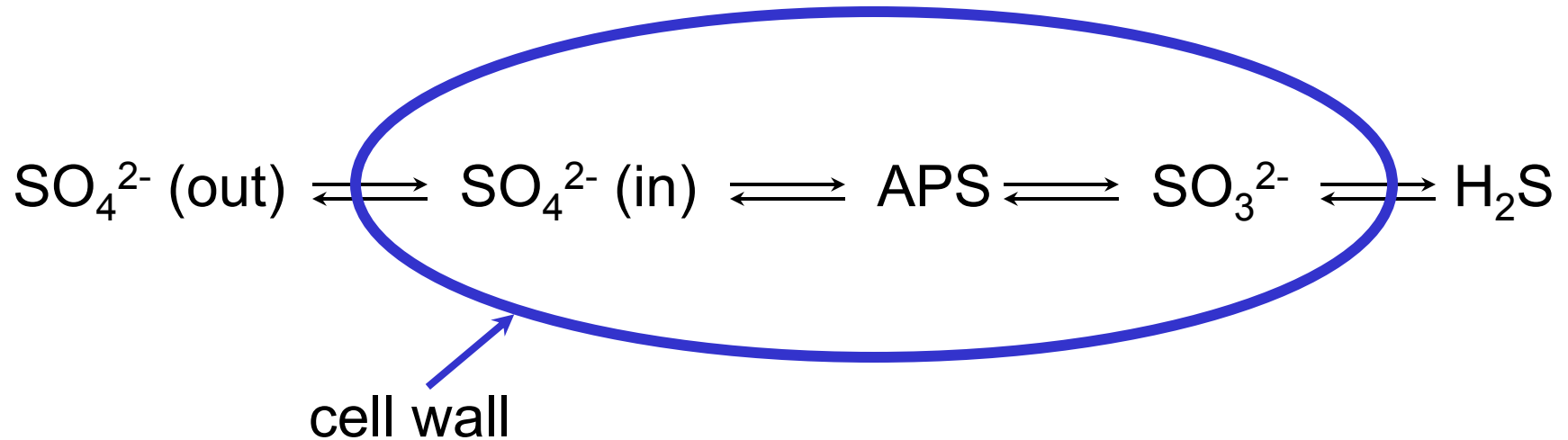
Sulfides become enriched in ^{32}S and depleted in ^{34}S

Sulfur isotope fractionation

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

$$\text{Fractionation } (\varepsilon_{\text{SR}}) = \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$$

Biochemical pathway of dissimilatory SR



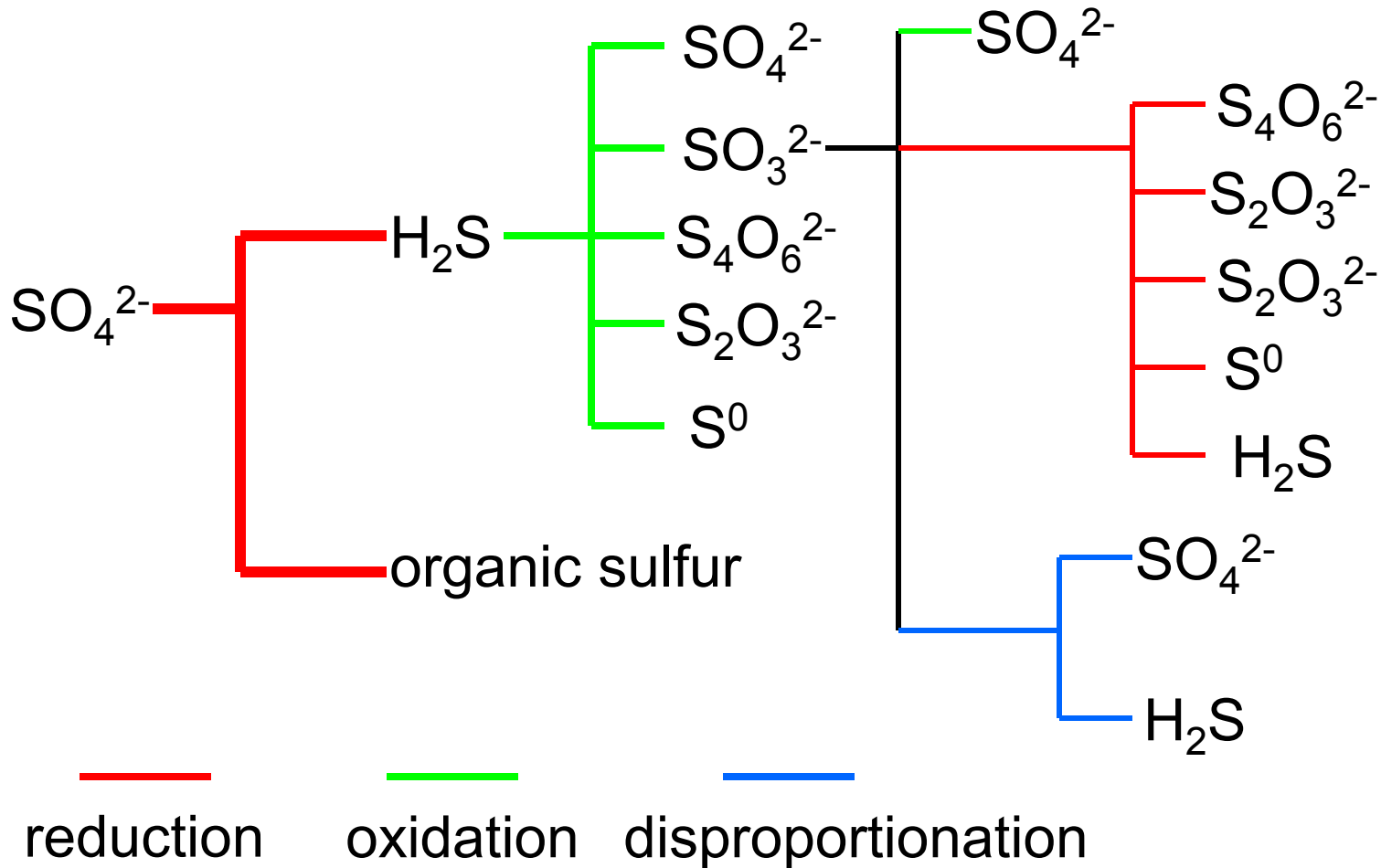
Fractionation -3‰

0‰

15‰

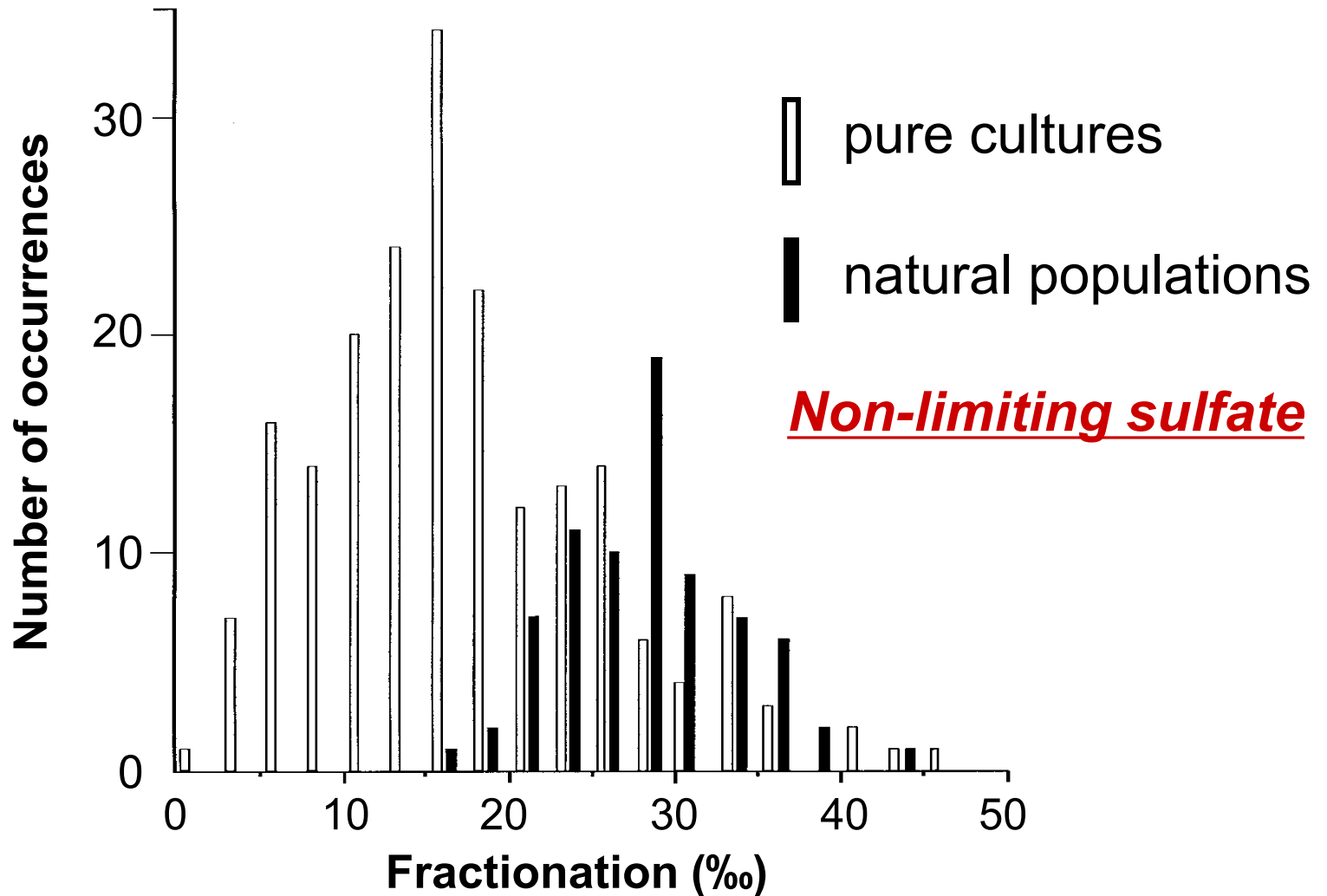
25‰

Tree of Biological Sulfur Cycle

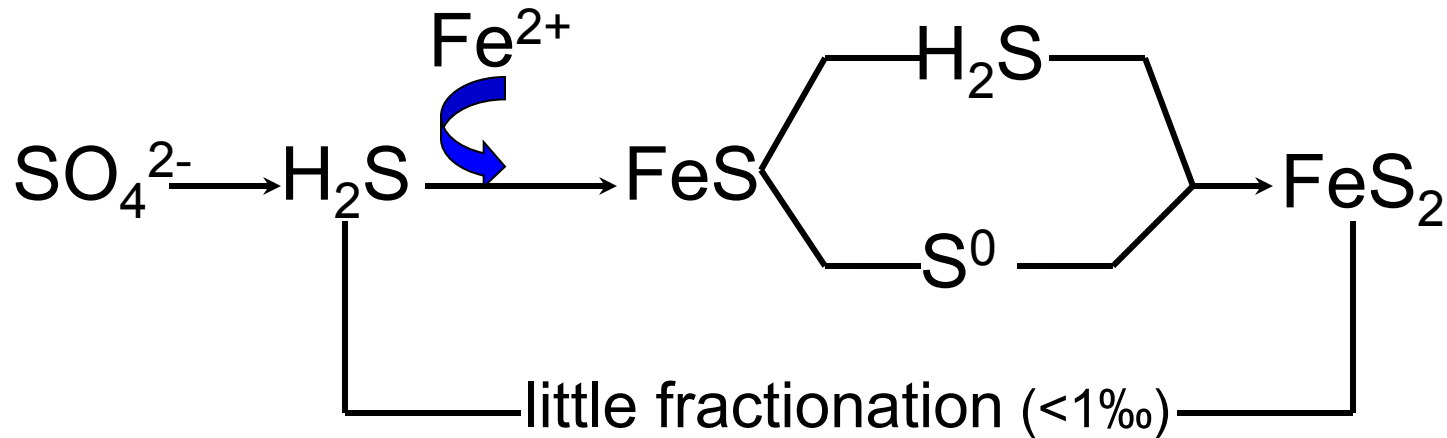


Empirical Measurements of S-isotopic fractionation during sulfate reduction

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



Pyrite formation and S-isotope preservation



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

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

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

Typical $\delta^{34}\text{S}$ values of some geological material (relative to CDT)

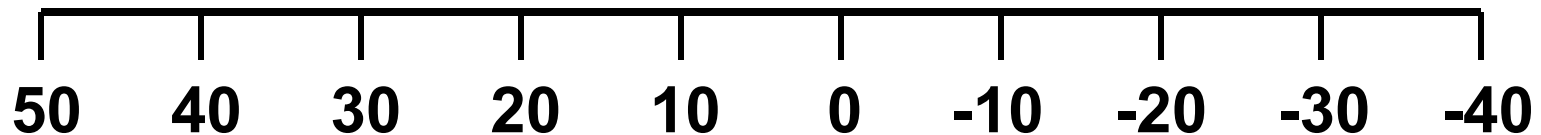
 ocean water

 sedimentary rocks

 metamorphic rocks

 granitic rocks

 basaltic rocks



$\delta^{34}\text{S}$ (‰)

Isotopic evidence for microbial sulfate reduction

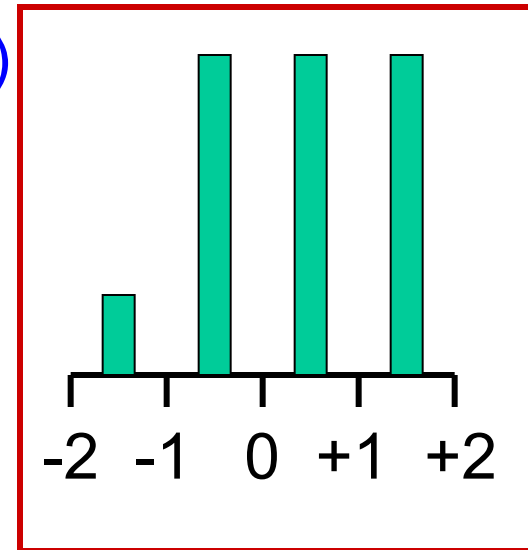
1. Isotope signature is primary from sedimentary rocks
2. $\delta^{34}\text{S}$ values are distinctly shifted to the negative values.
3. Fairly large spread of $\delta^{34}\text{S}$ values for sulfides, and thus large fractionations.

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

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

Narrow range $\delta^{34}\text{S}$ = ave. $0.5 \pm 0.9\text{‰}$

Similar to those of magmatic sulfides
and close to meteoritic ie solar system
values



Models for low fractionation of $0 \pm 5\text{‰}$

(~3.8 Ga – 2.7 Ga)
(Paytan, 2000. *Science*)

Non-biological
fractionation

Low pO_2
Low SO_4^{2-}
SRB not active

Low sulphate
concentration

$pO_2 = 10^{-12}$ atm
 $SO_4^{2-} < 1$ mM
SRB active

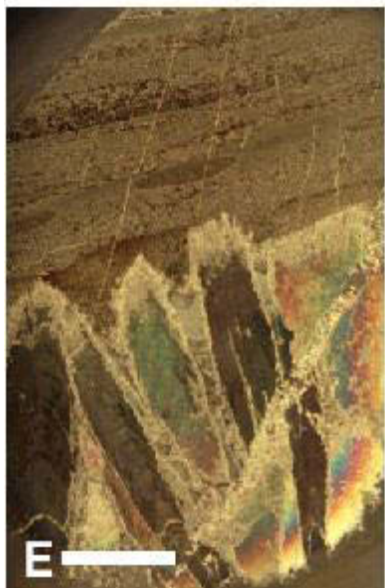
High SRR

$pO_2 = 10^{-2.5}$ atm
 $SO_4^{2-} > 10$ mM
SRB active
T ~ 40°C

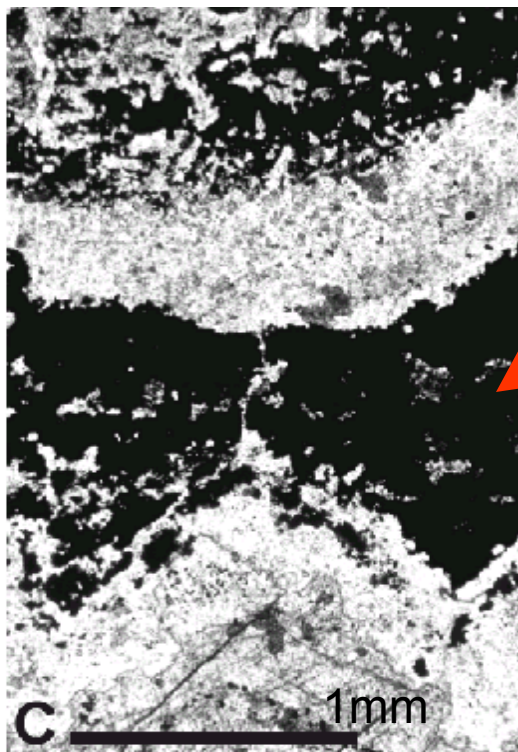
Closed system
effect

$pO_2 = 10^{-2.5}$ atm
 $SO_4^{2-} > 10$ mM
SRB active
SR Rates >
diffusion rates

3.48 Ga Barium Sulfate crystals from Western Australia

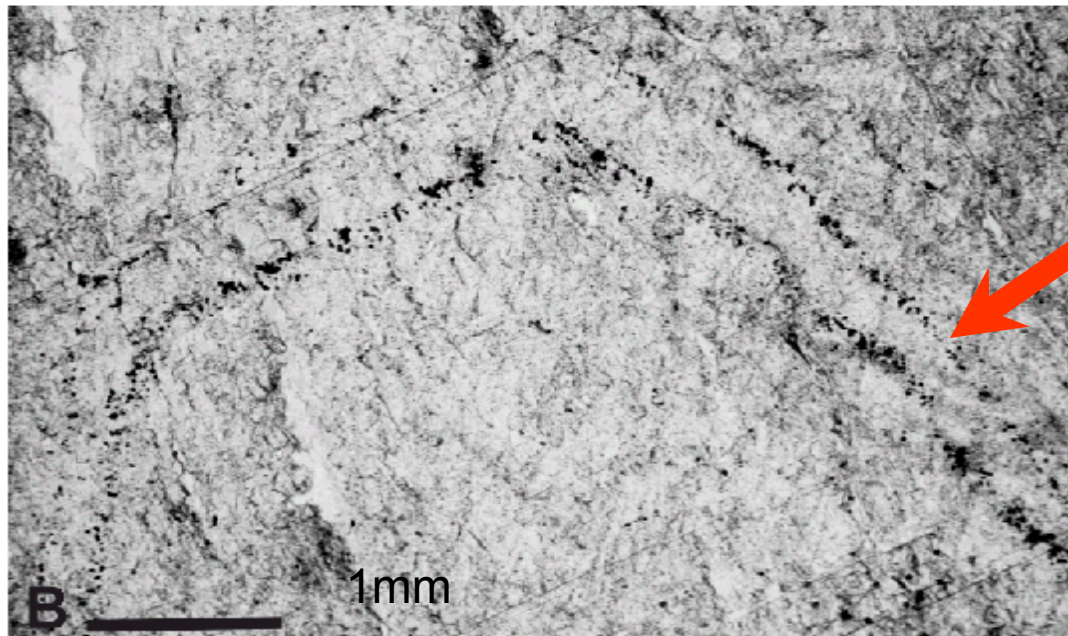


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macroscopic py

sulfate

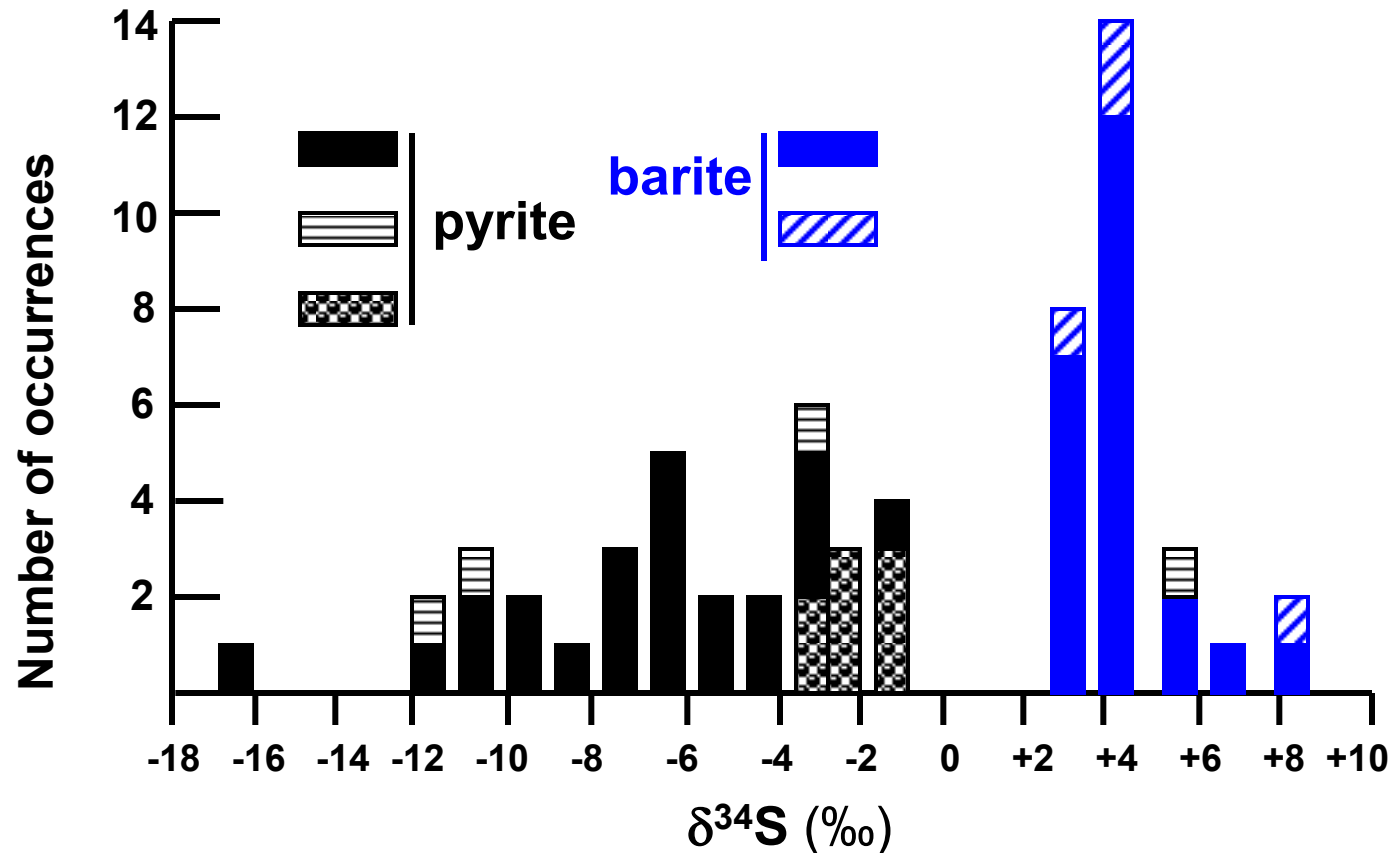


microscopic py

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The $\delta^{34}\text{S}$ of sulfur species from the 3.48Ga rocks in the North Pole of northwestern Australia

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



Courtesy of Nature Publishing Group. Used with permission. Source: Shen, Yanan, Roger Buick, et al. "Isotopic Evidence for Microbial Sulphate Reduction in the Early Archaean Era." *Nature* 410, no. 6824 (2001): 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 2001 p77-79

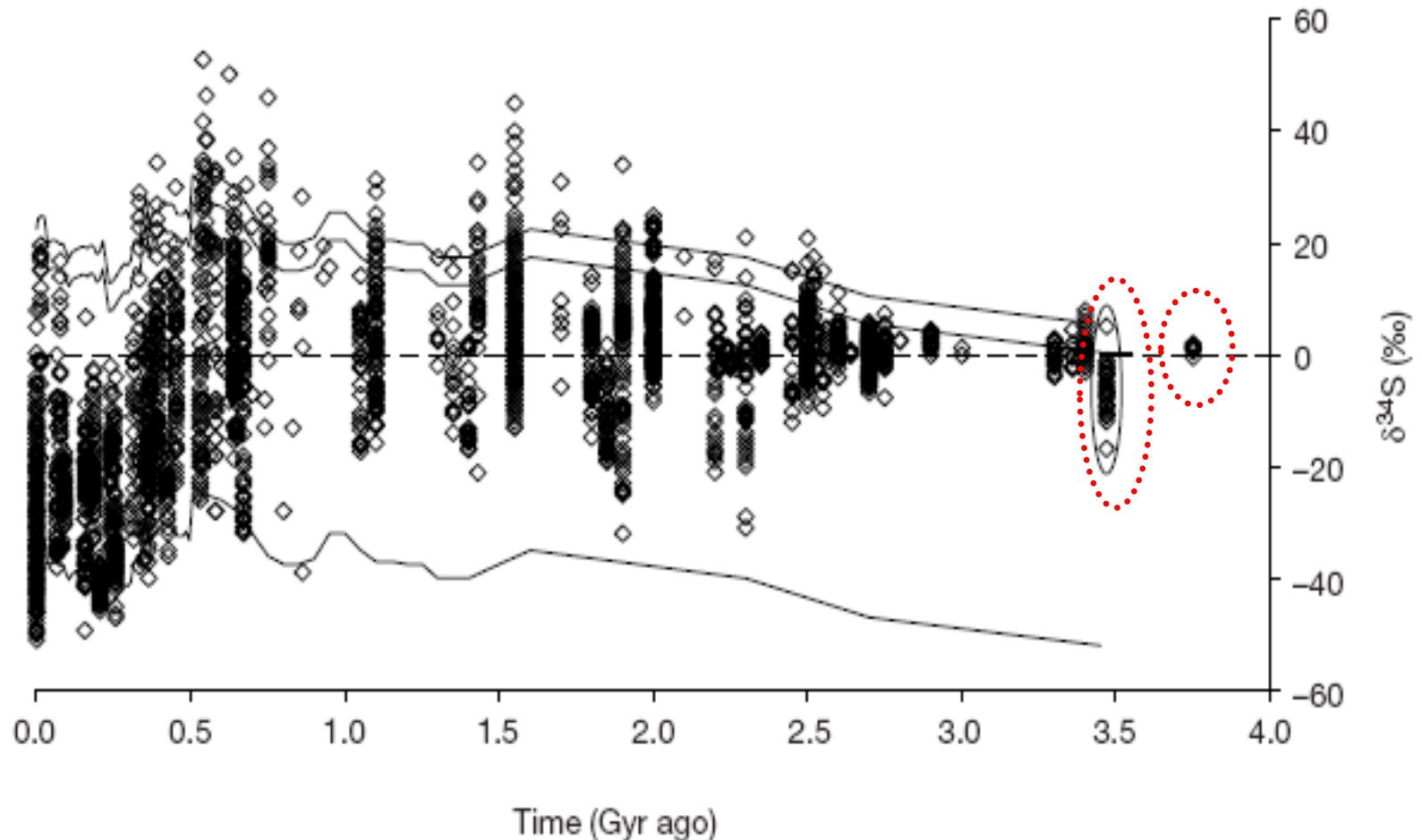
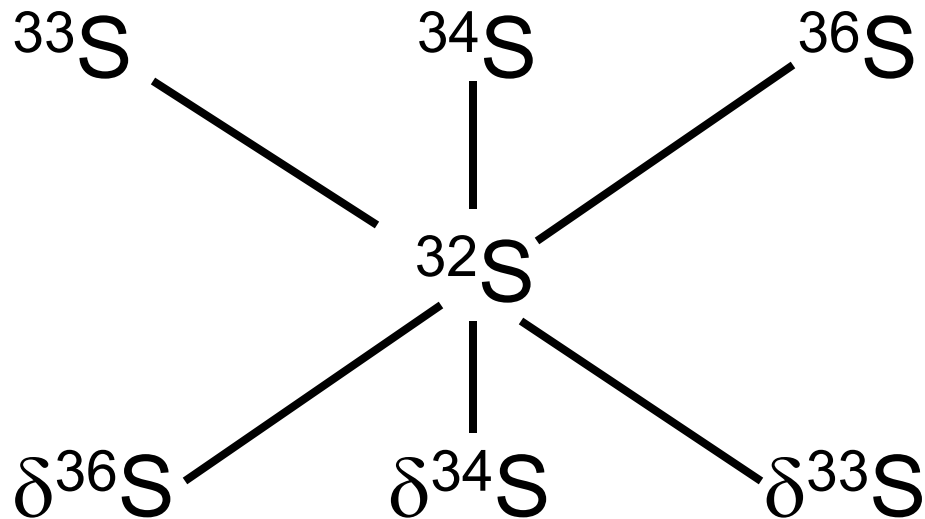


Figure 3 The secular trends in the isotopic composition of seawater sulphate and sulphide over geological time. Data within the oval are from this work, the other data are from refs 2, 29. The band (double line) in the upper part of the figure represents the isotopic composition of seawater sulphate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

Multiple sulfur isotopes



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

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 O₃, O₂, CO₂, CO, N₂O, H₂O₂ and sulfate aerosols. The isotopic anomalies are apparently linked to photochemical reactions
- A well-known example is the transfer, in the stratosphere, of ¹⁷O and ¹⁸O from molecular oxygen to CO₂ via ozone.
- Oxygenated sulfur species undergo gas phase reactions leading to MIF in the absence of O₂
- 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



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Earth and Planetary Science Letters 213 (2003) 15–30

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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

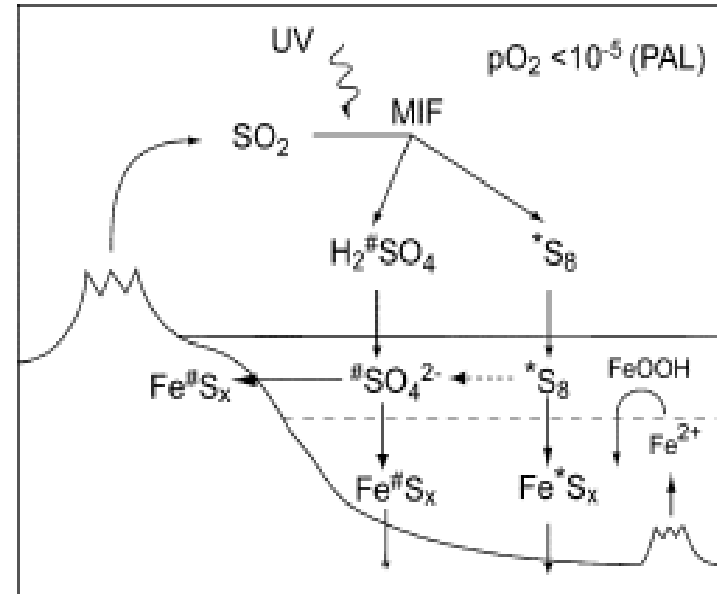
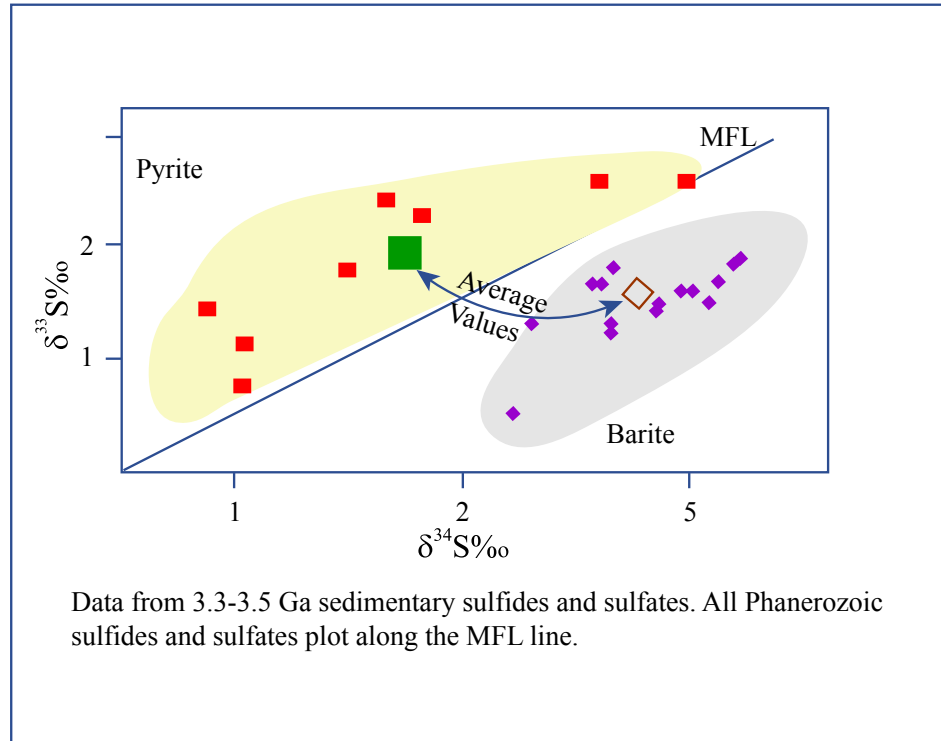


Fig. 3. A conceptual model of Archean sulfur cycle. Photochemistry in the atmosphere causes MIF in sulfur isotopes, and aerosols of S_8 and H_2SO_4 carry sulfur with positive (*S) and negative ($^{\#}S$) $\delta^{33}S$ signatures, respectively. The preservation of MIF signatures in the sediments implies incomplete oxidation of S_8 in the ocean (dashed arrow).

Mass Independent Fractionation



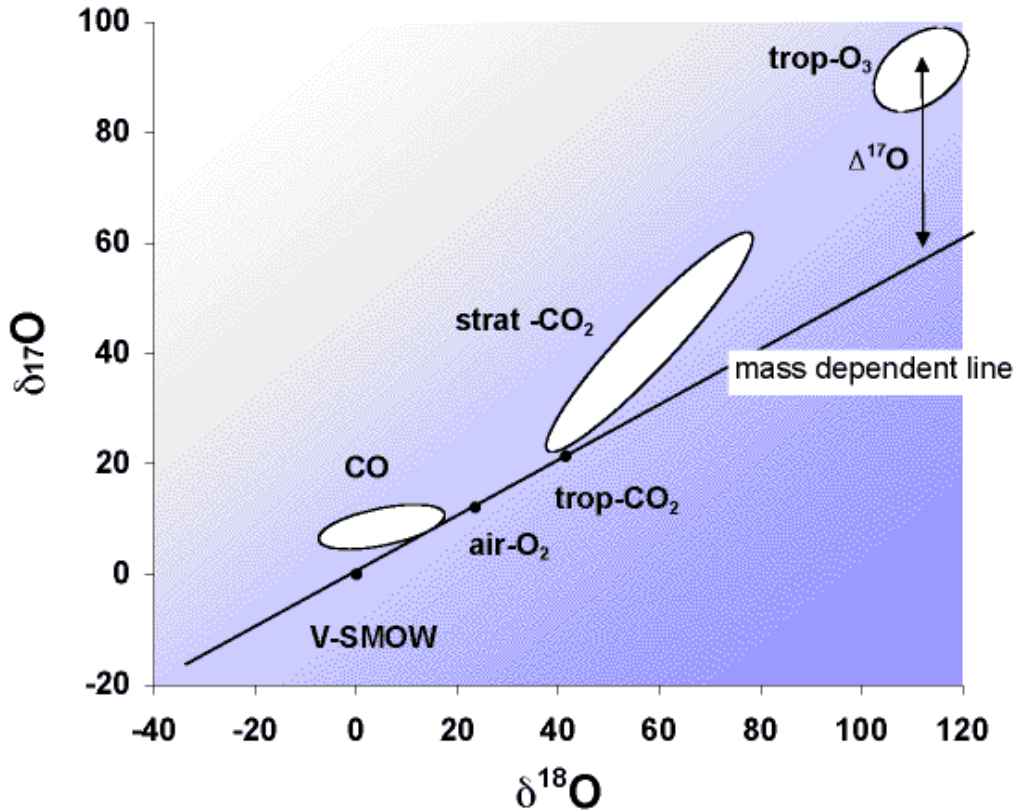
Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere

A.A. PAVLOV and J.F. KASTING **ASTROBIOLOGY** Volume 2, Number 1, 2002

Image by MIT OpenCourseWare. After Figure 3D in Farquhar, James et al. "Observation of Wavelength-Sensitive Mass-Independent Sulfur Isotope eEffects During SO₂ Photolysis: Implications for the Early Atmosphere.

" *Journal of Geophysical Research* 106, no. E12 (2001): 32829-32.

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



http://www.igacproject.org/sites/all/themes/bluemasters/images/NewsletterArchives/Issue_16_Mar_1999.pdf

Figure 3. A three-isotope plot showing the mass dependent line and the most important deviations for CO₂, CO, and tropospheric O₃. Stratospheric ozone (not shown here) is further enriched.

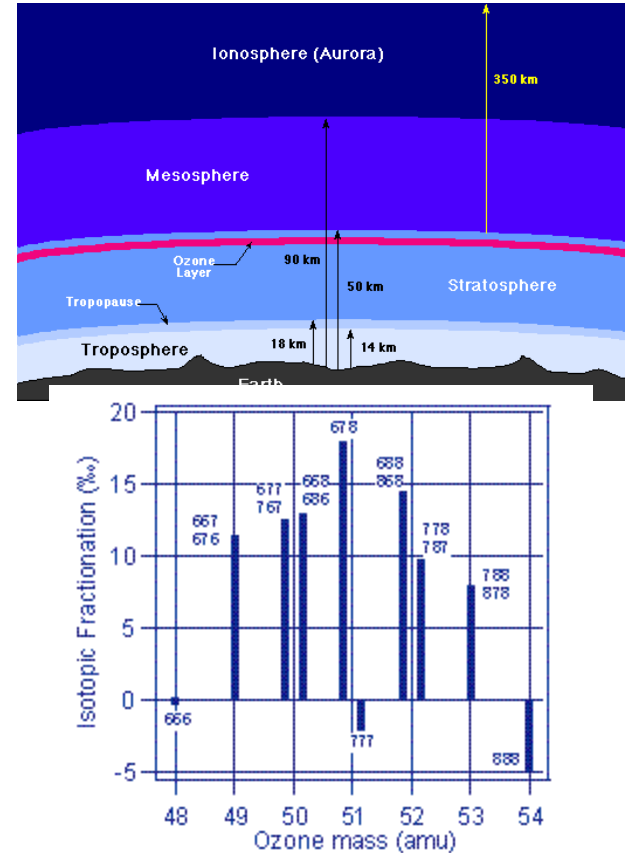


Figure 1. The distribution of ozone isotopomers measured by using enriched mixtures. The asymmetric molecules are formed preferentially. Numbers next to bars indicate molecular composition, e.g., "667" = ¹⁶O¹⁶O¹⁷O.

Sulfur Summary

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

The large S-isotopic fractionations in this localized and sulfate-rich environment, but not in other rocks imply that Archean ocean was **low in sulfate**, and, by implication, **low oxygen in the atmosphere**.

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