

The background of the slide is a photograph of a research vessel's deck. A CTD rosette, a metal frame holding several vertical sampling bottles, is suspended by a crane and being lowered towards the ocean. The scene is set at sunset or sunrise, with a colorful sky in shades of orange, yellow, and blue. The ocean surface is visible in the lower half of the image.

Triple Oxygen Isotopes for quantifying Gross Primary Production (GPP)

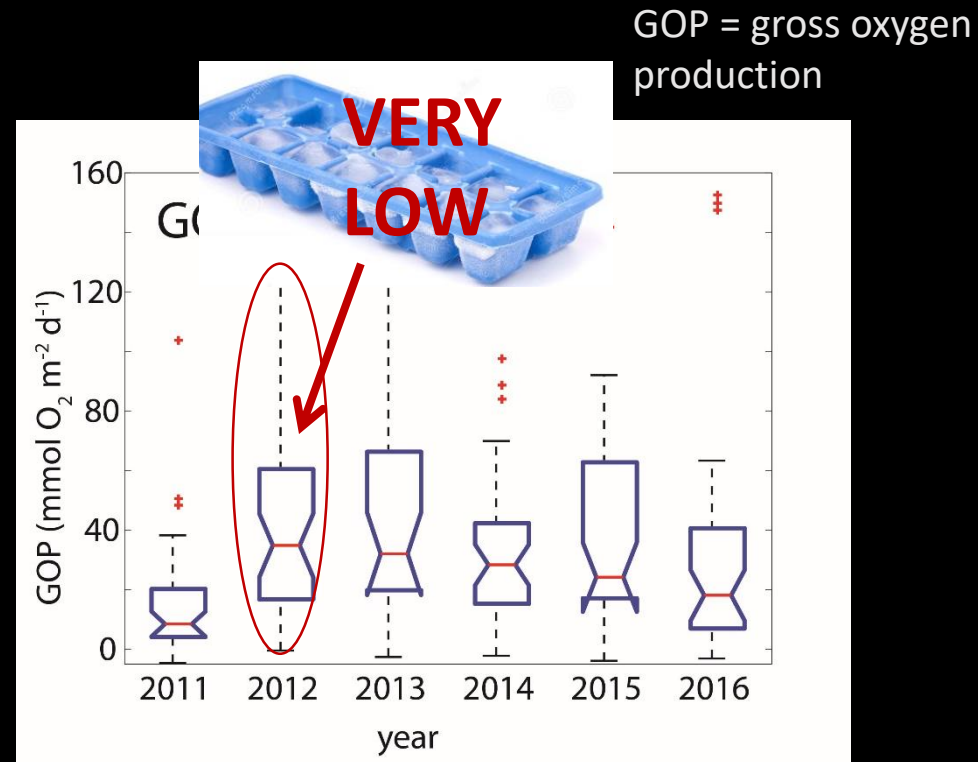
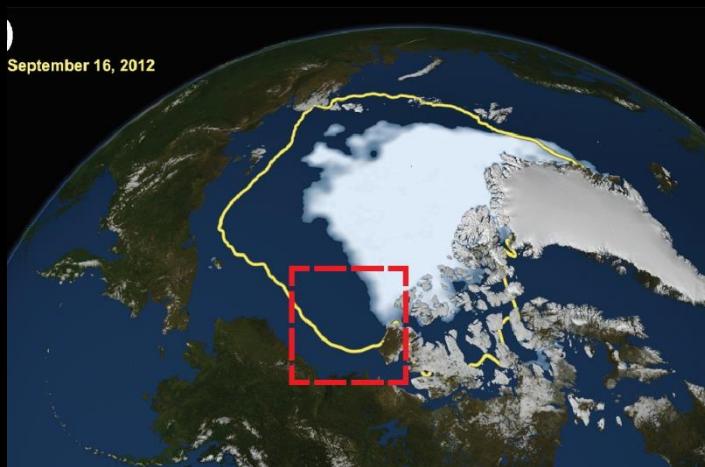
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Why measure GPP?

- GPP represents total energy available for the ecosystem (maximal production)
- interesting dynamics in combination with NCP

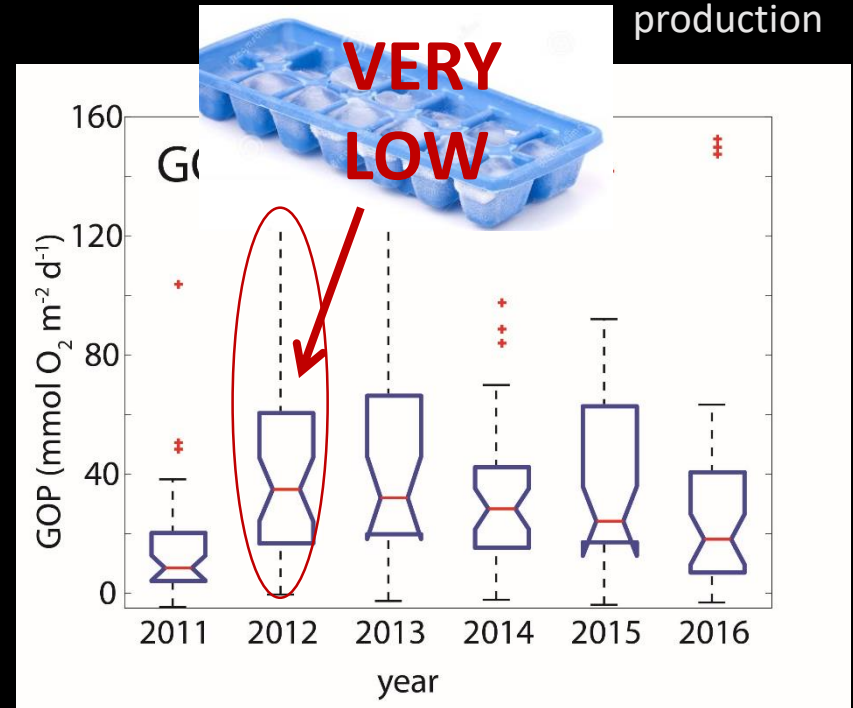
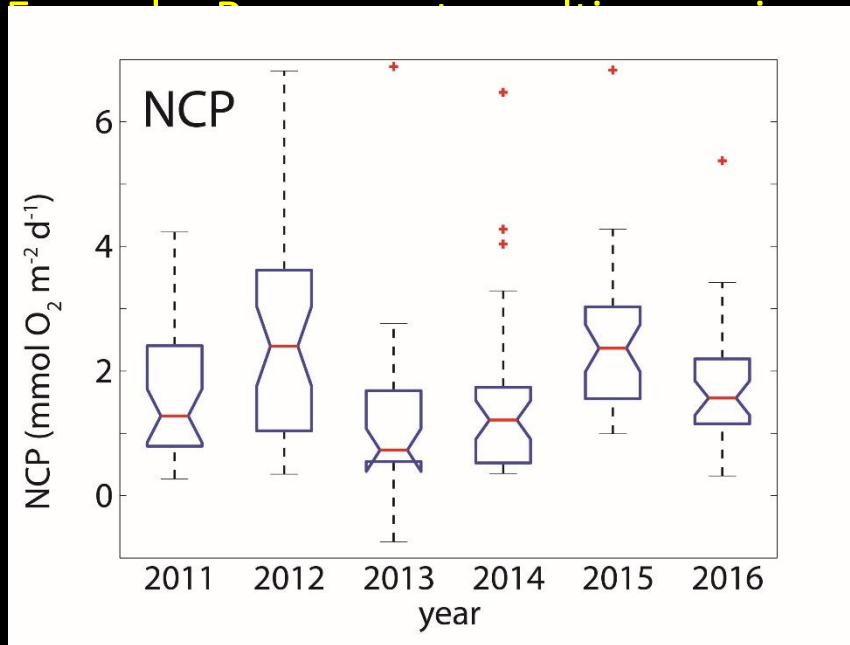
Example: Response to melting sea ice



From Ji et al., submitted

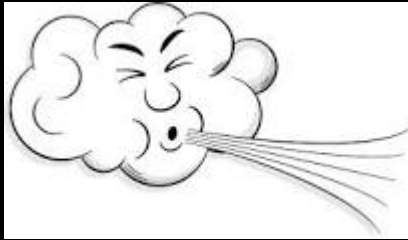
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- Particularly interesting dynamics in combination with NCP

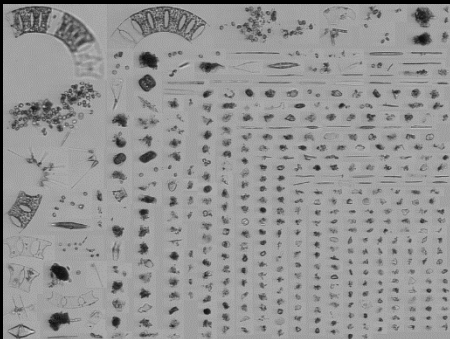


How does the method work?

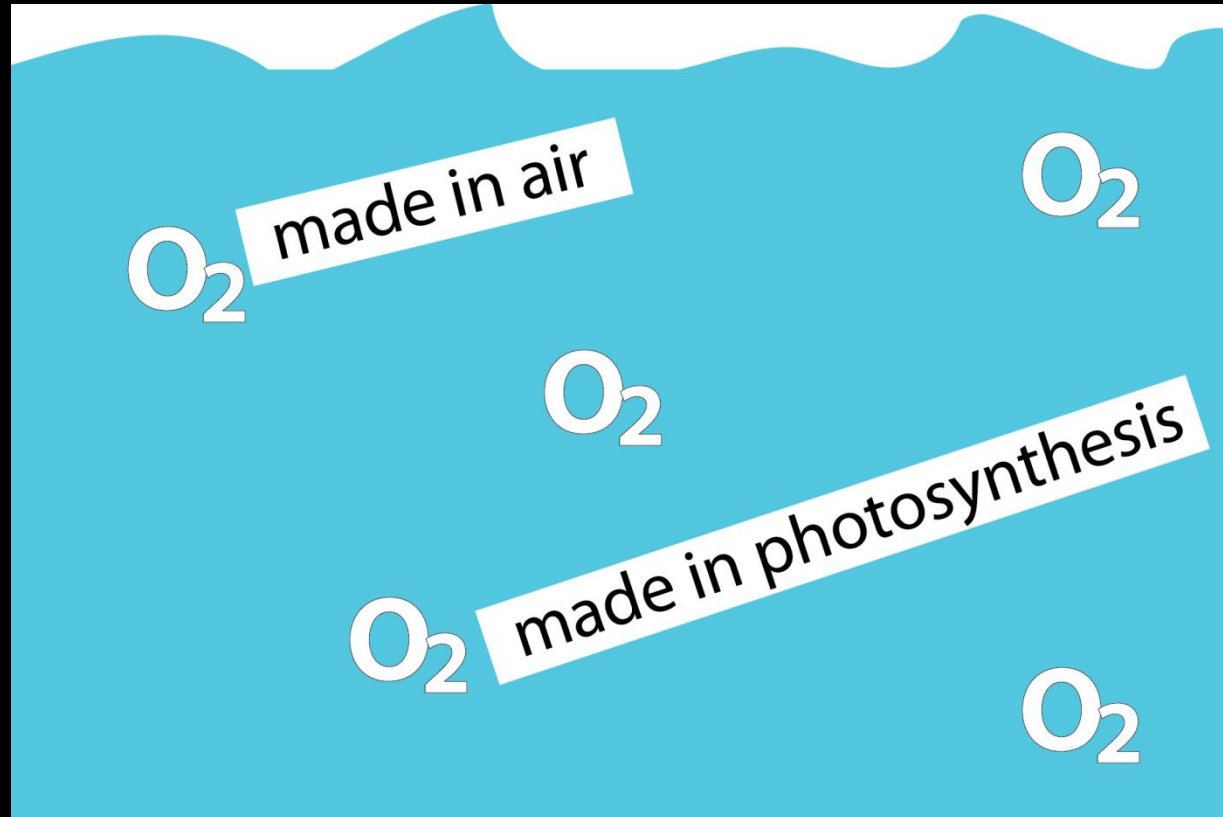
- Three isotopes of O: ^{16}O , ^{17}O , ^{18}O
- Ratio serves as a “made-in tag”



vs.



H. Sosik



GOP from Triple Oxygen Isotopes

$^{17}\Delta$ = measure of ratio of ^{16}O , ^{17}O , and ^{18}O
 $= \ln(\delta^{17}\text{O}/1000+1) - 0.5179 \ln(\delta^{18}\text{O}/1000+1) \times 10^6$

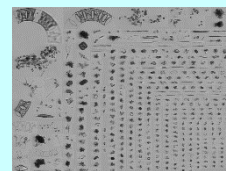
GOP = gross oxygen production

Atmosphere

UV Radiation \rightarrow Mass
mo

$$\text{GOP} = k\text{O}_{\text{eq}} \frac{\frac{X_{\text{dis}}^{17} - X_{\text{eq}}^{17}}{X_{\text{dis}}^{17}} - \lambda \frac{X_{\text{dis}}^{18} - X_{\text{eq}}^{18}}{X_{\text{dis}}^{18}}}{\frac{X_{\text{p}}^{17} - X_{\text{dis}}^{17}}{X_{\text{dis}}^{17}} - \lambda \frac{X_{\text{p}}^{18} - X_{\text{dis}}^{18}}{X_{\text{dis}}^{18}}}$$

Photosynthetic $\text{O}_2 \rightarrow$ Mass Dependent Fractionation
 derived from H_2O *more ^{18}O than ^{17}O*

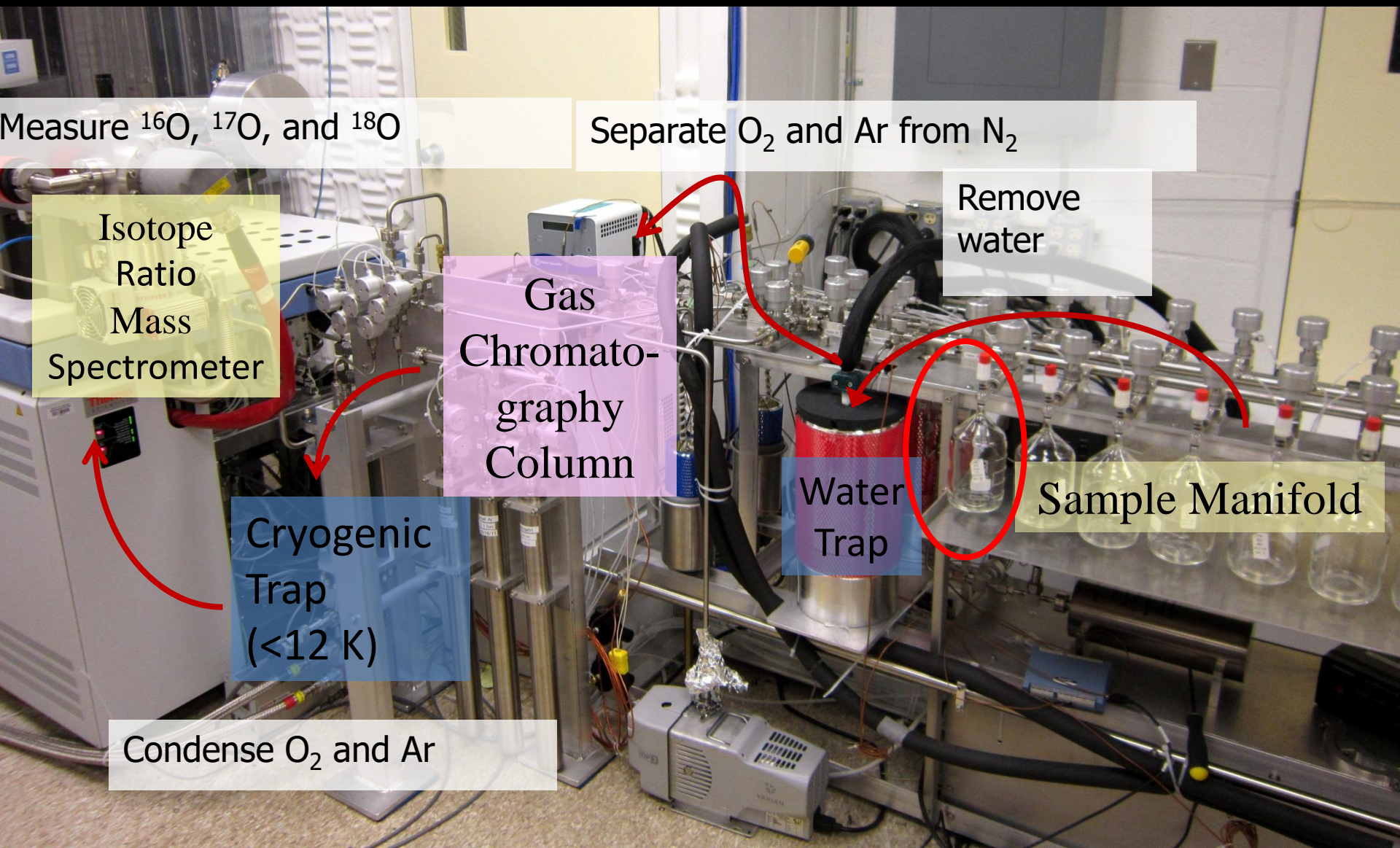


$^{17}\Delta$ of O_2 = 249 per meg

**Calculate
 GOP**

Ocean

Measuring Triple Oxygen Isotopes of O_2



Brief History

- Seminal papers by Luz et al. in 1999 and 2000 with simple equation
- Developed further by Michael Bender and Paul Quay in early 2000s...

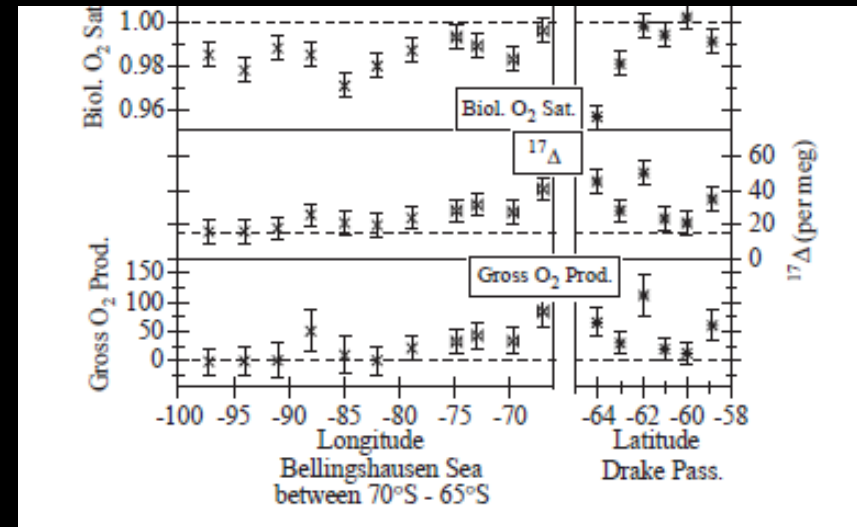
16 JUNE 2000 VOL 288 SCIENCE www.sciencemag.org

Assessment of Oceanic Productivity with the Triple-Isotope Composition of Dissolved Oxygen

Boaz Luz* and Eugeni Barkan

$$GP = KC_o(\Delta_{\text{diss}} - \Delta_{\text{eq}})/(\Delta_{\text{max}} - \Delta_{\text{diss}})$$

from Luz and Barkan, 2000



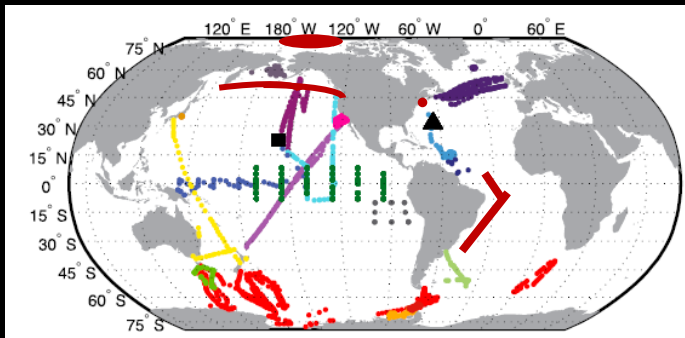
from Hendricks et al. 2004

Brief History

- Seminal papers by Luz et al. in 1999 and 2000 with simple equation
- Developed further by Michael Bender and Paul Quay in early 2000s...
- 2011 to present: equations developed further, 1D and 3D modeling, new considerations appear

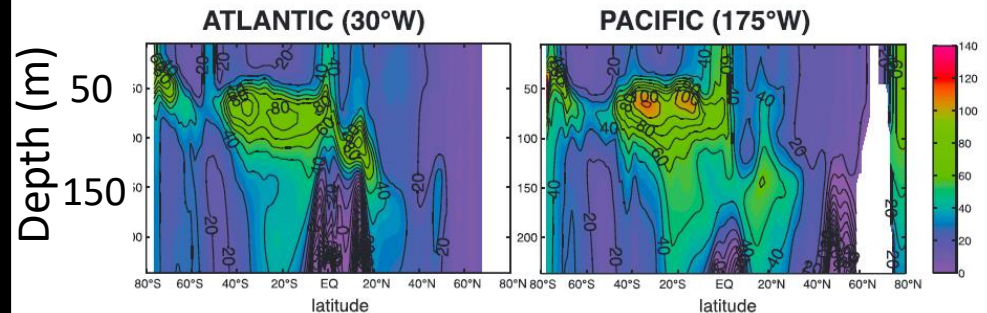
from Prokopenko et al., 2011

$$hO_{dis} \frac{\partial^{17}\Delta}{\partial t} = G \bullet \left[\frac{X_p^{17} - X_{dis}^{17}}{X_{dis}^{17}} - \lambda \frac{X_p^{18} - X_{dis}^{18}}{X_{dis}^{18}} \right] - kO_{eq} \bullet \left[\frac{X_{eq}^{17} - X_{dis}^{17}}{X_{dis}^{17}} - \lambda \frac{X_{eq}^{18} - X_{dis}^{18}}{X_{dis}^{18}} \right]$$



from Nicholson et al., 2014

$^{17}\Delta$ in 3D model



from Nicholson et al., 2014

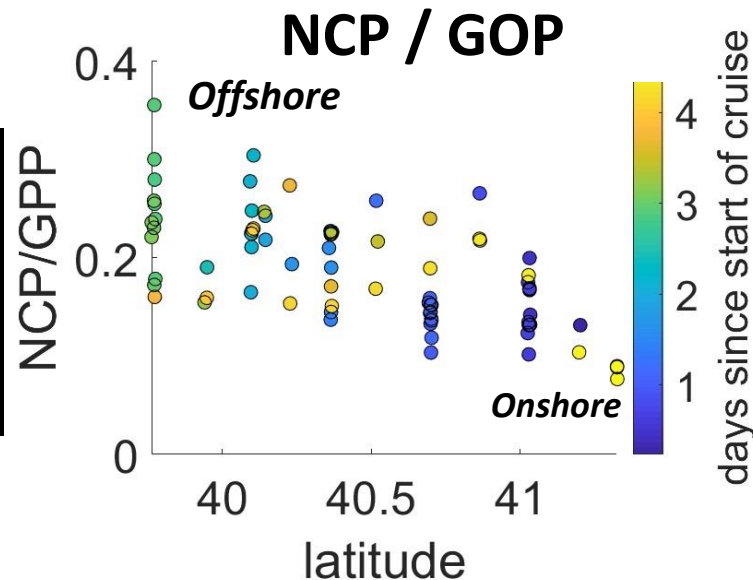
Advantages of TOI for GPP

- In situ technique: Doesn't disturb the biology!
- Don't need assumption that light = dark respiration
- Integrates over large spatial and temporal scales
- Relatively easy to collect (but hard to measure!) → enables hundred(s) of GOP rates per cruise
- Provides the NCP/GOP ratio: a measure of carbon cycle efficiency

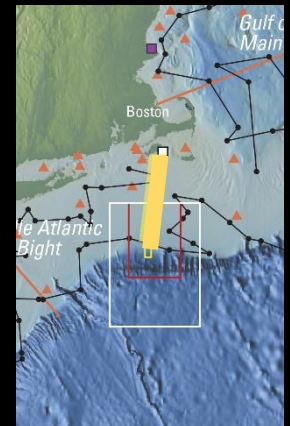


High Export =
Leaky

Low Export =
Efficient Recycling

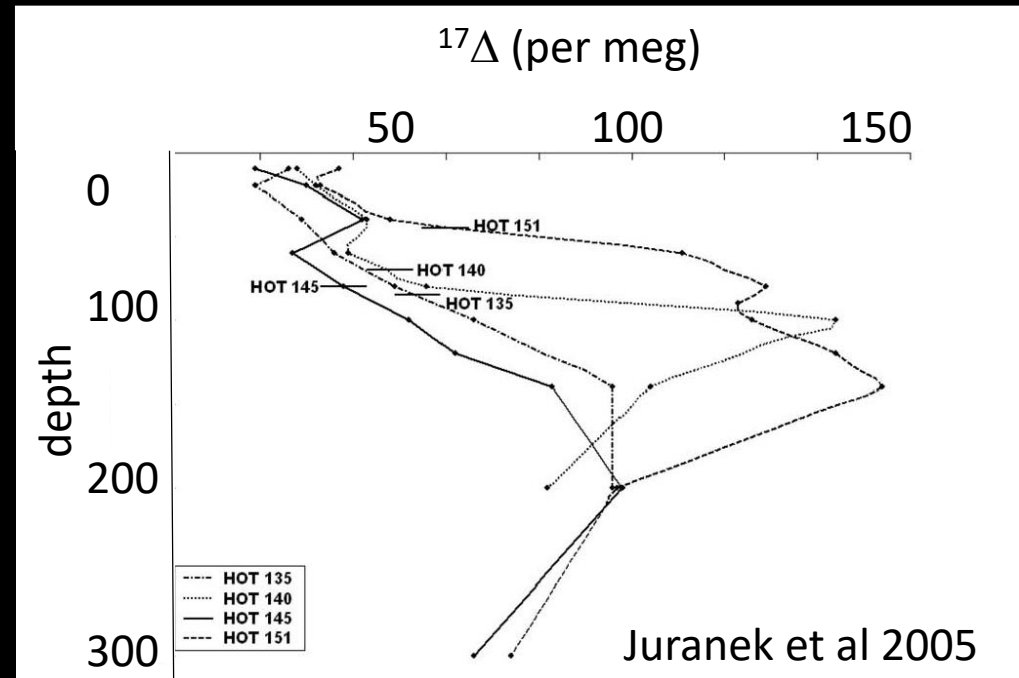
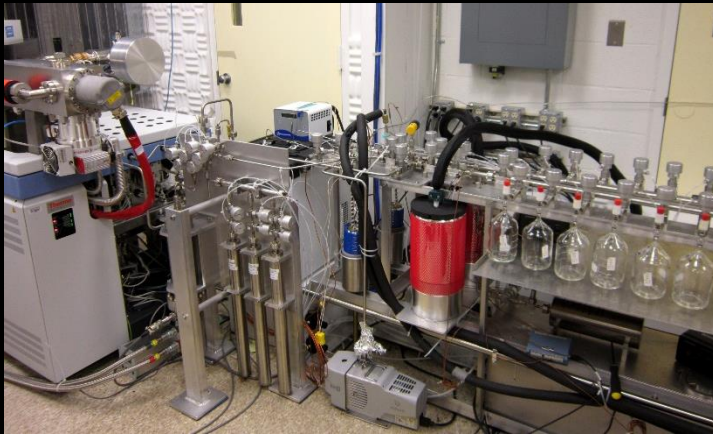


*Productivity on summer
New England shelf as
part of NES-LTER*



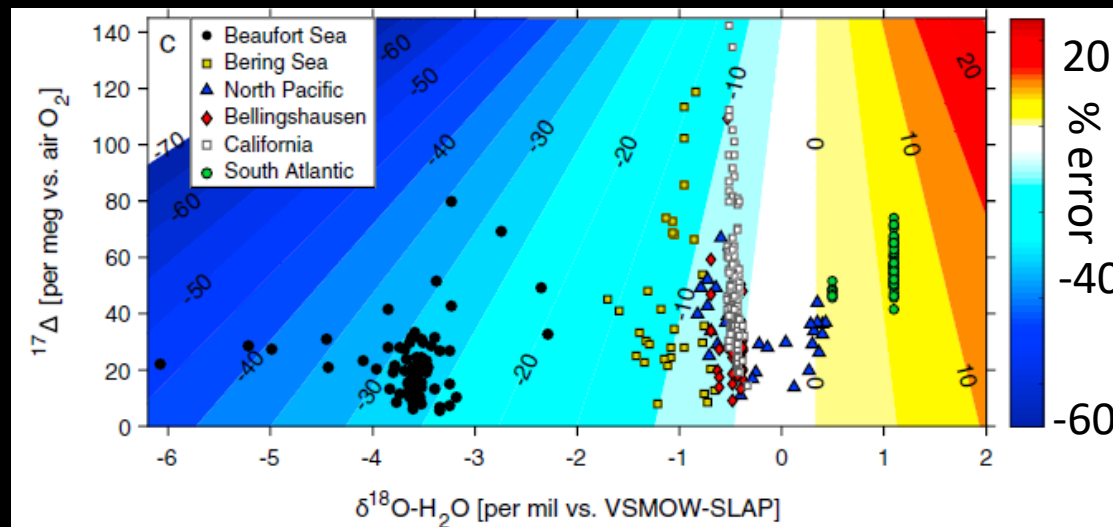
Disadvantages

- Need specialized equipment to measure samples
- Biases caused by physical transport and steady state assumption
- Usually used only to give rate integrated over mixed layer



Special Considerations

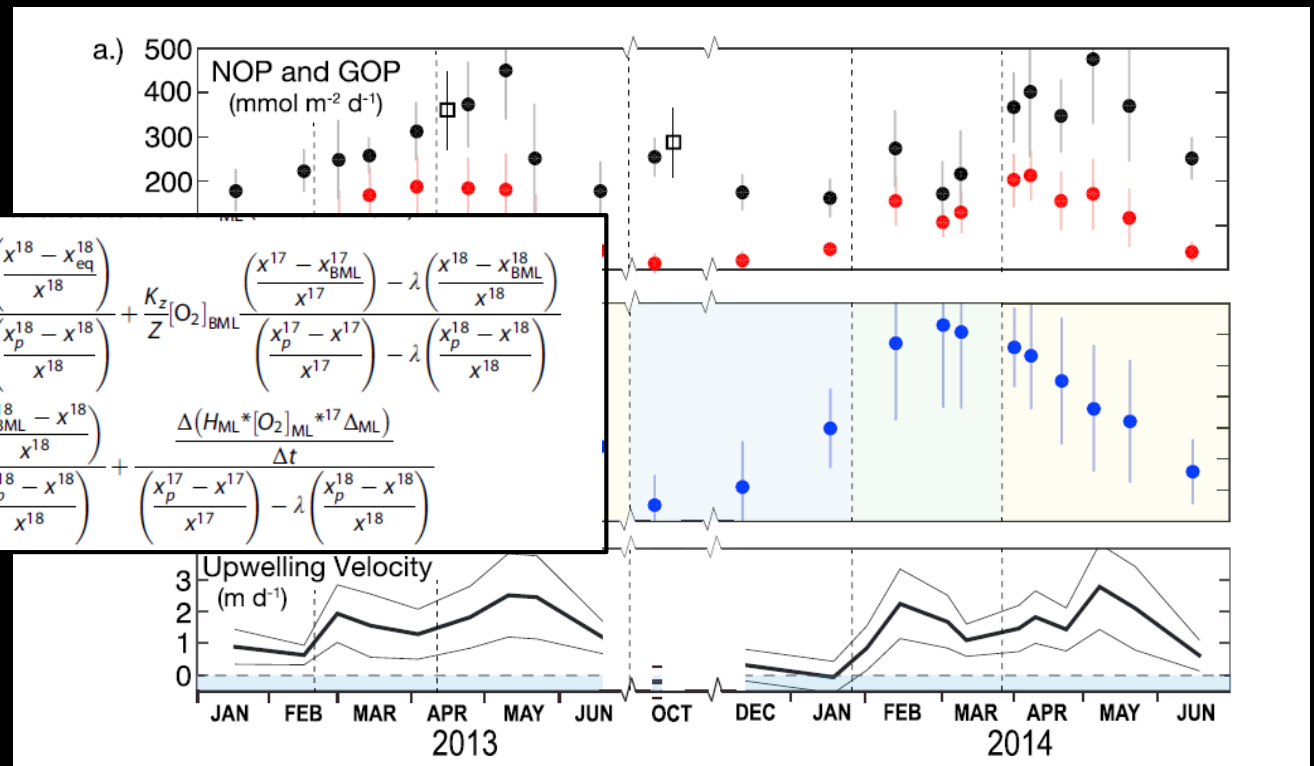
- Best to calculate photosynthetic end member from $\delta^{18}\text{O}$ of seawater (and $\delta^{17}\text{O}$ if possible)
- Cryogenic trapping really necessary in analysis
- Gives O_2 production \rightarrow Mehler reaction and photorespiration need to be taken into account if want carbon production



from Manning et al., 2017

Outstanding Questions

- How best to correct for lateral (and vertical) physical transport?
- What is best factor to use to estimate NPP from GPP?
- Are there processes that affect the $^{17}\Delta$ signature? Bubbles? Non-standard metabolism?

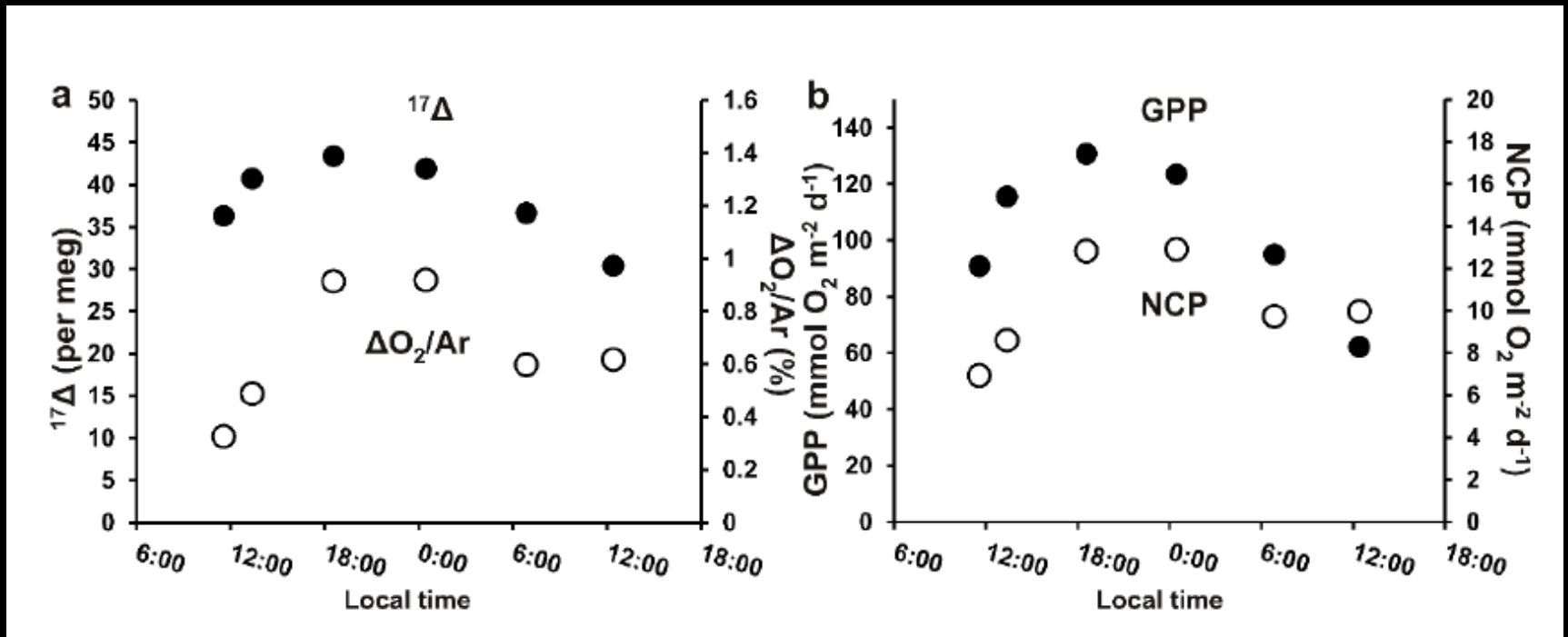


$$\begin{aligned}
 \text{GOP}_{\text{ML}} = & k[\text{O}_2]_{\text{eq}} \frac{\left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)}{\left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)} + \frac{K_z[\text{O}_2]_{\text{BML}} \left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)}{\left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)} \\
 & - w_H[\text{O}_2]_{\text{BML}} \frac{\left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)}{\left(\frac{x_p^{17} - x_p^{17}}{x^{17}} \right) - \lambda \left(\frac{x_p^{18} - x_p^{18}}{x^{18}} \right)} + \frac{\Delta(H_{\text{ML}}^*[\text{O}_2]_{\text{ML}}^{*17} \Delta_{\text{ML}})}{\Delta t}
 \end{aligned}$$

Extra slides

Diel Cycles in $^{17}\Delta$

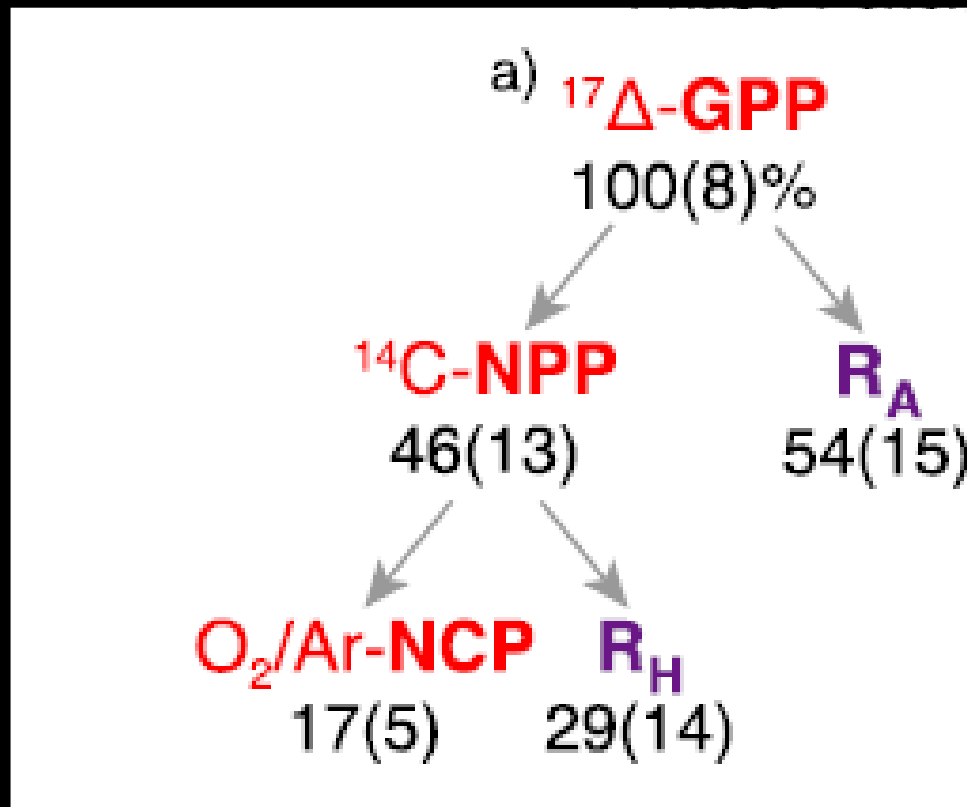
Sometimes diel cycles are observed despite expected time scale of O_2



From Howard et al., 2017

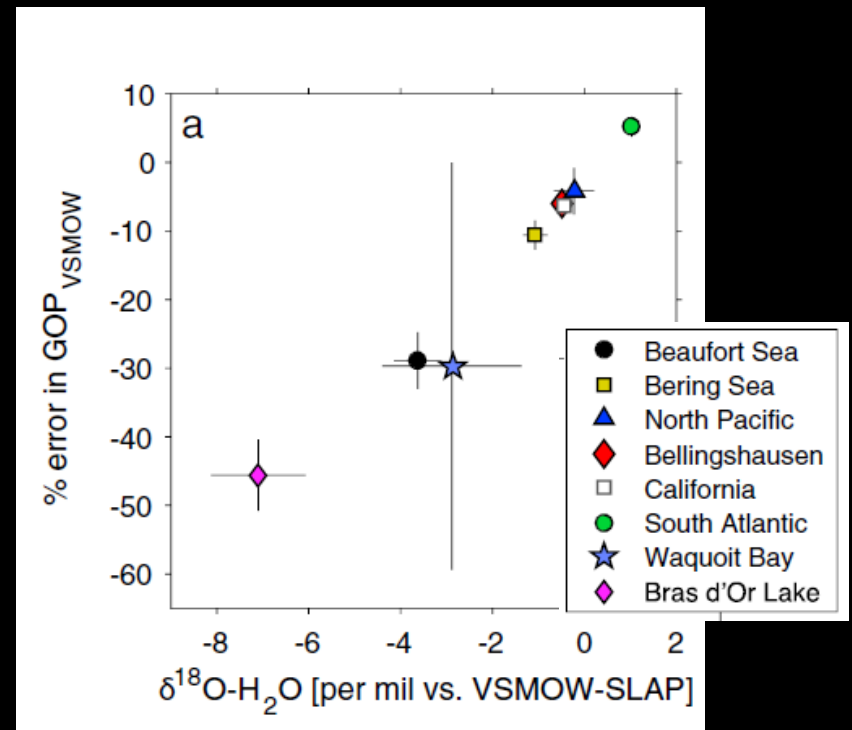
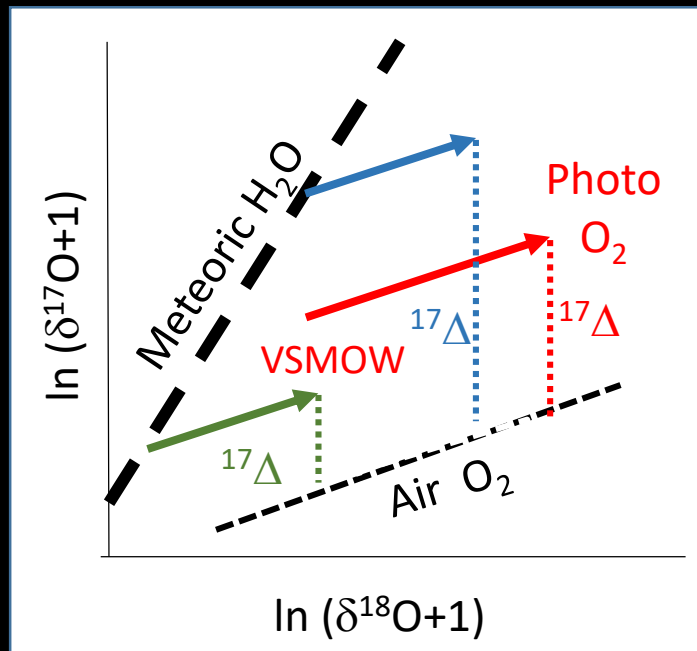
Energy flow diagrams

- Can be constructed if GPP, NPP and NCP are all measured



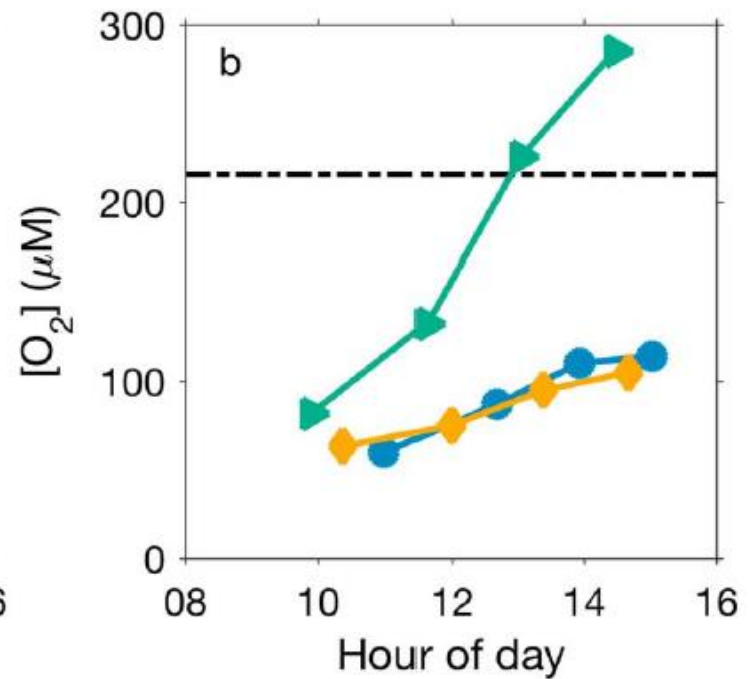
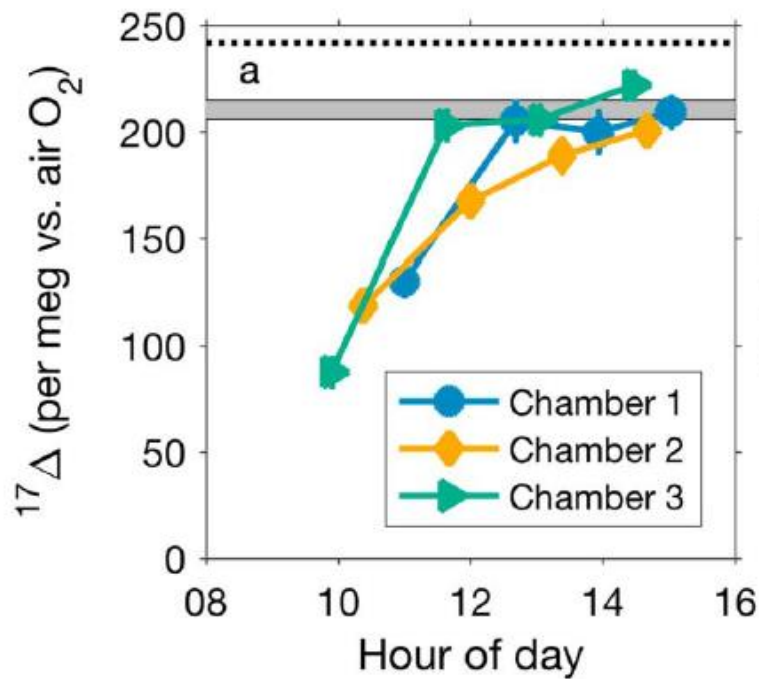
from Manning et al., 2017b

Why the isotopic composition of seawater matters



modified from Manning et al., 2017

Photosynthetic End Member



modified from Manning et al., 2017

Biases in GOP from $^{17}\Delta$ method

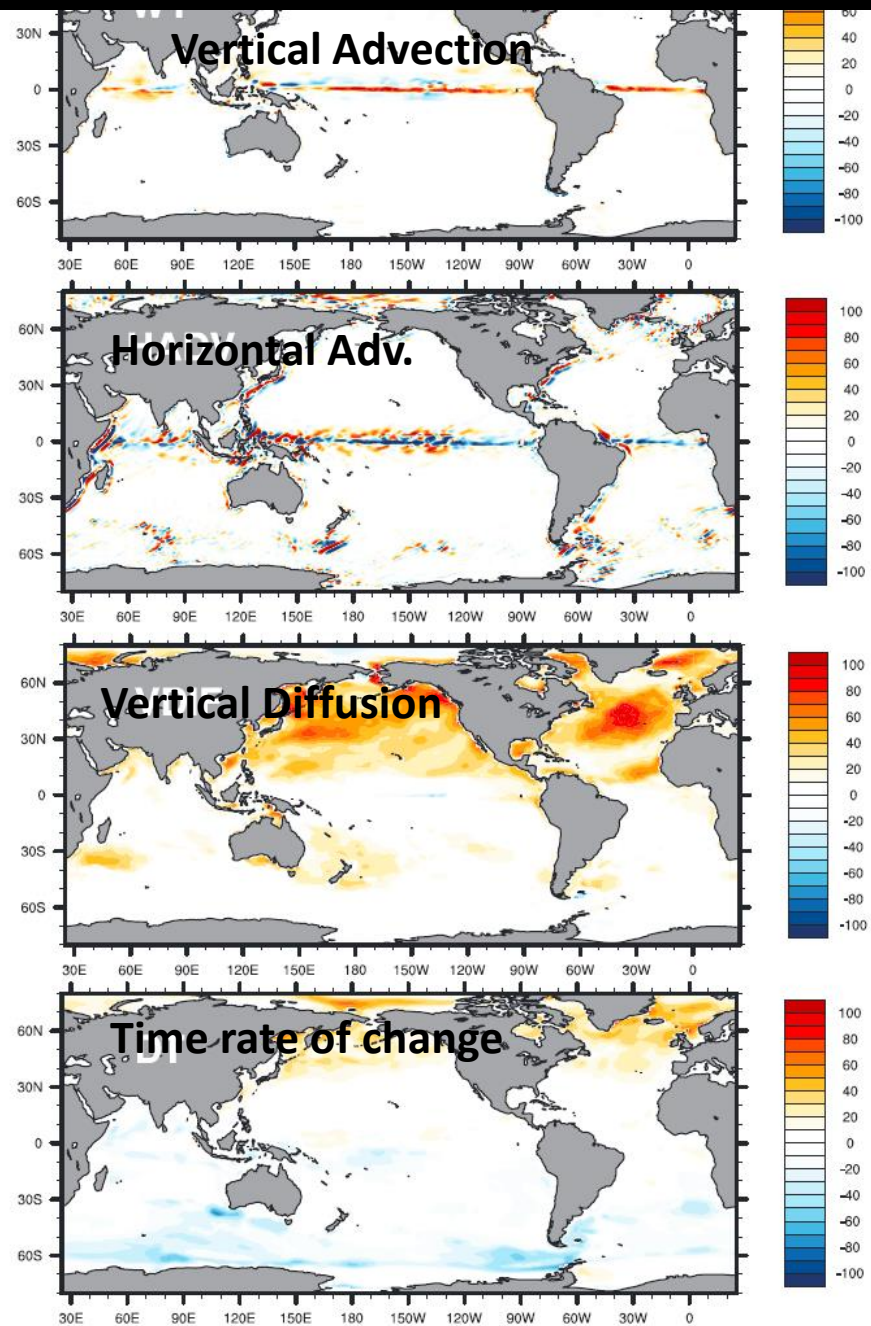


Figure 9

from Nicholson et al., 2014

Photosynthetic Electron Flow

