Introduction to Ocean Acidification

Steeve Comeau

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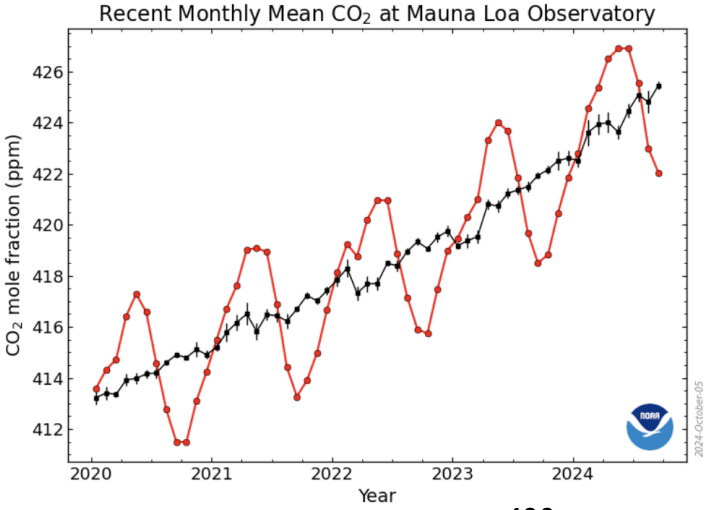
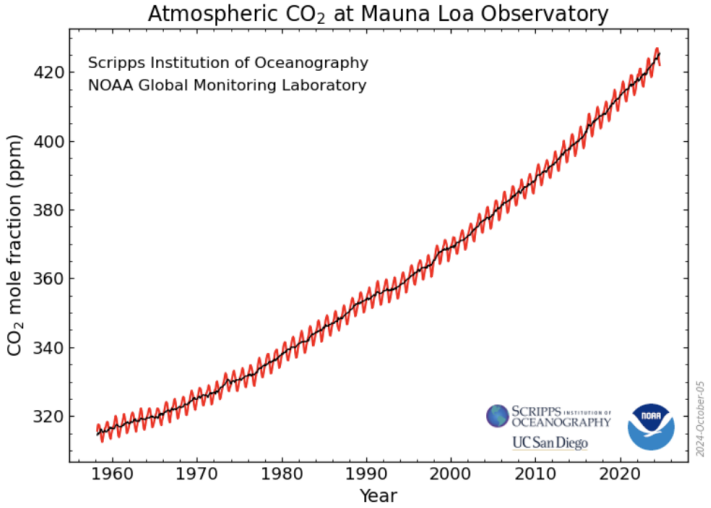
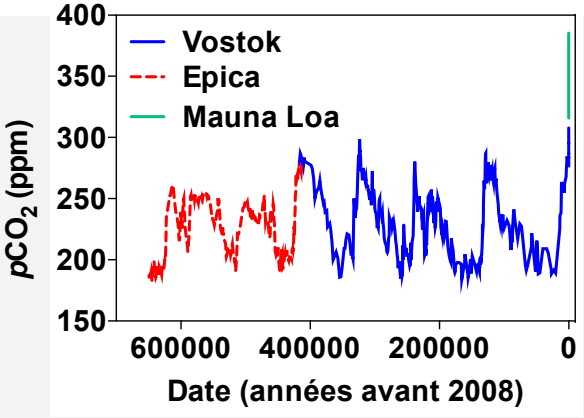
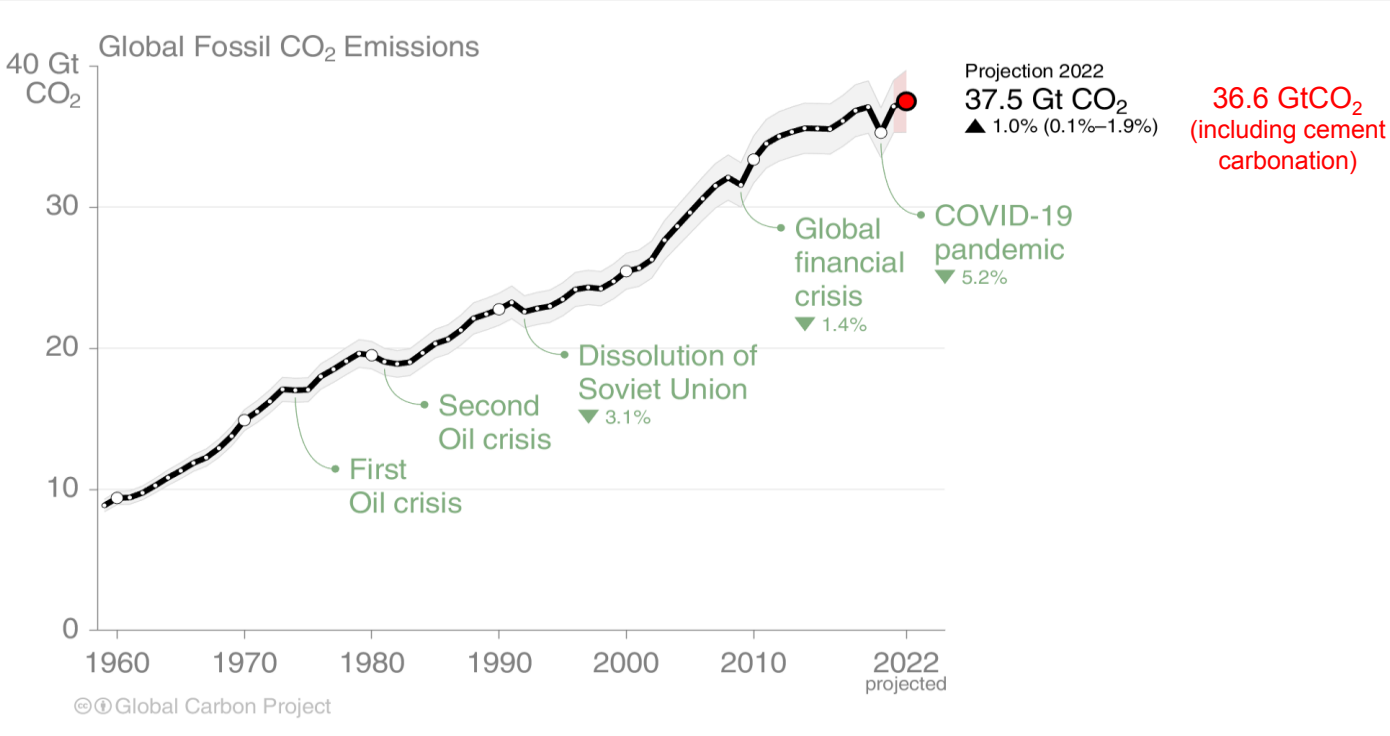
CO_2 level

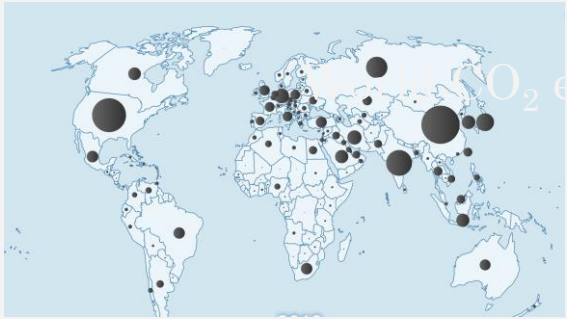

Recent Monthly Mean CO_2 at Mauna Loa Observatory
CO_2 mole fraction (ppm)
426
424
422
420
418
416
414
412
2020
2021
2022
2023
2024
Year
2024-October-05

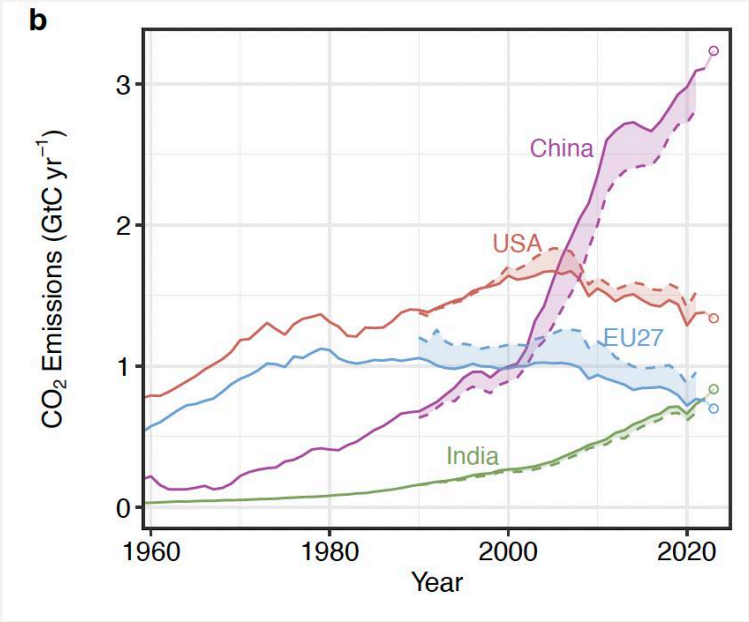

Atmospheric CO_2 at Mauna Loa Observatory
Scripps Institution of Oceanography
NOAA Global Monitoring Laboratory
CO_2 mole fraction (ppm)
420
400
380
360
340
320
1960
1970
1980
1990
2000
2010
2020
Year
SCRIPPS INSTITUTION OF OCEANOGRAPHY
UC San Diego
2024-October-05

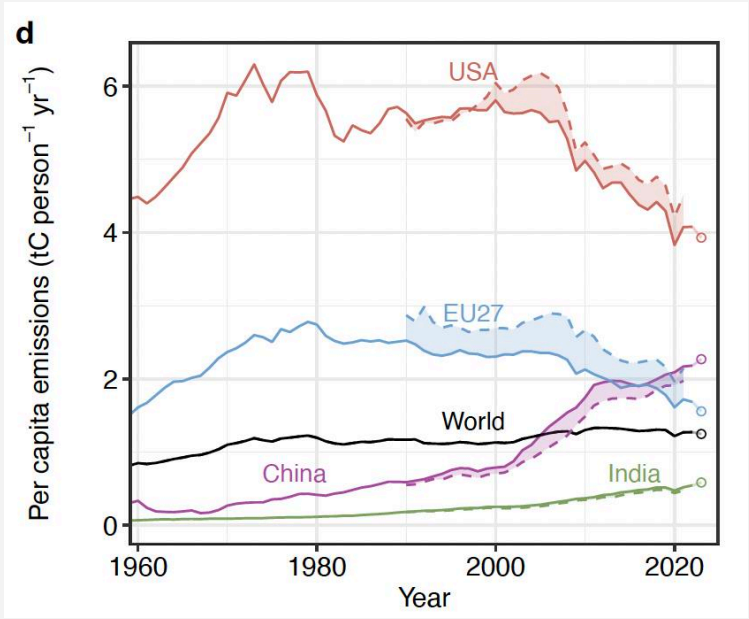

Vostok
Epica
Mauna Loa
pCO_2 (ppm)
400
350
300
250
200
150
600000
400000
200000
0
Date (années avant 2008)

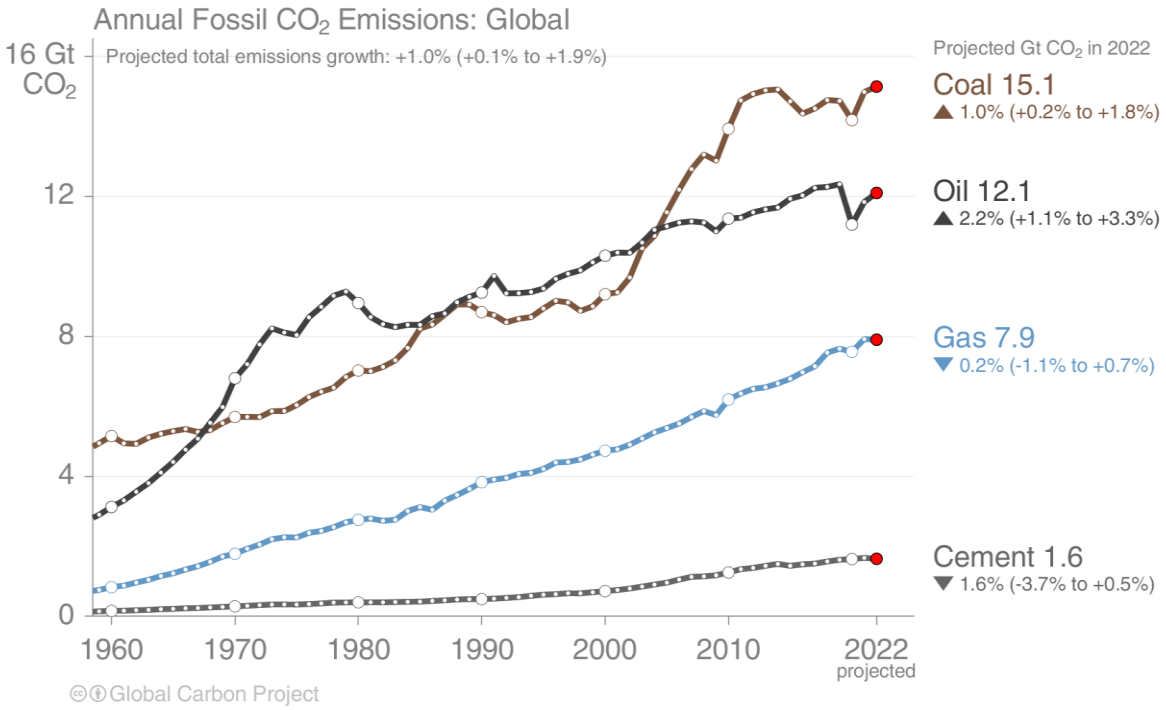
CO_2 emissions (covid effects)



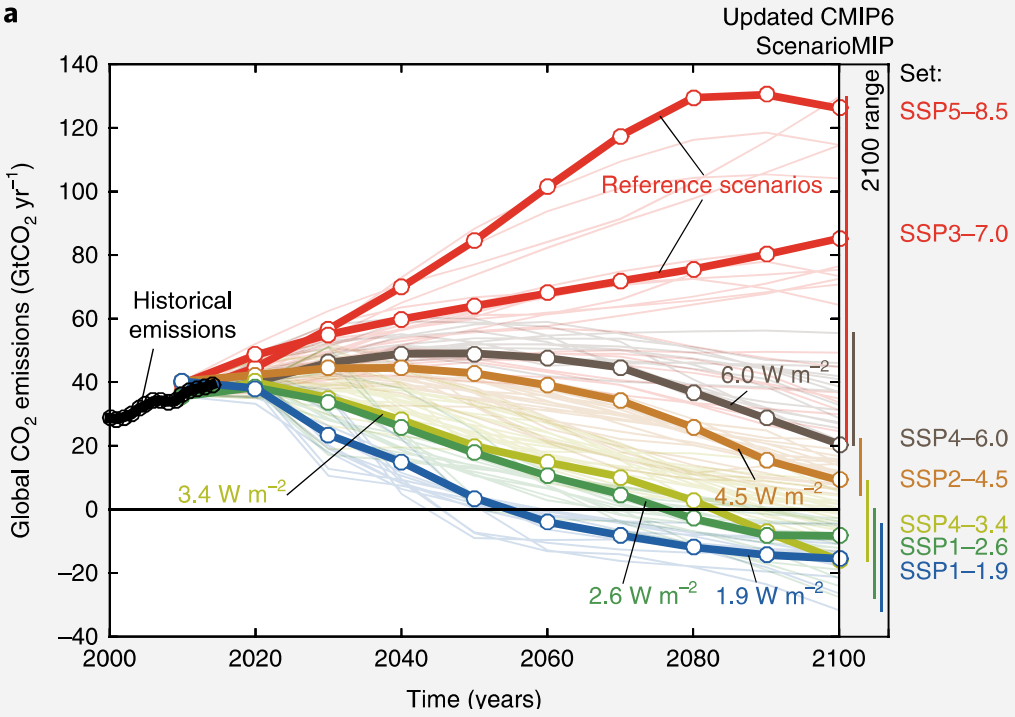



b
CO_2 Emissions (GtC yr^{-1})
3
2
1
0
China
USA
EU27
India
1960
1980
2000
2020
Year

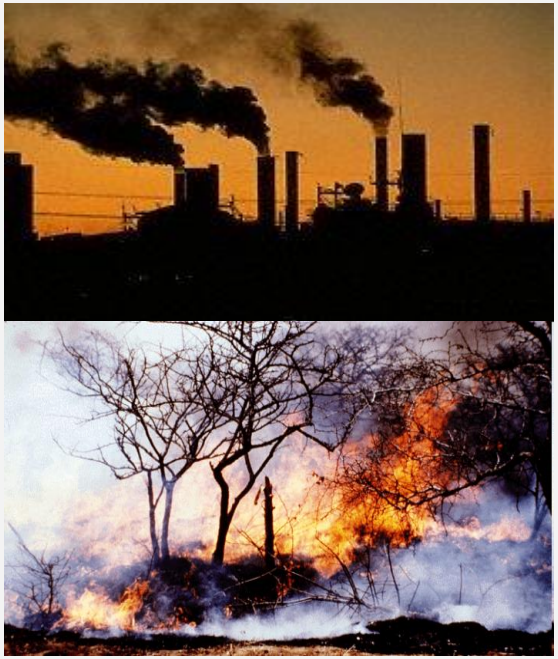

d
Per capita emissions (tC $person^{-1}$ yr^{-1})
6
4
2
0
USA
EU27
World
China
India
1960
1980
2000
2020
Year

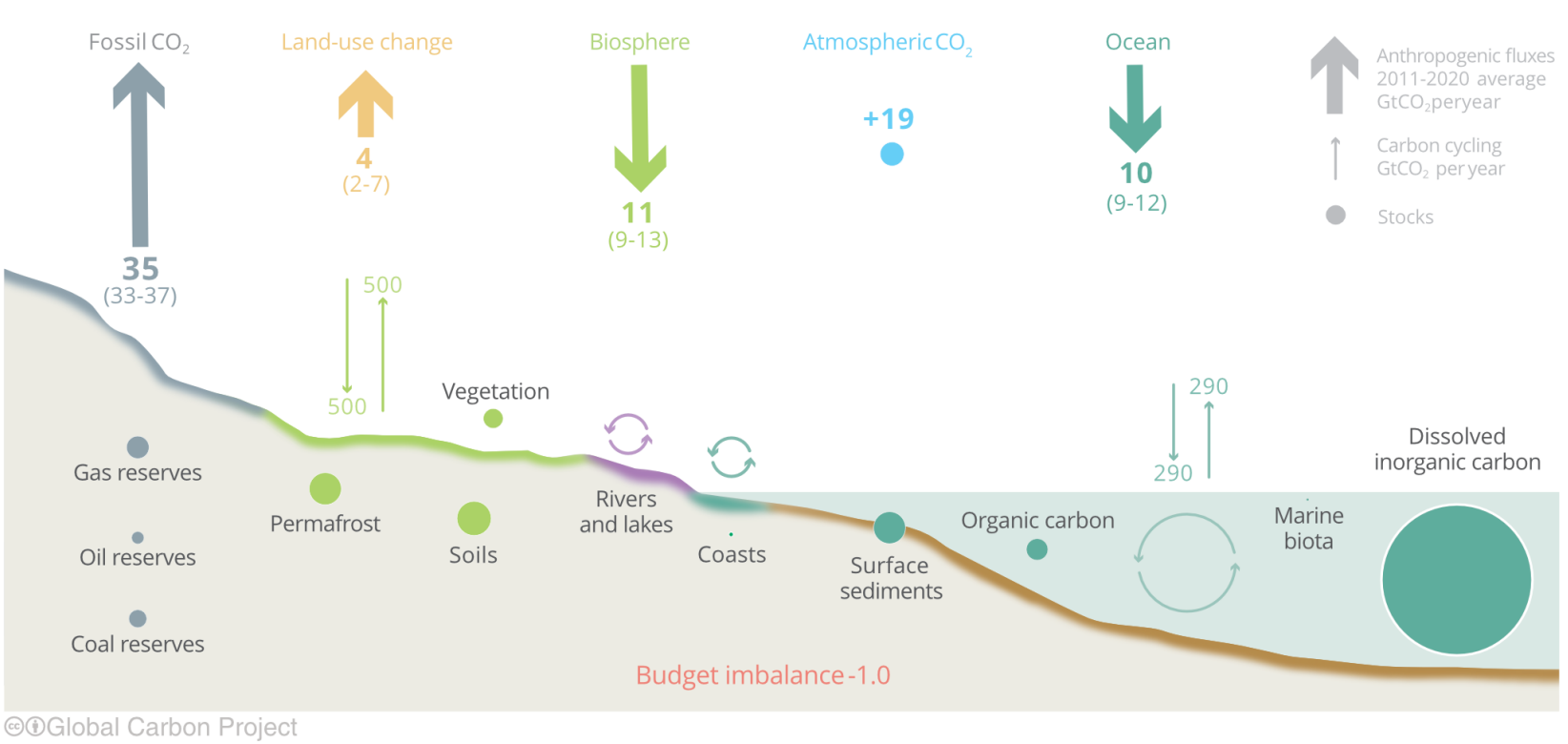

Annual Fossil CO_2 Emissions: Global
Projected total emissions growth: +1.0% (+0.1% to +1.9%)
16 Gt CO_2
12
8
4
0
1960
1970
1980
1990
2000
2010
2022
projected
Global Carbon Project
Projected Gt CO_2 in 2022
Coal 15.1
▲ 1.0% (+0.2% to +1.8%)
Oil 12.1
▲ 2.2% (+1.1% to +3.3%)
Gas 7.9
▼ 0.2% (-1.1% to +0.7%)
Cement 1.6
▼ 1.6% (-3.7% to +0.5%)

CO_2 emissions (SSP – Shared Socio-economic Pathways)

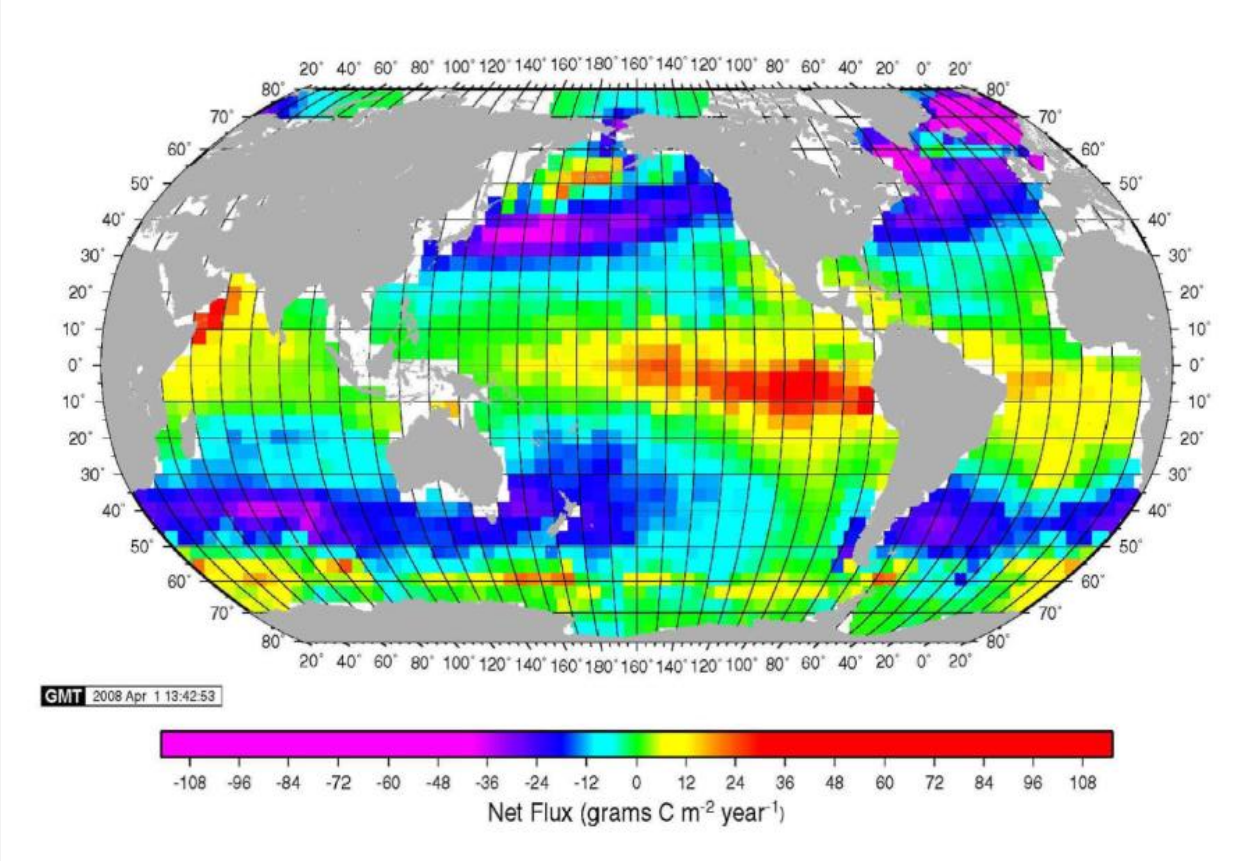


Where is CO_2 stored?



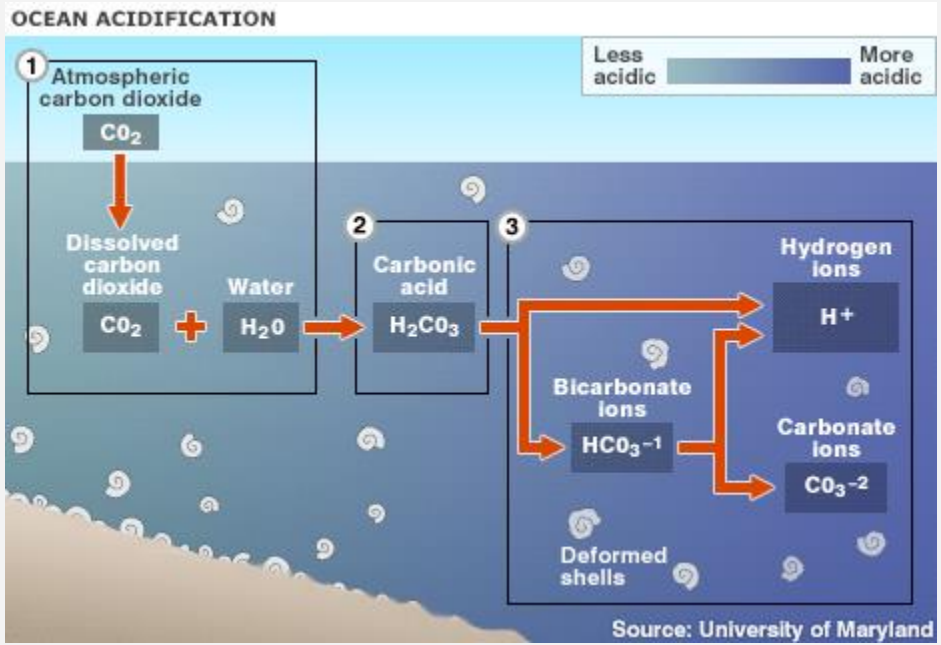

Fossil CO_2
35
(33-37)
Land-use change
4
(2-7)
Biosphere
11
(9-13)
Atmospheric CO_2
+19
Ocean
10
(9-12)
Anthropogenic fluxes
2011-2020 average
$GtCO_2$ per year
Carbon cycling
$GtCO_2$ per year
Stocks
500
500
Vegetation
290
290
Dissolved
inorganic carbon
Gas reserves
Oil reserves
Coal reserves
Permafrost
Soils
Rivers
and lakes
Coasts
Surface
sediments
Organic carbon
Marine
biota
Budget imbalance -1.0
©Global Carbon Project

Air-sea CO_2 fluxes



Takahashi et al. 2010

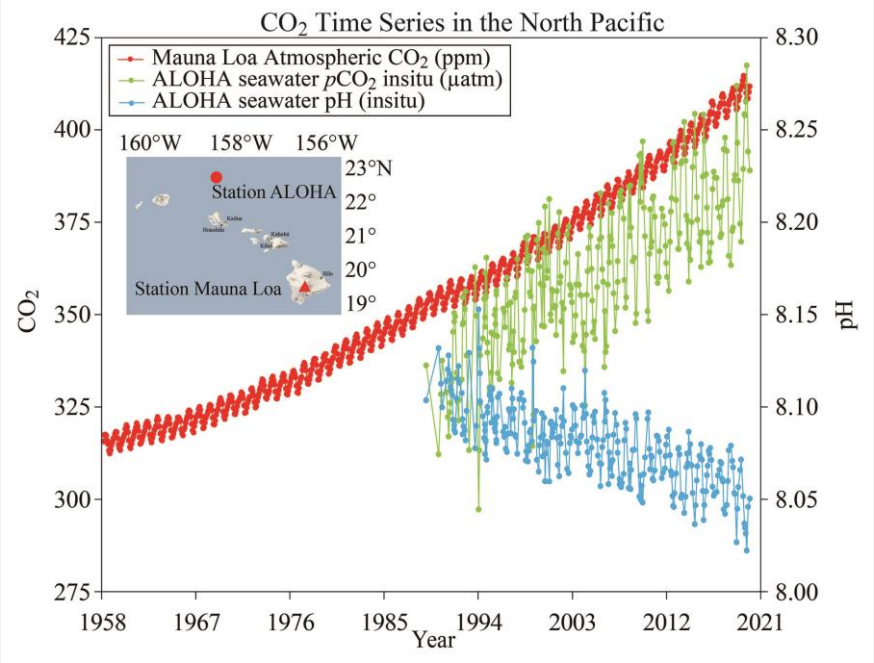
Ocean Acidification



pH = - log [H^+]

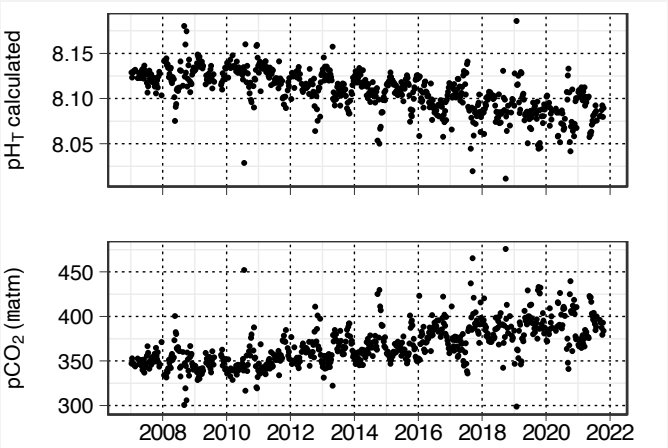
pH has already decreased by 0.1 unit since 1800

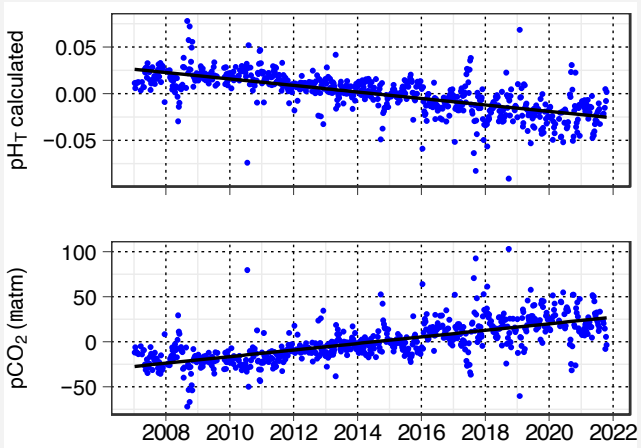
Ocean acidification can already be measured



AOAN

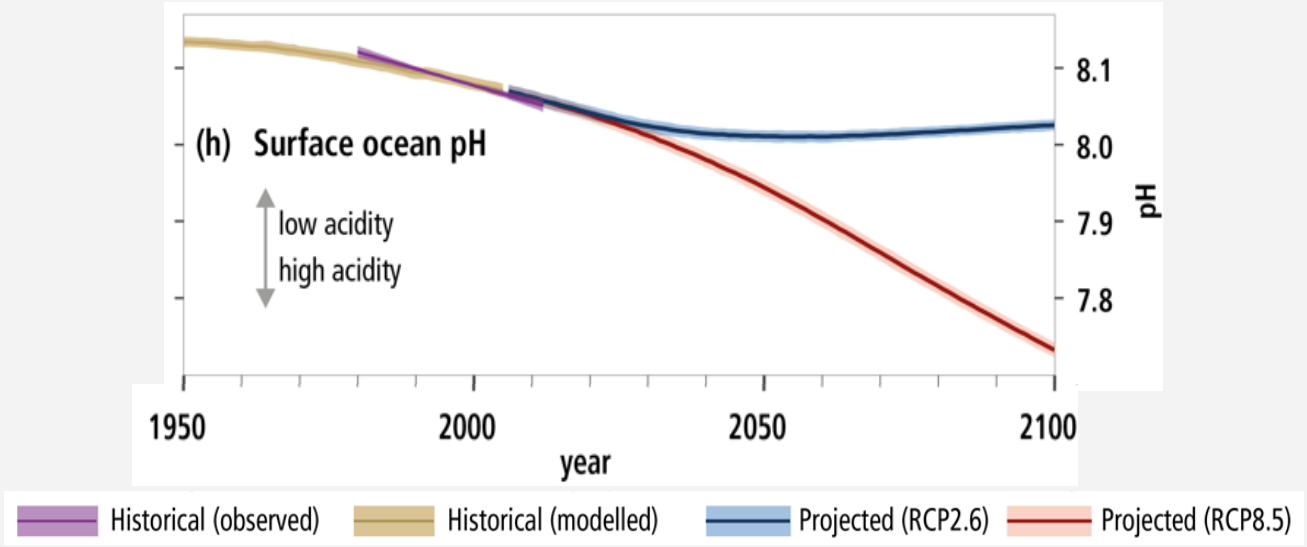
Ocean acidification can already be measured





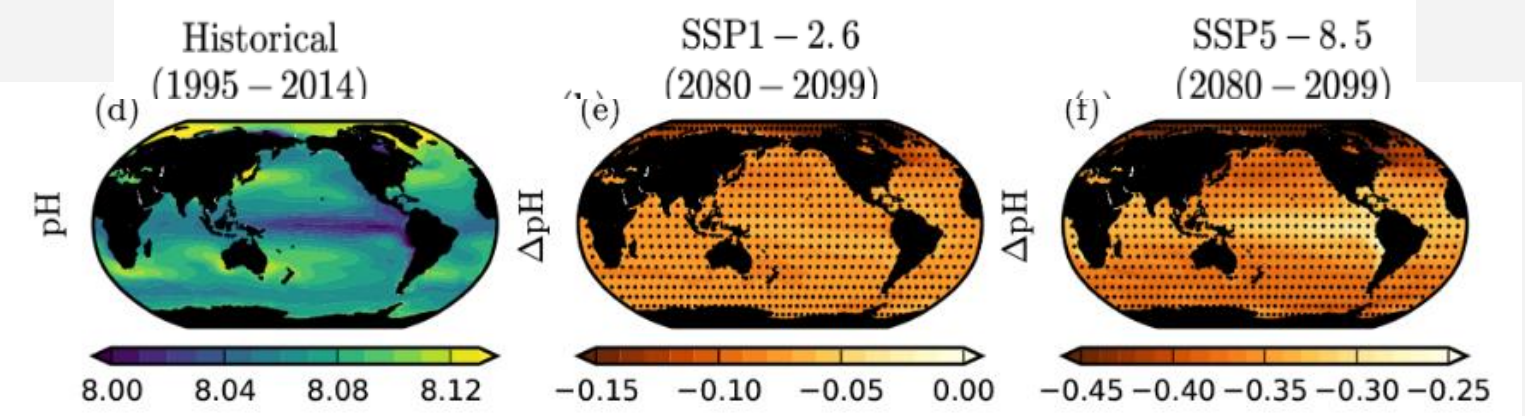
Kapsenberg et al. 2017, Ocean Sci.

pH change…



IPCC-SROCC 2019

pH change…



Kwiatkowski et al. 2020

A bit of chemistry

$$CO_2(g) \rightleftharpoons CO_2(aq), \quad (1)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq), \quad (2)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq), \quad (3)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq); \quad (4)$$

The equilibrium relationships between the concentrations of these various species can then be written as

$$K_0 = [CO_2^*] / f(CO_2), \quad (7)$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*], \quad (8)$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]. \quad (9)$$

A bit of chemistry

4.4 Total hydrogen ion concentration

The hydrogen ion concentration in sea water is usually reported as pH:

$$\mathrm{pH} = -\log[\mathrm{H}^+]. \tag{14}$$

Although the concept of a total hydrogen ion concentration is somewhat confusing[2], it is needed to define acid dissociation constants accurately in sea water (Dickson, 1990). Total hydrogen ion concentration is defined as

$$[\mathrm{H}^+] = [\mathrm{H}^+]_F \cdot (1 + S_T / K_S). \tag{15}$$

$[\mathrm{H}^+]_F$ is the *free* hydrogen ion concentration, S_T is the total sulfate concentration ($[\mathrm{SO}_4^{2-}] + [\mathrm{HSO}_4^-]$) and K_S is the acid dissociation constant for HSO_4^-. At pH values above 4, equation (15) can be approximated as

$$[\mathrm{H}^+] = [\mathrm{H}^+]_F + [\mathrm{HSO}_4^-]. \tag{16}$$

$CaCO_3$ solubility and saturation

- **Saturation state** $\Omega = [CO_3^{2-}] [Ca^{2+}] / Ks$
  - *K_s is the solubility product of $CaCO_3$*
    - Ks differs between the different polymorphs of calcium carbonate (mostly aragonite and calcite), aragonite being 30% more soluble than calcite
    - Ks depends on temperature, salinity and pressure
      - $\Omega > 1 \rightarrow$ supersaturation $\rightarrow$ precipitation
      - $\Omega < 1 \rightarrow$ undersaturation $\rightarrow$ dissolution
  - **The surface ocean is almost completely oversaturated with respect to aragonite (but that will change….)**
  - **Saturation decreases with depth (pressure increase, temperature, more CO_2)**
  - **$CaCO_3$ becomes undersaturated below the lysocline**
  - **Below the carbonate compensation depth (CCD) no $CaCO_3$ in the sediments**

A bit of chemistry…

Total dissolved inorganic carbon

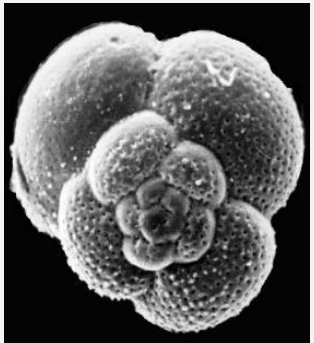
$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$$

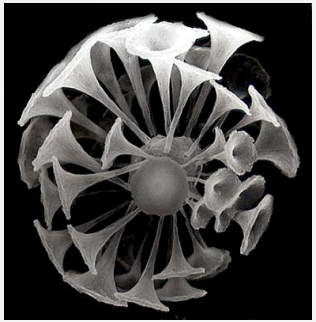
Total alkalinity: "Numbers of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors…"

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$
$$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots$$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$$

Biological processes

- **Net calcification vs dissolution**
  - $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$

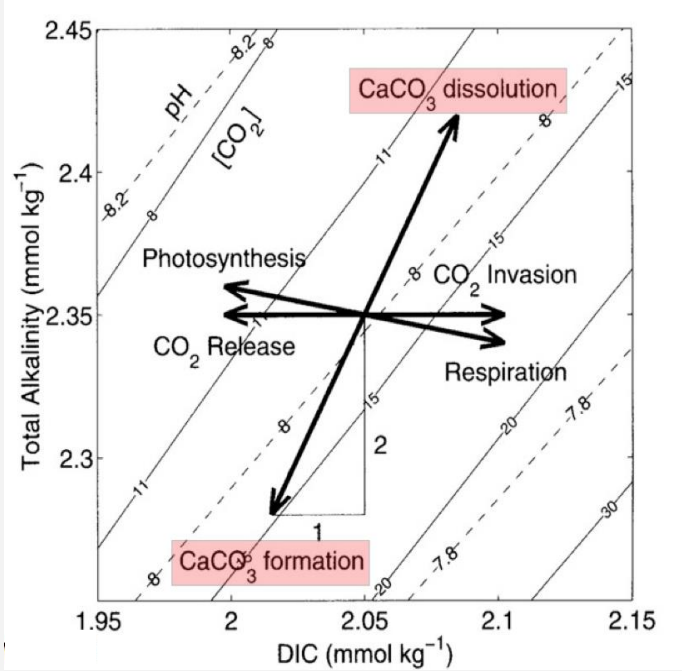




Biological processes vs. Carbon chemistry

- **Calcification/Dissolution**

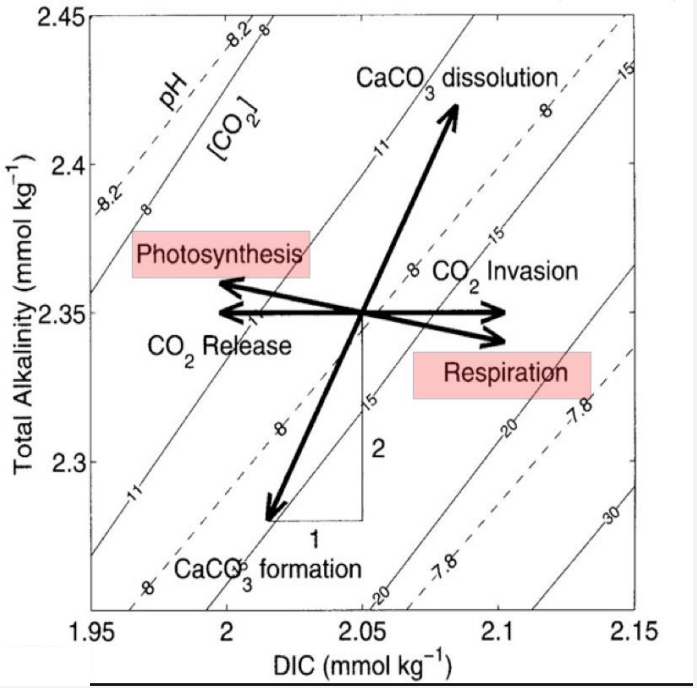
$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$



- Calcification
  - CO_2 production
  - DIC and alkalinity consumption
- Dissolution
  - CO_2 consumption
  - DIC and alkalinity production

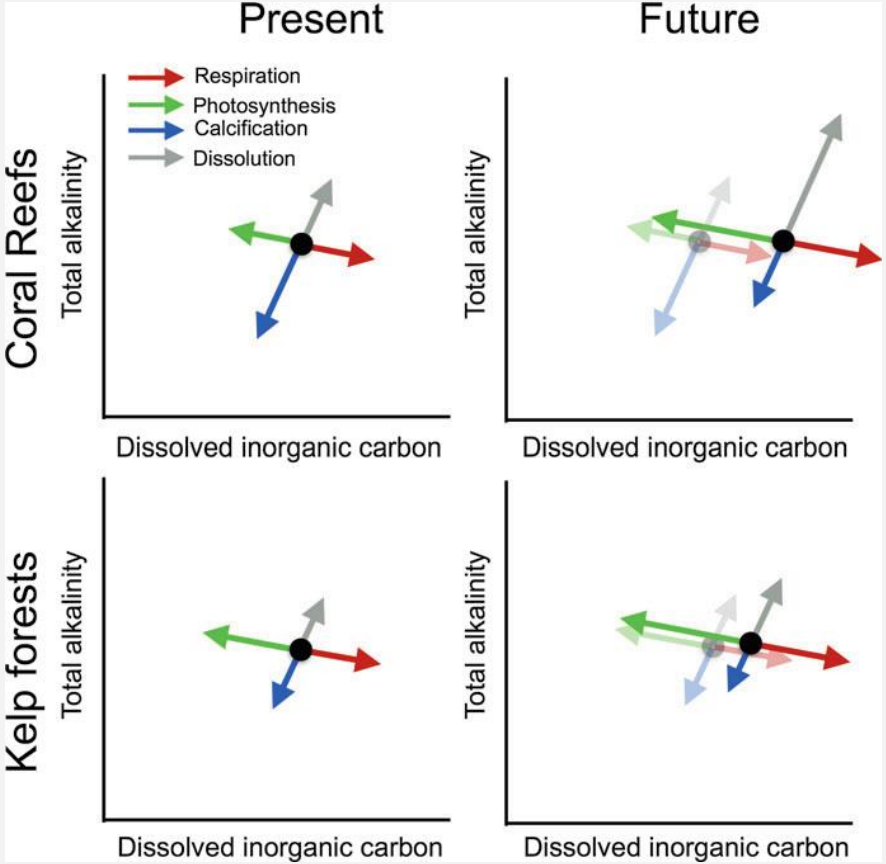
Biological processes vs. Carbon chemistry

- **Photosynthesis / Respiration**



- Photosynthesis
  - CO_2 and DIC consumption
  - Alkalinity production
- Respiration
  - CO_2 and DIC production
  - Alkalinity consumption

- Play a very significant role in determining an ecosystem as a source or a sink of atmospheric CO_2

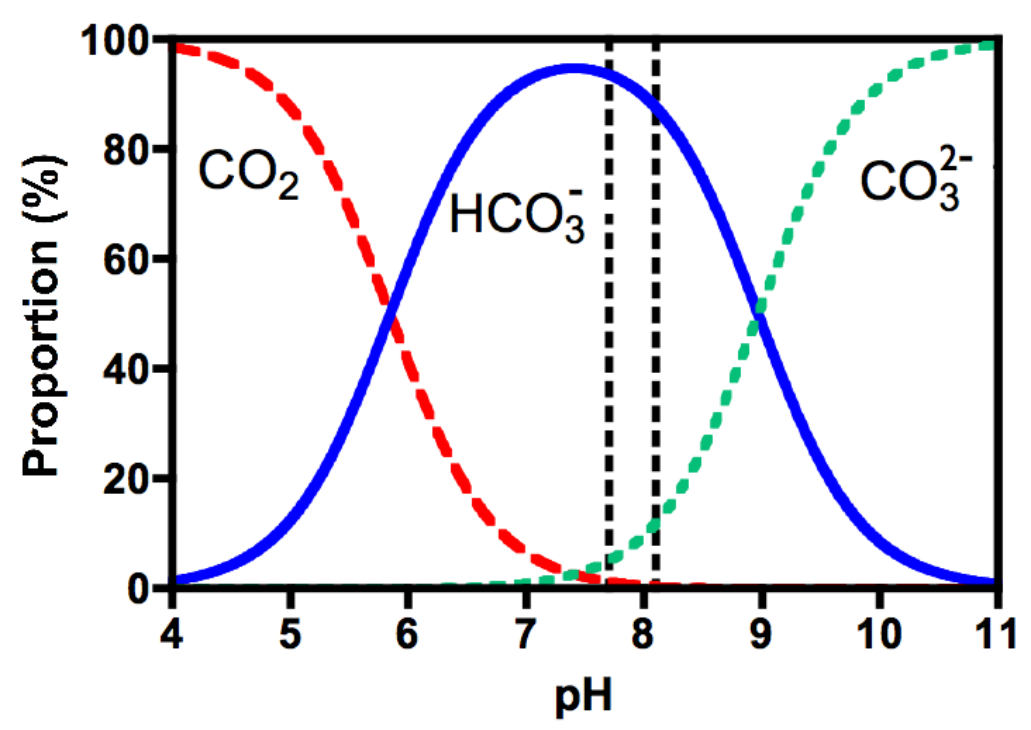

Present
Future
Respiration
Photosynthesis
Calcification
Dissolution
Coral Reefs
Kelp forests
Total alkalinity
Dissolved inorganic carbon

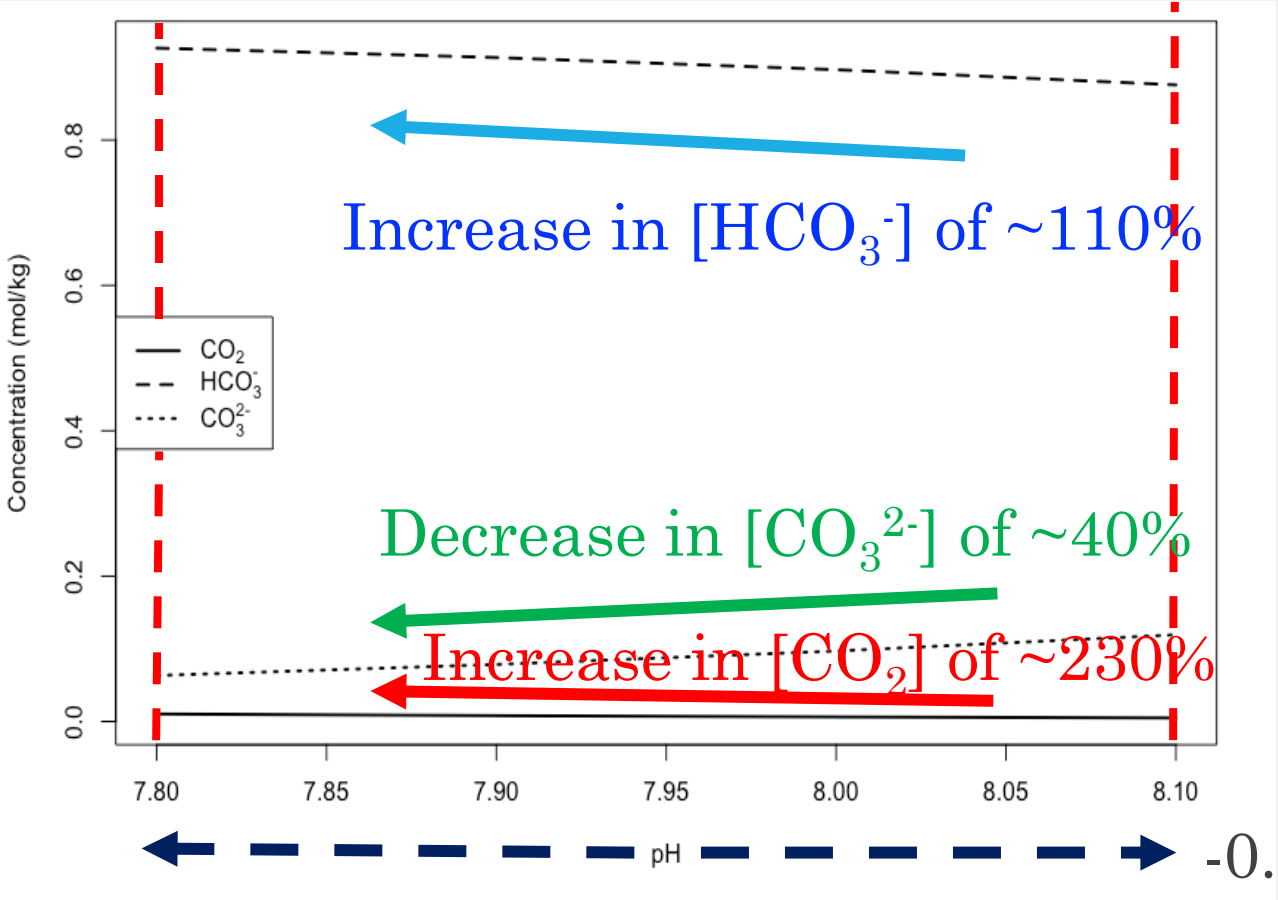
The process of calcification

Some equations

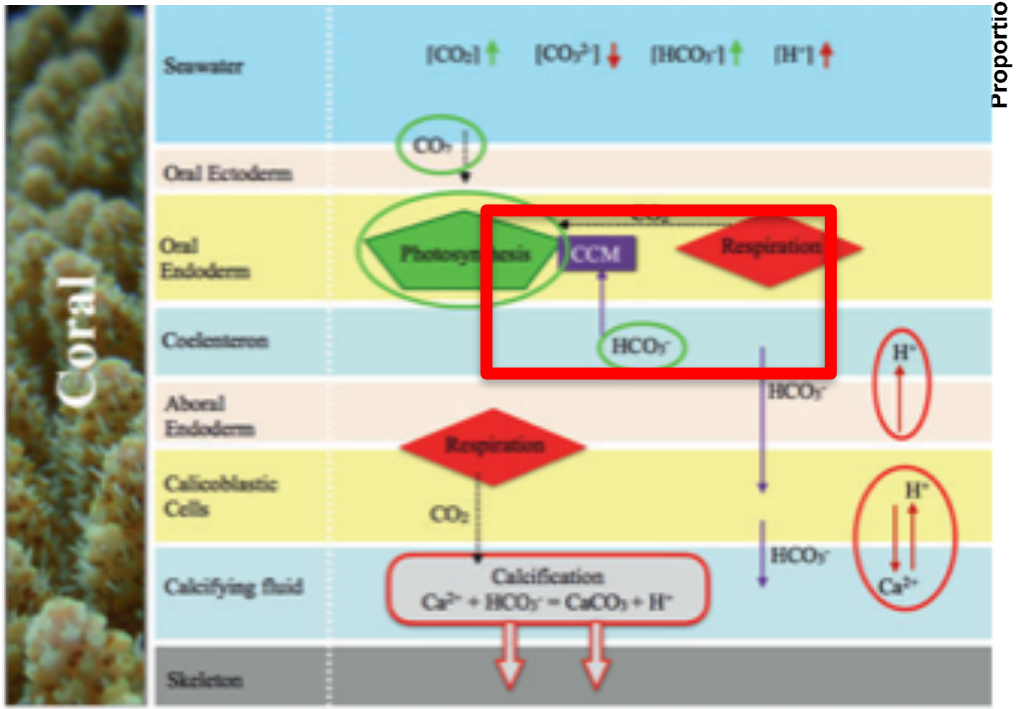
- $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ → Need to compensate for CO_3^{2-} loss
- $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ → Proton production
- $HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$ → Use of H^+ by proton acceptor
- $Ca^{2+} + \cancel{CO_3^{2-}} + HCO_3^- + HCO_3^- + \cancel{H^+} \leftrightarrow CaCO_3 + \cancel{CO_3^{2-}} + \cancel{H^+} + CO_2 + H_2O$
- $Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$ → Shows that calcification PRODUCES CO_2

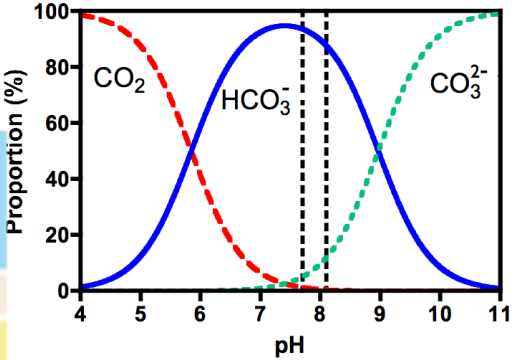
Ocean acidification




Concentration (mol/kg)
0.0
0.2
0.4
0.6
0.8
CO2
HCO3-
CO3 2-
Increase in [HCO3-] of ~110%
Decrease in [CO3 2-] of ~40%
Increase in [CO2] of ~230%
7.80
7.85
7.90
7.95
8.00
8.05
8.10
pH
-0.3

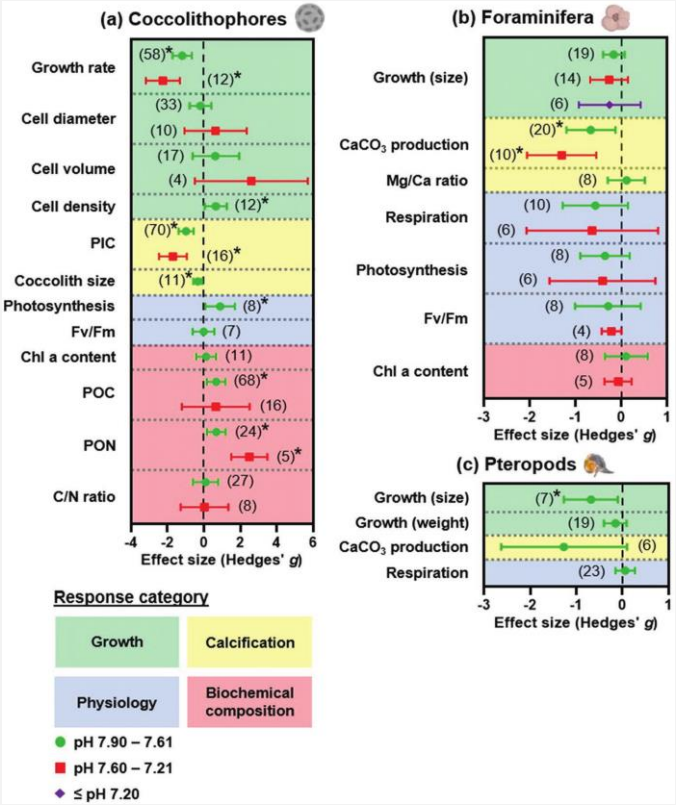
Ocean acidification …not that simple!





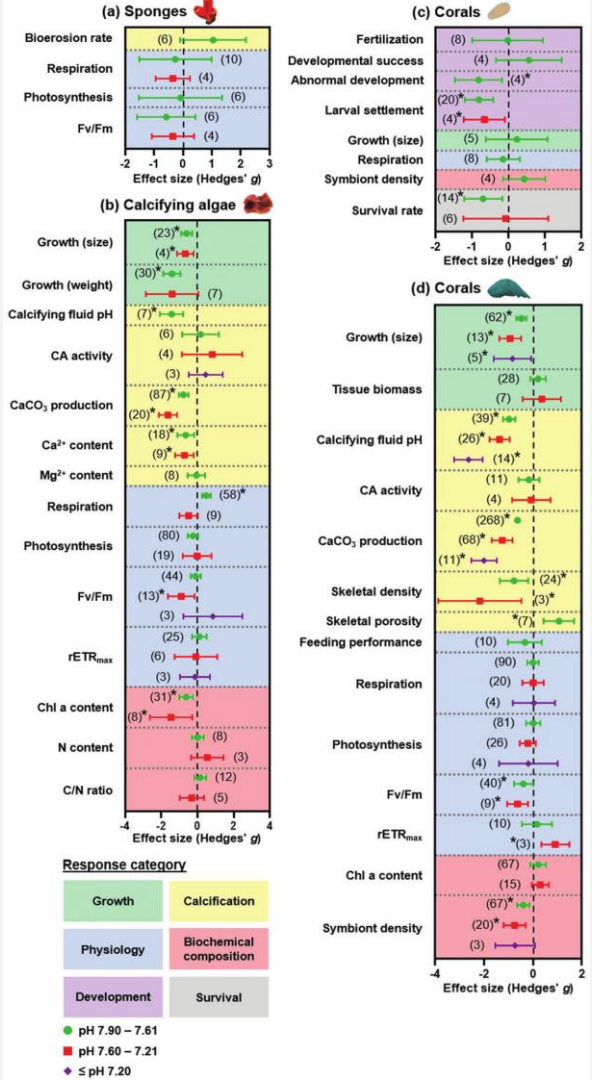
Comeau and Cornwall 2017

Is Ocean acidification a threat for marine organisms?



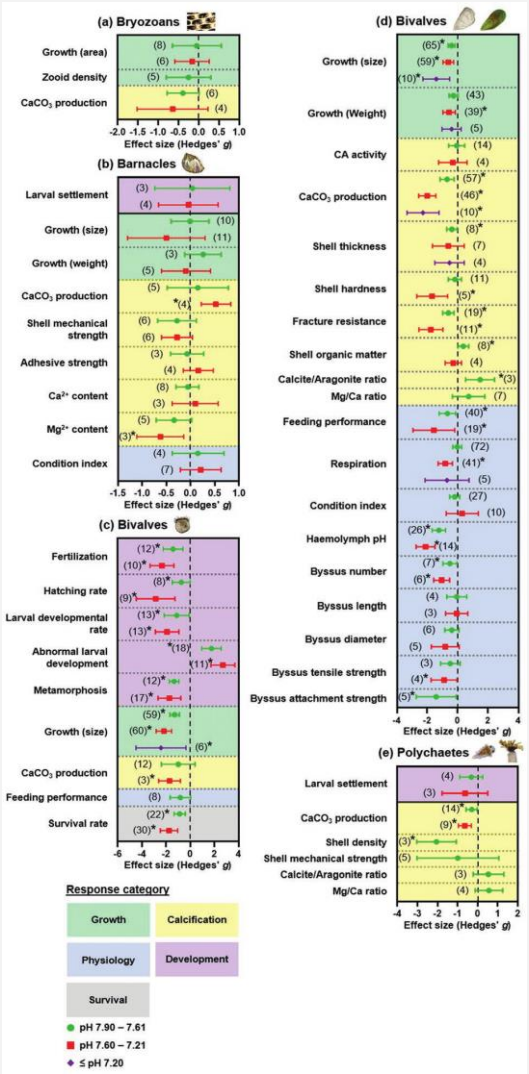
Leung et al. 2022

Is Ocean acidification a threat for marine organisms?



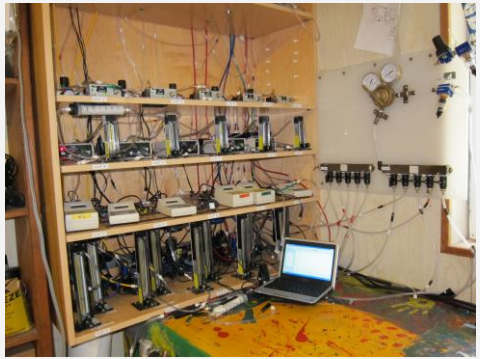
Leung et al. 2022

Is Ocean acidification a threat for marine organisms?

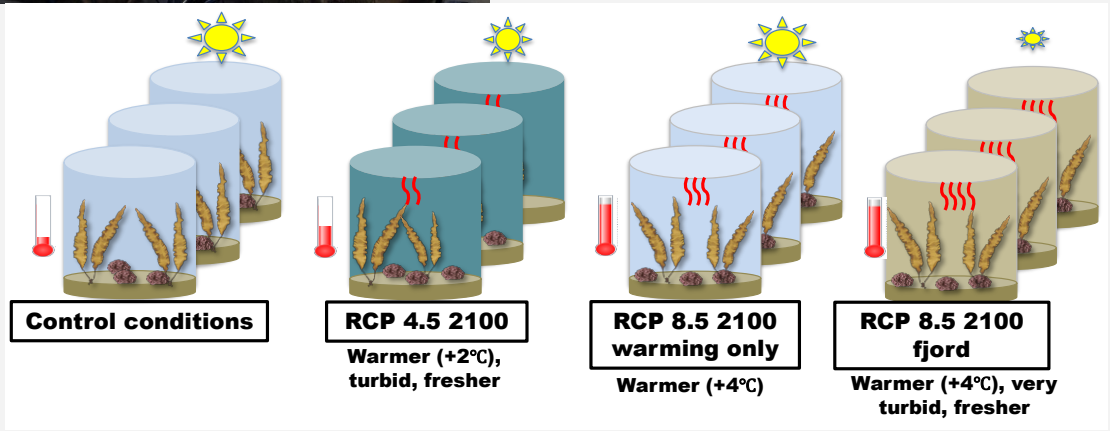


Leung et al. 2022

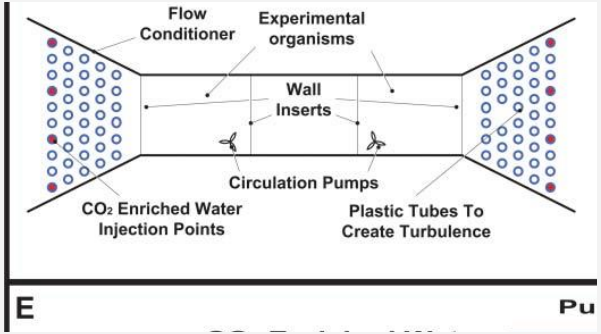
How to test the effects of ocean acidification/warming: Laboratory work

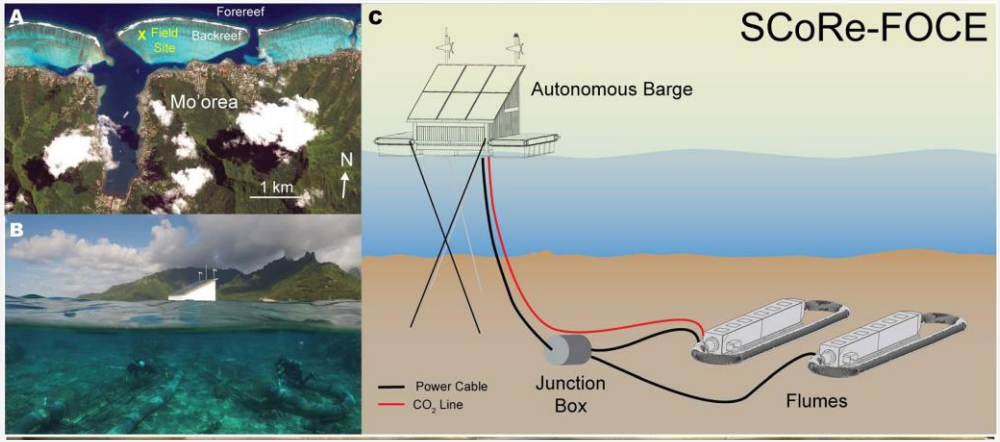


Mesocosms approach

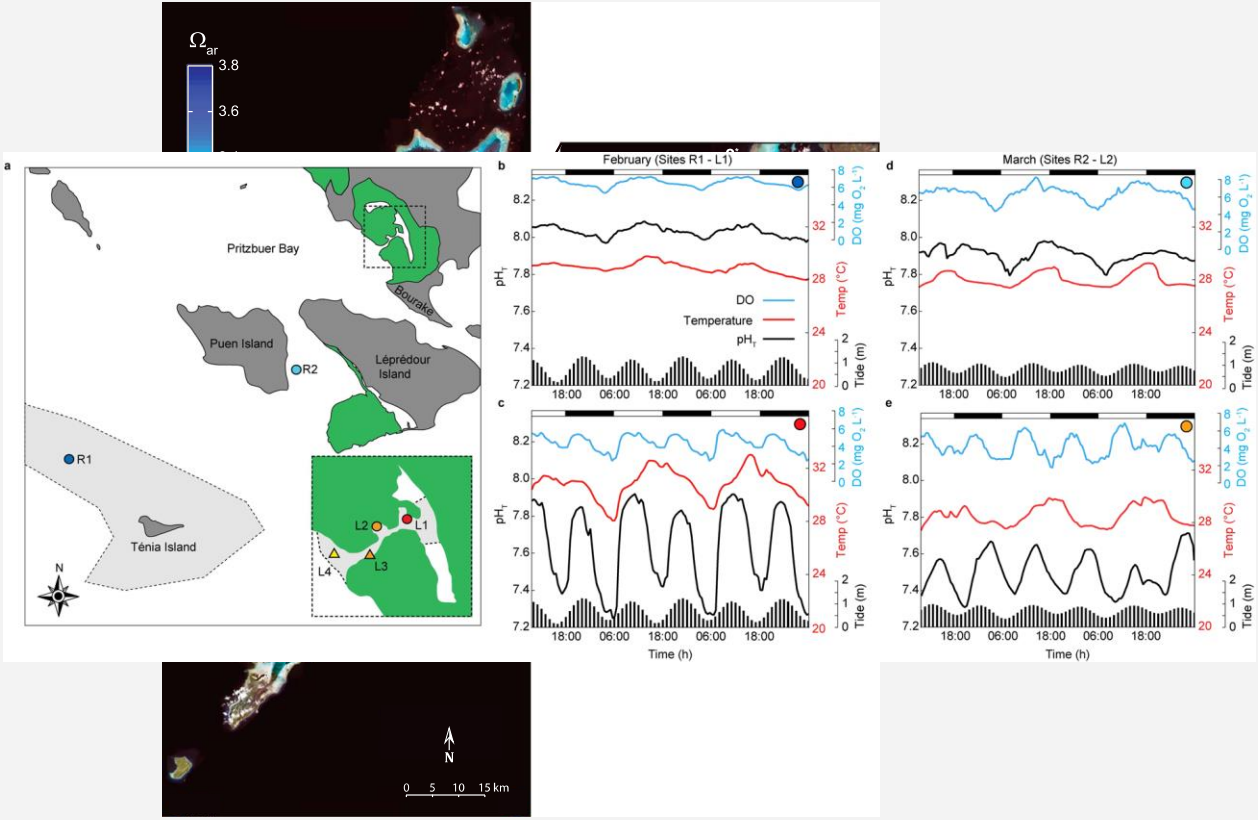


In situ manipulations : Free Ocean Carbon Enrichment (FOCE)

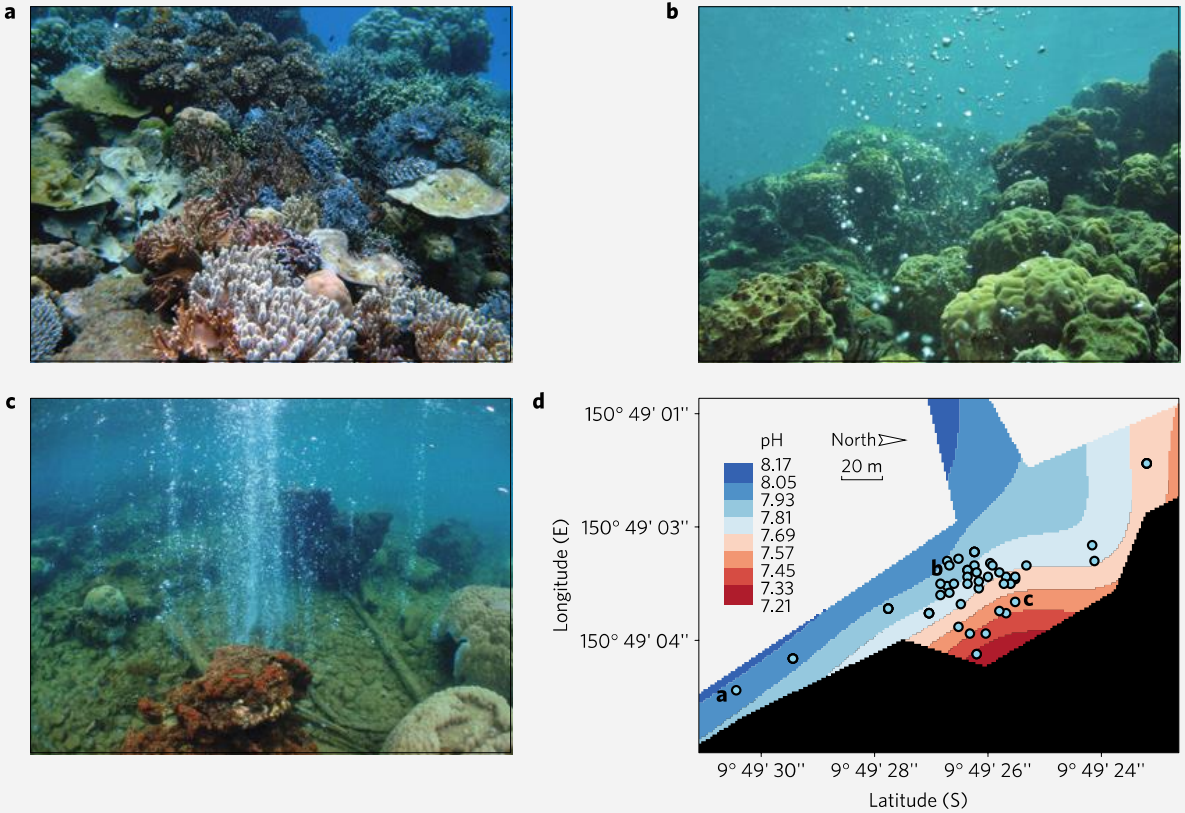




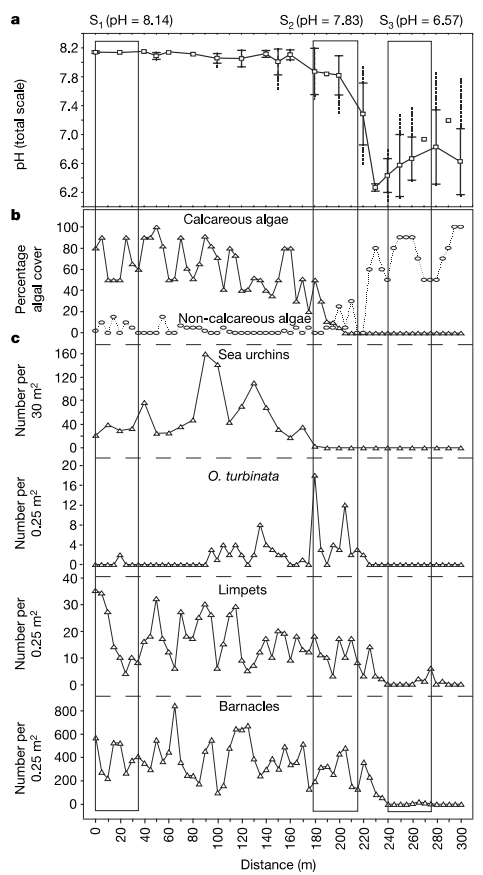
In situ approach: Sites with naturally low pH



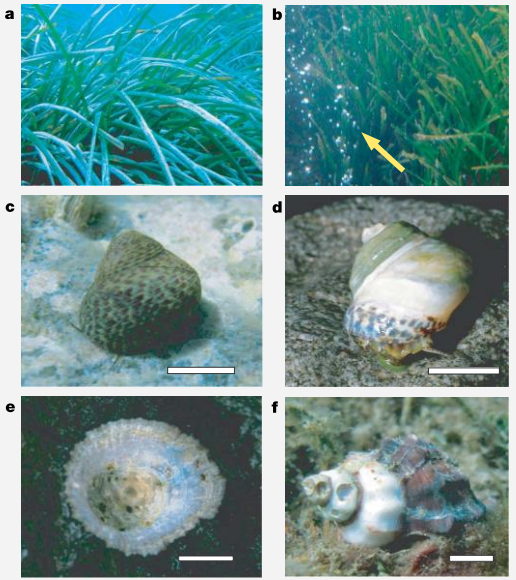
CO2 vents: Palau



CO2 vents : Ischia

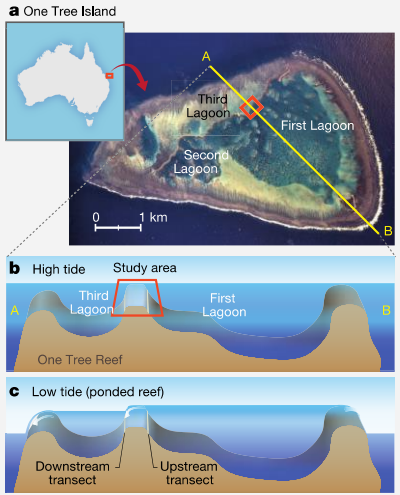


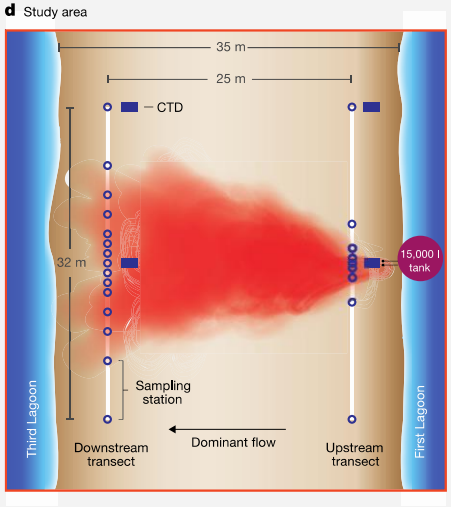
Decreasing pH

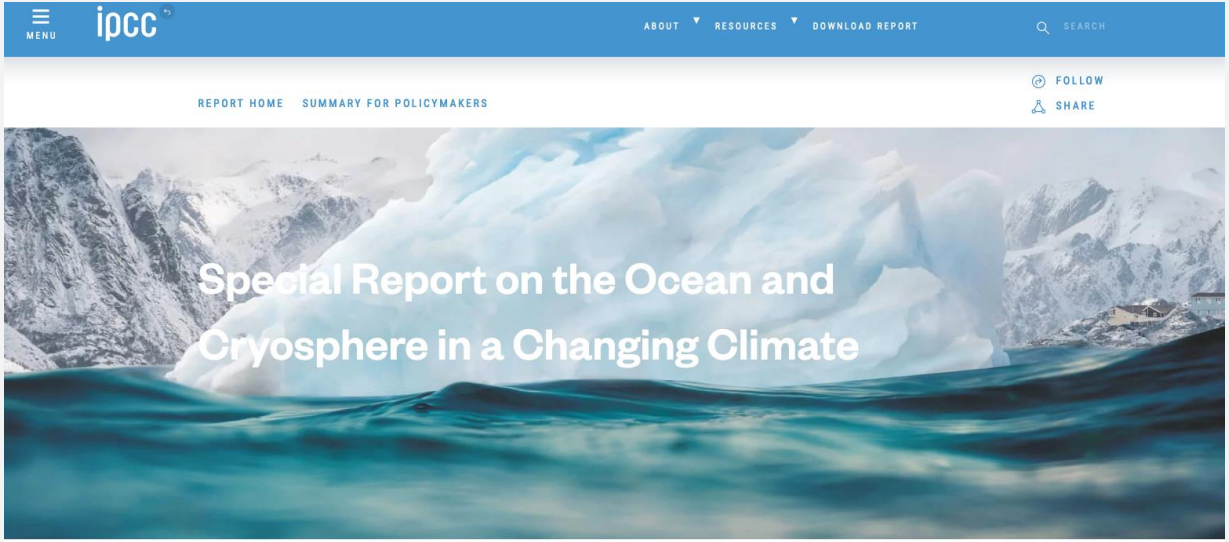


Other methods to test the effects of climate change

- In situ manipulation
- Use of the thermocline
- Use of human activities (Power plants, hotels, etc.)
- ….







The IPCC approved and accepted *Special Report on the Ocean and Cryosphere in a Changing Climate* at its 51st Session held on 20 – 23 September 2019. The approved Summary for Policymakers (SPM) was presented at a press conference on 25 September 2019.

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