IFM-GEOMAR
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an der Universität Kiel

Experimental approaches of carbonate chemistry manipulation in CO_2 pertubation studies

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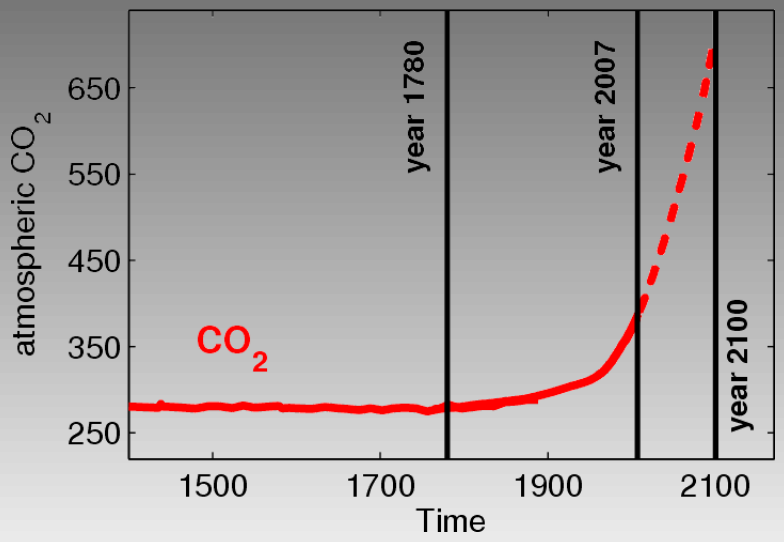
Monaco, 06.-09.10.2008

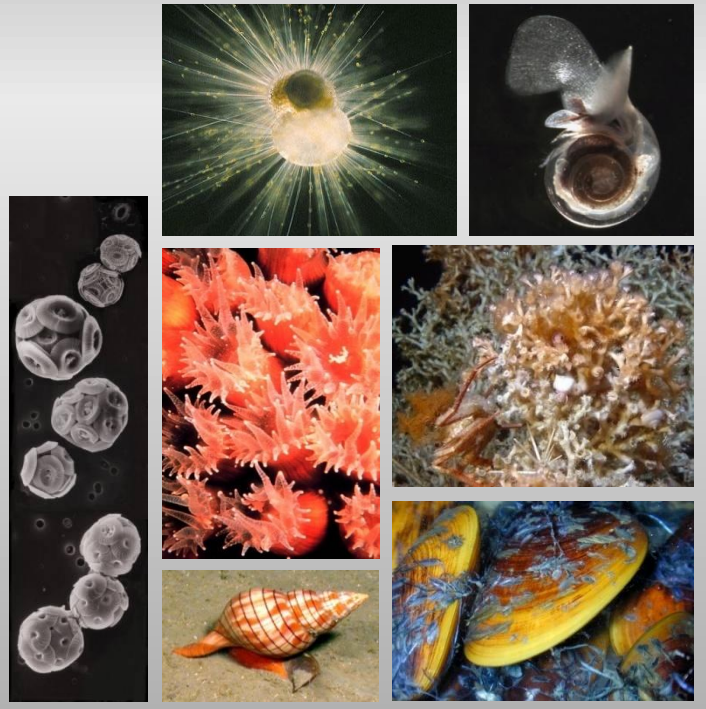
Atmospheric CO_2 variability and marine life



Siegenthaler et al. 2005, Dr. Peter Tans (NOAA/ESRL), IPCC 2001

increase to about 700 ppmv until the year 2100 (IS92a)

100 ppmv increase since industrial revolution



especially of interest for marine calcifiers , such as mussels, snails, Corals, foraminifera, pteropods or coccolithophorids

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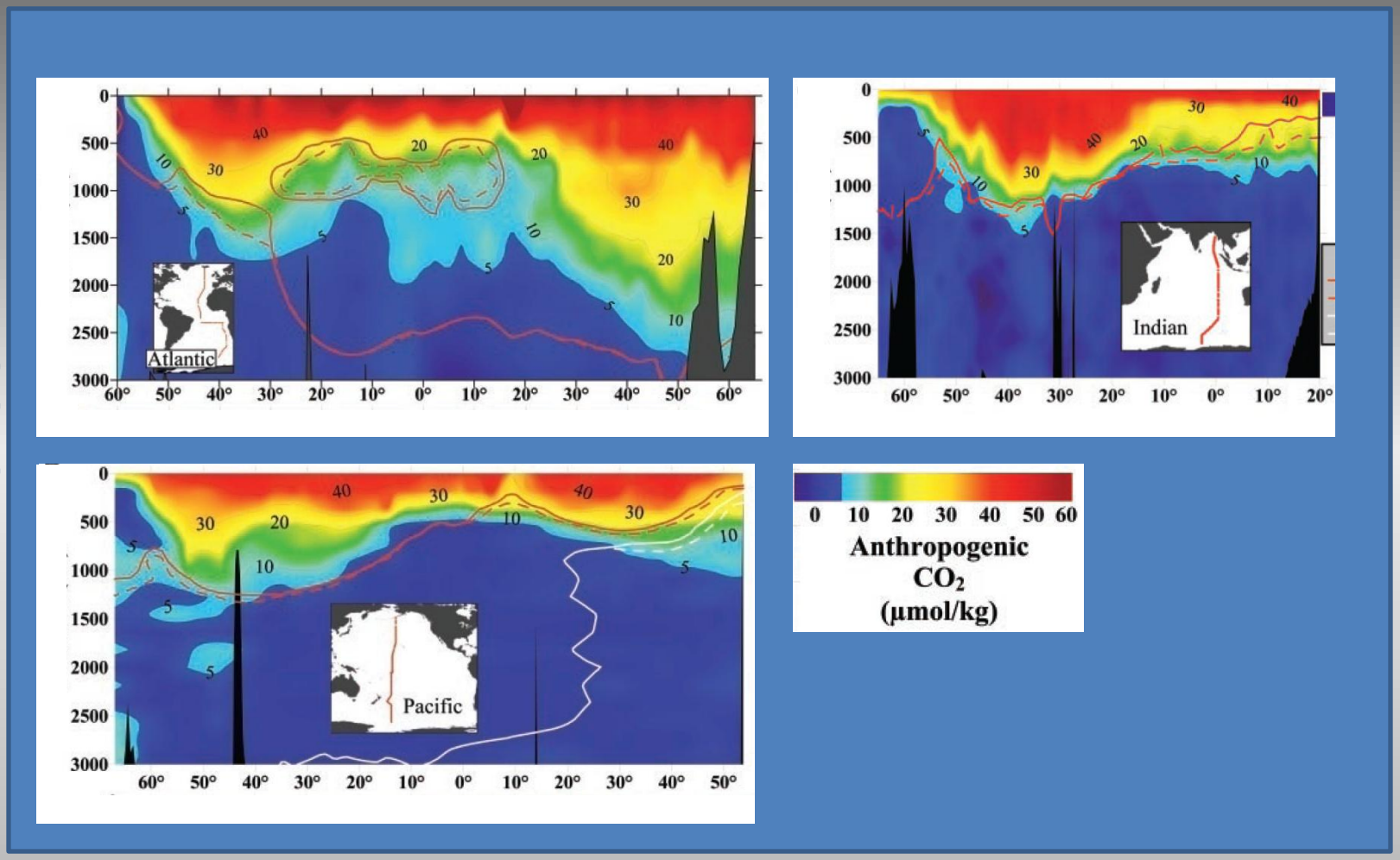
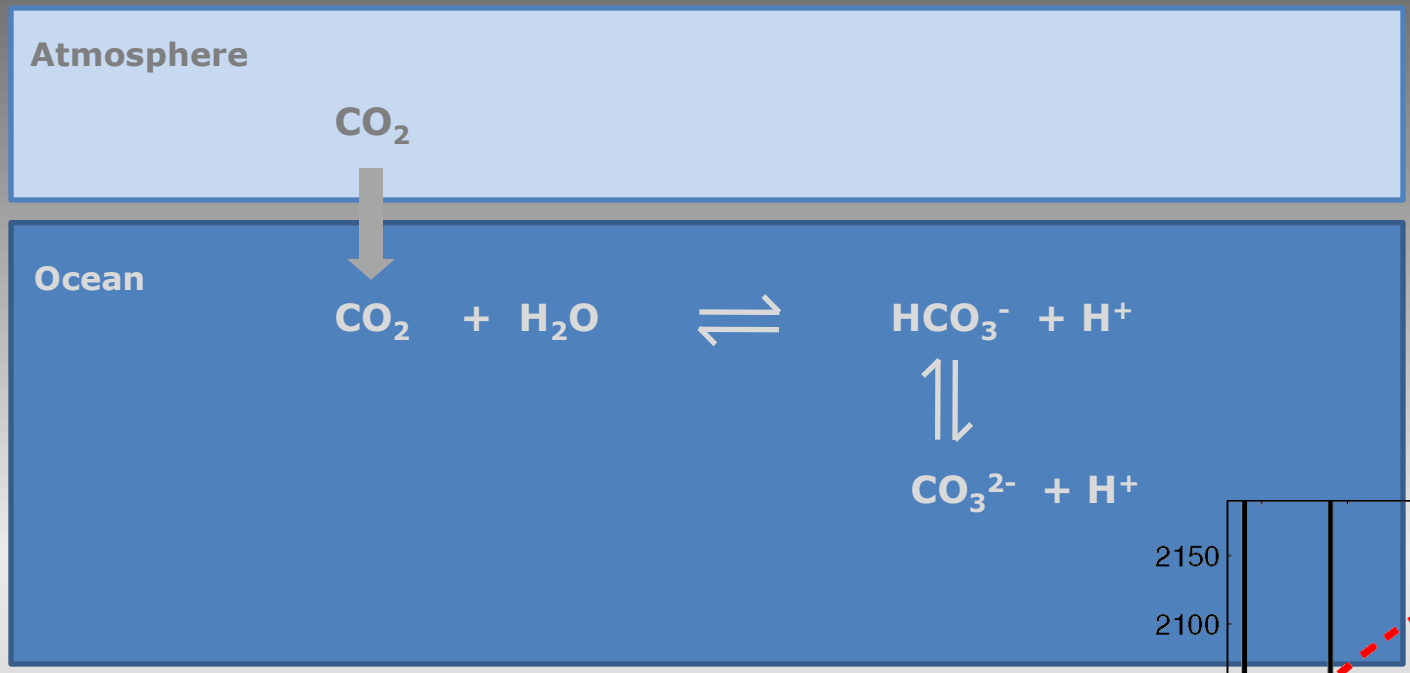
Anthropogenic CO_2 invasion until present day



Feely et al. 2004

CO_2 dissociation in seawater

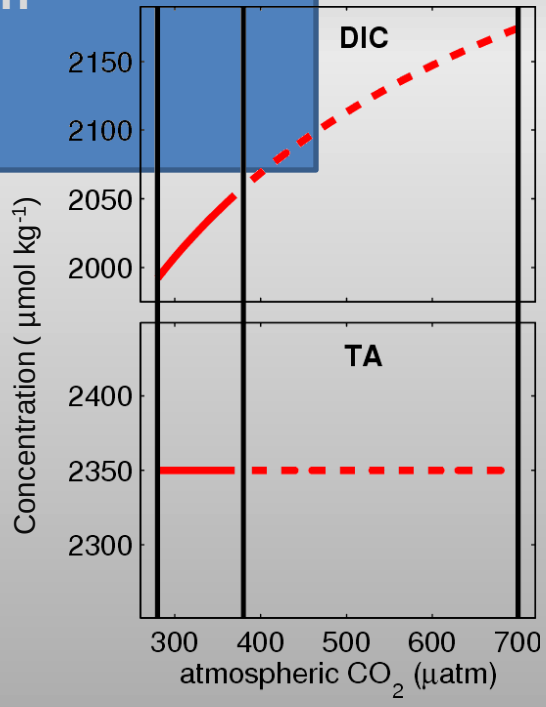


dissolved inorganic carbon

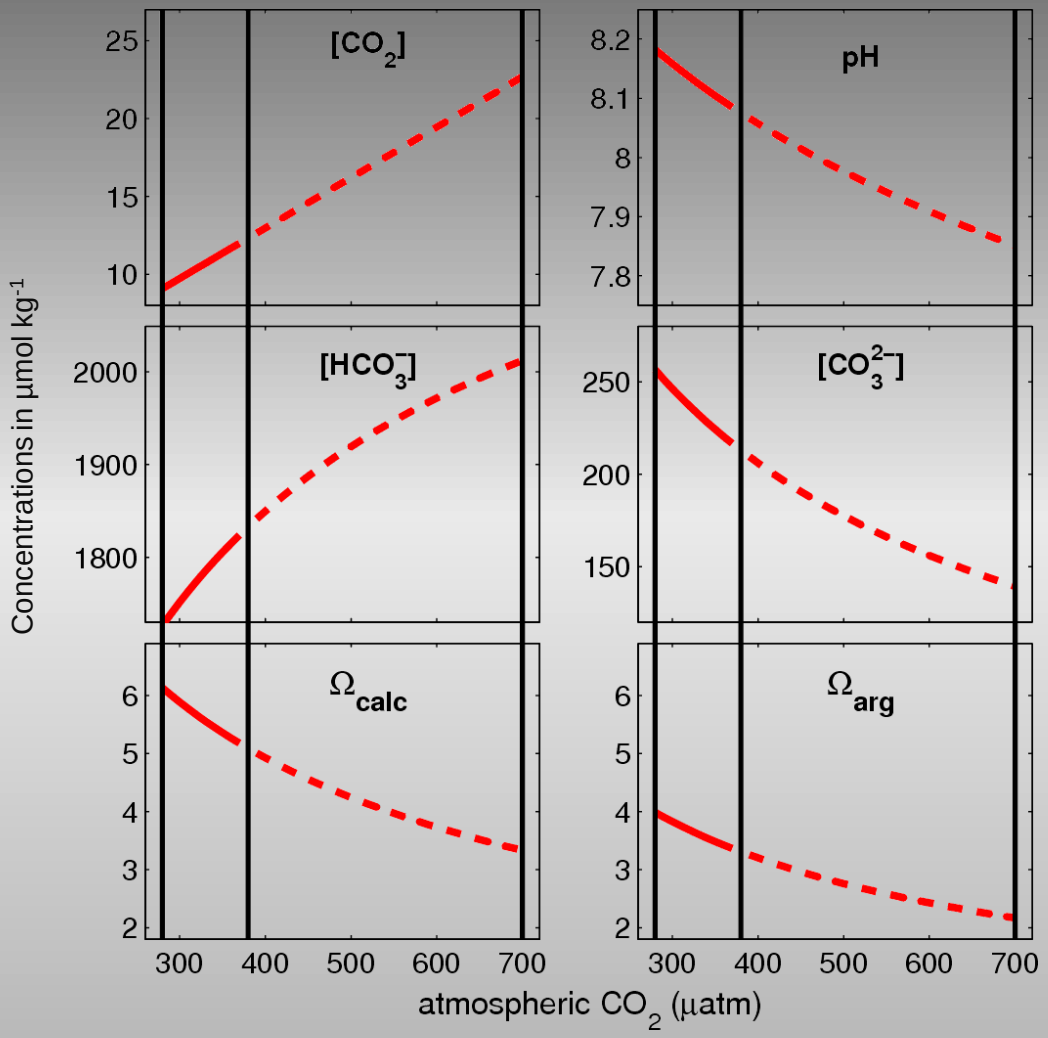
$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

total alkalinity (excluding some minor components)

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$



Surface seawater carbonate chemistry redistribution



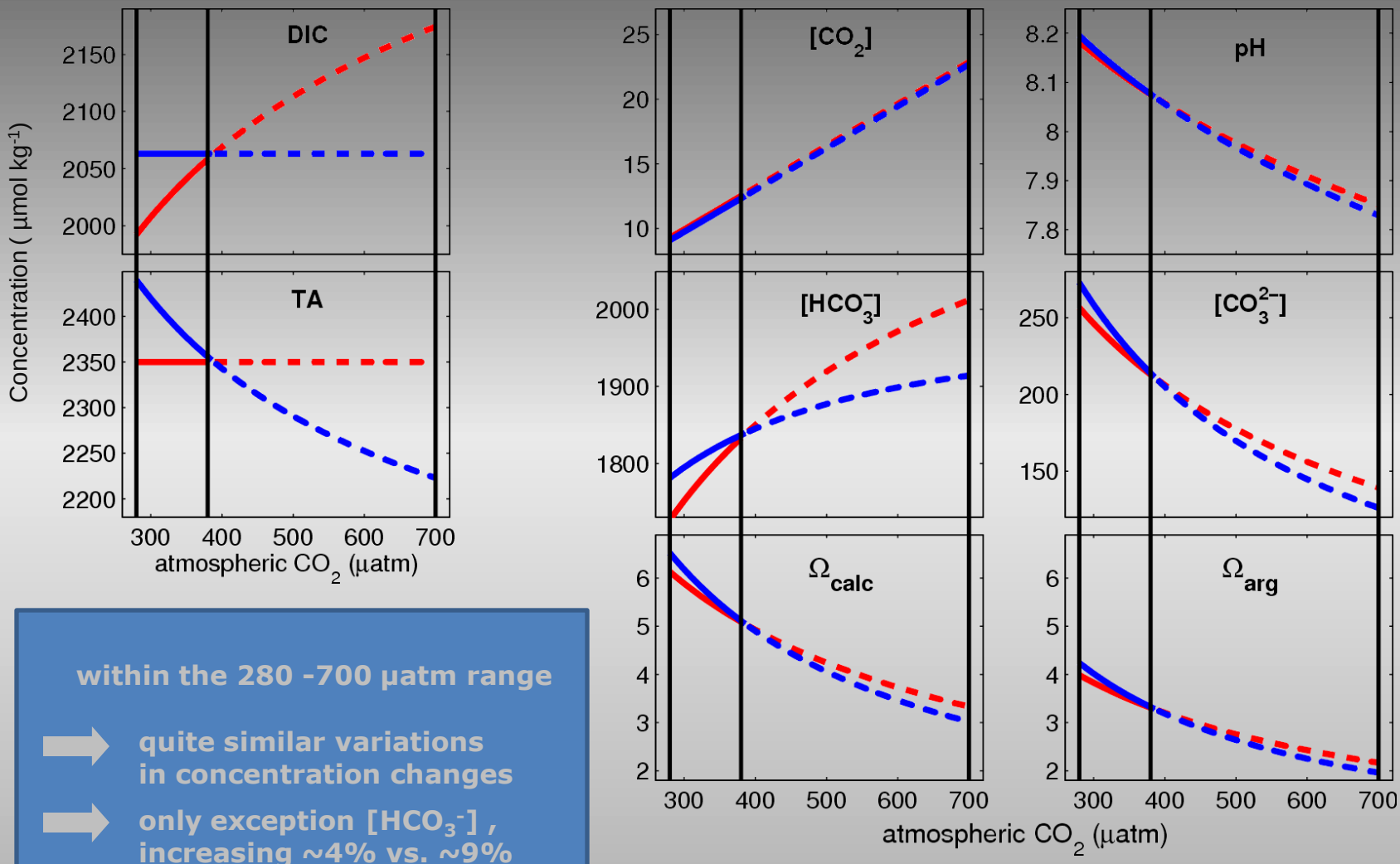
increasing DIC at constant TA

↑ $[CO_2]$, $[HCO_3^-]$

↓ pH, $[CO_3^{2-}]$, Ω_{calc} , Ω_{arg}

Seawater carbonate redistributions also occur by variations in TA at constant DIC

Changes in DIC and TA



within the 280 -700 µatm range

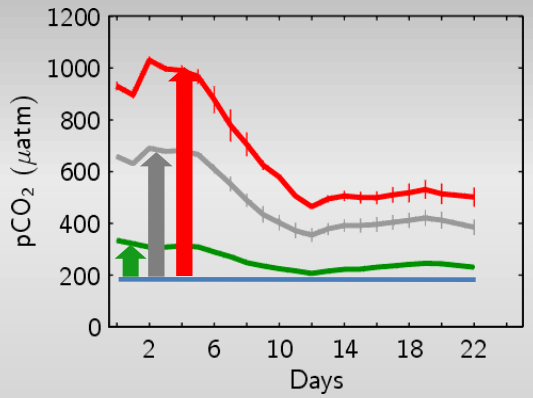
- **quite similar variations in concentration changes**
- **only exception [HCO_3^-] , increasing ~4% vs. ~9% between 380 and 700 µatm**

Different approaches for different experimental setups

- **Which organism / ecosystem is studied?**
  autotrophs, heterotrophs, mixed communities
- **What is the size of the experiment?**
  liters vs. cubic meters of seawater
- **What are the main processes impacting the carbonate system?**
  photosynthesis vs. calcification or respiration
- **What is the duration of the experiment?**
  hours/days vs. weeks
- **What is the main question?**
  physiology vs. biogeochemistry

Leads ideally to a perfect way to manipulate, maintain and monitor the experimental carbonate system

DIC manipulation : aeration of seawater at target CO_2 levels



HOWTO: aeation of the mesocosms (~30m³ each) with air enriched with CO_2 at target levels

aeration was stopped when levels were reached after about two days

Phytoplankton bloom was studied for about 3 weeks

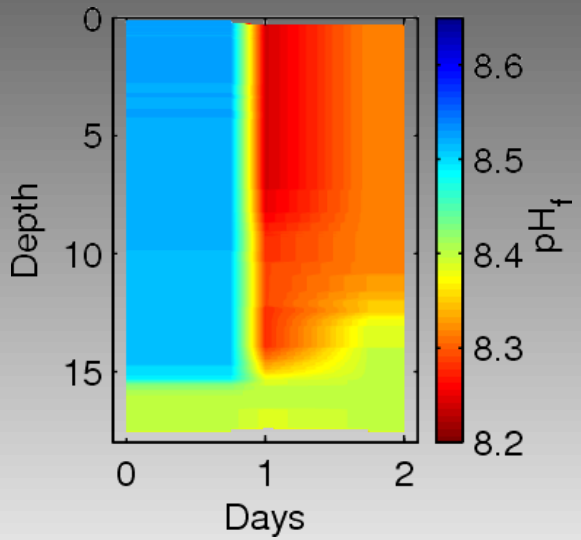
→ CO_2 / pH change gradual

→ relatively easy to adjust although equilibration might take some time

→ simultaneous supply of O_2 during aeration

→ direct seawater aeration might disturb organisms or impact dissolved organics pool

DIC manipulation : injection of CO_2 enriched water



HOWTO:

aeration of filtered seawater with pure CO_2

injection of CO_2 saturated seawater into mesocosms

about 100 l per 60m^3 for ~0.3 pH drop

- **works extremely well for large volumes**
- **does not require a lot of infrastructure**
- **not so easy to adjust to desired CO_2 level**

DIC manipulation : $NaHCO_3$ or Na_2CO_3 additions together with HCl

HOWTO: addition of $NaHCO_3$ to increase DIC to target values together with equimolor additions of HCl to counterbalance the otherwise increase of TA

additions of Na_2CO_3 with twice as much HCl

→ ideal for small scale bottle experiments

→ manipulations can be extremely precise up to a couple of micromoles.

dissolved inorganic carbon

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

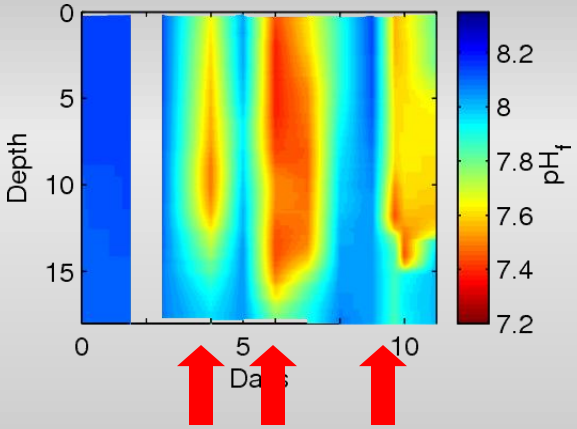
total alkalinity (excluding some minor components)

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

TA manipulation : NaOH / HCl additions

HOWTO:

increasing pCO_2 by additions of HCl and decreasing by NaOH



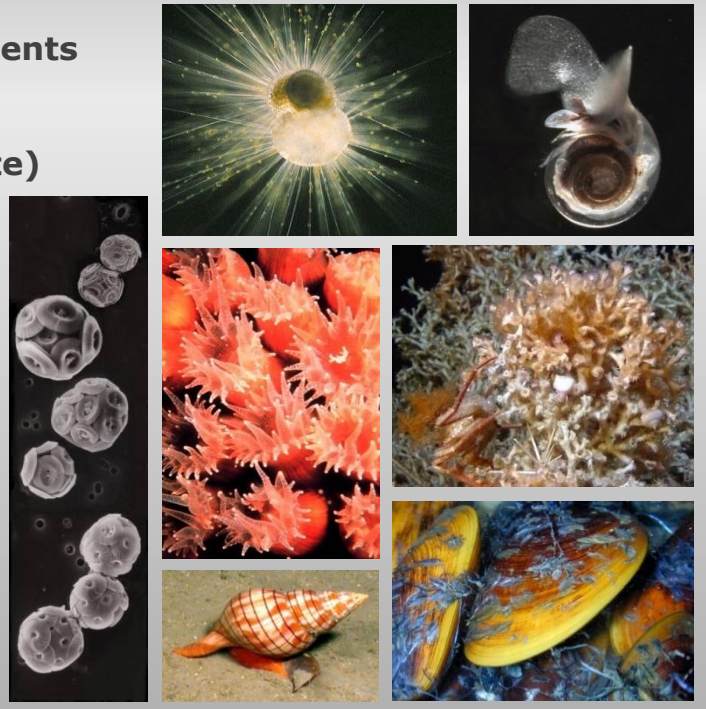
3 acidifications

- **widely used, relativley easy way for manipulation**
- **does not require any complicated infrastructure**
- **feasible for small and large scale applications**

Final remarks and summary

- Type of manipulation depends on application,
  e.g. aeration at target pCO_2 might be necessary to supply O_2 for heterotrophs
- Manipulation is first step, equally important is monitoring
- Measure at least 2 parameters of the carbonate system
  to ensure that the manipulation has worked as intended
- Be sure to know how DIC and TA is impacted
  in the experiments as this will ultimately
  determine pCO_2 changes (long-term experiments
  With calcifiers at constant pCO_2)
- High nutrient (ammonium, silicate, phosphate)
  concentrations have to be considered
  as TA components

Thank you



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