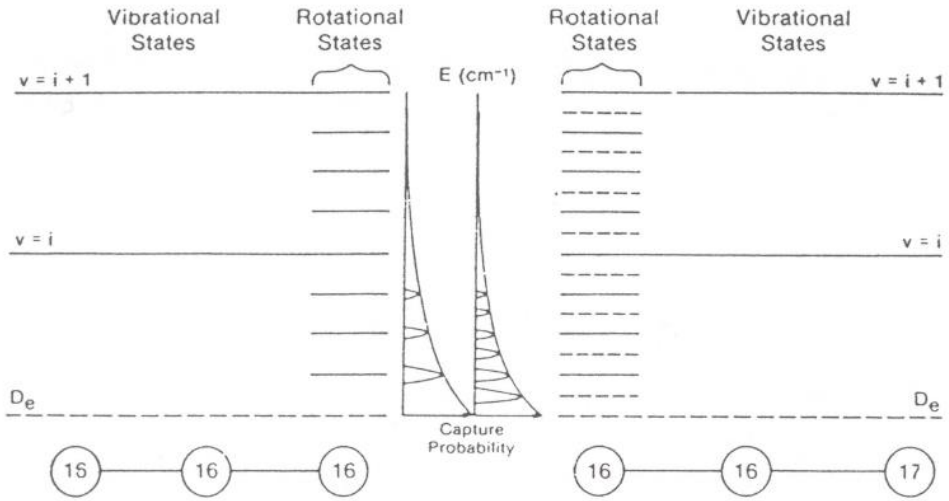
Mass Independent Fractionation!

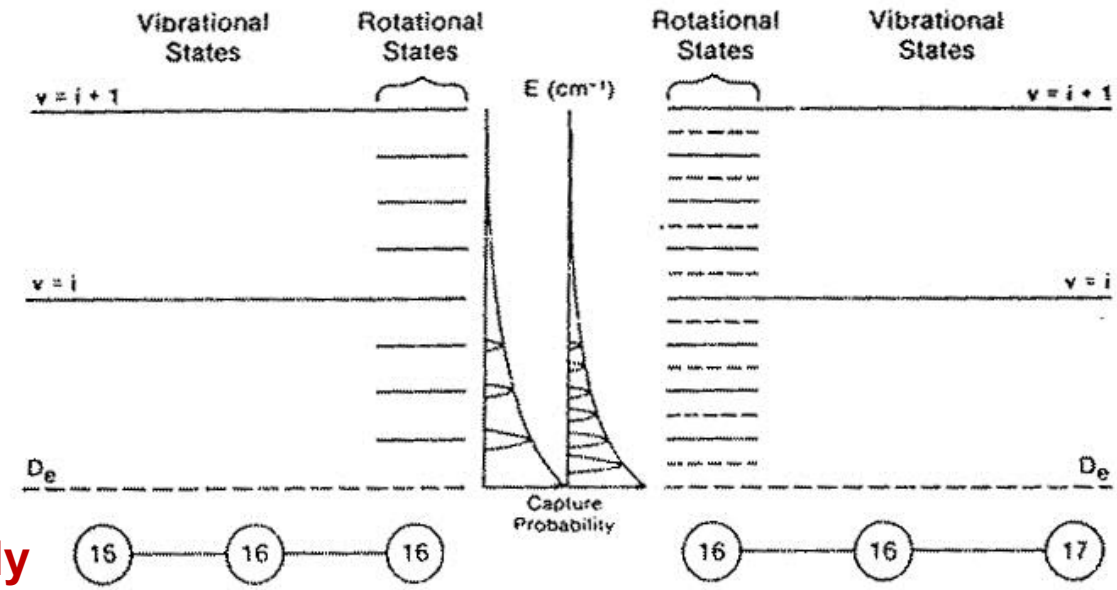
- Quantum mechanical ozone predissociation rotational state symmetry breaking:
  - Non-symmetric molecules have more rotational states



Schematic diagram of the process of inverse predissociation for $O + O_2$ reaction. Note that the asymmetric isotopic species has double the number of rotational states and an increased probability of stabilization.

Mass-Independent Fractionation

Mechanism: Available rotational states affect transition probability (Gao & Markus, 2002)



Rotationally Symmetric

Rotationally Asymmetric

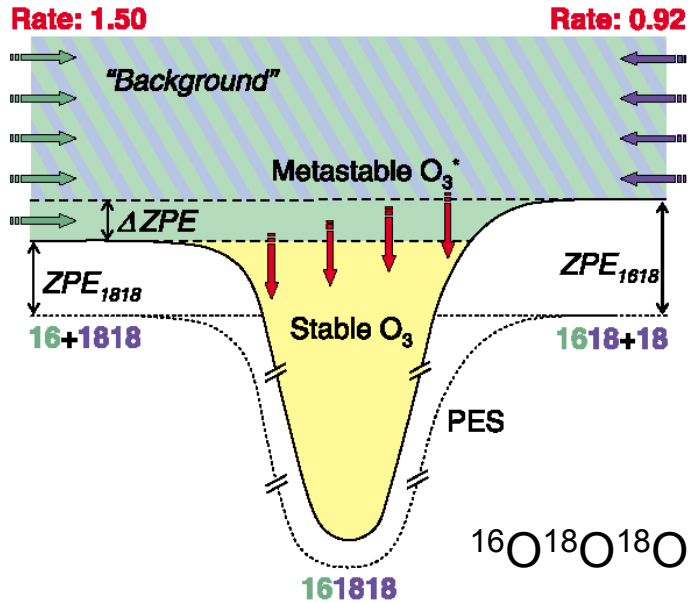
Figure 8. Schematic diagram of the process of inverse predissociation for $O + O_2$ reaction. Note that the asymmetric isotopic species has double the number of rotational states and an increased probability of stabilization.

Molecular rotational symmetry is broken when ^{18}O or ^{17}O is substituted for ^{16}O in O_2 and O_3 *doubling* the available quantum states available for transition.

Babikov et al. (2003) cartoon summarizing their calculations

$^{16}O + {}^{18}O^{18}O$

s lower ZPE
ha



$^{16}O^{18}O + {}^{18}O$

$^{16}O^{18}O^{18}O$ Ozone

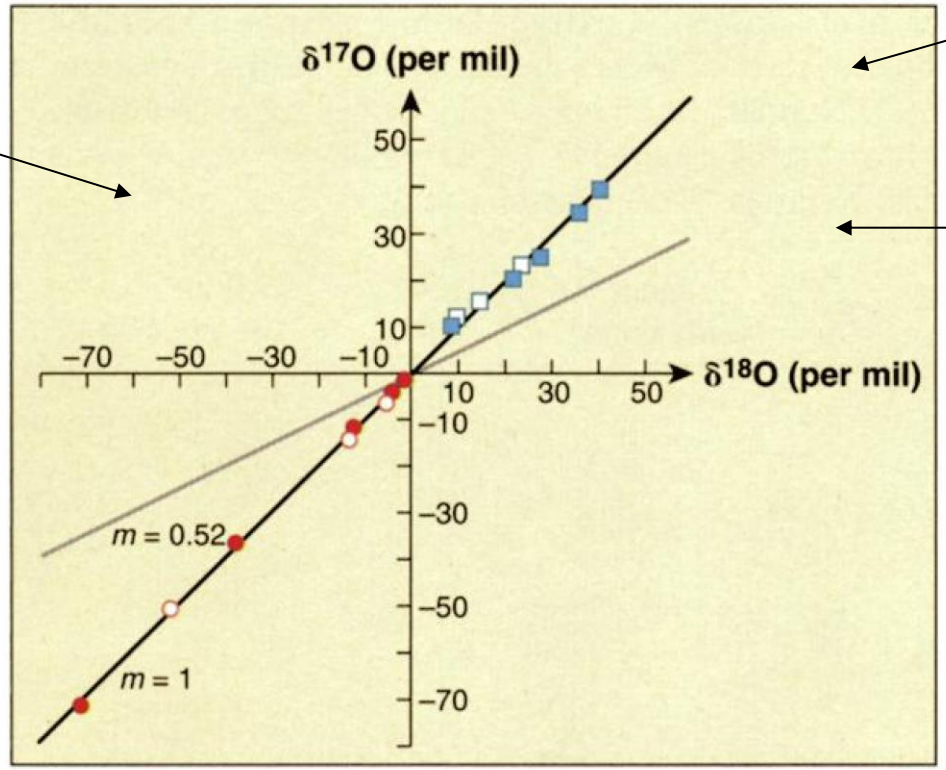
Fig. 2. Schematic for recombination processes forming ozone $^{16}O^{18}O^{18}O$. Stable ozone molecules are formed in the potential well (yellow part) as a result of collisional stabilization of metastable states formed above the well (in the green and striped blue/green part). The stabilization process is shown schematically as red descending arrows. Metastable states in the striped part of the spectrum can be formed from both entrance channels: $^{16}O + {}^{18}O^{18}O$ on the left (green arrows) and $^{16}O^{18}O + {}^{18}O$ on the right (blue arrows). Metastable states in the ΔZPE part of spectrum (green) are formed exclusively from the $^{16}O + {}^{18}O^{18}O$ entrance channel. The PES (dotted line) and the ZPE for both channels are shown (not to scale). Experimental relative rates of ozone formation for the two channels are given at the top.

Source: Babikov, Dmitri, B. K. Kendrick, et al. "Quantum Origin of an Anomalous Isotope Effect in Ozone Formation." *Chemical Physics Letters* 372, no. 5 (2003): 686-91.

Demonstration of "Mass-independent Fractionation" in the Laboratory

O_3 created in the lab from O_2, via electric discharge (Thiemens & Heidenreich, 1983)

Later demonstrated in nature by high altitude air samples (Thiemens et al., 1995)



m = 1.0

m ~ 0.52

Blue = O_3
Red = O_2
Two labs

Plot of the first demonstration of a chemically produced mass independent isotope effect. Square symbols, ozone samples; circles, molecular oxygen reservoirs; $m = \delta^{17}O/\delta^{18}O$. The report Gao and Marcus successfully explains these observations.

Source: Thiemens, Mark H. "The Mass-Independent Ozone Isotope Effect." *Science* 293, no. 5528 (2001): 226.

Mass-independent Fractionation of Oxygen in the Stratosphere

Can define anomalous ^{17}O signal as:

$$\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$$

average air used as standard, reported as parts per meg (1 in 10^6)

empirically determined

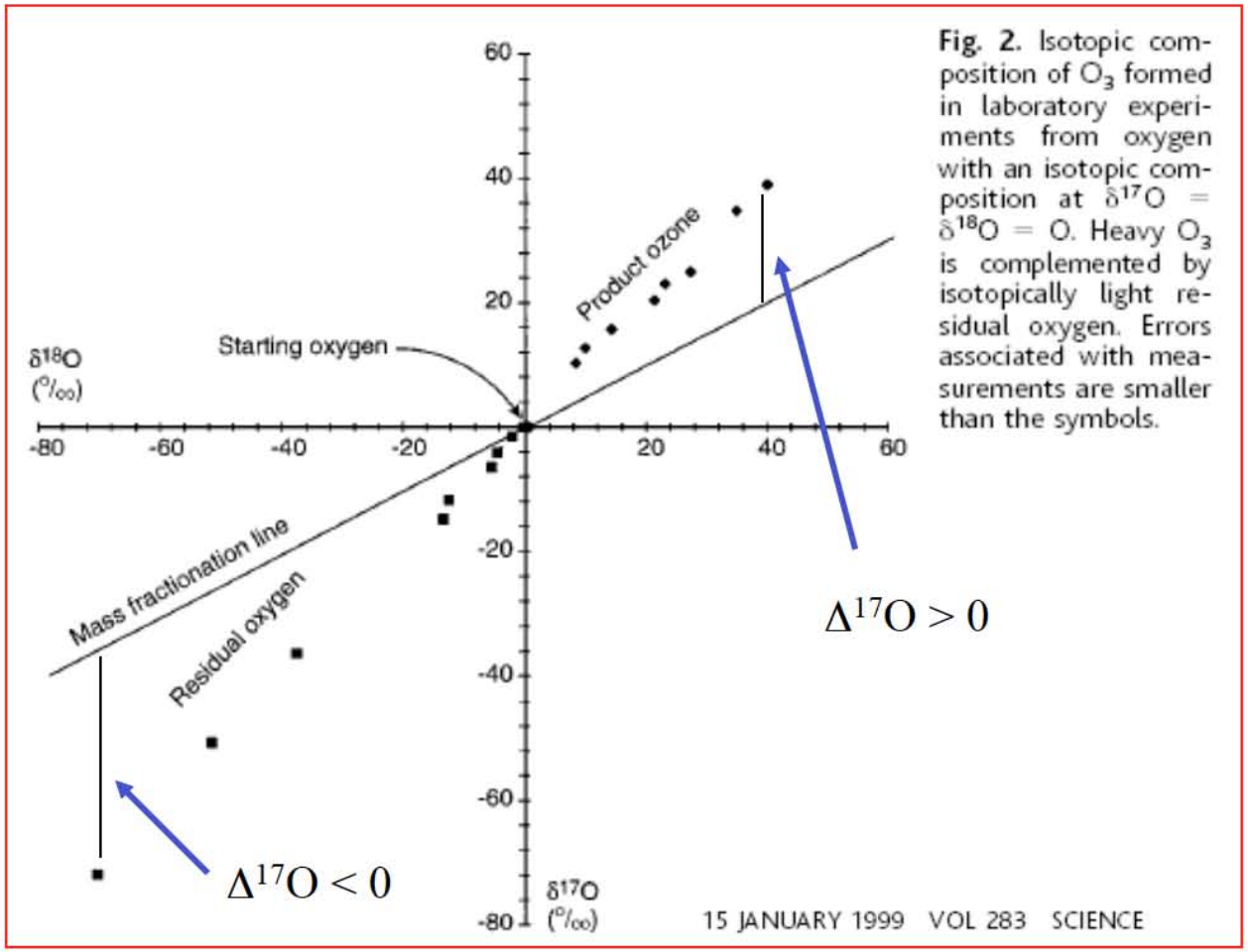


Fig. 2. Isotopic composition of O_3 formed in laboratory experiments from oxygen with an isotopic composition at $\delta^{17}O = \delta^{18}O = 0$. Heavy O_3 is complemented by isotopically light residual oxygen. Errors associated with measurements are smaller than the symbols.

Thiemens and Heidenreich, 1983; Theimens, 1999 (review)

Source: Thiemens, Mark H. "Mass-Independent Isotope Effects in Planetary Atmospheres and the Early Solar System." *Science* 283, no. 5400 (1999): 341-5.

Primary Production

- Gross primary production
  - Total amount of carbon fixed per unit time
- Net primary production
  - Net carbon fixed (gross minus respiration/dark)
- Net community production
  - That net biomass production
- New production
  - Production arising from influx of new nitrate
    - Dugdale & Goering (1967) L&O v12 p196
    - f-ratio = New/Net
      - Varies from 0.05 to 0.5 (oligotrophic→ eutrophic)

        Eppley & Peterson (1979) Nature v282 p677
- Export production
  - Flux of carbon leaving euphotic zone
    - e-ratio = Export/Net ~ f-ratio

Triple-Oxygen Isotope Pathways

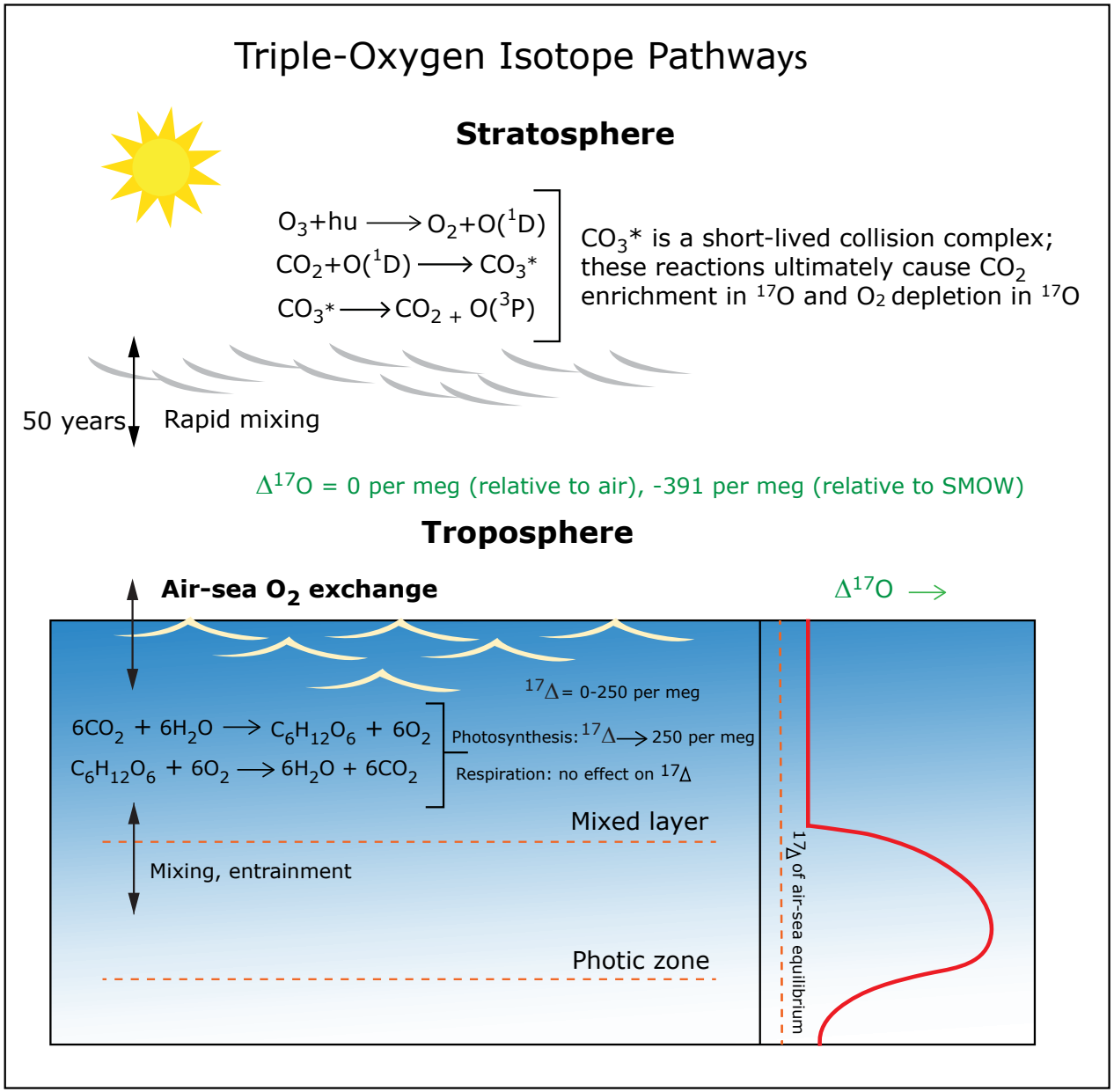
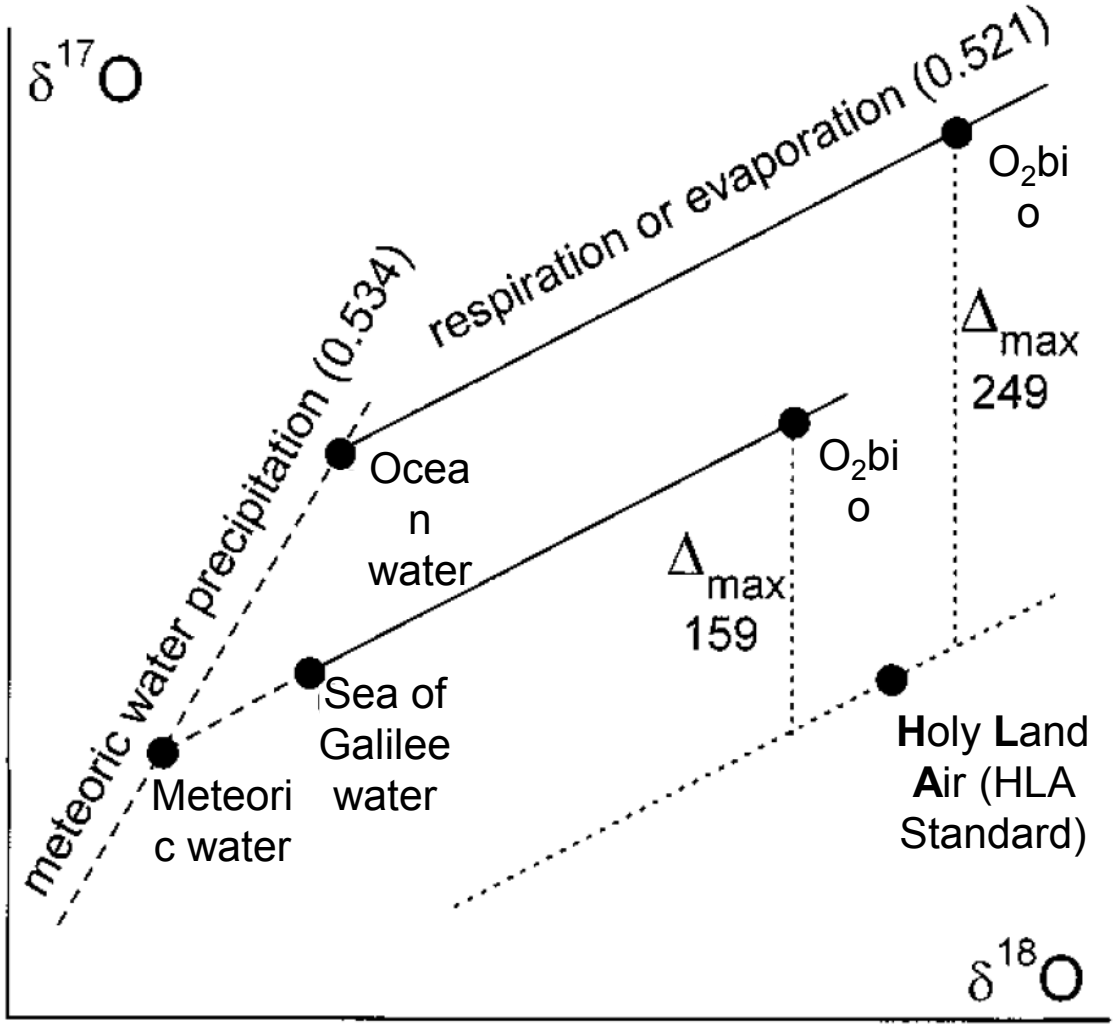


Image by MIT OpenCourseWare.

modified from Juranek & Quay (2012)

Schematic Oxygen Isotope Relationships



Source: Luz, Boaz, and Eugeni Barkan. "Assessment of Oceanic Productivity with the Triple-Isotope Composition of Dissolved Oxygen." *Science* 288, no. 5473 (2000): 2028-31.

Remember – Mass-Dependent Fractionation:

Equilibrium Fractionation:

$\alpha_{2/1} = (\alpha_{3/1})^{\beta}$ with $\beta = (1/m_1 - 1/m_2) / (1/m_1 - 1/m_3)$

with $m_1 = {}^{32}S$ (31.97207070), $m_2 = {}^{33}S$ (32.97145854), $m_3 = {}^{34}S$ (33.9678665), $m_4 = {}^{36}S$ (35.96708062)

$\beta = 0.5158_8$

Kinetic Fractionation:

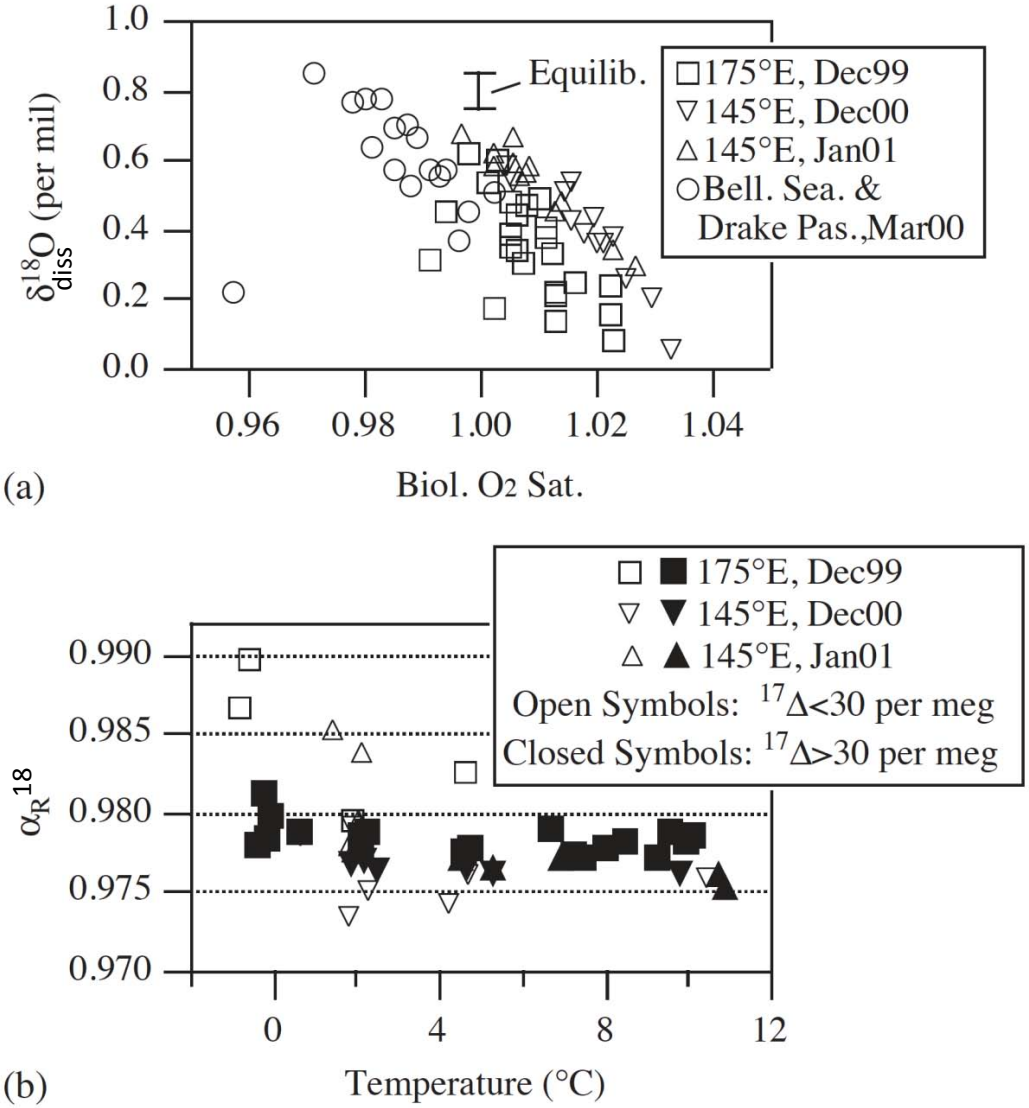
$\alpha_{2/1} = (\alpha_{3/1})^{\beta}$ with $\beta = [\ln (m_1/m_2)] / [\ln (m_1/m_3)]$

with $m_1 = {}^{32}S$ (31.97207070), $m_2 = {}^{33}S$ (32.97145854), $m_3 = {}^{34}S$ (33.9678665), $m_4 = {}^{36}S$ (35.96708062)

$\beta = 0.5083_1$

Ref.: Young ED, A Galy, H Nagahara, 2002, Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, GCA 66 (6), 1095-1104.

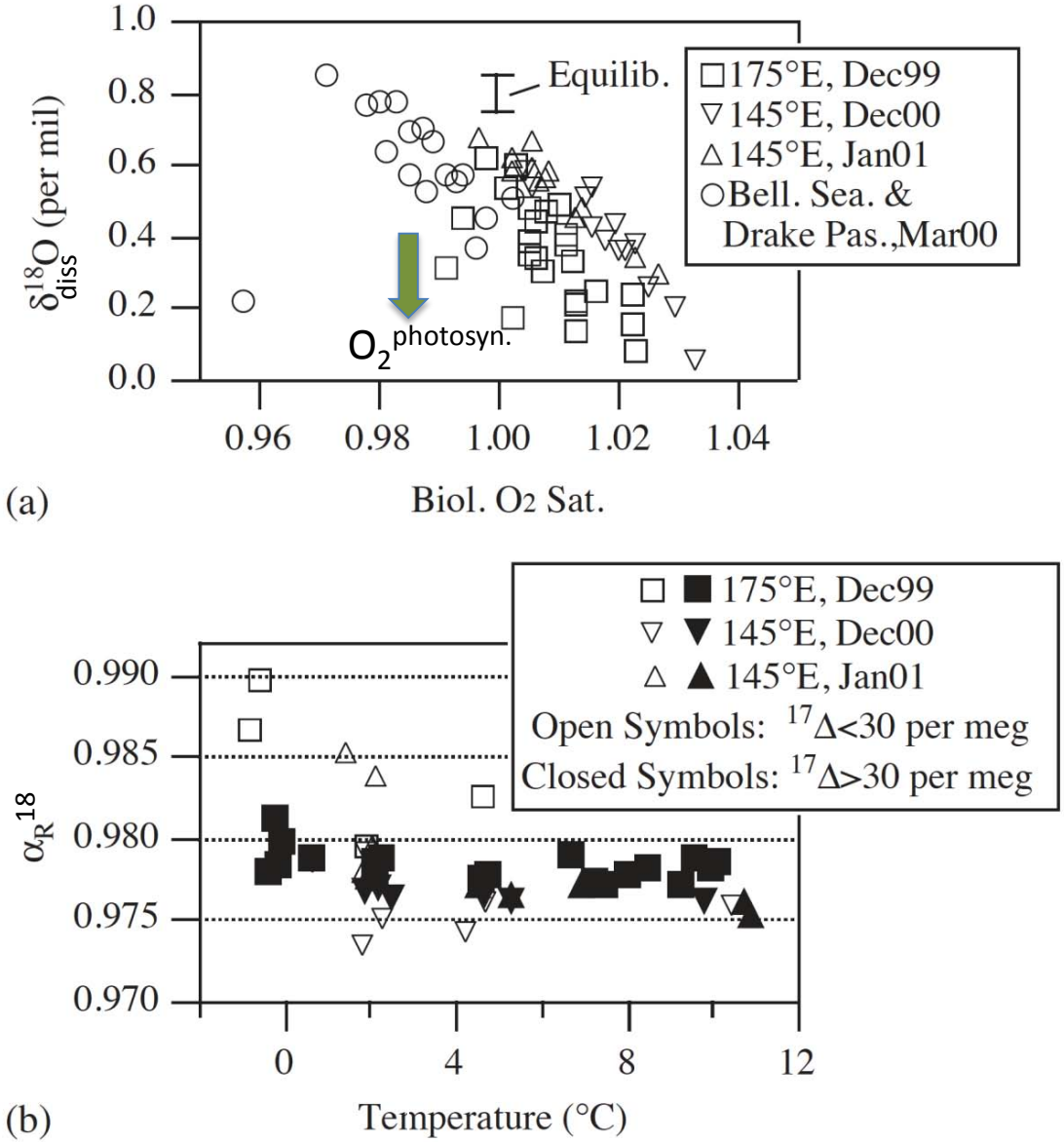
Isotope Fractionation during Respiration



Equilibrium refers to $\delta_{sat}{}^{18}O$ at surface temperatures of the study region (Southern Ocean) = + 0.8 per mil

Source: Hendricks, Melissa B., Michael L. Bender, et al. "Net and Gross O_2 Production in the Southern Ocean from Measurements of Biological O_2 Saturation and its Triple Isotope Composition." *Deep Sea Research Part I: Oceanographic Research Papers* 51, no. 11 (2004): 1541-61.

Isotope Fractionation during Respiration



Photosynthetic O_2:

$\delta^{18}O$ of atmospheric O_2 w.r.t SMOW is +23.5 per mil (Kroopnick & Graig, 1972) – i.e. *Dole Effect*.

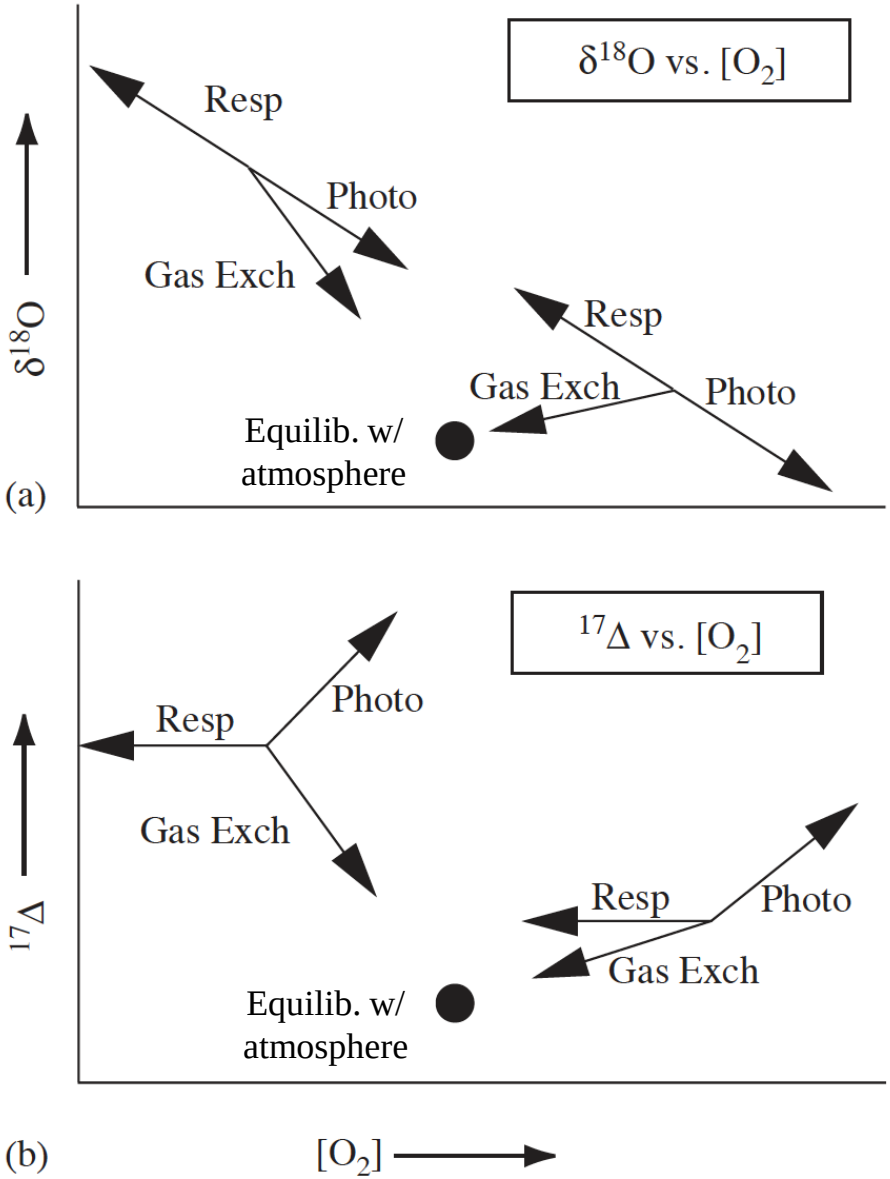
--Then – relative to air:

$\delta^{18}O_{SMOW} = (X^{18}_{SMOW}/X^{18}_{atm} - 1)\ 10^3$

$= -22.96$

--Note that for small $^{17}\Delta$ values, N/G, and thus α^{18}_R is not well constrained.

Source: Hendricks, Melissa B., Michael L. Bender, et al. "Net and Gross O_2 Production in the Southern Ocean from Measurements of Biological O_2 Saturation and its Triple Isotope Composition." *Deep Sea Research Part I: Oceanographic Research Papers* 51, no. 11 (2004): 1541-61.



Definitions:

$$\Delta^{17}O = \ln(X^{17}/X^{17}_{std}) - 0.516\,(X^{18}X^{18}_{std})\,10^6$$

or

$$\Delta^{17}O = \ln(\delta^{17}O/10^3 + 1) - 0.516\,\ln(\delta^{18}O/10^3 + 1)\,10^6$$

or

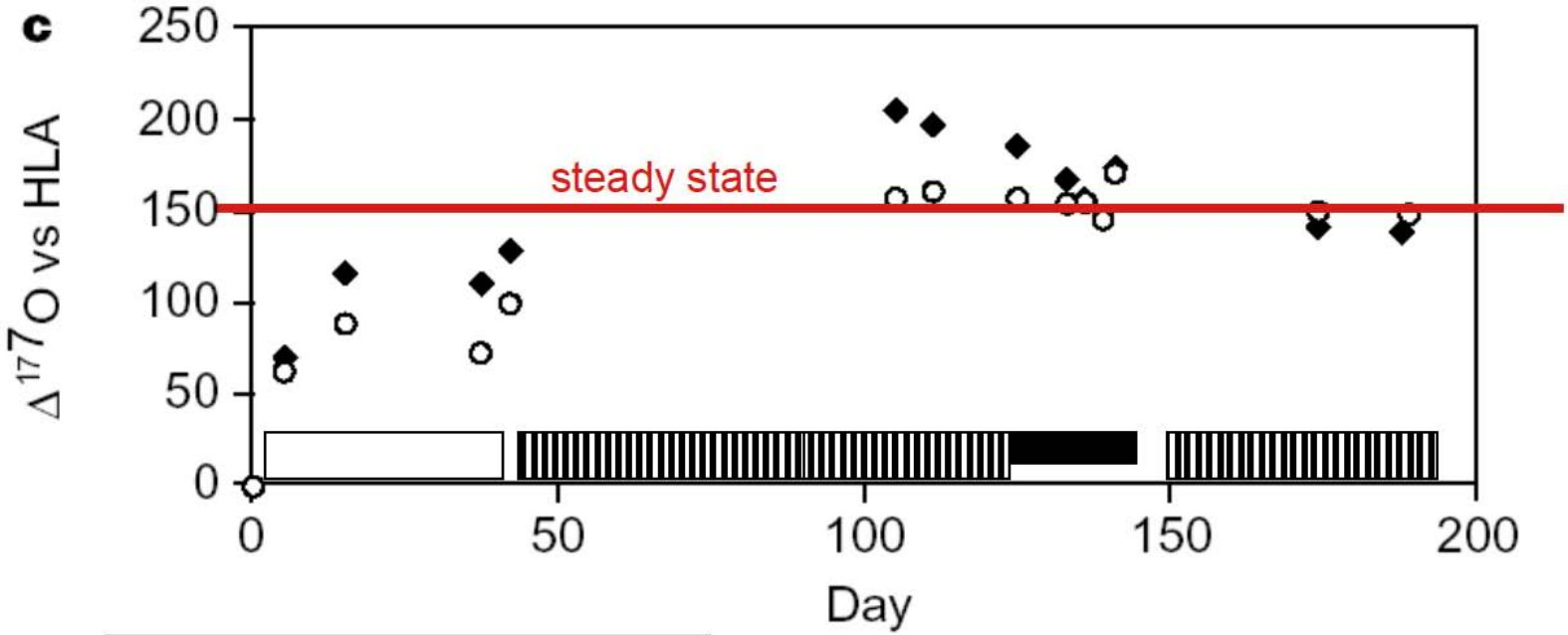
$$\Delta^{17}O = (\delta^{17}O - 0.516\,\delta^{18}O)\,10^3$$

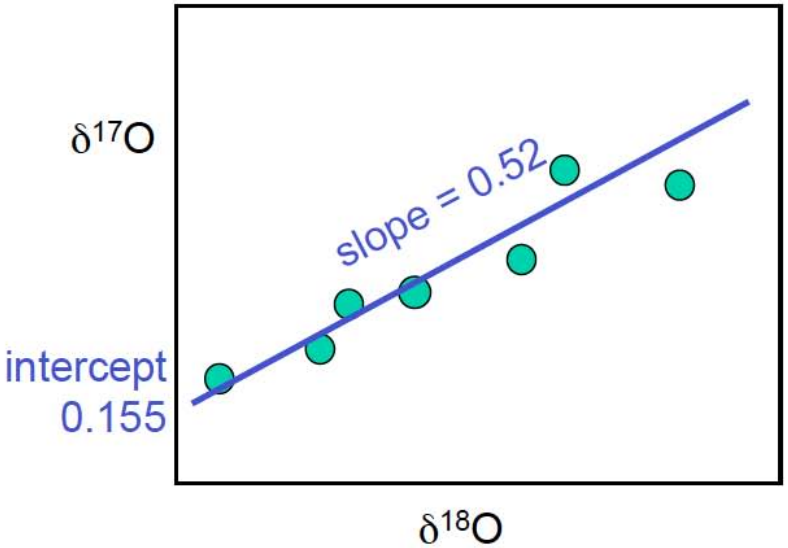
<u>Note</u>: the slope in $\delta^{17}O$ vs. $\delta^{18}O$ space varies between studies from 0.516 to 0.521. It is chosen so that $\Delta^{17}O$ is insensitive to respiration.

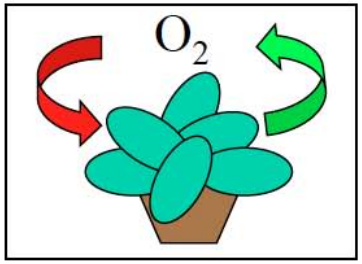
Because variations are so small, differences are expressed as parts per million (per meg).

Source: Hendricks, Melissa B., Michael L. Bender, et al. "Net and Gross O_2 Production in the Southern Ocean from Measurements of Biological O_2 Saturation and its Triple Isotope Composition." *Deep Sea Research Part I: Oceanographic Research Papers* 51, no. 11 (2004): 1541-61.

Closed biological system – steady state $\Delta^{17}O$ (wrt air)







Luz and Barkan, 2000

Schematic Oxygen Isotope Relationships in the Mixed Layer

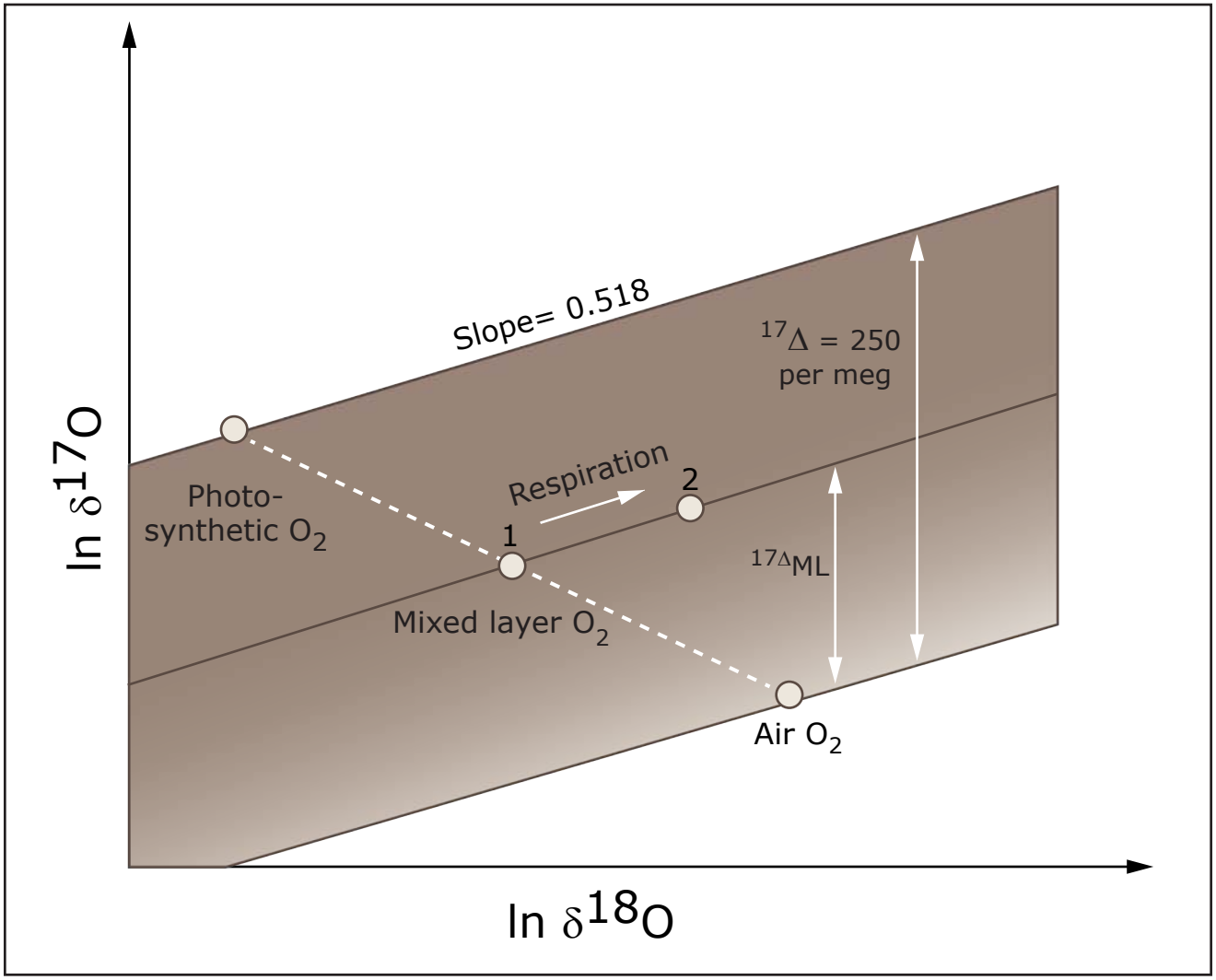


Image by MIT OpenCourseWare.

Oxygen Concentration in the Mixed Layer

O_2 concentration = Gross O_2 production – Respiration + Gas exchange

$$h\,\mathrm{d}C/\mathrm{d}t = G - R + k\,(C_{sat} - C)$$

G = Gross O_2 production by photosynthesis (e.g. in mmol O_2 m^{-2} d^{-1})
R = O_2 consumption by respiration
h = Average height of mixed layer
C = Concentration; $_{sat}$ = at saturation (e.g. in mmol O_2 m^{-3})
k = Gas exchange coefficient for O_2 (m d^{-1}), proxy: Ar

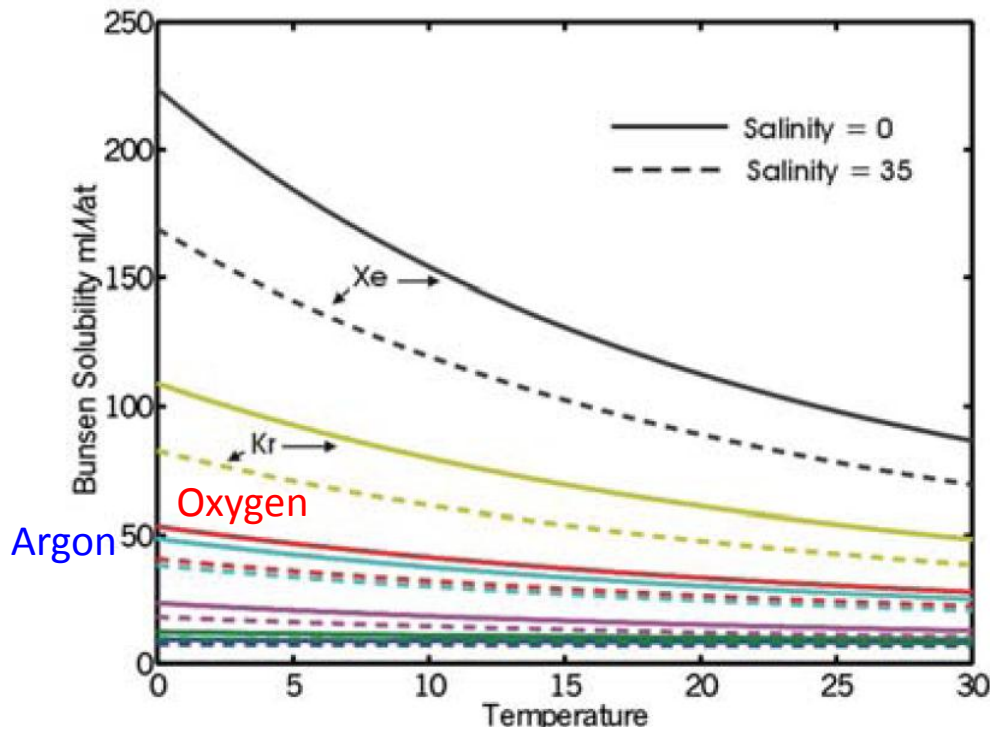
For the isotopomers $^{17}O^{16}O$ and $^{18}O^{16}O$ dissolved in the mixed layer, we introduce the isotope ratio X_{diss} and the fractionation factors for photosynthesis α_P and respiration α_R. Subscripts $_w$ and $_{sat}$ denote isotope ratios of oxygen in seawater (H_2O) and dissolved O_2 in equilibrium with the atmosphere, respectively. Then:

$$h\,\mathrm{d}(CX_{diss})/\mathrm{d}t = GX_w\underbrace{\alpha_P}_{=1} - RX_{diss}\alpha_R + k\,(C_{sat}X_{sat} - CX_{diss})$$

Gas Solubility

- Gas solubility generalities:
  - heavier, more polar gases are more soluble
  - all gases are more soluble at ***lower*** temperatures*
    - more soluble gases have greater temperature dependence
  - salinity depresses solubility

Note the similarity in solubility between oxygen and argon



Triple-Oxygen Isotope Pathways

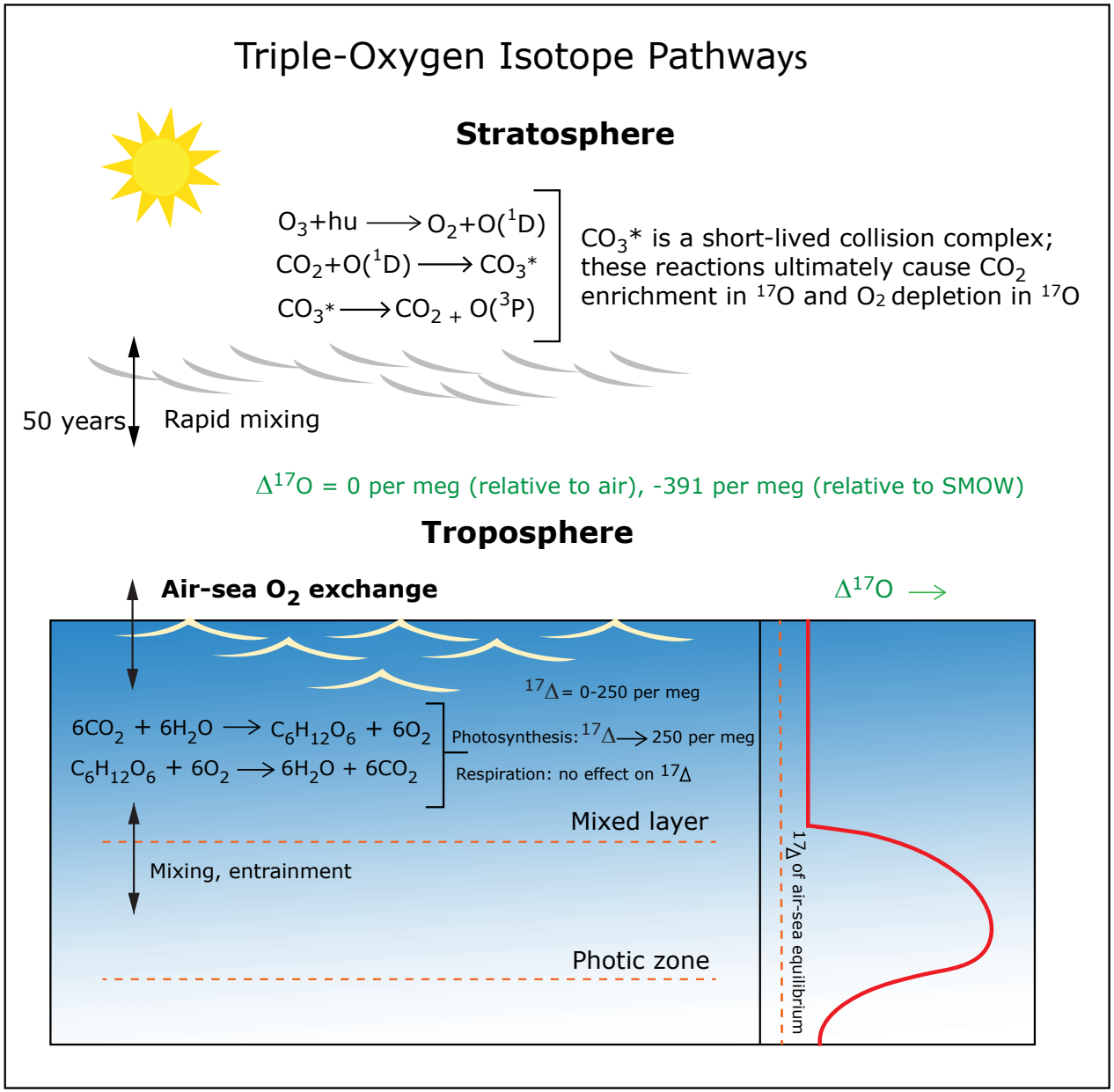
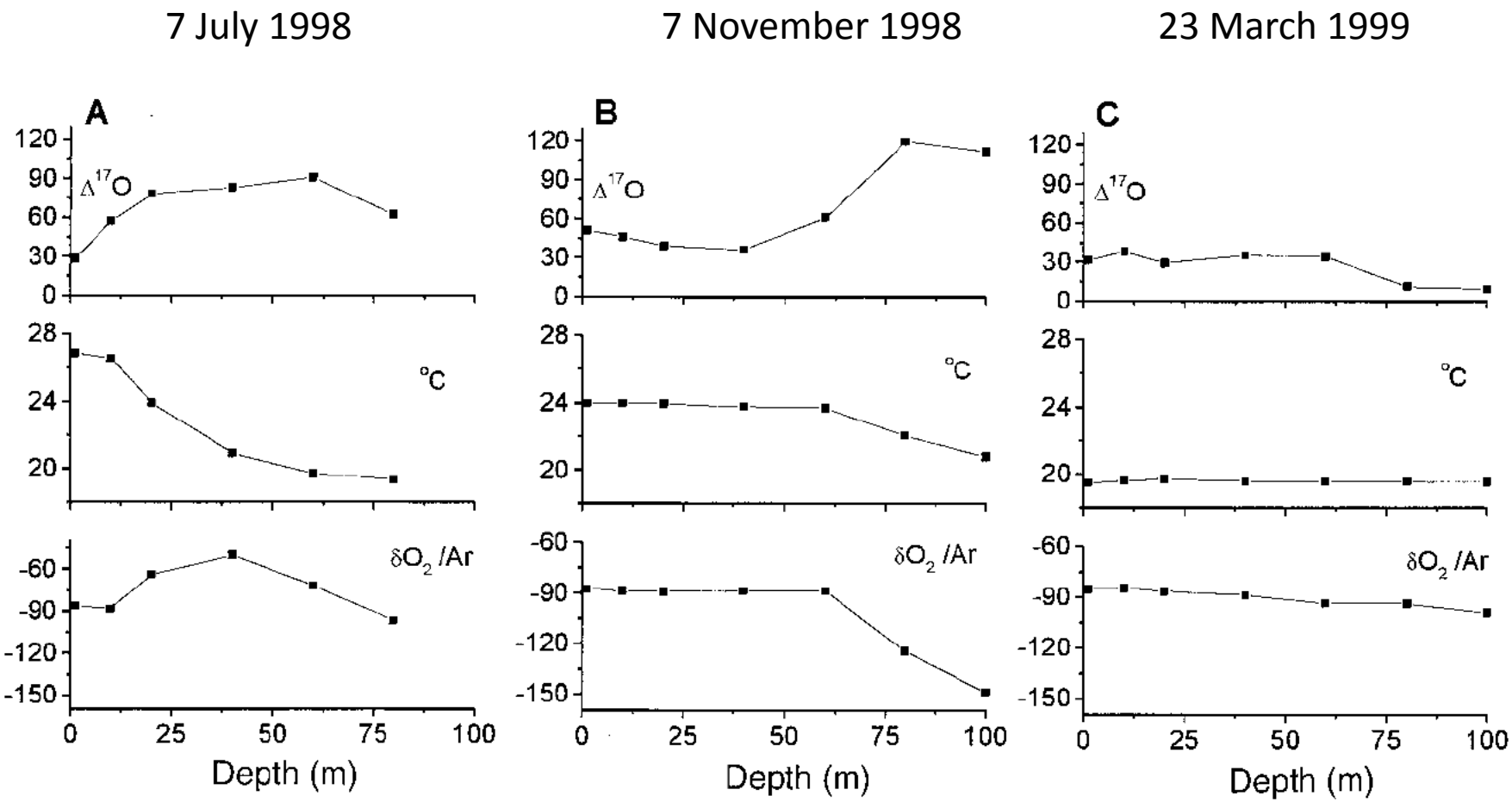


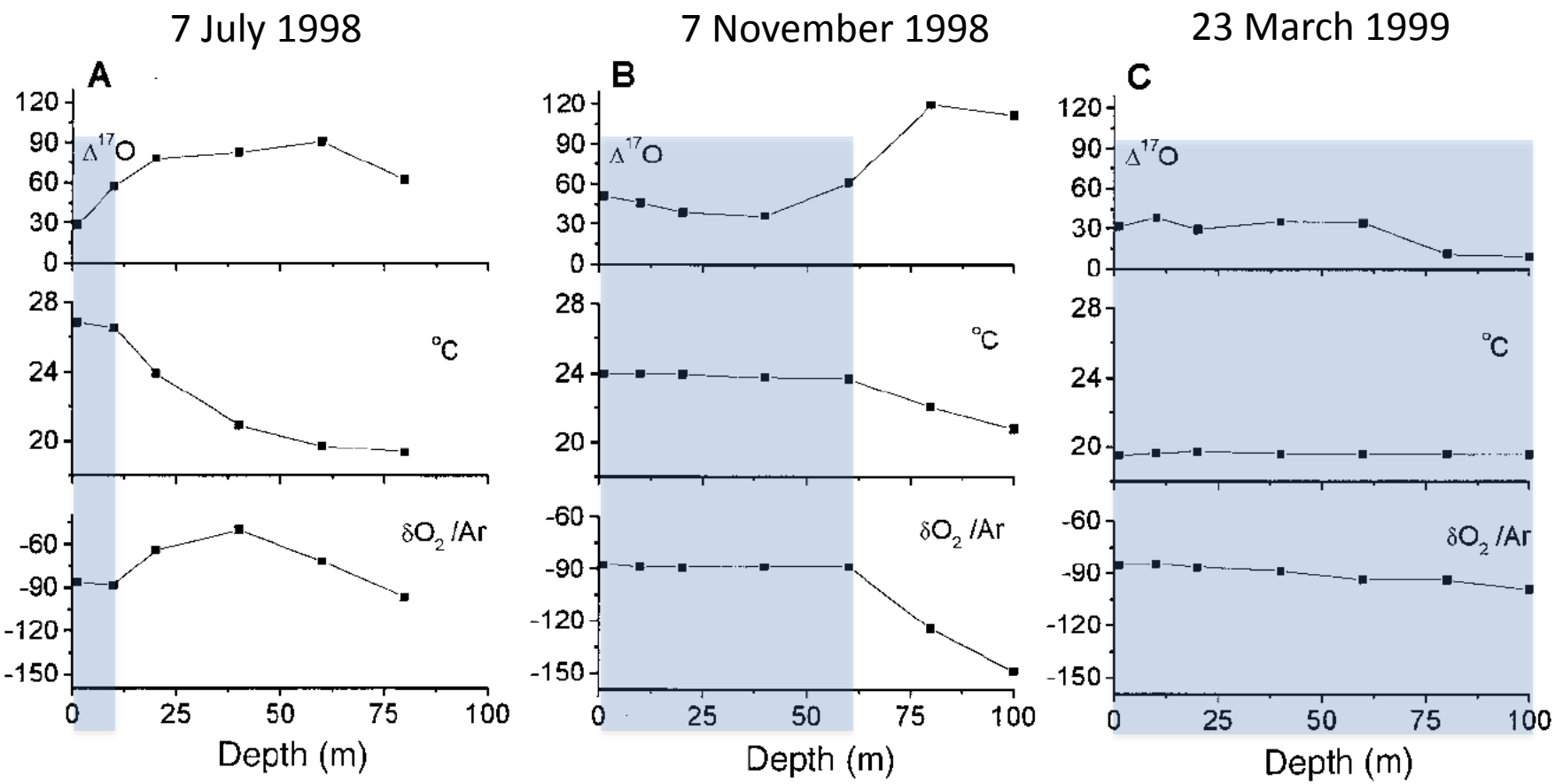
Image by MIT OpenCourseWare.

Triple-Oxygen, Temperature and O_2/Ar at Bermuda (BATS)



Source: Luz, Boaz, and Eugeni Barkan. "Assessment of Oceanic Productivity with the Triple-Isotope Composition of Dissolved Oxygen." *Science* 288, no. 5473 (2000): 2028-31.

Triple-Oxygen, Temperature and O_2/Ar at Bermuda (BATS)



Thermocline O_2 max due to net accumulation of $O_2^{photosyn}$

In situ O_2 production, but uptake > production

Mixed layer > photic zone
No photosyn. in thermocline

Source: Luz, Boaz, and Eugeni Barkan. "Assessment of Oceanic Productivity with the Triple-Isotope Composition of Dissolved Oxygen." *Science* 288, no. 5473 (2000): 2028-31.

$$h\, d(CX_{diss})/dt = GX_w\underbrace{\alpha_P}_{=1} - RX_{diss}\alpha_R + k\,(C_{sat}X_{sat} - CX_{diss})$$

By replacing R with $G + k\,(C_{sat}\ldots C)$ and dividing each side by X_{std}, the isotope ratio of the standard (atmospheric O_2), we can express $\delta_{diss}O$ as a function of G/kC, C/C_{sat} and α_R according to:

$$\delta_{dis}O / 10^3 = \frac{\{(G/kC_{sat})\,(\delta_w O/10^3 + 1) + (\delta_{sat}O/10^3 + 1)\}}{\{(G/kC_{sat}) + 1 - [(G/kC_{sat}) + 1 - (C/C_{sat})]\,(1 - \alpha_R)\}} - 1$$

This equation can also be expressed in terms of the ratio of net O_2 production (N) to gross O_2 production (G), C/C_{sat} and α_R:

$$\delta_{dis}O / 10^3 = \frac{\{(C/C_{sat} - 1)\,(\delta_w O/10^3 + 1) + (N/G)\,(\delta_{sat}O/10^3 + 1)\}}{\{(C/C_{sat}) - 1 + (N/G) - [1 - (N/G)]\,[(C/C_{sat}) - 1]\,(1 - \alpha_R)\}} - 1$$

Melissa Hendricks and colleagues (*Deep-Sea Res. 1*, 51, 1541-1561, 2004) derive equivalent equations for expressions of $\Delta^{17}O_{dis}$ in the appendix of their paper, e.g.

$$N/G = (C/C_{sat} - 1)\,(\Delta^{17}O_{diss} - \Delta^{17}O_w) / (\Delta^{17}O_{sat} - \Delta^{17}O_{dis})$$

Triple-Isotope Measurements of Dissolved Oxygen Since 2000

World map with locations where the triple isotopic composition of dissolved oxygen has been used to assess marine productivity has been removed due to copyright restrictions.

See figure 1 in Juranek, L. W., and P. D. Quay. "Using Triple Isotopes of Dissolved Oxygen to Evaluate Global Marine Productivity." *Annual Review of Marine Science* 5 (2013): 503-524.

Table with summary of previously published comparisons of various quantities has been removed due to copyright restrictions.

See table 1 in Juranek, L. W., and P. D. Quay. "Using Triple Isotopes of Dissolved Oxygen to Evaluate Global Marine Productivity." *Annual Review of Marine Science* 5 (2013): 503-24.

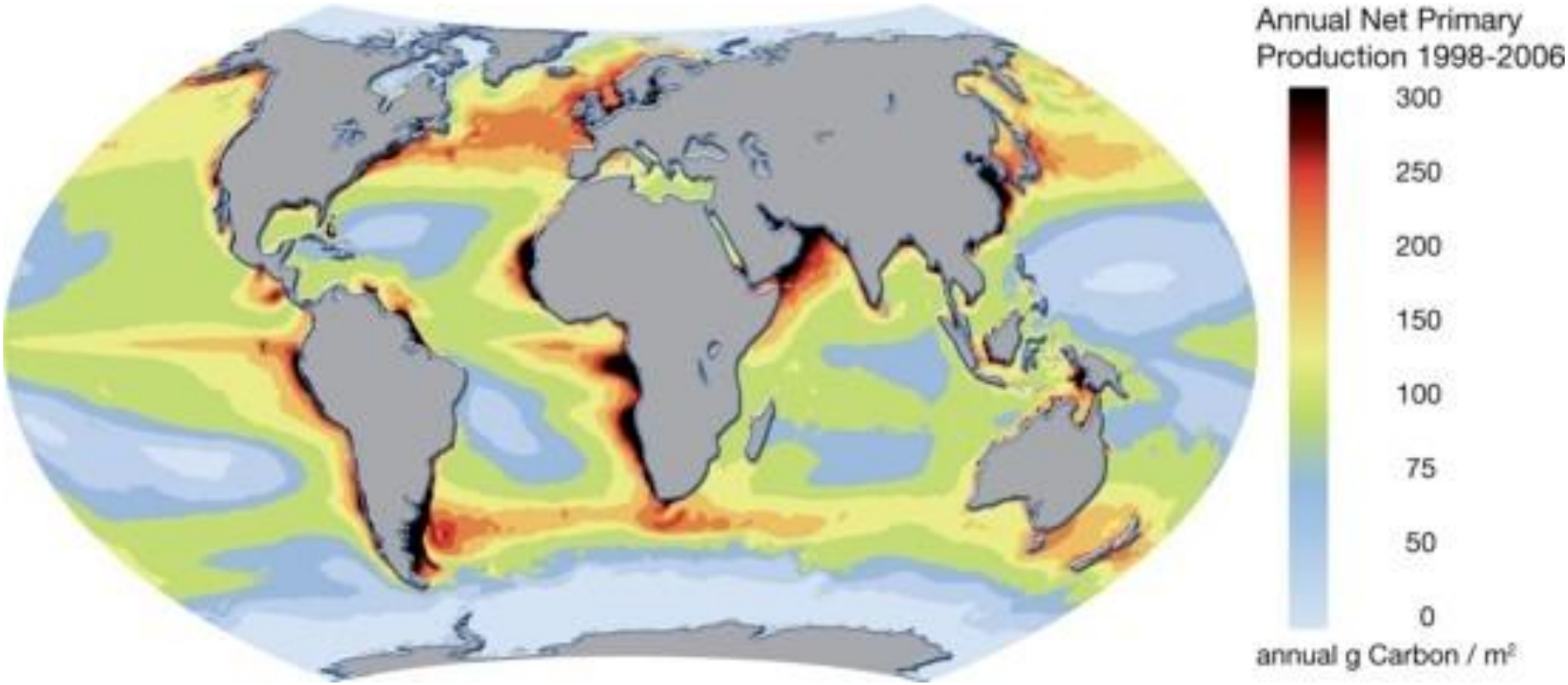
Comparison of Primary Production and Gross Oxygen Production Methods

Table with summary of previously published comparisons of various quantities has been removed due to copyright restrictions.

See table 1 in Juranek, L. W., and P. D. Quay. "Using Triple Isotopes of Dissolved Oxygen to Evaluate Global Marine Productivity." *Annual Review of Marine Science* 5 (2013): 503-24.

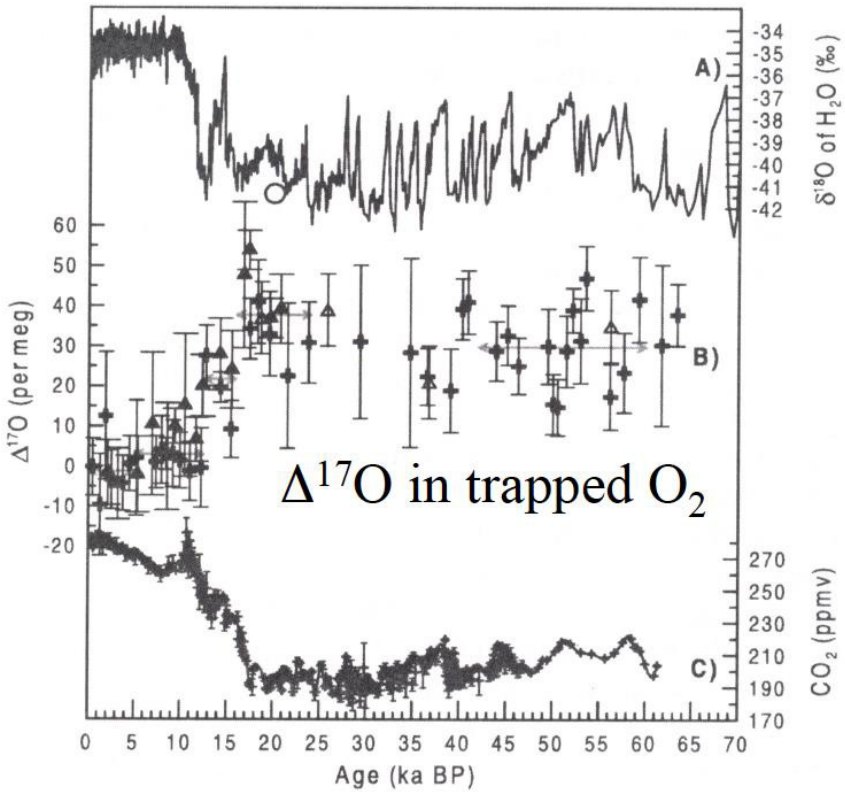
Satellite-based Primary Production Estimates

VGPM = Vertically Generalized Productivity Model (Behrenfeld & Falkowski, 1997)
CbPM = C-based Productivity Model (Behrenfeld et al., 1995, Westberry et al., 2008)



Courtesy of Hugo Ahlenius, UNEP/GRID-Arendal. Used with permission.

Net Terrestrial Productivity Record



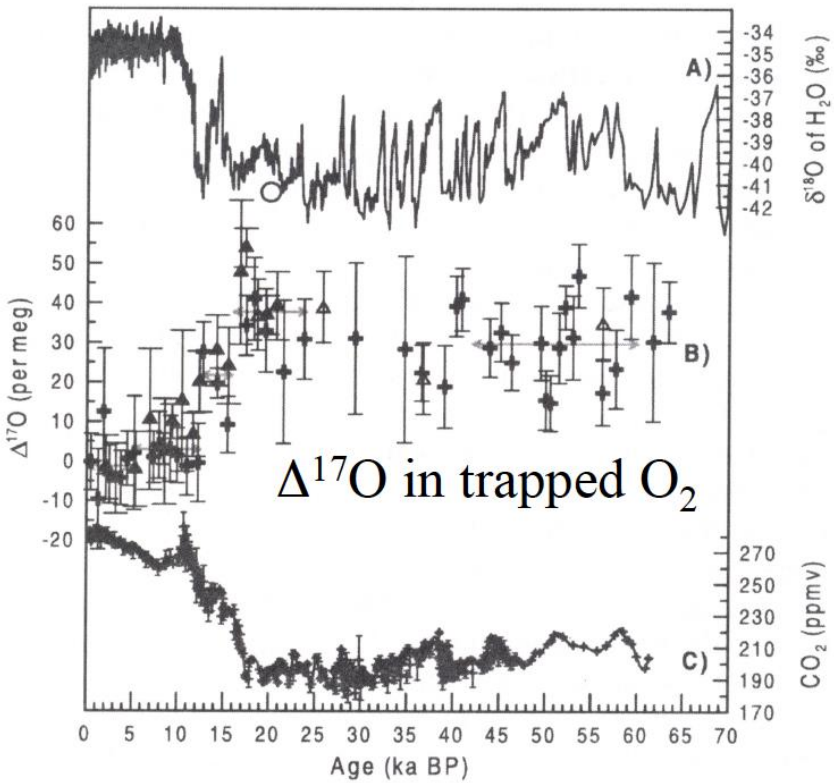
Results from the Greenland Ice Sheet Project 2 (GISP2) and Siple Dome ice cores. (a) $\delta^{18}O$ of the ice, a proxy for local temperature [*Grootes et al.*, 1993] from the GISP2 ice core, Greenland. (b) $\Delta^{17}O$ values, where open triangles are results from *Luz et al.* [1999] and crosses and solid triangles are individual measurements from GISP2 and Siple Dome, respectively.

Total biogenic productivity was only 76-83% of today during the last glacial period!

Note that two processes compete: 1) During LGM less CO_2 was available for exchange reactions, leading to less anomalous O_2 being formed, making $\Delta^{17}O$ rise to its biological value (Effect: +70).
2) Biological productivity was lower during the LGM, leading to lower $\Delta^{17}O$
Process 1) dominated

Source: Blunier, Thomas, Bruce Barnett, et al. "Biological Oxygen Productivity During the Last 60,000 Year from Triple Oxygen Isotope Measurements." *Global Biogeochemical Cycles* 16, no. 3 (2002): 3-1-3-13.

Net Terrestrial Productivity Record



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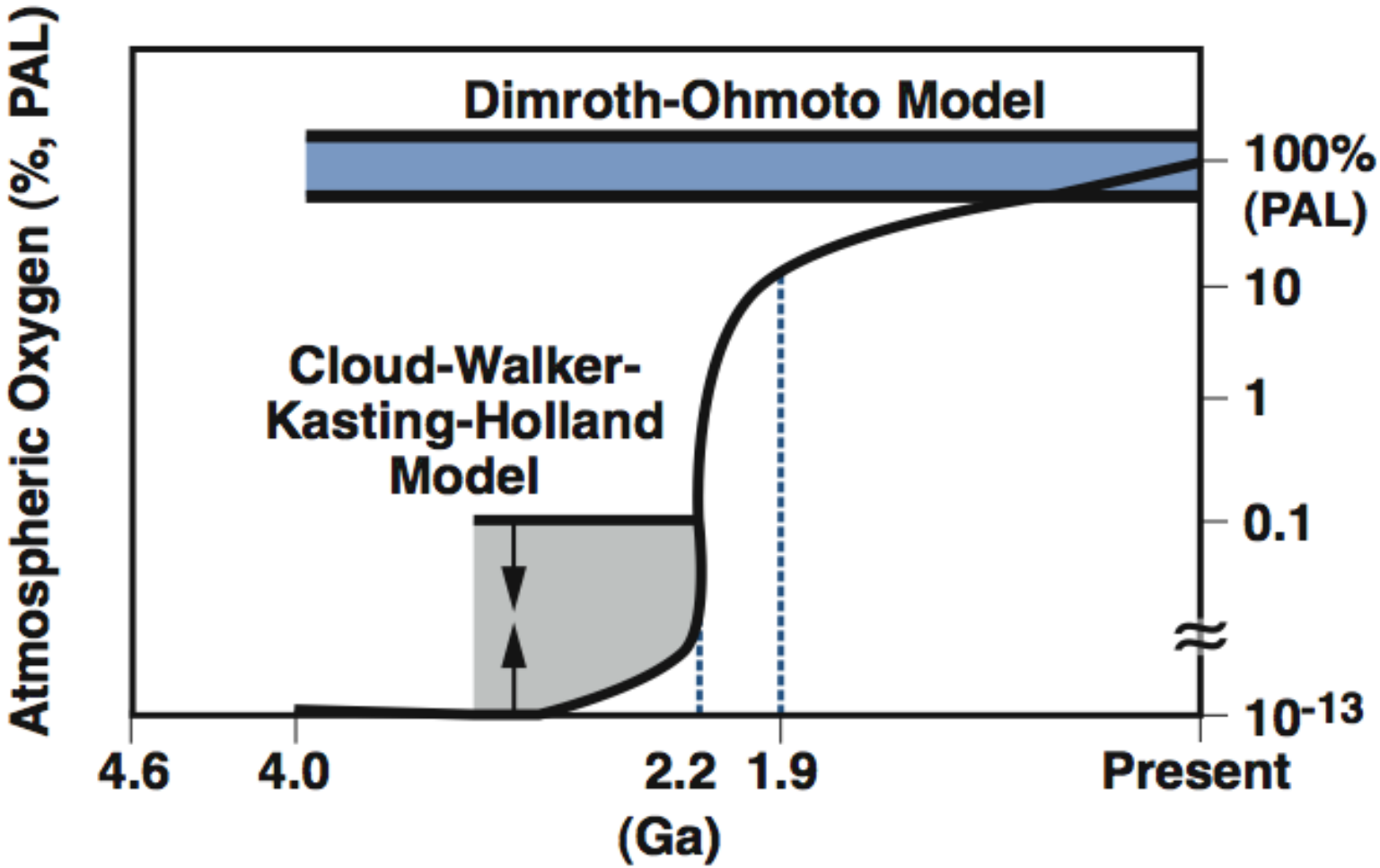
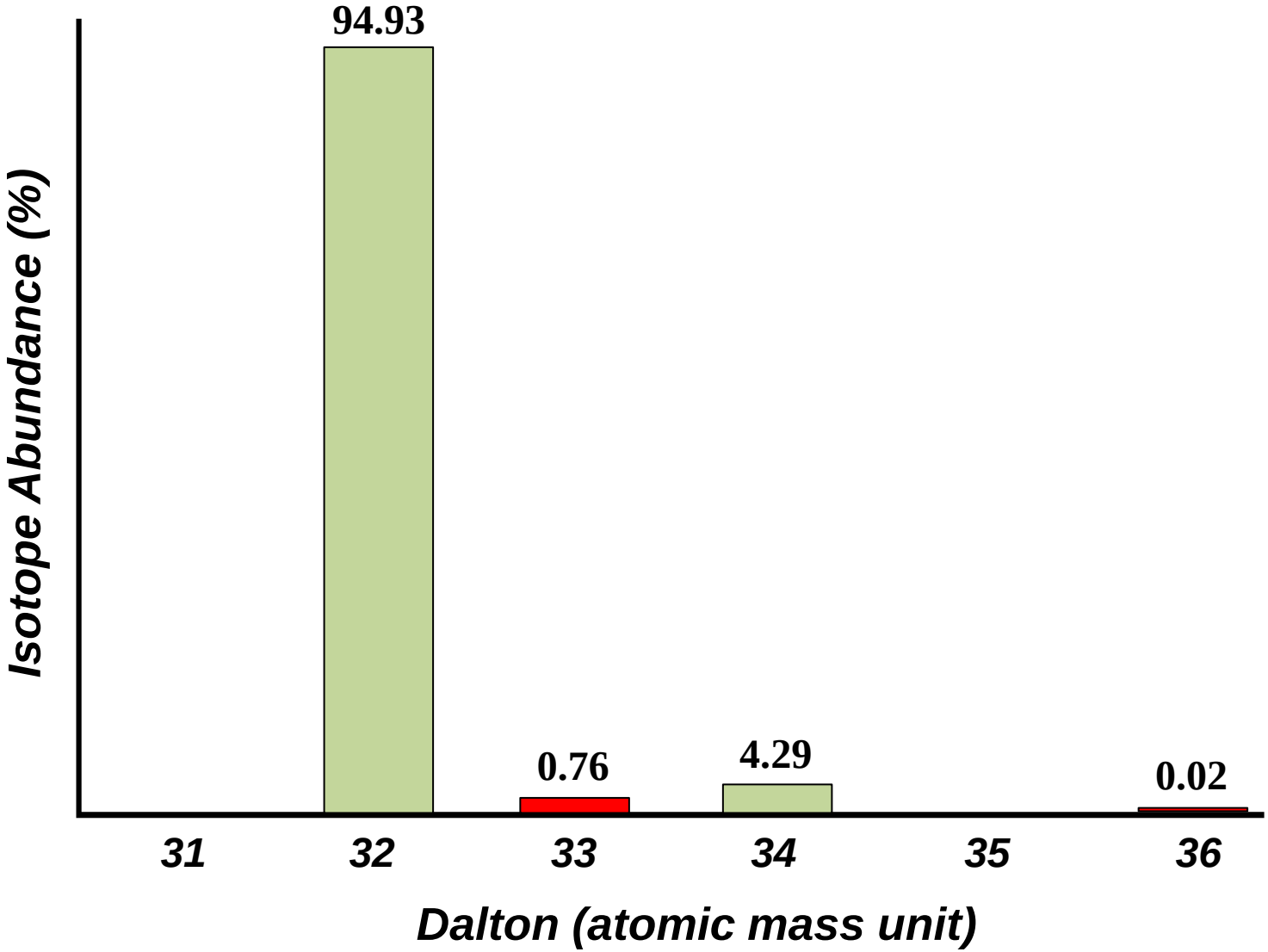
Two contrasting models for the evolution of atmospheric O_2

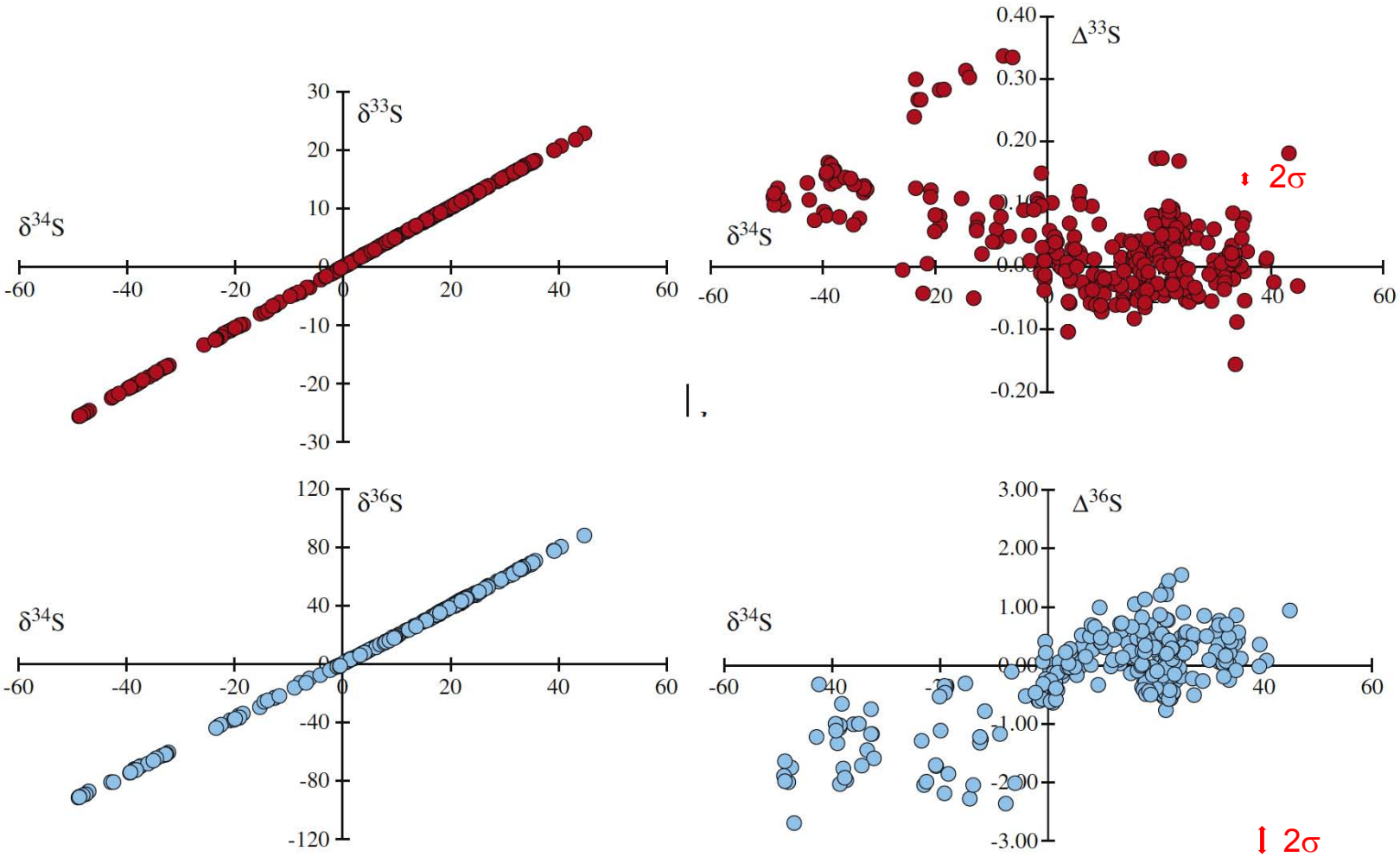
from Ohmoto, Geochem. News #93, Fall 1997



Stable Sulfur Isotopes



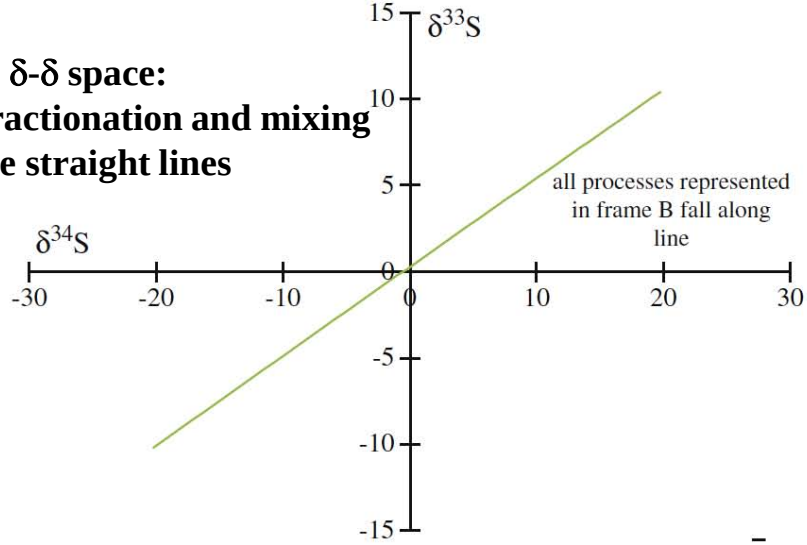
Conventional vs. Modern mass spectrometry



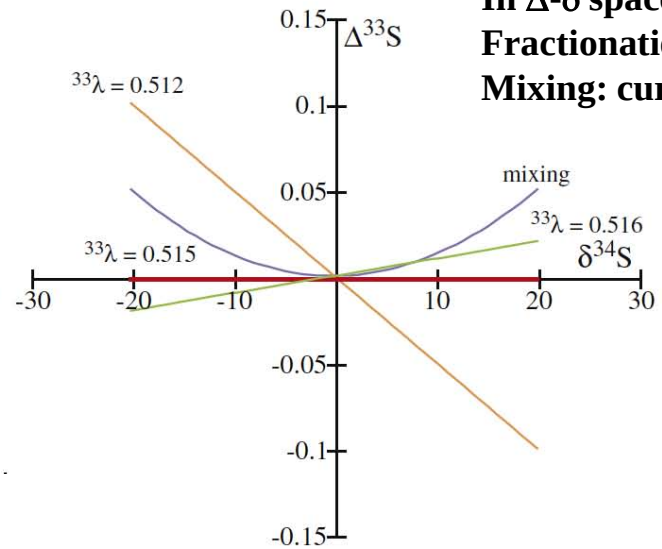
Source: Figure 2 of Johnston, David T. "Multiple Sulfur Isotopes and the Evolution of Earth's Surface Sulfur Cycle." *Earth-Science Reviews* 106, no. 1 (2011): 161-83.

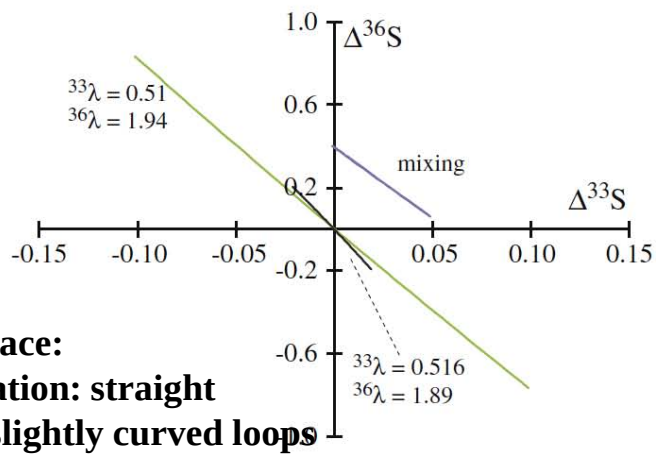
Slopes of Fractionation and Mixing Trends

In δ-δ space:
Fractionation and mixing are straight lines

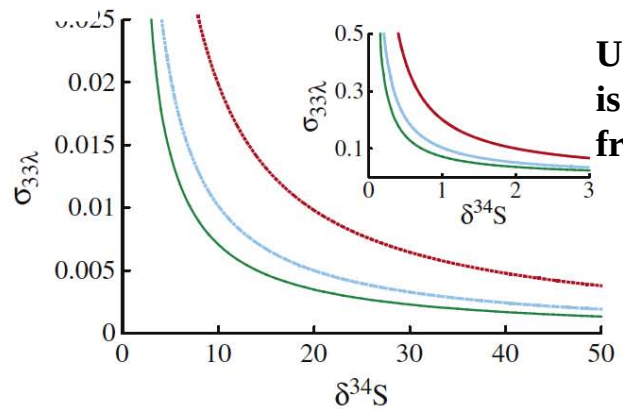


In Δ-δ space:
Fractionation: straight
Mixing: curved





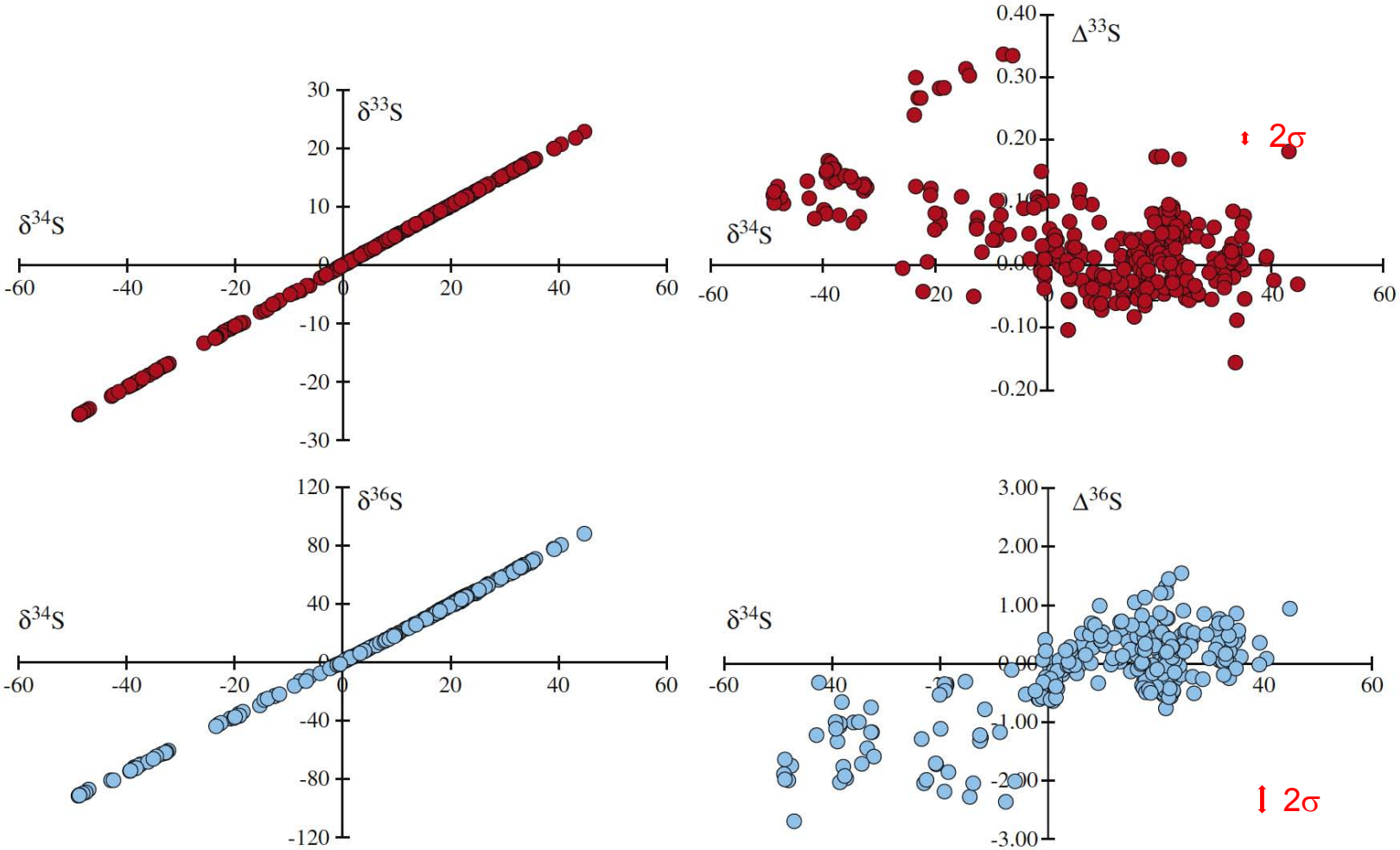
In Δ-Δ space:
Fractionation: straight
Mixing: slightly curved loops



Uncertainty (σ) is a function of fractionation

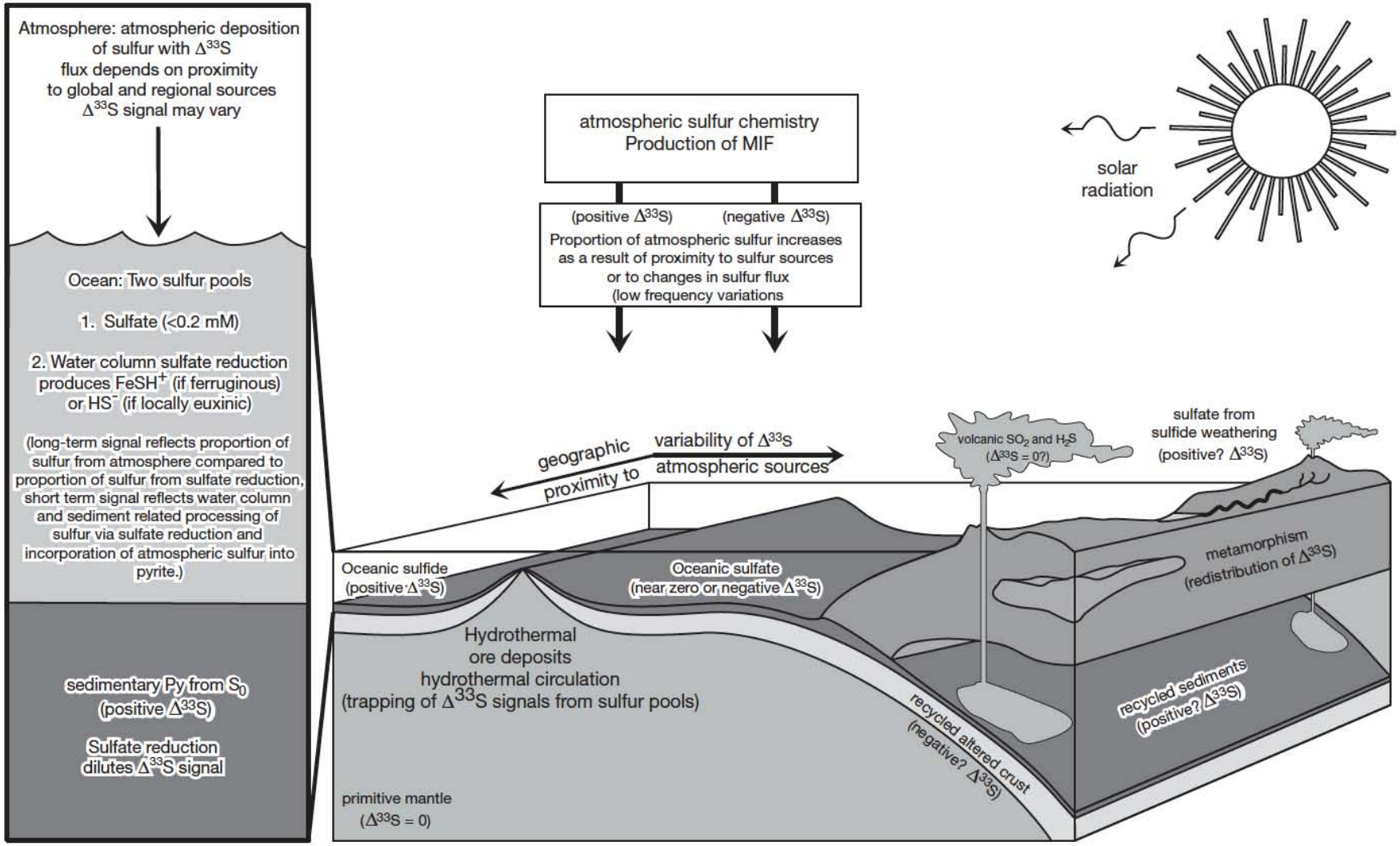
Source: Figure 2 of Johnston, David T. "Multiple Sulfur Isotopes and the Evolution of Earth's Surface Sulfur Cycle." *Earth-Science Reviews* 106, no. 1 (2011): 161-83.

Conventional vs. Modern mass spectrometry



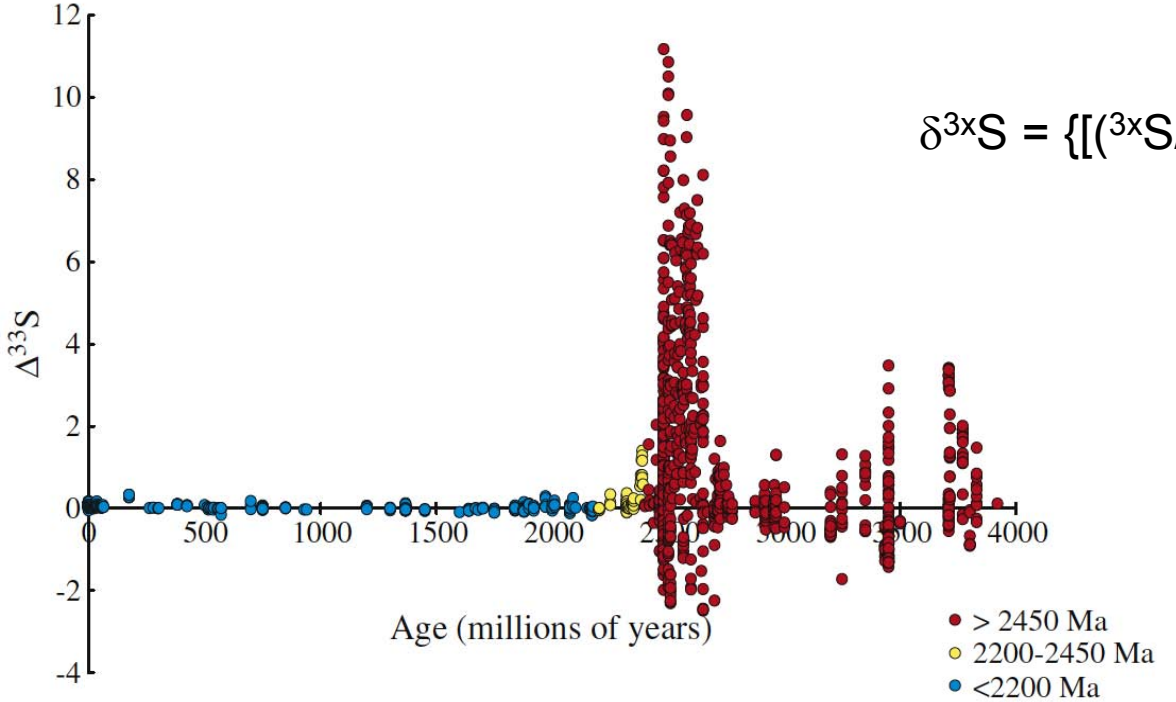
Source: Figure 2 of Johnston, David T. "Multiple Sulfur Isotopes and the Evolution of Earth's Surface Sulfur Cycle." *Earth-Science Reviews* 106, no. 1 (2011): 161-83.

Processes Affecting the Sulfur Isotope Cycle



Source: Figure 5 in Farquhar, James, Nanping Wu, et al. "Connections between Sulfur Cycle Evolution, Sulfur Isotopes, Sediments, and Base Metal Sulfide Deposits." *Economic Geology* 105, no. 3 (2010): 509-33.

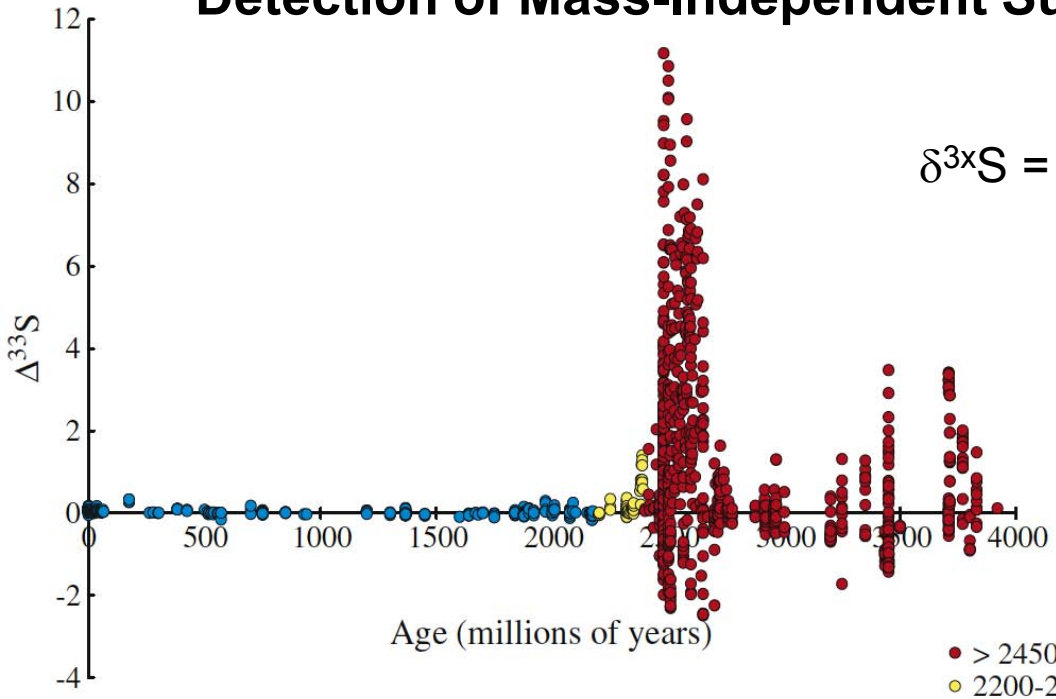
Detection of Mass-Independent Sulfur Isotope Variations



$$\delta^{3x}S = \{[(^{3x}S/^{32}S)_s] / [(^{3x}S/^{32}S)_{std}] - 1\}\ 10^3$$

Source: Figure 2 of Johnston, David T. "Multiple Sulfur Isotopes and the Evolution of Earth's Surface Sulfur Cycle." *Earth-Science Reviews* 106, no. 1 (2011): 161-83.

Detection of Mass-Independent Sulfur Isotope Variations

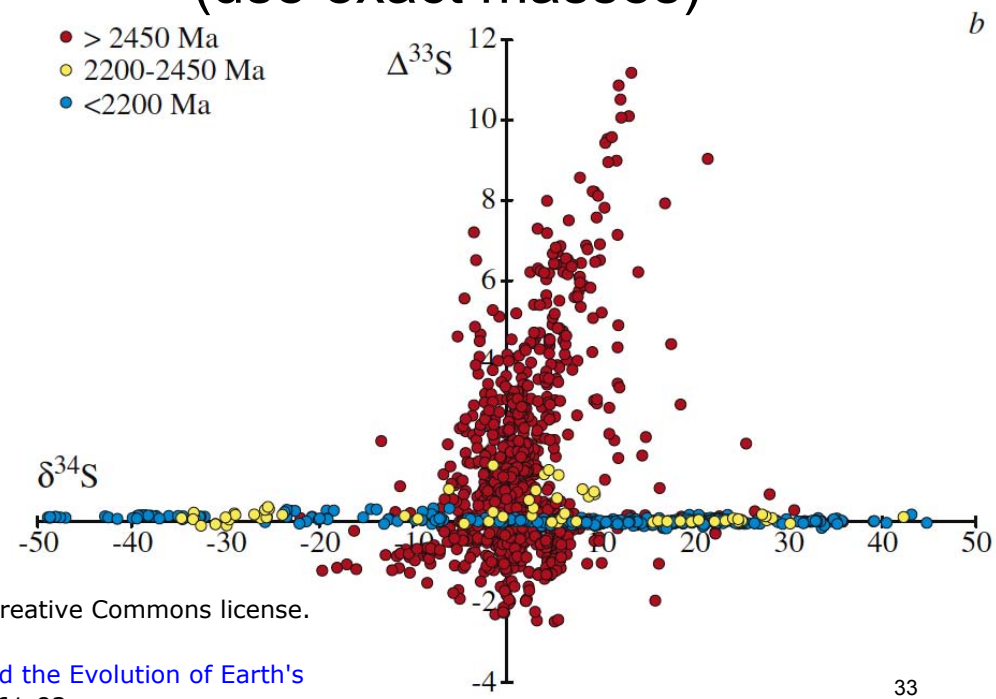


$$\delta^{3x}S = \{[(^{3x}S/^{32}S)_s] / [(^{3x}S/^{32}S)_{std}] - 1\}\ 10^3$$

$$\Delta^{3x}S = \delta^{3x}S - {}^{3x}\lambda\ \delta^{34}S$$

$$\lambda = (1/m_1 - 1/m_2) / (1/m_1 - 1/m_3)$$

$m_1 = 32$, $m_2 = 33$, $m_3 = 34$
(use exact masses)



Source: Figure 2 of Johnston, David T. "Multiple Sulfur Isotopes and the Evolution of Earth's Surface Sulfur Cycle." *Earth-Science Reviews* 106, no. 1 (2011): 161-83.

Definition of Mass-Independent Sulfur Isotope Variations

$$\Delta^{3x}S = \delta^{3x}S - 1000 \times \left[\left(1 + \frac{\delta^{34}S}{1000}\right)^{{}^{3x}\lambda} - 1\right]$$

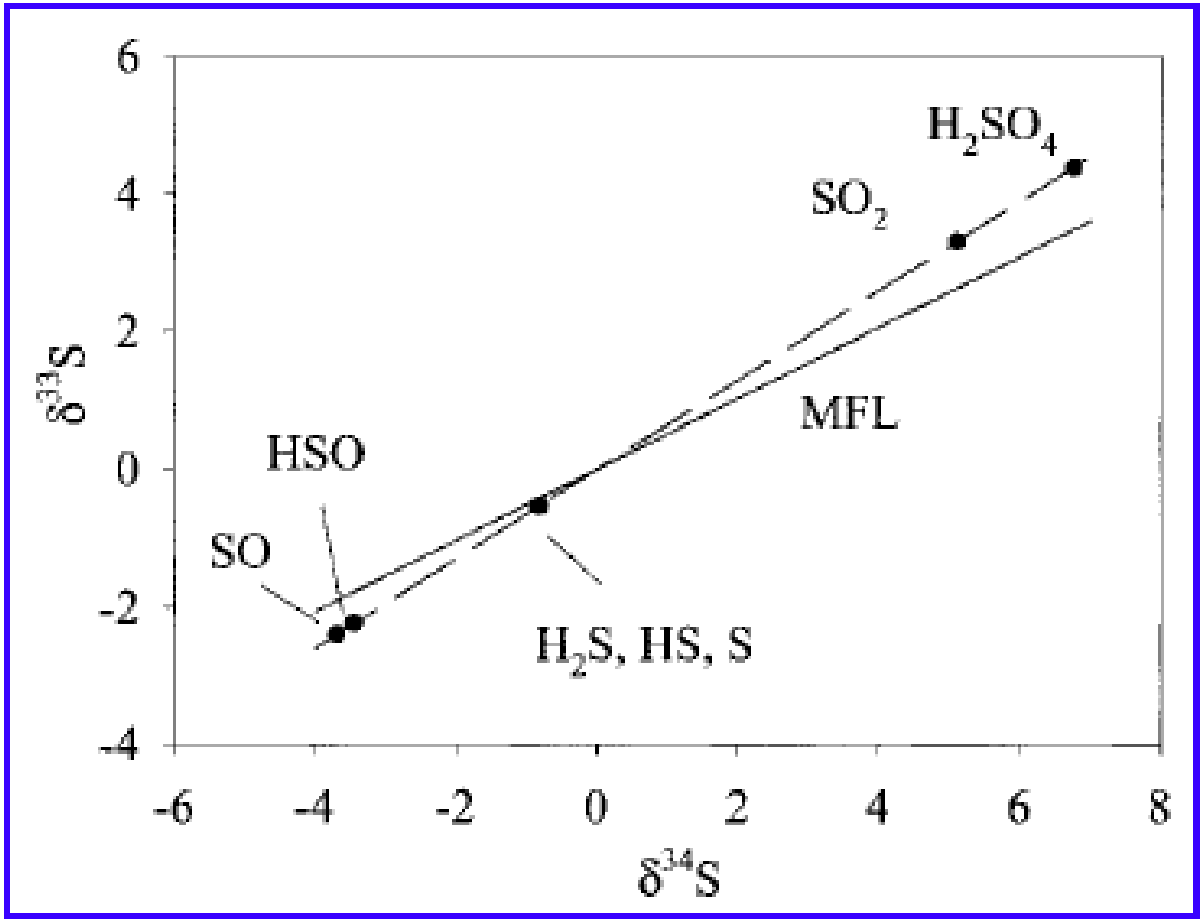
$$\Delta^{3x}S = 1000 \times \left[\ln\left(1 + \frac{\delta^{3x}S}{1000}\right) - {}^{3x}\lambda \times \ln\left(1 + \frac{\delta^{34}S}{1000}\right)\right]$$

These two expressions yield very similar solutions for the range of Earth materials ($\delta^{34}S$ variations between -5% and 5%). λ can be solved by measuring fractionations, even if the processes involve multiple steps.

$${}^{3x}\lambda = \frac{\ln\left(1 + \frac{\delta^{3x}S_A}{1000}\right) - \ln\left(1 + \frac{\delta^{3x}S_B}{1000}\right)}{\ln\left(1 + \frac{\delta^{34}S_A}{1000}\right) - \ln\left(1 + \frac{\delta^{34}S_B}{1000}\right)}$$

Johnston, 2011

Stratospheric Photolyses Reactions

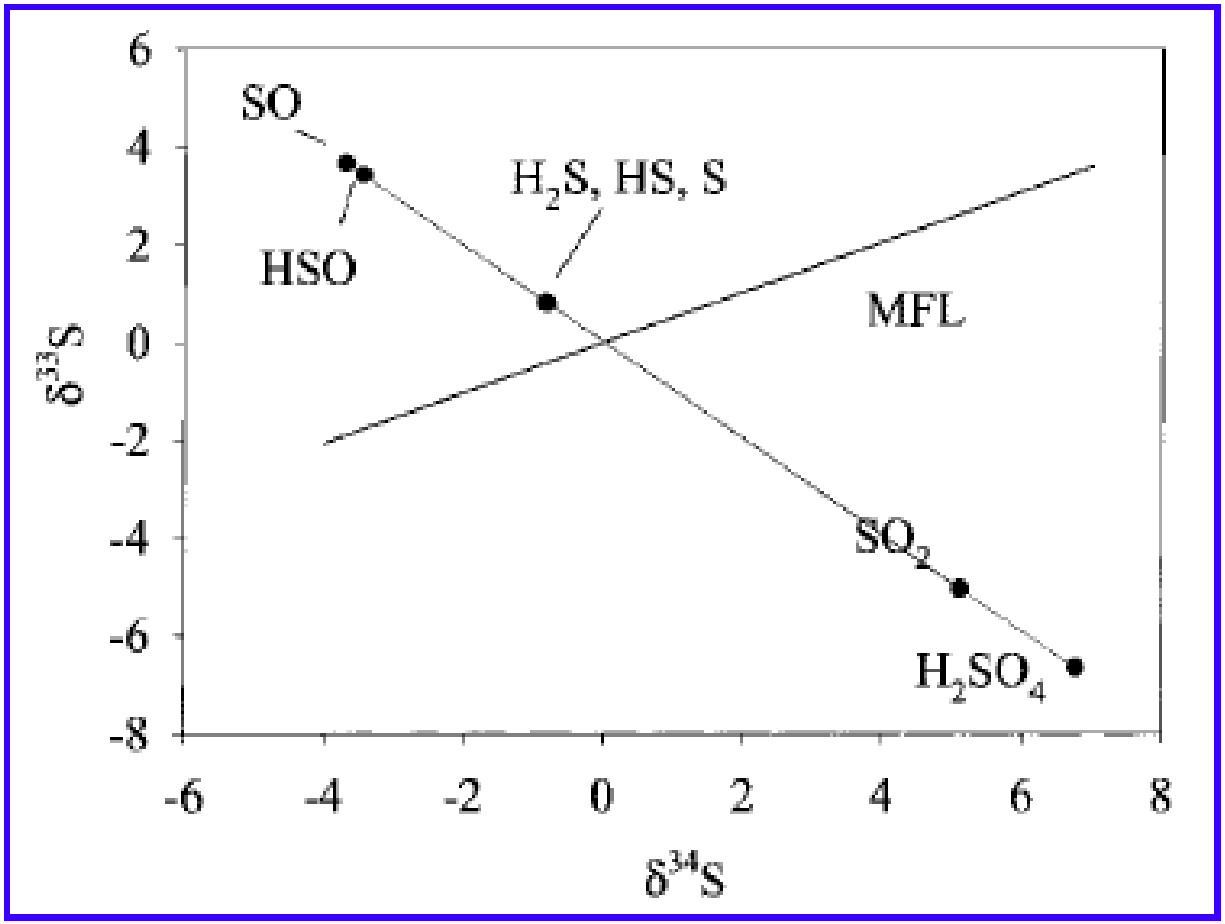


$SO_2 + h\nu \longrightarrow SO + O$ with $J(^{34}SO_2) = 0.99\ J(^{32}SO_2)$

$J(^{33}SO_2) = 0.99351\ J(^{32}SO_2)$

Source: Pavlov, A. A., and J. F. Kasting. "Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere." *Astrobiology* 2, no. 1 (2002): 27-41.

Stratospheric Photolyses Reactions

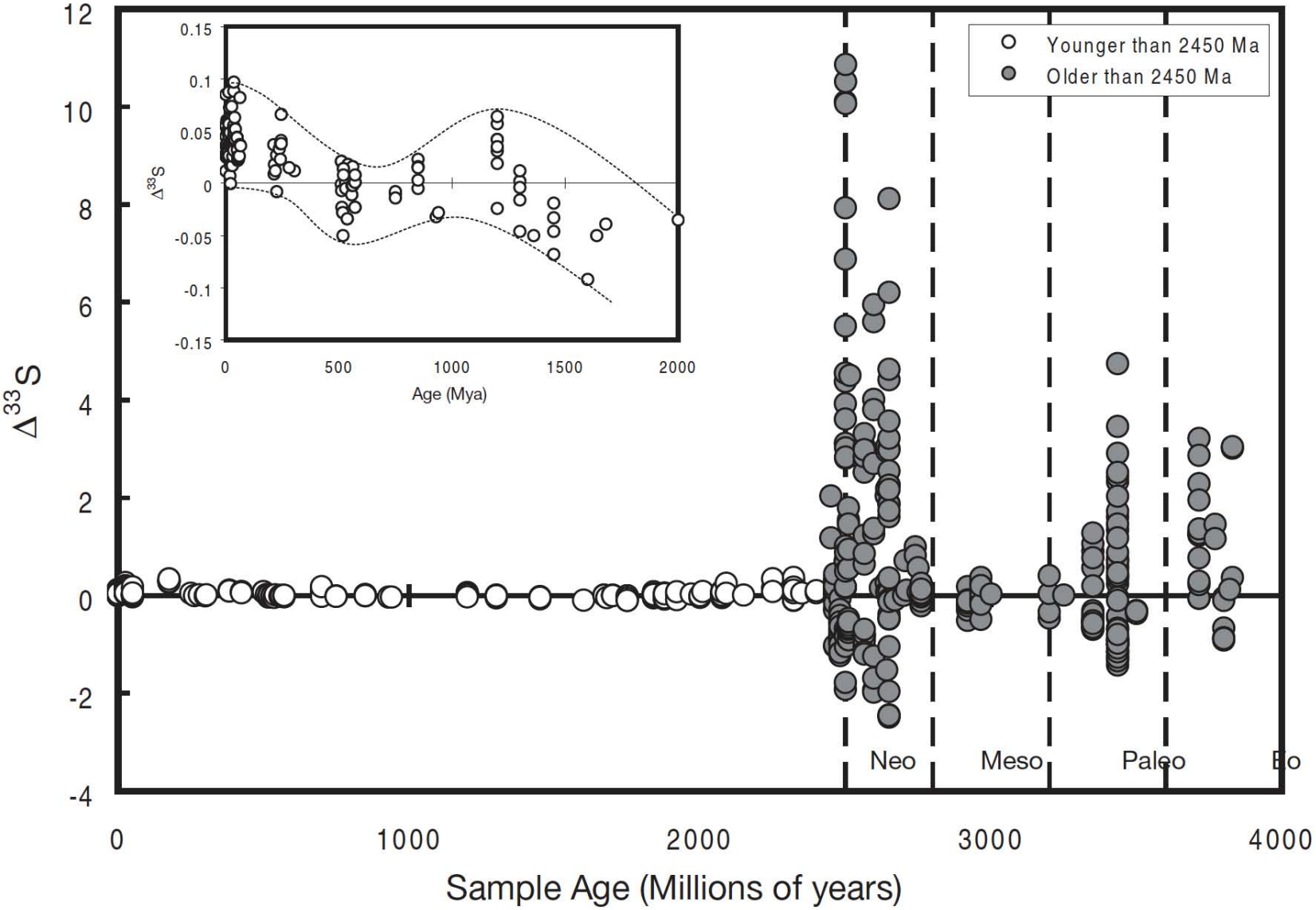


$SO_2 + h\nu \longrightarrow SO + O$ with $J(^{34}SO_2) = 0.99\ J(^{32}SO_2)$

$J(^{33}SO_2) = 1.01\ J(^{32}SO_2)$

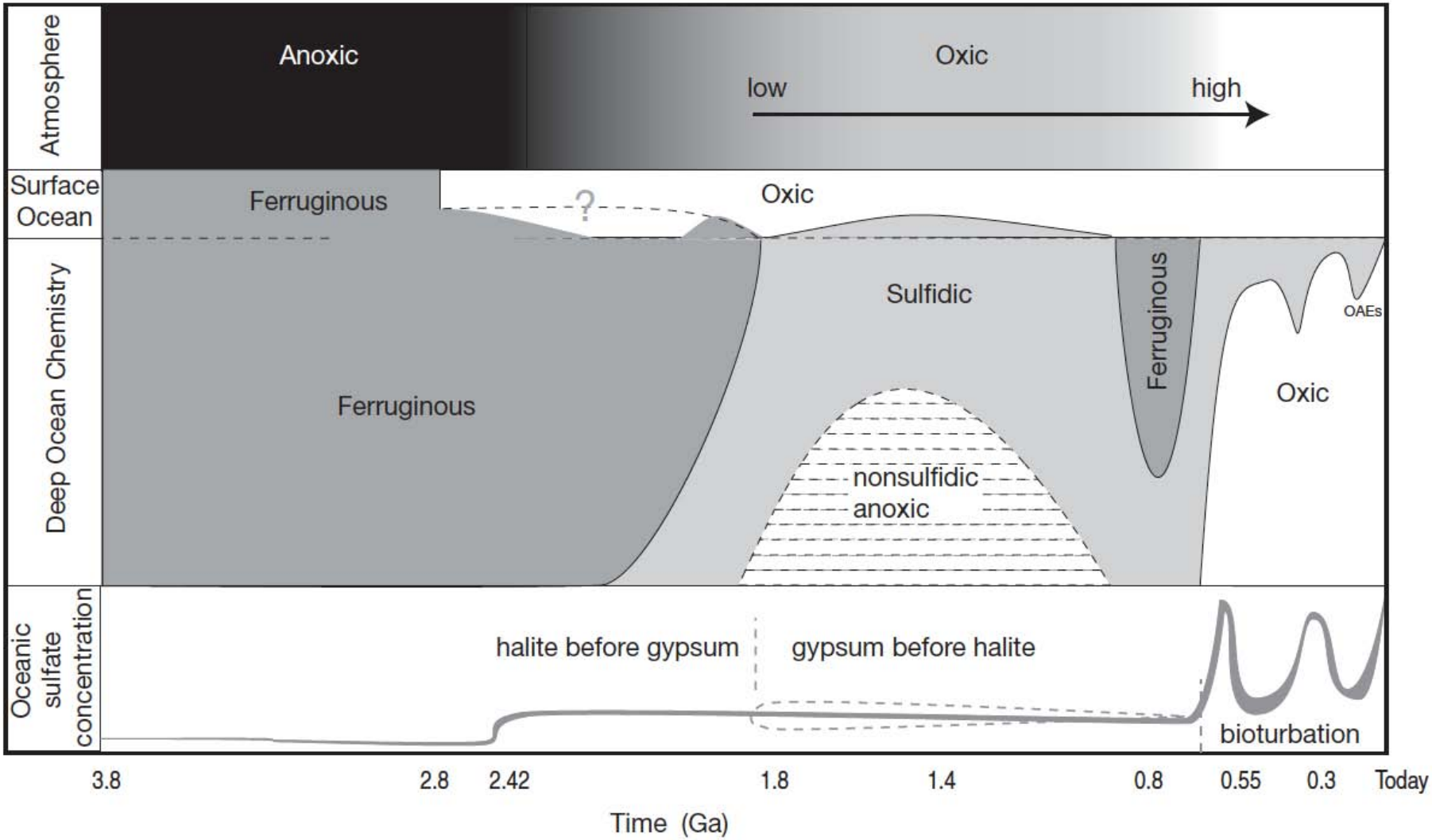
Source: Pavlov, A. A., and J. F. Kasting. "Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere." *Astrobiology* 2, no. 1 (2002): 27-41.

Record of Mass-Independent Sulfur Isotope Variations



Source: Figure 5 in Farquhar, James, Nanping Wu, et al. "Connections between Sulfur Cycle Evolution, Sulfur Isotopes, Sediments, and Base Metal Sulfide Deposits." *Economic Geology* 105, no. 3 (2010): 509-33.

Ideas and Models of Oxygenation of Atmosphere and Ocean



Source: Figure 5 in Farquhar, James, Nanping Wu, et al. "Connections between Sulfur Cycle Evolution, Sulfur Isotopes, Sediments, and Base Metal Sulfide Deposits." *Economic Geology* 105, no. 3 (2010): 509-33.

12.744 Marine Isotope Chemistry
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