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 $\text{O} + \text{O}_2$ 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)

Figure 8. Schematic diagram of the process of inverse predissociation for O + O₂ 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 ¹⁸O or ¹⁷O is substituted for ¹⁶O in O₂ and O₃ doubling the available quantum states available for transition.
Babikov et al. (2003) cartoon summarizing their calculations

\[ ^{16}\text{O} + ^{18}\text{O}^{18}\text{O} \]

ha

\[ ^{16}\text{O}^{18}\text{O} + ^{18}\text{O} \]

Fig. 2. Schematic for recombination processes forming ozone \(^{15}\text{O}^{18}\text{O}^{18}\text{O}\). 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: \(^{18}\text{O} + ^{15}\text{O}^{18}\text{O}\) on the left (green arrows) and \(^{16}\text{O}^{18}\text{O} + ^{18}\text{O}\) on the right (blue arrows). Metastable states in the \(\Delta\text{ZPE}\) part of spectrum (green) are formed exclusively from the \(^{16}\text{O} + ^{15}\text{O}^{18}\text{O}\) 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.

© Elsevier. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
Demonstration of “Mass-independent Fractionation” in the Laboratory

O₃ created in the lab from O₂, via electric discharge (Thiemens & Heidenreich, 1983)

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

Blue = O₃
Red  = O₂
Two labs

Plot of the first demonstration of a chemically produced mass independent isotope effect. Square symbols, ozone samples; circles, molecular oxygen reservoirs; m = δ¹⁷O/δ¹⁸O. The report Gao and Marcus successfully explains these observations.

© AAAS. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
Can define anomalous $^{17}\text{O}$ signal as:

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

average air used as standard, reported as parts per meg (1 in $10^5$)

empirically determined

Fig. 2. Isotopic composition of O$_3$ formed in laboratory experiments from oxygen with an isotopic composition at $\delta^{17}\text{O} = \delta^{18}\text{O} = 0$. Heavy O$_3$ is complemented by isotopically light residual oxygen. Errors associated with measurements are smaller than the symbols.

$\Delta^{17}\text{O} > 0$

$\Delta^{17}\text{O} < 0$

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

© AAAS. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

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 $\rightarrow$ eutrophic)
        - Eppley & Peterson (1979) Nature v282 p677
- Export production
  - Flux of carbon leaving euphotic zone
    - e-ratio = Export/Net $\sim$ f-ratio
Triple-Oxygen Isotope Pathways

**Stratosphere**

- $\text{O}_3 + \text{hu} \rightarrow \text{O}_2 + \text{O}^{(1D)}$
- $\text{CO}_2 + \text{O}^{(1D)} \rightarrow \text{CO}_3^*$
- $\text{CO}_3^* \rightarrow \text{CO}_2 + \text{O}^{(3P)}$

$\text{CO}_3^*$ is a short-lived collision complex; these reactions ultimately cause $\text{CO}_2$ enrichment in $^{17}\text{O}$ and $\text{O}_2$ depletion in $^{17}\text{O}$

50 years Rapid mixing

$\Delta^{17}\text{O} = 0$ per meg (relative to air), -391 per meg (relative to SMOW)

**Troposphere**

Air-sea $\text{O}_2$ exchange

- $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2$
- $\text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{H}_2\text{O} + 6\text{CO}_2$

Photosynthesis: $^{17}\Delta \rightarrow 250$ per meg
Respiration: no effect on $^{17}\Delta$

$\Delta^{17}\text{O} \rightarrow$

$^{17}\Delta = 0$-250 per meg

Modified from Juranek & Quay (2012)

Image by MIT OpenCourseWare
Schematic Oxygen Isotope Relationships

Meteoric water precipitation (0.534)
Ocean water
Sea of Galilee water
Holy Land Air (HLA Standard)

© AAAS. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
Remember – Mass-Dependent Fractionation:

**Equilibrium Fractionation:**

\[ \alpha_{2/1} = (\alpha_{3/1})^\beta \quad \text{with} \quad \beta = \frac{1/m_1 - 1/m_2}{1/m_1 - 1/m_3} \]

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

\( \beta = 0.5158 \)

**Kinetic Fractionation:**

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

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

\( \beta = 0.5083 \)

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

© Elsevier. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse. 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:  
\[
\delta^{18}O_{\text{SMOW}} = (X_{18}^\text{SMOW}/X_{18}^\text{atm} - 1) 10^3
\]
  
  = -22.96  
--Note that for small \(^{17}\Delta\) values, N/G, and thus \(\alpha^{18}_R\) is not well constrained.
Definitions:

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

or

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

or

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

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

- Steady state indicated at $\Delta^{17}$O vs HLA.
- Linear relationship between $\delta^{17}$O and $\delta^{18}$O with slope 0.52 and intercept 0.155.
- Diagram showing oxygen cycle with $O_2$.

Luz and Barkan, 2000

© source unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
Schematic Oxygen Isotope Relationships in the Mixed Layer

\[ \ln \delta^{17}O \]

\[ \ln \delta^{18}O \]

Slope = 0.518

\[ {\Delta}^{17} = 250 \text{ per meg} \]

Air O₂

Mixed layer O₂

Photo-synthetic O₂

Respiration

Image by MIT OpenCourseWare.
Oxygen Concentration in the Mixed Layer

O₂ concentration = Gross O₂ production − Respiration + Gas exchange

\[ h \frac{dC}{dt} = G - R + k (C_{sat} - C) \]

\[ G = \text{Gross O}_2 \text{ production by photosynthesis (e.g. in mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}) \]

\[ R = \text{O}_2 \text{ consumption by respiration} \]

\[ h = \text{Average height of mixed layer} \]

\[ C = \text{Concentration; } C_{sat} = \text{at saturation (e.g. in mmol O}_2 \text{ m}^{-3}) \]

\[ k = \text{Gas exchange coefficient for O}_2 \text{ (m d}^{-1}), \text{ proxy: Ar} \]

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 $\alpha_P$ and respiration $\alpha_R$. Subscripts $w$ and $sat$ denote isotope ratios of oxygen in seawater (H$_2$O) and dissolved O$_2$ in equilibrium with the atmosphere, respectively. Then:

\[ h \frac{d(CX_{diss})}{dt} = GX_w \alpha_p - RX_{diss} \alpha_R + k (C_{sat} X_{sat} - CX_{diss}) \]

=1
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

© source unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
Triple-Oxygen Isotope Pathways

**Stratosphere**

\[\text{O}_3^{\text{hu}} \rightarrow \text{O}_2 + \text{O}(^{1}\text{D})\]

\[\text{CO}_2 + \text{O}(^{1}\text{D}) \rightarrow \text{CO}_3^{*}\]

\[\text{CO}_3^{*} \rightarrow \text{CO}_2 + \text{O}(^{3}\text{P})\]

CO\(_3^*\) is a short-lived collision complex; these reactions ultimately cause CO\(_2\) enrichment in \(^{17}\)O and O\(_2\) depletion in \(^{17}\)O

50 years Rapid mixing

\[\Delta^{17}\text{O} = 0\text{ per meg (relative to air),} -391\text{ per meg (relative to SMOW)}\]

**Troposphere**

Air-sea O\(_2\) exchange

\[6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2\]

\[\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{H}_2\text{O} + 6\text{CO}_2\]

Photosynthesis: \[\Delta^{17}\text{O} \rightarrow 250\text{ per meg}\]

Respiration: no effect on \(^{17}\Delta\)

Mixed layer

Mixing, entrainment

Photic zone

\[\Delta^{17}\text{O} \rightarrow \]
Triple-Oxygen, Temperature and O₂/Ar at Bermuda (BATS)

7 July 1998

7 November 1998

23 March 1999

© AAAS. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

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

- **7 July 1998**: Thermocline $O_2$ max due to net accumulation of $O_2^{\text{photosyn}}$
- **7 November 1998**: In situ $O_2$ production, but uptake > production
- **23 March 1999**: Mixed layer > photic zone
  No photosyn. in thermocline

© AAAS. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

\[
    h \frac{d(CX_{\text{diss}})}{dt} = GX_w \alpha_p - RX_{\text{diss}} \alpha_R + k (C_{\text{sat}} X_{\text{sat}} - CX_{\text{diss}}) = 1
\]

By replacing \( R \) with \( G + k \left( C_{\text{sat}} \ldots C \right) \) and dividing each side by \( X_{\text{std}} \), the isotope ratio of the standard (atmospheric O\(_2\)), we can express \( \delta_{\text{diss}} O \) as a function of \( G/kC \), \( C/C_{\text{sat}} \) and \( \alpha_R \) according to:

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

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

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

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

\[
    \frac{N}{G} = (C/C_{\text{sat}} - 1) \left( \Delta^{17}O_{\text{diss}} - \Delta^{17}O_w \right) / \left( \Delta^{17}O_{\text{sat}} - \Delta^{17}O_{\text{dis}} \right)
\]
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.


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

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.

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

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

Note that two processes compete: 1) During LGM less CO₂ was available for exchange reactions, leading to less anomalous O₂ being formed, making Δ¹⁷O rise to its biological value (Effect: +70).
2) Biological productivity was lower during the LGM, leading to lower Δ¹⁷O.
Process 1) dominated

Results from the Greenland Ice Sheet Project 2 (GISP2) and Siple Dome ice cores. (a) δ¹⁸O of the ice, a proxy for local temperature [Groottes et al., 1993] from the GISP2 ice core, Greenland. (b) Δ¹⁷O 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.

© John Wiley & Sons. All rights reserved. This content is excluded from our Creative Commons license. For more information, see [http://ocw.mit.edu/help/faq-fair-use/](http://ocw.mit.edu/help/faq-fair-use/).
Net Terrestrial Productivity Record

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

Note that two processes compete: 1) During LGM less CO₂ was available for exchange reactions, leading to less anomalous O₂ being formed, making $\Delta^{17}\text{O}$ rise to its biological value (Effect: +70).
2) Biological productivity was lower during the LGM, leading to lower $\Delta^{17}\text{O}$

Process 1) dominated

Results from the Greenland Ice Sheet Project 2 (GISP2) and Siple Dome ice cores. (a) $\delta^{18}\text{O}$ of the ice, a proxy for local temperature [Grootes et al., 1993] from the GISP2 ice core, Greenland. (b) $\Delta^{17}\text{O}$ 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.

© John Wiley & Sons. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.
Two contrasting models for the evolution of atmospheric $O_2$

from Ohmoto, Geochem. News #93, Fall 1997
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 $\delta-\delta$ space:
- Fractionation: straight lines
- All processes represented in frame B fall along line

In $\Delta-\delta$ space:
- Fractionation: straight
- Mixing: curved loops

In $\Delta-\Delta$ space:
- Fractionation: straight
- Mixing: slightly curved loops

Uncertainty ($\sigma$) is a function of fractionation

© Elsevier. All rights reserved. This content is excluded from our Creative Commons license.
For more information, see http://ocw.mit.edu/fairuse.
Conventional vs. Modern mass spectrometry

© Elsevier. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
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

© Society of Economic Geologists, Inc. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

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

\[ \delta^{3x}S = \left\{ \left[ \frac{(^{3}S/^{32}S)_{s}}{(^{3}S/^{32}S)_{std}} \right] - 1 \right\} \times 10^{3} \]

© Elsevier. All rights reserved. This content is excluded from our Creative Commons license. For more information, see [http://ocw.mit.edu/fairuse](http://ocw.mit.edu/fairuse).

Detection of Mass-Independent Sulfur Isotope Variations

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

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

\[ \lambda = \frac{1/m_1 - 1/m_2}{1/m_1 - 1/m_3} \]

\[ m_1 = 32, \quad m_2 = 33, \quad m_3 = 34 \]

(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

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

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

These two expressions yield very similar solutions for the range of Earth materials (\(\delta^{34} S\) variations between -5% and 5%). \(\lambda\) 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

\[ \text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O} \quad \text{with} \quad J^{(34}\text{SO}_2) = 0.99 \; J^{(32}\text{SO}_2) \]

\[ J^{(33}\text{SO}_2) = 0.99351 \; J^{(32}\text{SO}_2) \]

 Courtesy of Mary Ann Liebert, Inc. Used with permission.
SO$_2$ + $h\nu$ → SO + O  with  $J^{(34}\text{SO}_2) = 0.99 J^{(32}\text{SO}_2)\$

$J^{(33}\text{SO}_2) = 1.01 J^{(32}\text{SO}_2)\$

Stratospheric Photolyses Reactions

Courtesy of Mary Ann Liebert, Inc. Used with permission.
Record of Mass-Independent Sulfur Isotope Variations

© Society of Economic Geologists, Inc. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
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

© Society of Economic Geologists, Inc. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.
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.