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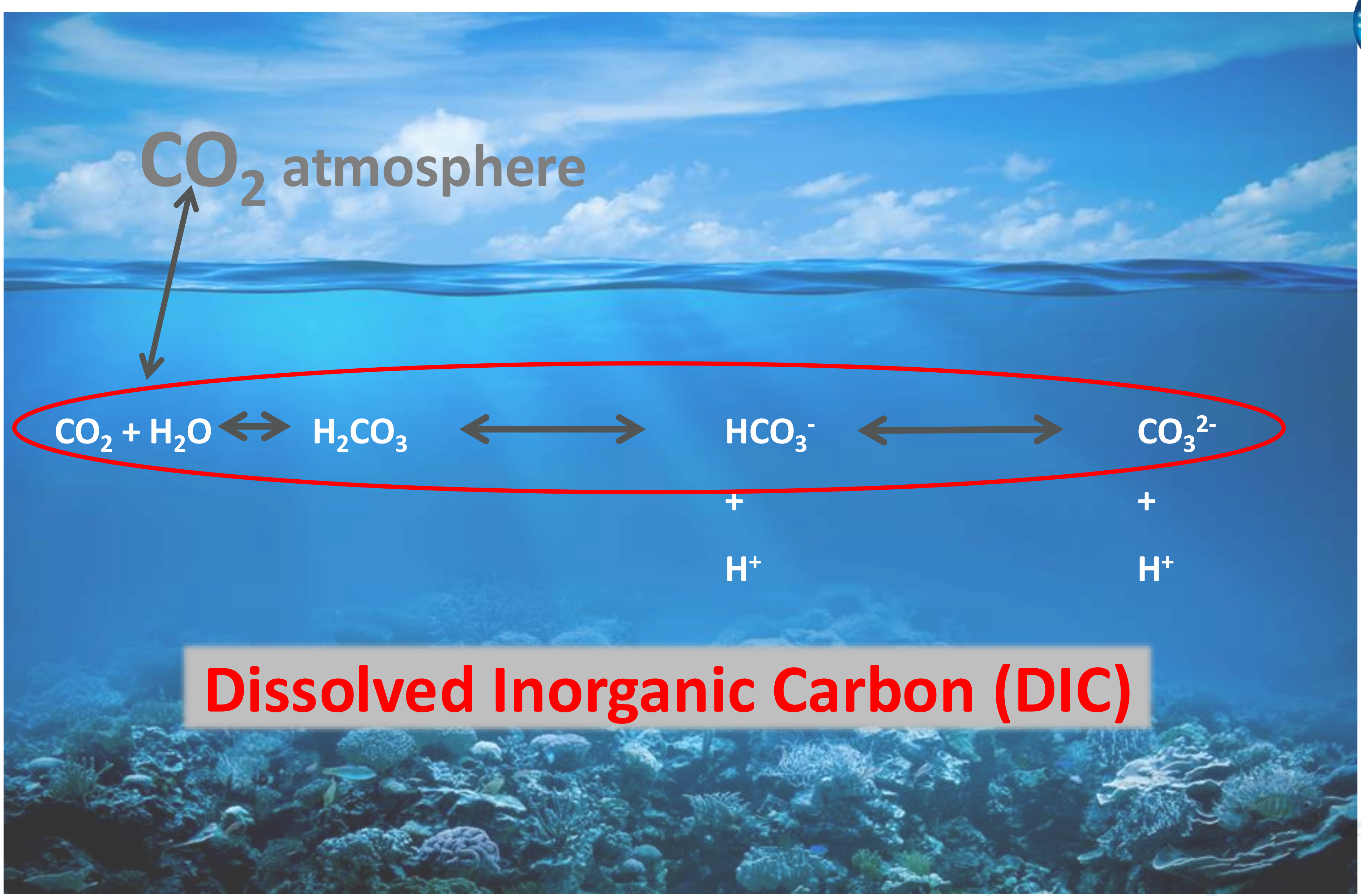
EUROMARINE SUMMER SCHOOL

"PulseOcean: Taking an interdisciplinary pulse on ocean under global change"

"Ocean Acidification and Macrophytes: Photosynthesis, Respiration, & Calcification"

Irene Olivé, Stazione Zoologica Anton Dohrn

Inorganic Carbon chemistry in seawater


CO_2 atmosphere
$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$
$+ H^+$
$+ H^+$
Dissolved Inorganic Carbon (DIC)

Quantifying C chemistry in seawater

- If we want to evaluate the DIC "status" of the ocean and know "how" will behave the ocean in the future ("Sink or Source of CO_2") we need to have estimates of ALL elements (DIC, pH, CO_2, HCO_2^-, CO_3^{2-}, pCO_2, Ω, A_T)

- Measuring pH, DIC; A_T, pCO_2 is feasible
- Measuring CO_2, HCO_2^-, CO_3^{2-} in seawater is DIFFICULT

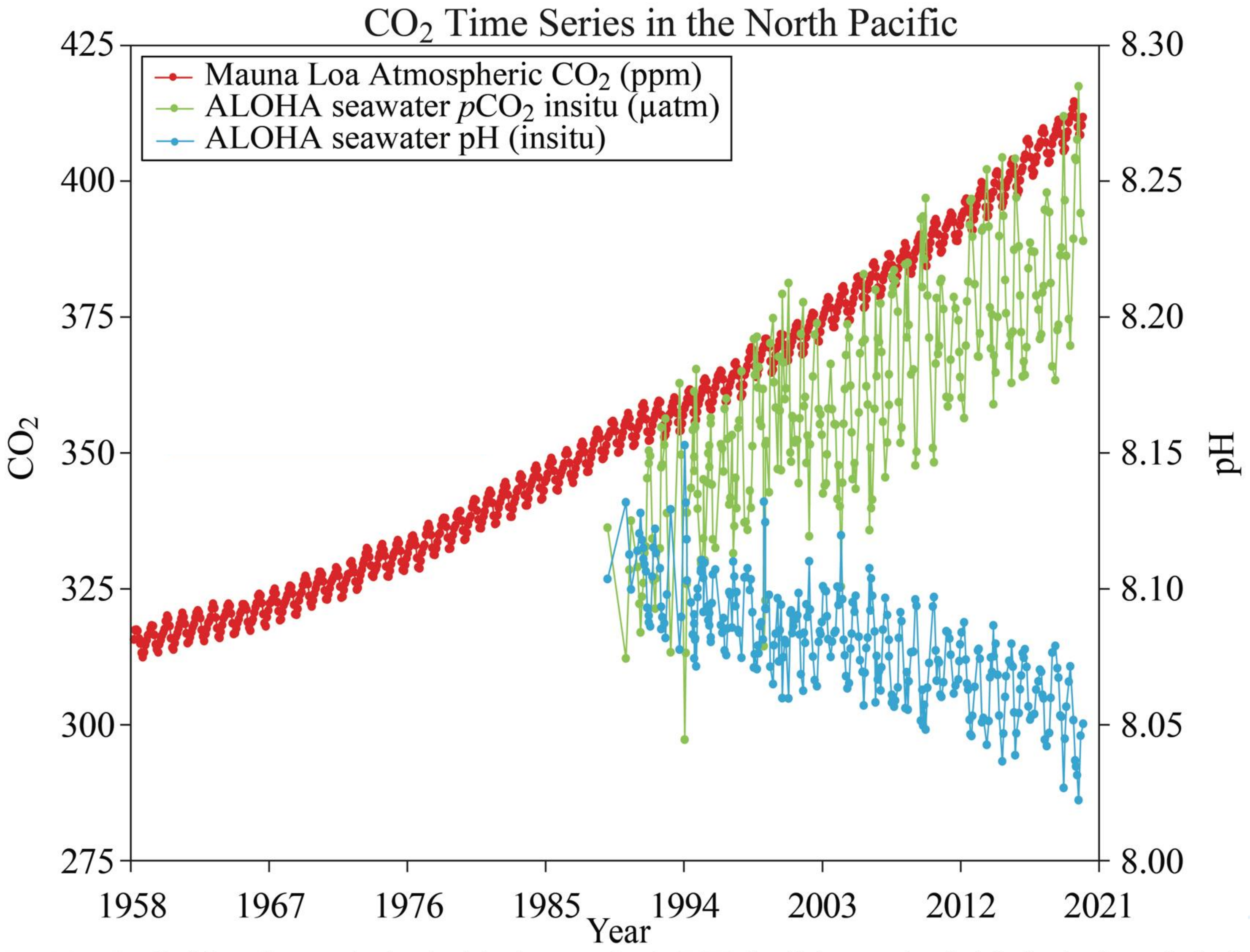
BUT since 3 equilibrium constants (K_0, K_1, K_2) links all concentrations...

$$K_0 = \frac{[CO^2]}{mCO_2 \cdot p} \qquad K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \qquad K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3-]}$$

- There are only 2 degrees of freedom –> This implies that only two of the aqueous concentrations can be varied independently of one another.

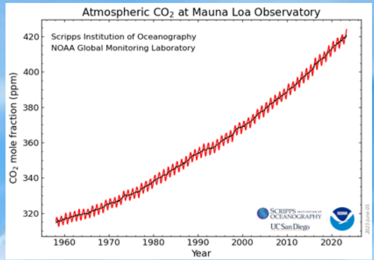
In other words**, If we measure 2 parameters, we can have it all**

Atmospheric CO_2 is rising and seawater too



Data: Mauna Loa (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_mm_mlo.txt) ALOHA (http://hahana.soest.hawaii.edu/hot/hot-dogs/bextraction.html)
ALOHA pH & pCO_2 are calculated at in-situ temperature from DIC & TA (measured from samples collected on Hawaii Ocean Times-series (HOT) cruises)
using co2sys (Pelletier, v25b06) with constants: Lueker et al. 2000, KSO4: Dickson, Total boron: Lee et al. 2010, & KF: seacarb

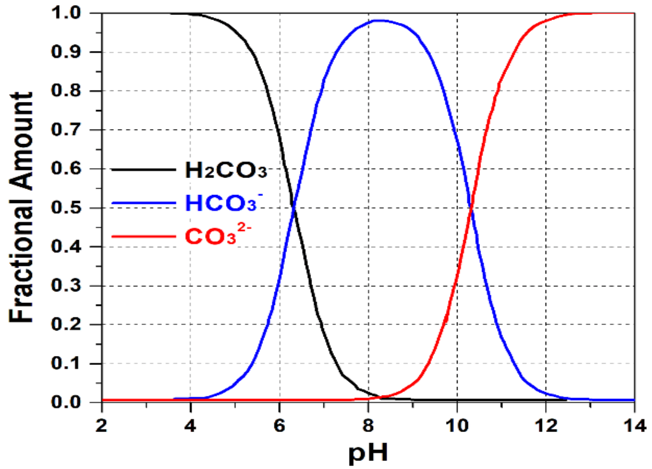
$\uparrow$ CO_2 atmosphere



$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+$

$\uparrow$ DIC $\downarrow$ pH

Ocean Acidification



- Increase Dissolved CO_2
- Increased DIC
- Increase bicarbonate HCO_3^-

- Decrease carbonate CO_3^{2-}
- Increase H^+, decrease pH
- Decrease saturation state calcium carbonate (Ω)

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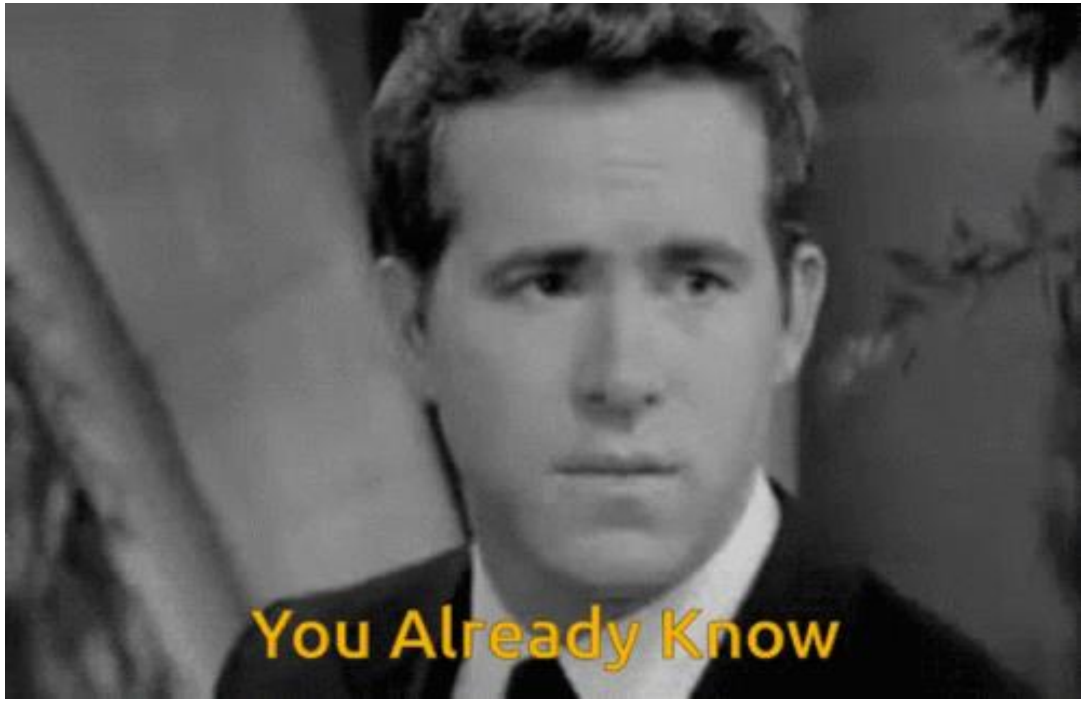
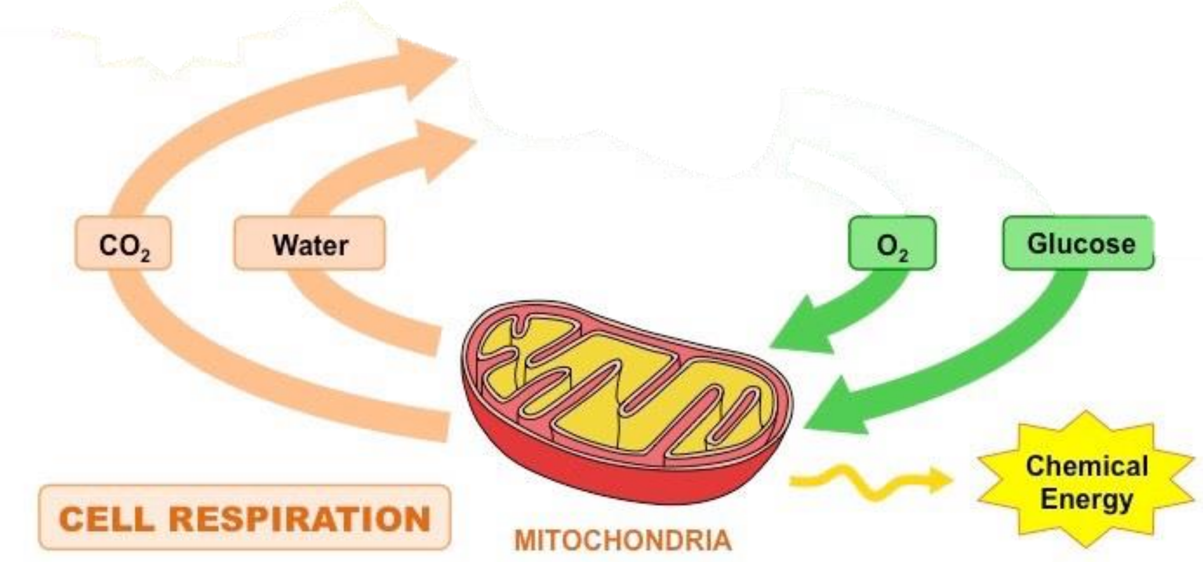
Biology also affects carbon chemistry in seawater



IF YOU ARE ALIVE, YOU BREATH

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

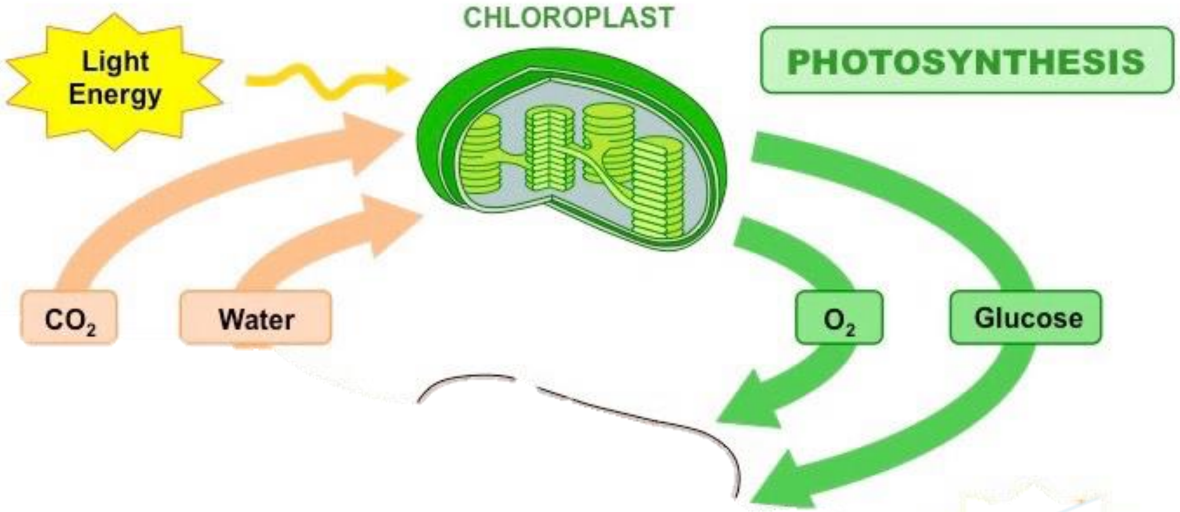
Respiration (R)



If you also have chloroplasts

Photosynthesis (P)

$$CO_2 + H_2O \longrightarrow CH_2O + O_2$$

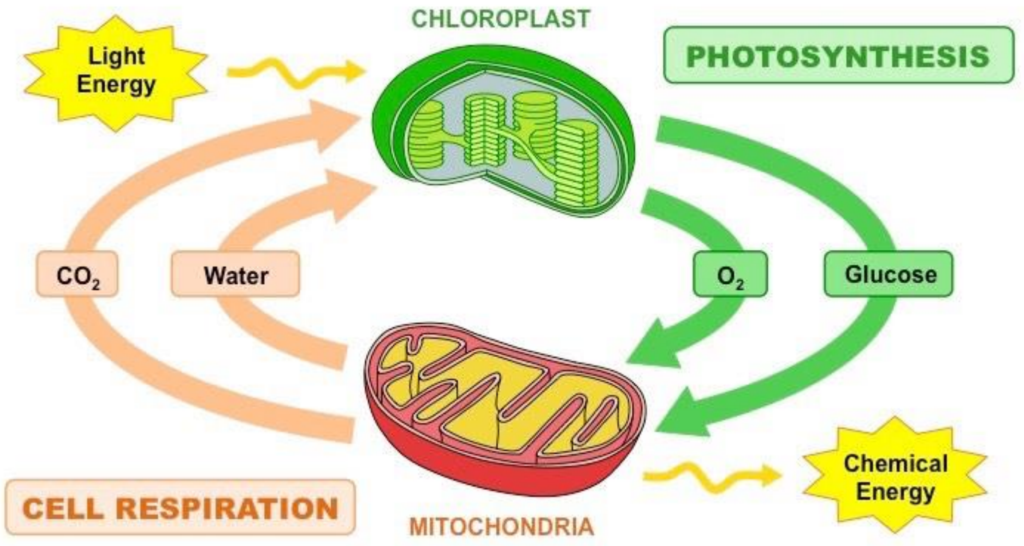


If you are alive and have chloroplasts

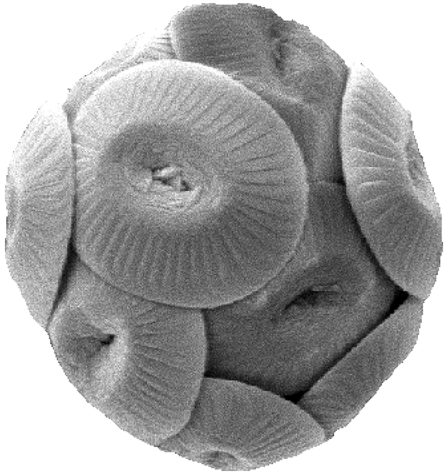
Photosynthesis (P)

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

Respiration (R)



If an organism feels it "ROCKS"



Calcification (C)

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O$$

Dissolution (decalcification) (D)

Biology also affects C chemistry in seawater

Photosynthesis (P)

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

Respiration (R)

Calcification (C)

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O$$

Dissolution (D)

- **P and D removes CO_2**
- **R and C releases CO_2**

Biology also affects C chemistry in seawater

How can we evaluate changes due to biological activity?

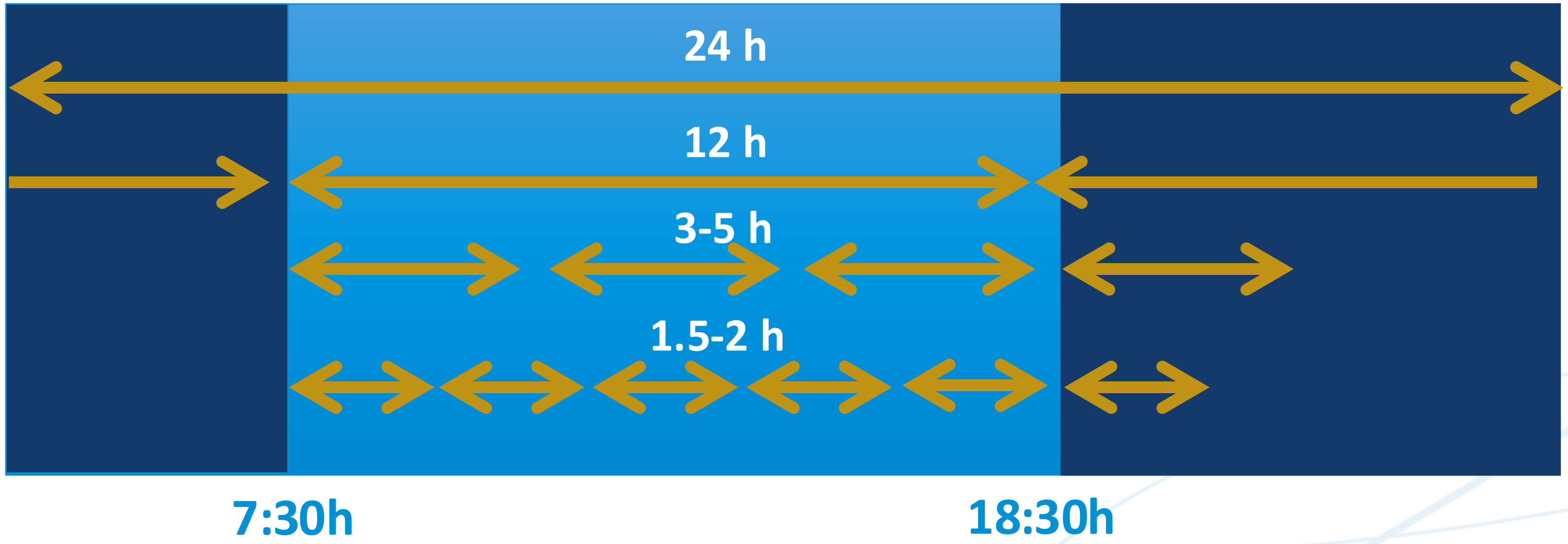
Some examples

Estimation of NCP of *Posidonia oceanica*

- Net Community Production (NCP)
- *Posidonia oceanica*
- Incubation chambers
- Oxygen by Winkler method by spectrophotometry

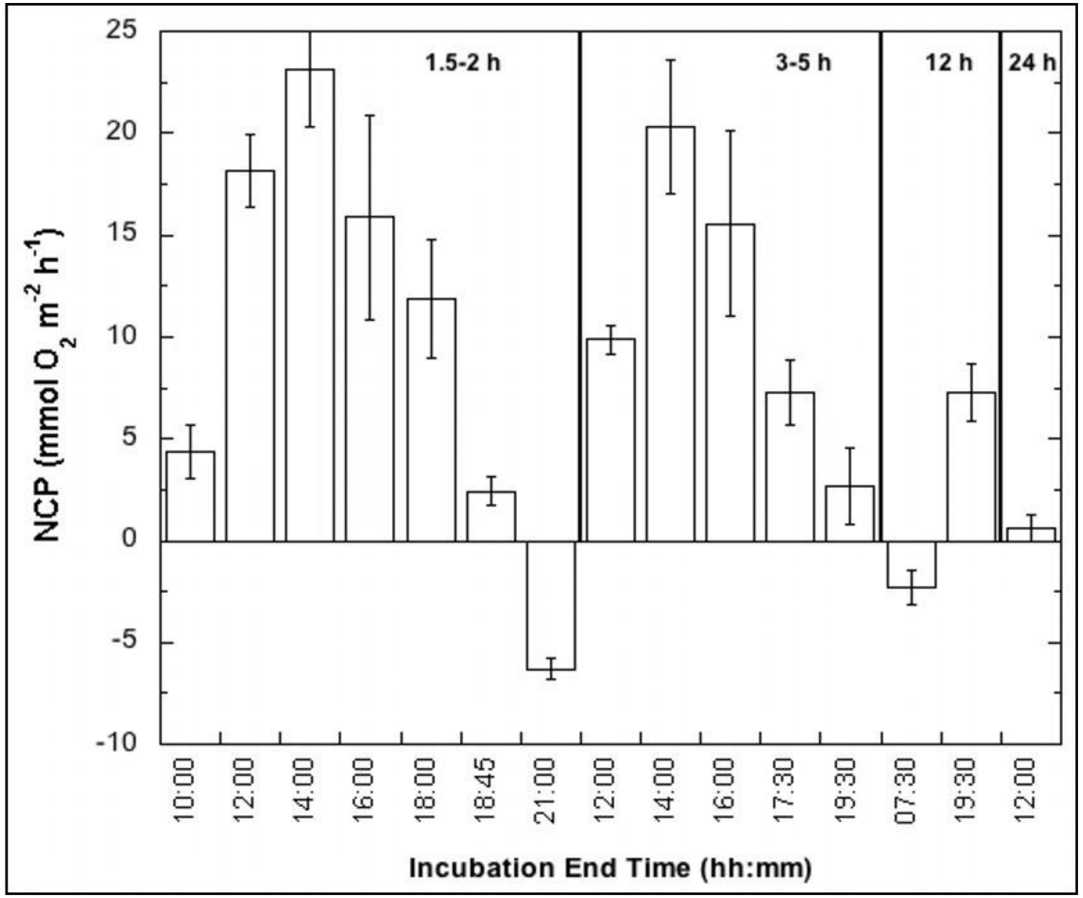
Olivé et al. (2016)

Estimation of NCP of *Posidonia oceanica*



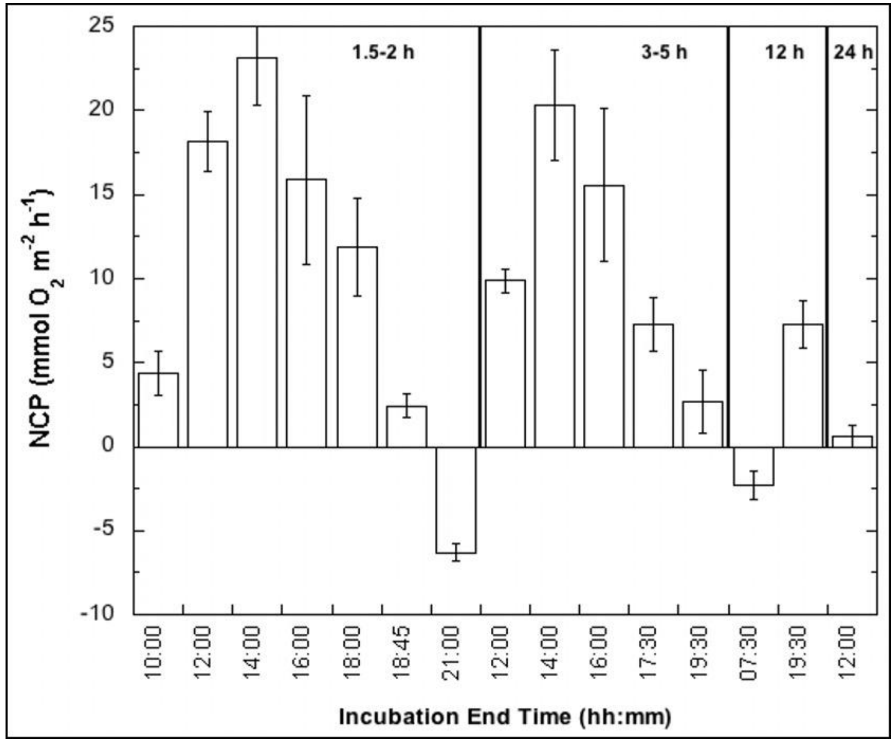
Olivé et al. (2016)

Estimation of NCP of *Posidonia oceanica*



Olivé et al. (2016)

Estimation of NCP of *Posidonia oceanica*



Incubation duration	Light budget	Night budget	Daily budget
(Hours)	(mmol $O_2 \cdot m^{-2}$)	(mmol $O_2 \cdot m^{-2}$)	(mmol $O_2 \cdot m^{-2} \cdot d^{-1}$)
1.5-2	143.3 ± 21.7	-81.7 ± 11.3	61.7 ± 24.5
3-5	102.8 ± 15.7	(na)	(na)
12	80.0 ± 8.7	-30.1 ± 6.9	49.9 ± 11.1
24	-	-	14.8 ± 5.4

UNDERESTIMATION of:

28% “light NCP budget” (3-5h)
44% “light NCP budget” (12h)

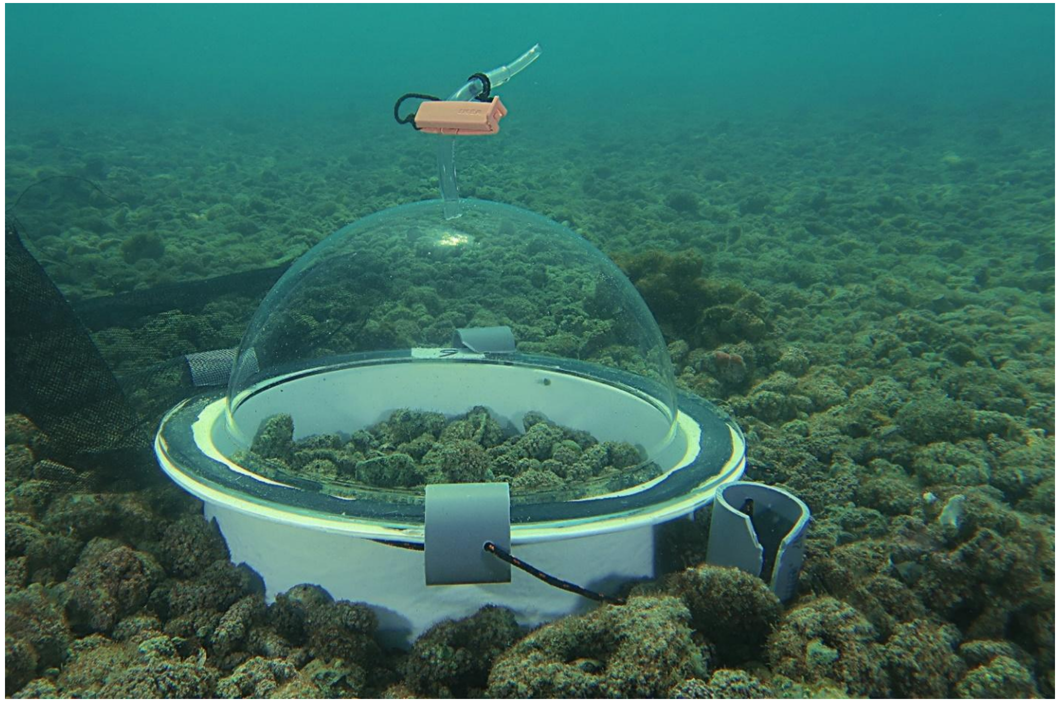
63% “night NCP budget” (12h)

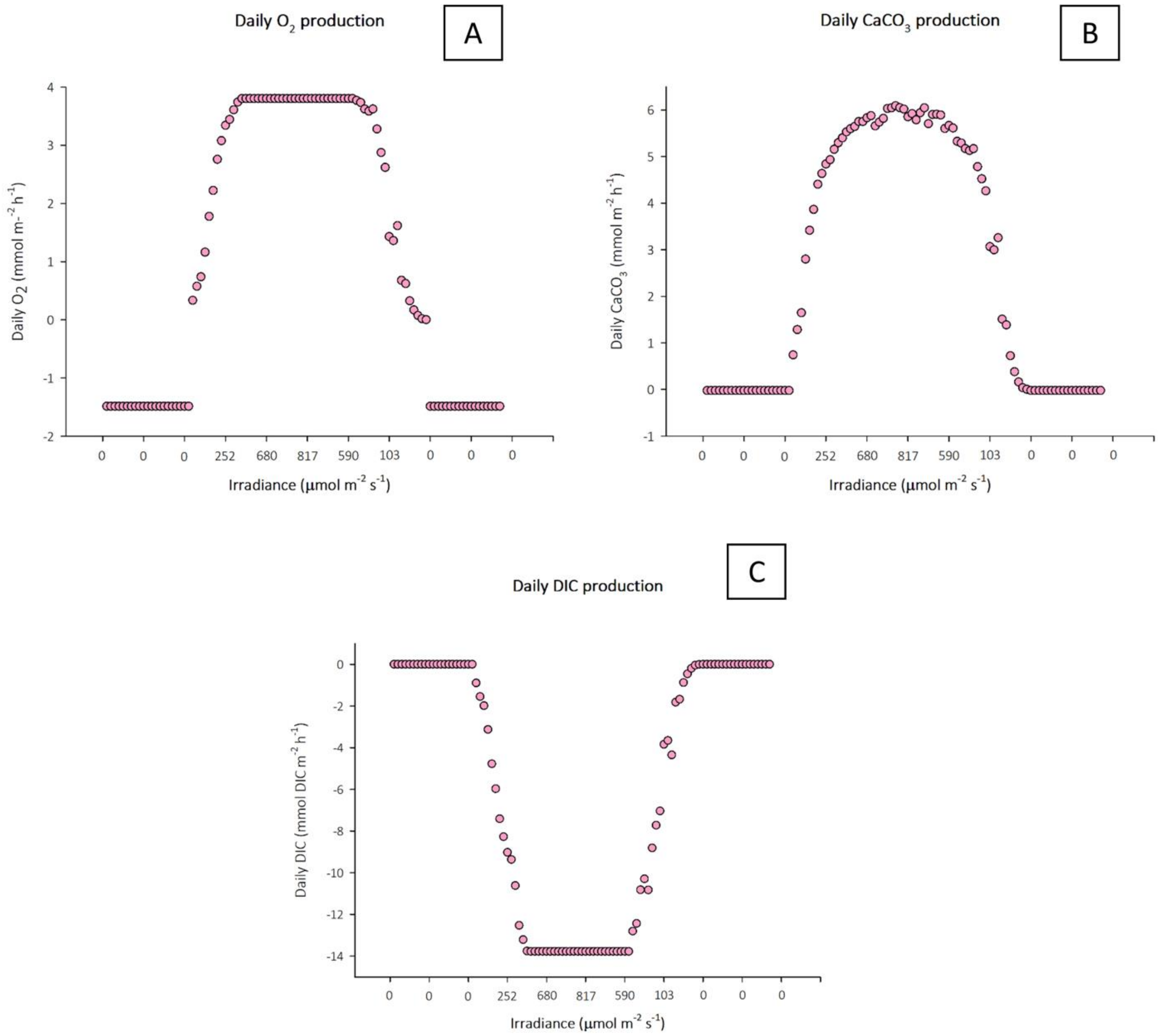
19% daily NCP budget (12h)
76% daily NCP budget (24h)

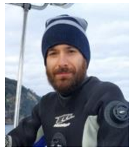
Olivé et al. (2016)

Calcareous

Rhodoliths







PhD Thesis. M. Nannini

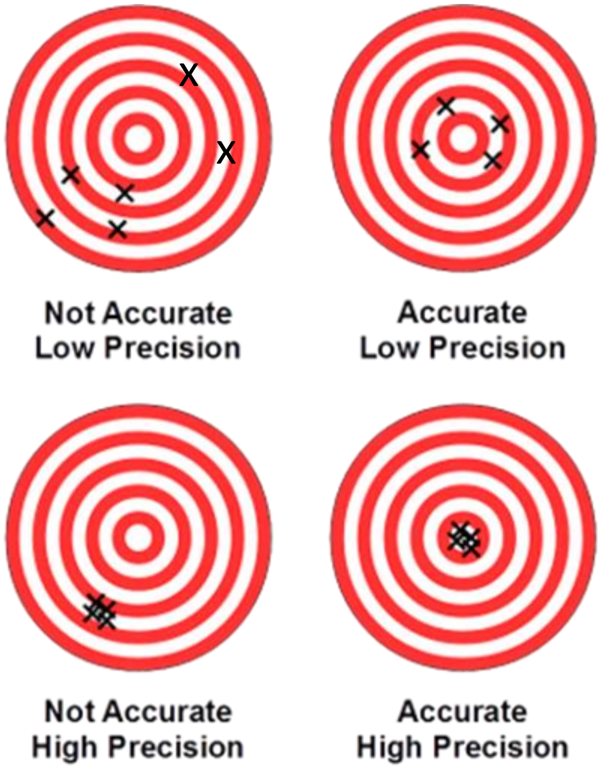
Biology also affects C chemistry in seawater

How can we evaluate changes due to biological activity?

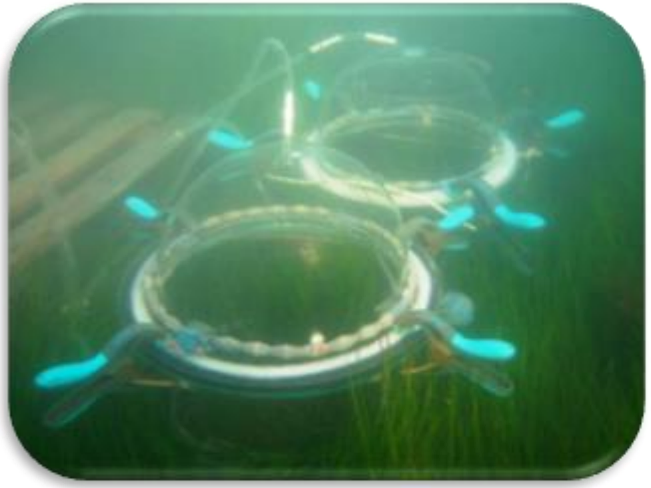
- Measure changes in biological activity
- Measure under “optimized” conditions
- Measure under “controlled” conditions
- Account for the changes not due to our object of study

How well should we measure?

Accuracy and Precision



How much precision is needed?

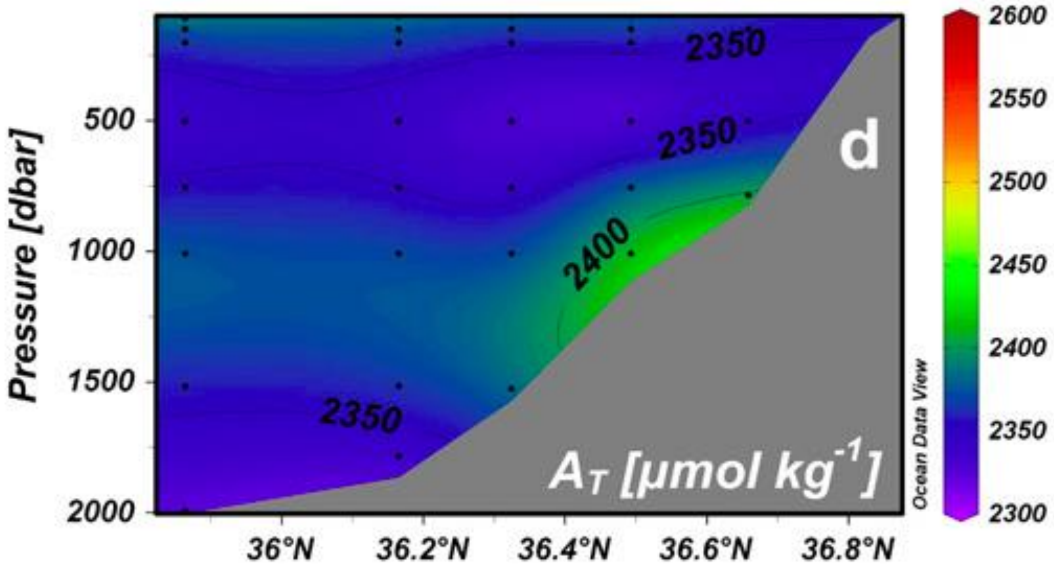


1st exp.	pH	TA (umol Kg^{-1})
Mean	8.11	2641.80
SD	0.12	156.85

2nd exp.	pH (T,S corrected)	TA (umol/Kg^{-1}) (corrected)
Mean	8.06	2615.84
SD	0.09	58.0646

How much precision is needed?

in oceanography changes <50 uM are quantified



Flecha et al. (2012)

1st exp.	pH	TA (umol Kg^{-1})
Mean	8.11	2641.80
SD	0.12	156.85

2nd exp.	pH (T,S corrected)	TA (umol/Kg^{-1}) (corrected)
Mean	8.06	2615.84
SD	0.09	58.0646

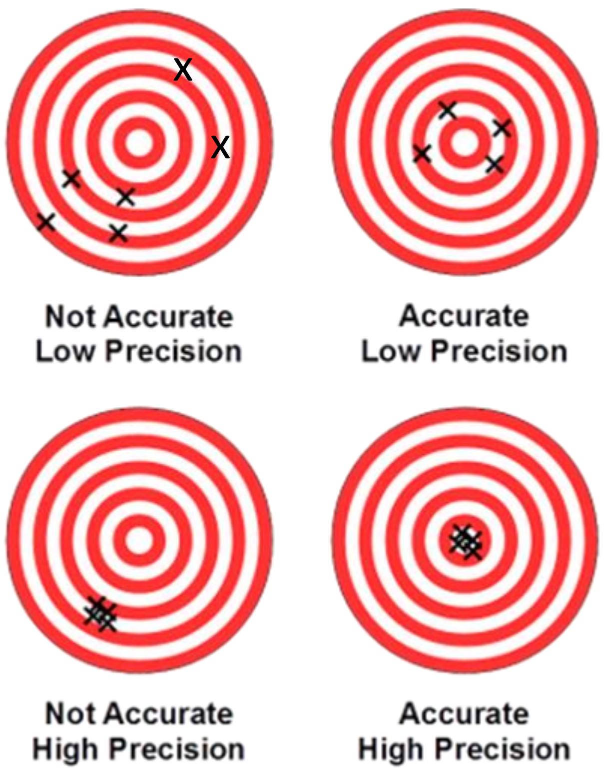
How much accuracy is needed?

The U.S. NSF funded the development of certified reference materials (CRMs) for the measurement of oceanic CO_2 parameters (Dickson Lab USA)

1st exp.	pH	TA (umol Kg^{-1})
Mean	8.11	2641.80
SD	0.12	156.85

2nd exp.	pH (T,S corrected)	TA (umol/Kg^{-1}) (corrected)
Mean	8.06	2615.84
SD	0.09	58.0646

Accuracy and Precision



Accuracy -> Use of CRM

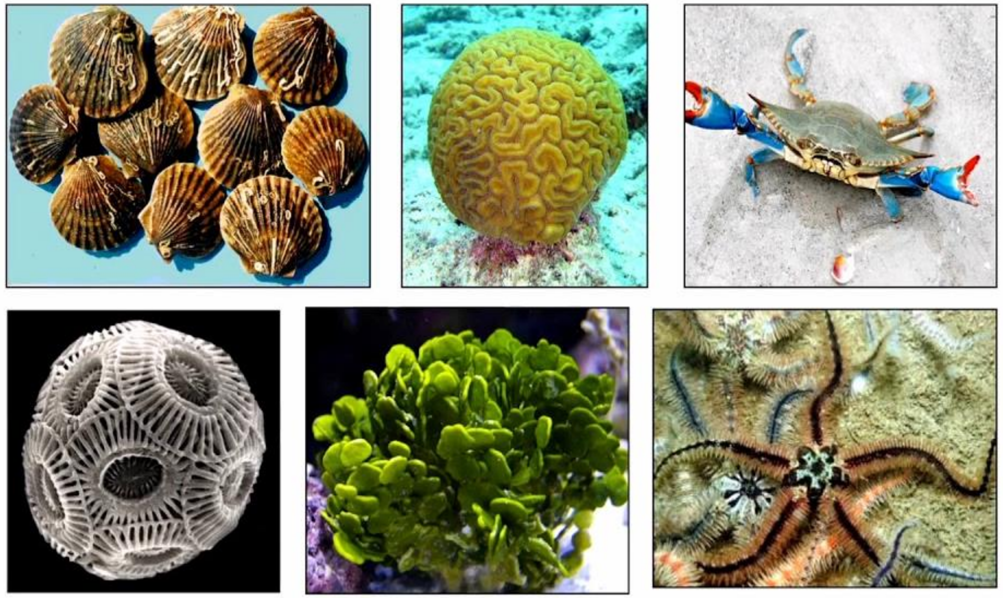
Precision -> Lower the SD

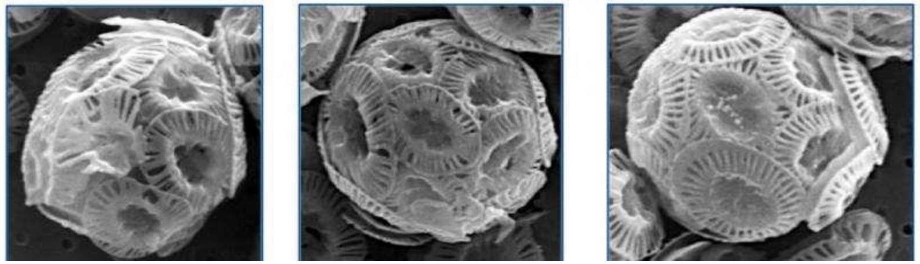
Biology is also affected (and affects) OA

Ocean Acidification and Marine Organisms

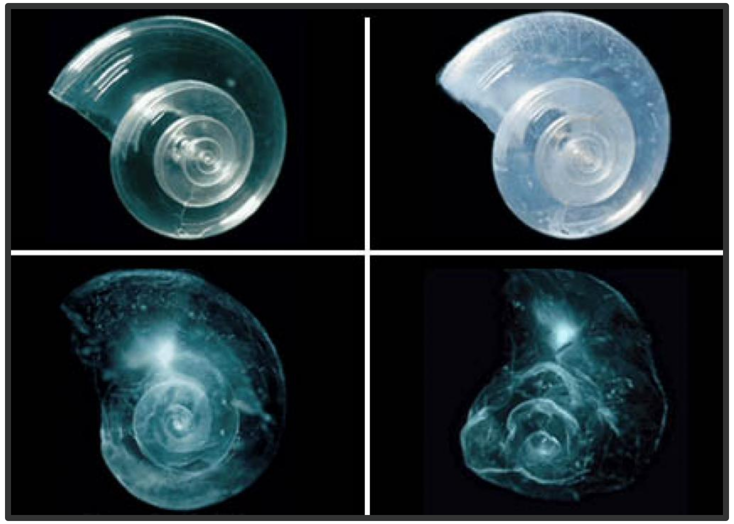
Calcifying organisms vulnerable to ocean acidification

(Orr et al 2005; Doney et al 2009; Reise et al 2009; Talmage and Gobler 2009, 2010, 2011, 2012)

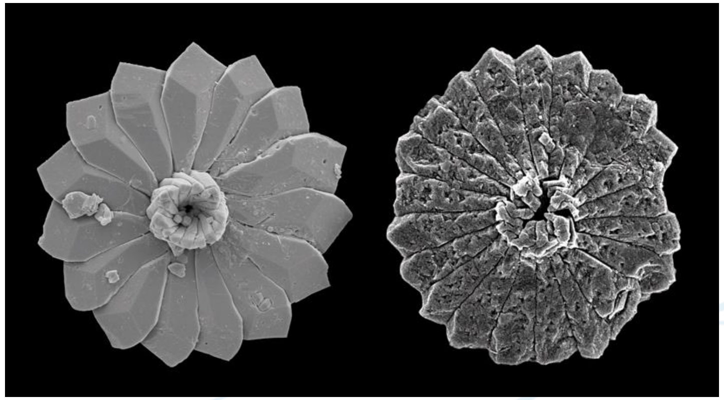




Milner et al. 2016

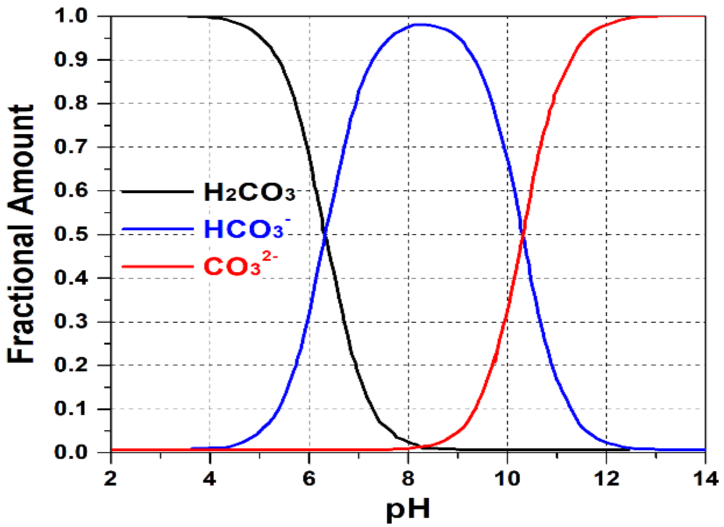


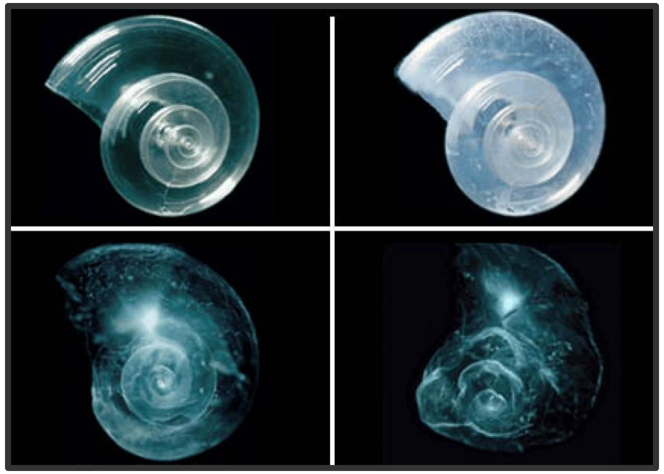
David Littschwager/National Geographic Society



P. Ziveri

Ωi and pH decreases





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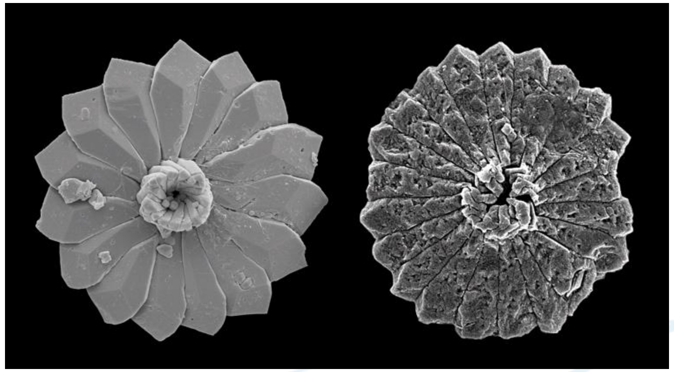


P. Ziveri

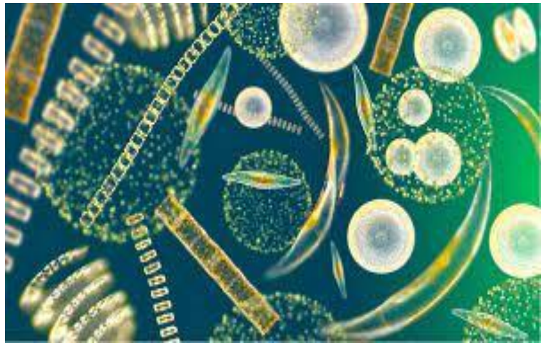
Calcification (C)

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O$$

Decalcification (D)

Ocean Acidification and Marine Organisms

Are all organisms threatened by OA?



With Ocean Acidification

CO_2 increases

DIC increases

Photosynthesis (P)

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

Respiration (R)

Marine Primary producers as

- **OA buffers**
- **Nature Based Solutions**

Some examples

(spoiler: going for some controversy now)

Ocean Acidification and Macrophytes

CO2 vents

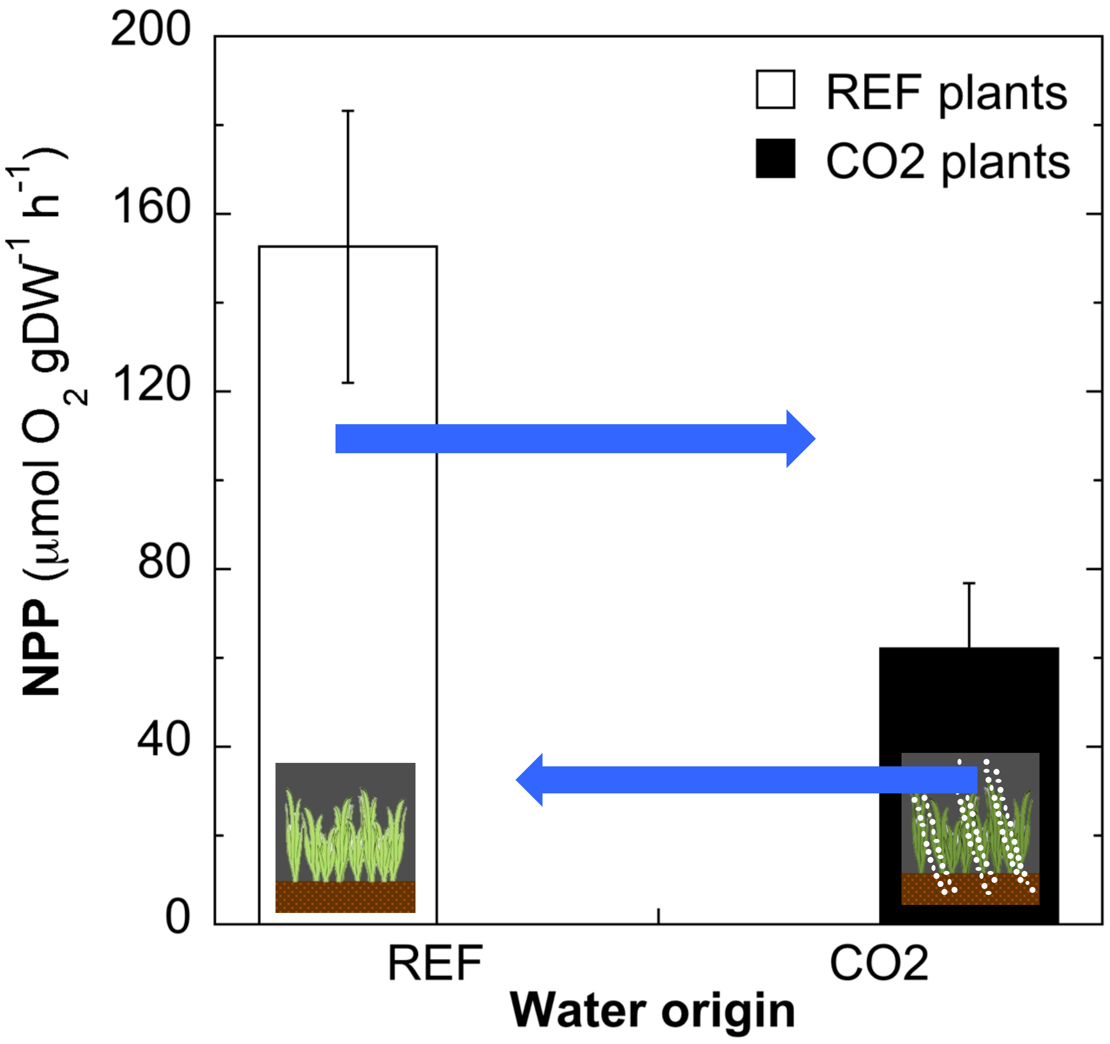
Vulcano Island (Sicily, Italy)

- Shallow CO_2 Vents (< 5 m)
- *Cymodocea nodosa*
- *In situ* incubations (*in loco* vs transplants)
- Gene expression and Plant productivity

Site	pH (NBS)	pCO_2 (uatm)	DIC (umol kg SW^{-1})	S (psu)	T (ºC)
Ref	8.18	427	2244	37.5	20.3
CO_2	7.98	737	2377	37.5	19.8

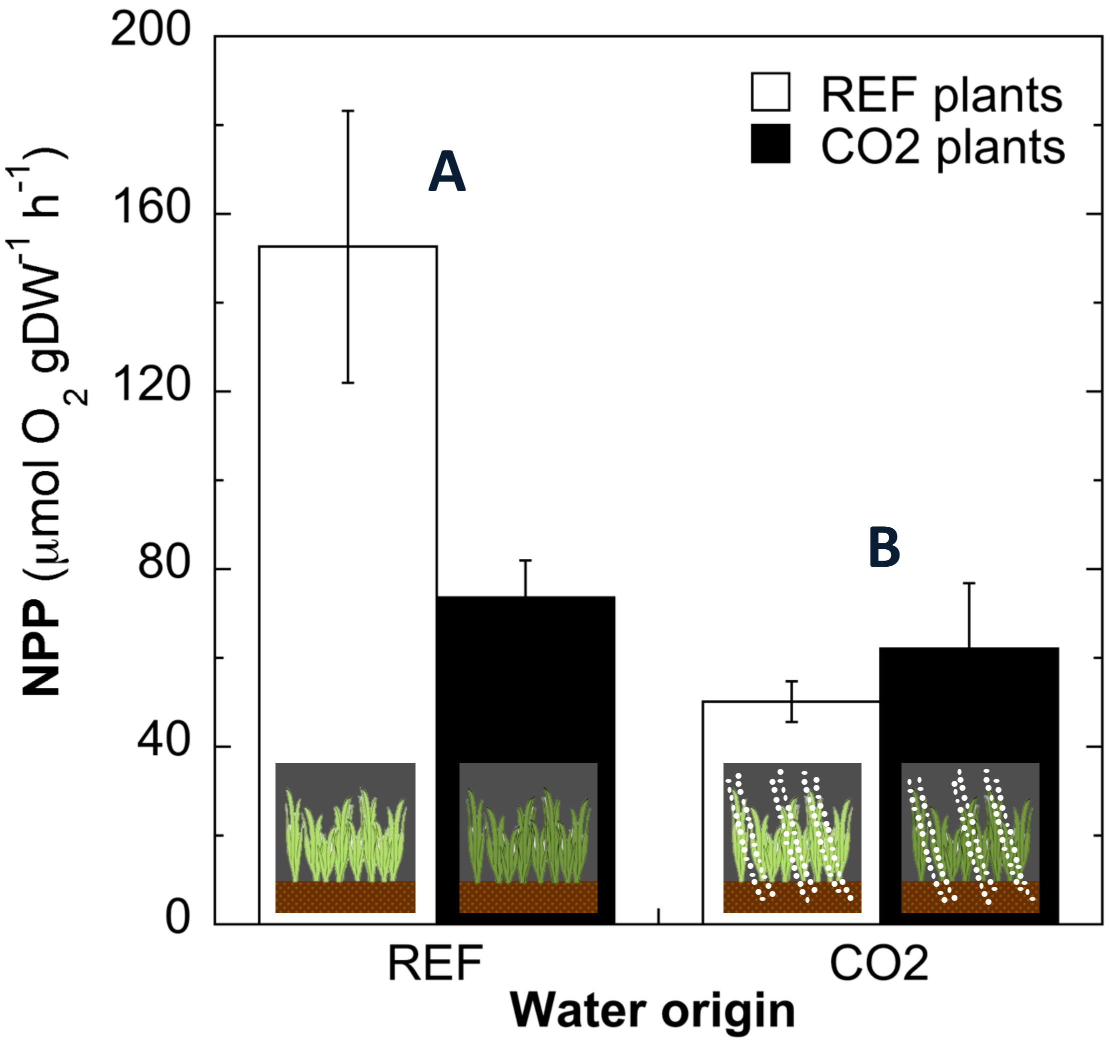
Olivé *et al.* (2017)

Ocean Acidification and Macrophytes



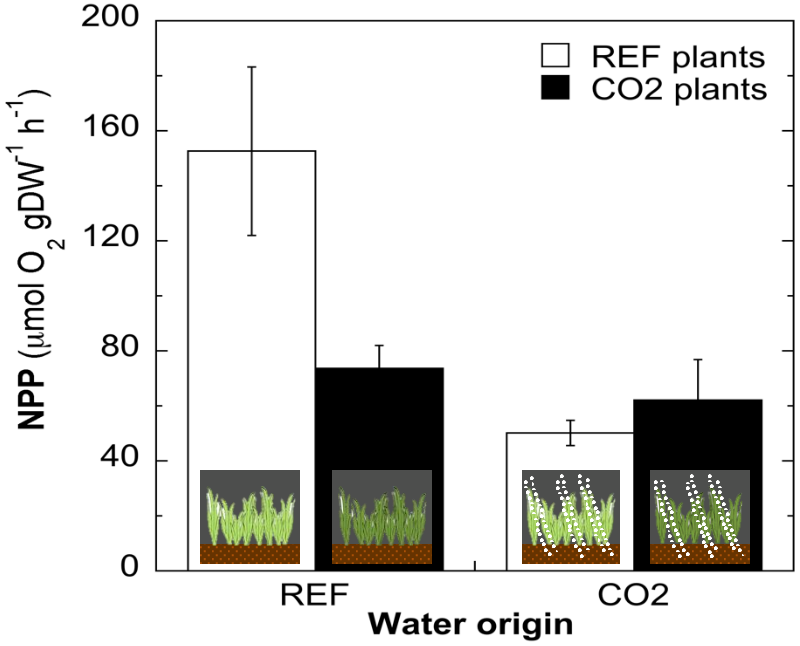
Olivé *et al.* (2017)

Ocean Acidification and Macrophytes



Olivé *et al.* (2017)

Ocean Acidification and Macrophytes



Net balance autotrophic
(NPP>0)

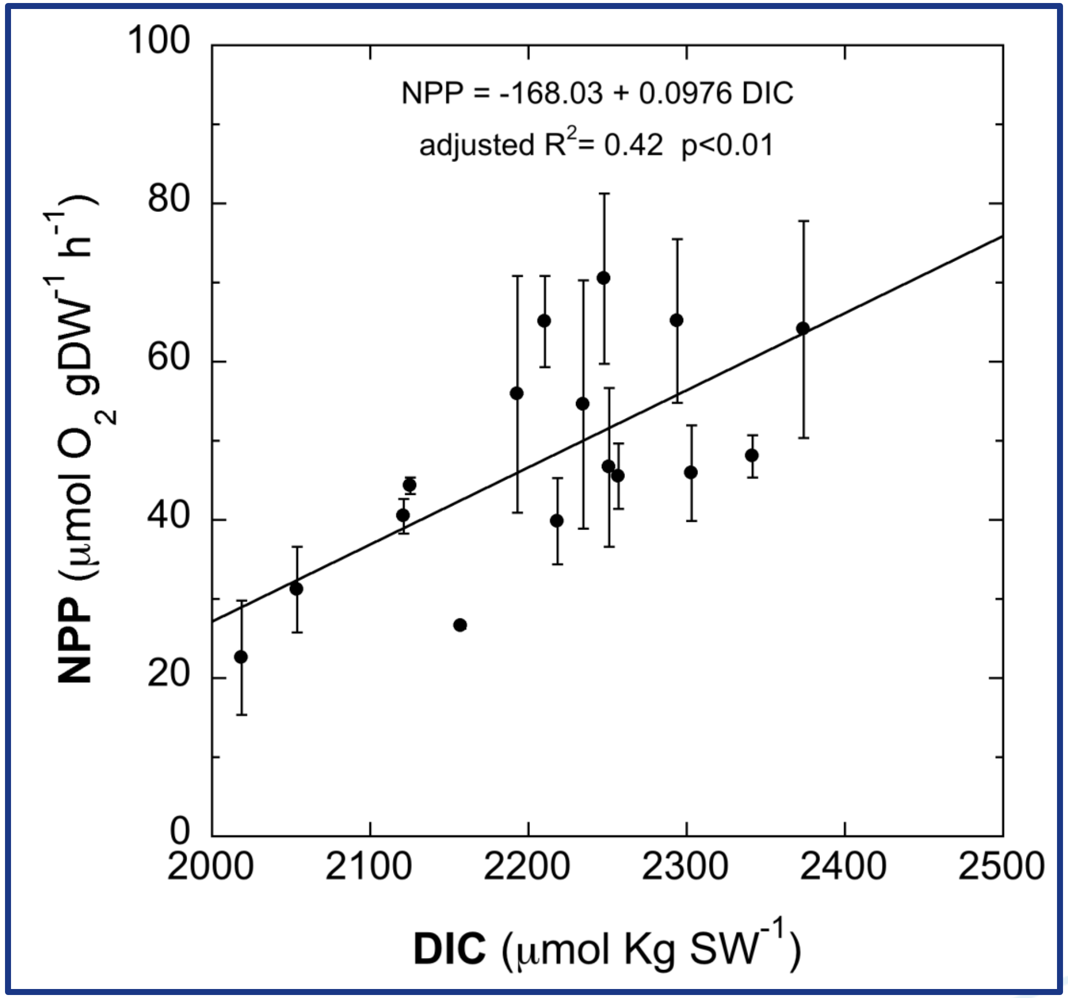
~~**Hypothesis:**~~
~~**Ocean Acidification stimulates seagrass productivity**~~

Olivé *et al.* (2017)

Controlled conditions

NPP increases with DIC

Hypothesis:
Ocean Acidification stimulates seagrass productivity



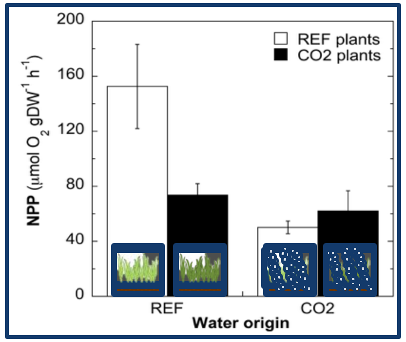
Olivé *et al.* (2017)

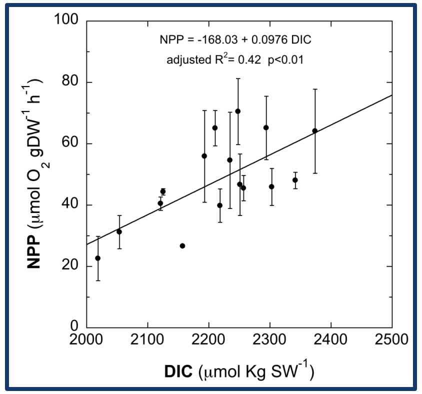
Ocean Acidification and Macrophytes

- In Vulcano CO_2 vents, **seagrass productivity decreases** in plants exposed to high CO_2 (**CO_2 vents**)

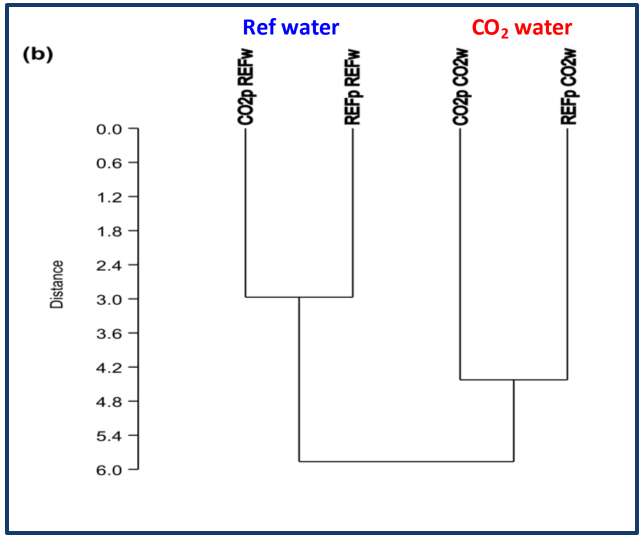
BUT

- Under **controlled conditions**, seagrass **productivity significantly correlates** (increases) with **CO_2** availability





Is there something in the (CO_2 vents) water?



Olivé *et al.* (2017)

Ocean Acidification and Macrophytes

CO2 vents

Ischia

- *Posidonia oceanica*
- CO_2 “pure” (Tedesco 1996)

Panarea

- *Posidonia oceanica*
- CO_2 & Other gases (Gugliando *et al*. 2006)

Ocean Acidification and Macrophytes

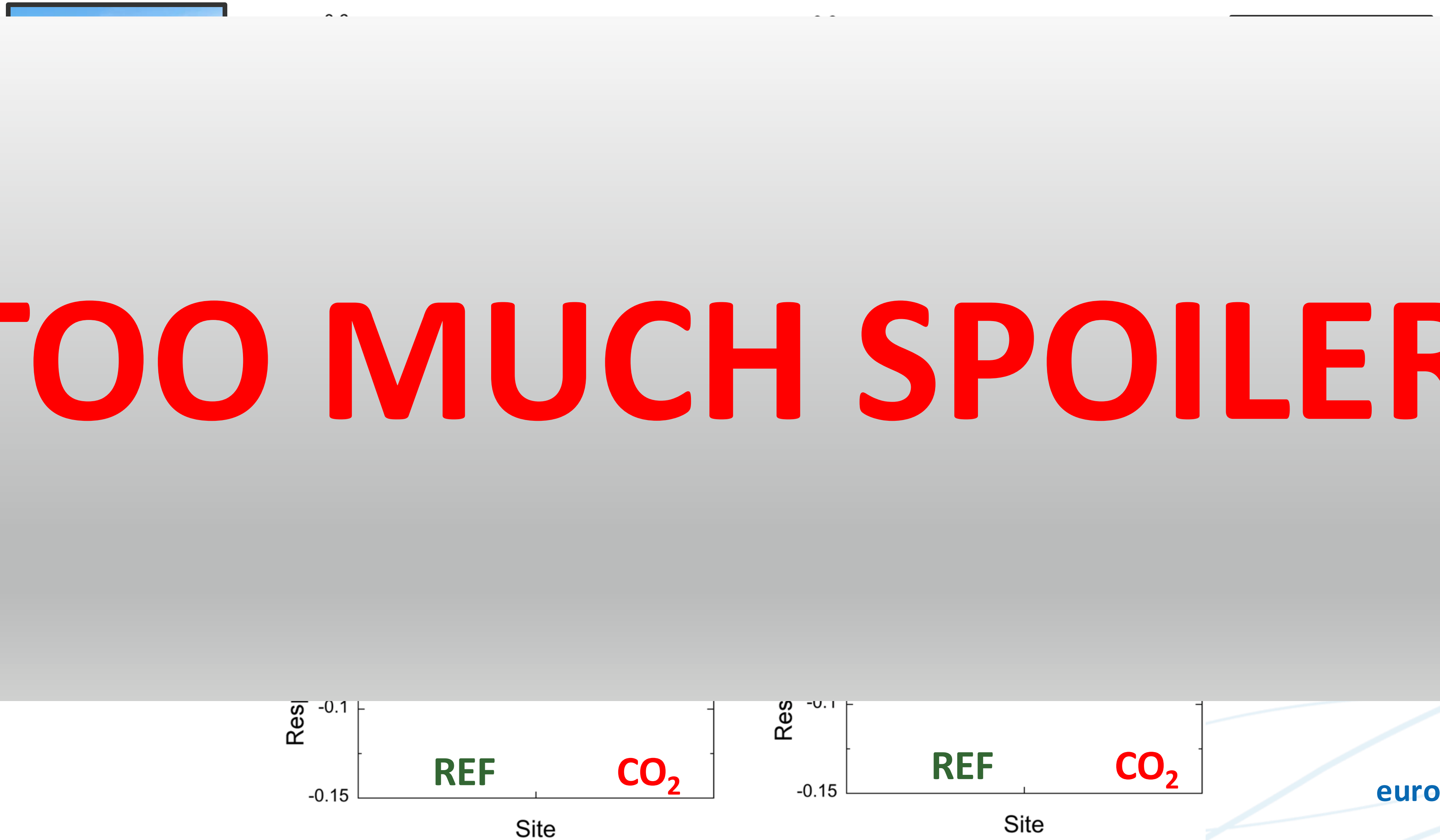
Ischia

“pure” CO_2

Panarea

CO_2 + ??

TOO MUCH SPOILER



Your turn to work