Workshop on Analytical Methods in Aquatic Biogeochemistry

Dissolved inorganic carbon (DIC) & Total alkalinity (TA)

Pete Brown
National Oceanography Centre,
Southampton, UK

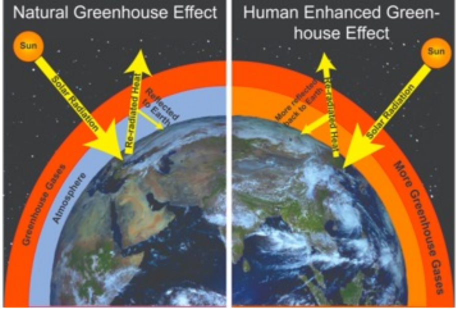
1ST-12TH OCTOBER 2018

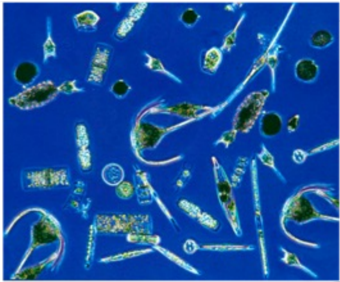
Contents

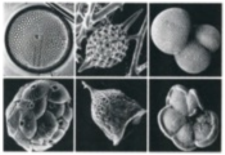
- Why is it important to understand the global CO_2 system?
- What are the drivers of ocean CO_2 uptake / outgassing?
- Consequences of elevated atmospheric CO_2 levels, and associated climate change
- Carbonate system in seawater
- Water sampling and storage
- Seawater carbon system analysis
- Data quality

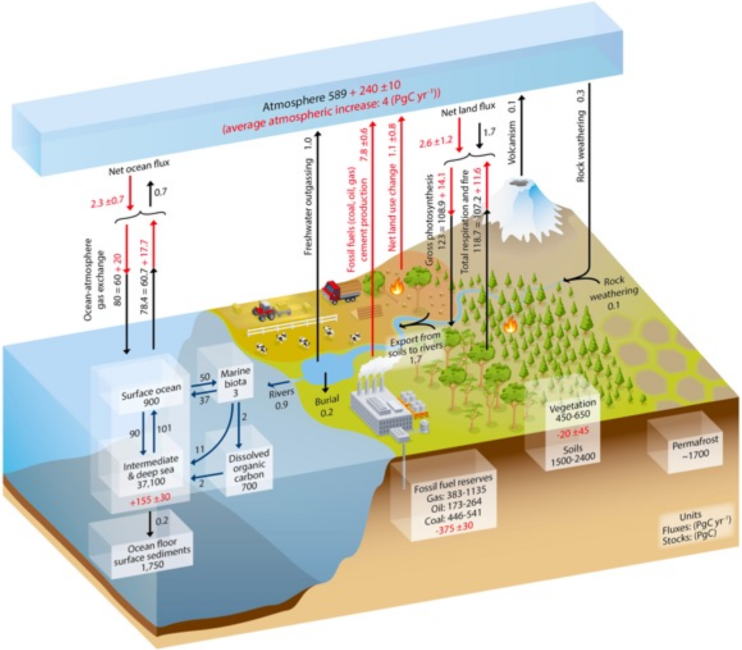
Why is it important to understand the CO_2 system?

- CO_2 controls the fraction of inbound radiation that remains trapped in the atmosphere (greenhouse effect), which controls planetary climate
- CO_2 is the raw material used to build organic matter
- CO_2 controls the pH of the oceans
- Distribution of CO_2 species affects preservation of $CaCO_3$ deposited on the sea floor



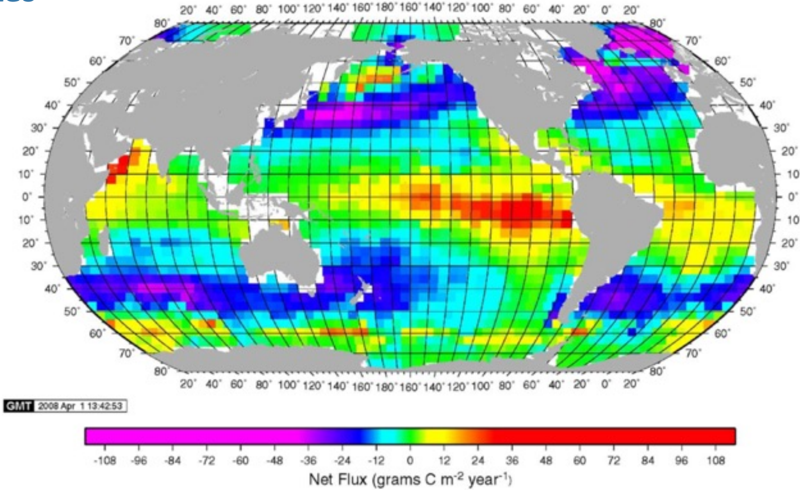





Atmosphere 589 + 240 ±10
(average atmospheric increase: 4 (PgC yr⁻¹))
Net ocean flux
2.3 ±0.7
0.7
Ocean-atmosphere gas exchange
80 = 60 + 20
78.4 = 60.7 + 17.7
Freshwater outgassing 1.0
Fossil fuels (coal, oil, gas) cement production 7.8 ±0.6
Net land use change 1.1 ±0.8
Net land flux
2.6 ±1.2
1.7
Gross photosynthesis 123 = 108.9 + 14.1
Total respiration and fire 118.7 = 107.2 + 11.6
Volcanism 0.1
Rock weathering 0.3
Rock weathering 0.1
Export from soils to rivers 1.7
Surface ocean 900
Marine biota 3
50
37
Rivers 0.9
Burial 0.2
90
101
2
11
Intermediate & deep sea 37,100
+155 ±30
Dissolved organic carbon 700
2
0.2
Ocean floor surface sediments 1,750
Vegetation 450-650
-20 ±45
Soils 1500-2400
Permafrost ~1700
Fossil fuel reserves
Gas: 383-1135
Oil: 173-264
Coal: 446-541
-375 ±30
Units
Fluxes: (PgC yr⁻¹)
Stocks: (PgC)

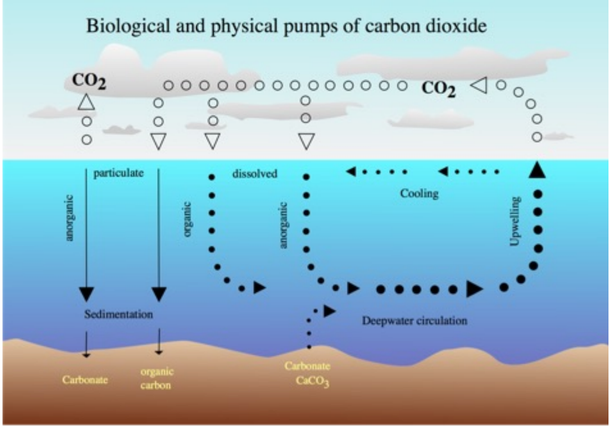
Air-sea carbon dioxide fluxes

Annual flux of contemporary CO_2



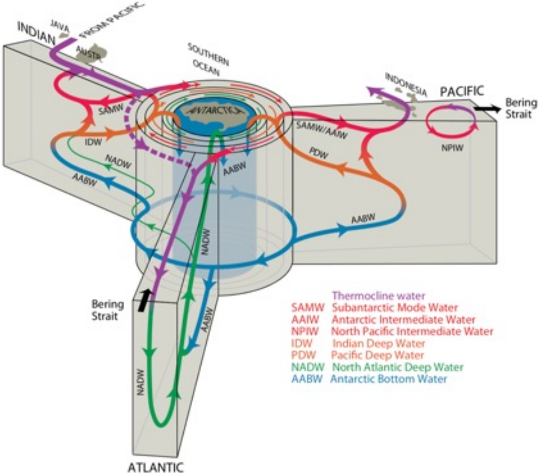
Takahashi et al (2009) DSR

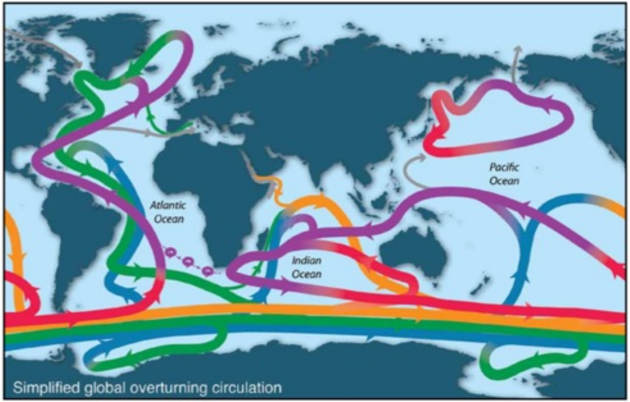
What are the drivers of the ocean CO_2 sink?



What are the drivers of the ocean CO_2 sink?

- Ocean Circulation

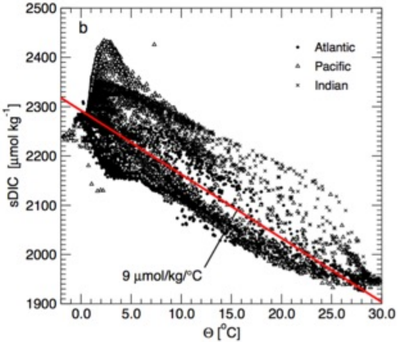


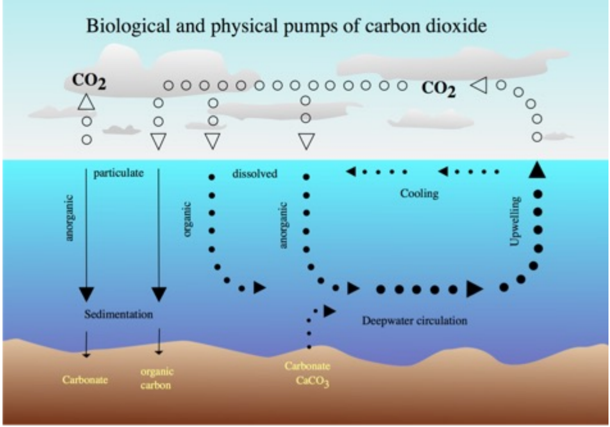


Talley 2013

What are the drivers of the ocean CO_2 sink?

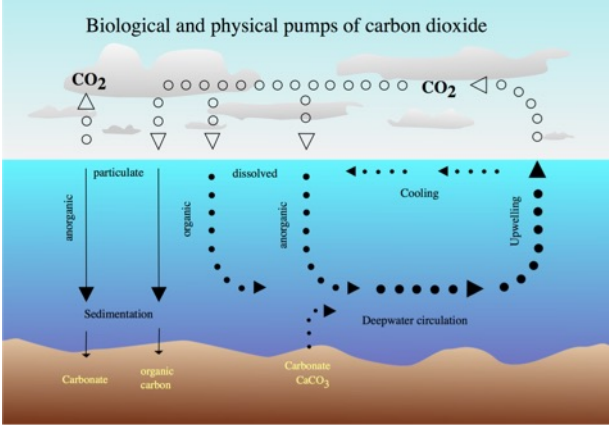
- Ocean Circulation
  - Transport of heat
  - Heat fluxes – cooling / warming of surface waters drives CO2 uptake / outgassing through impact on CO_2 solubility





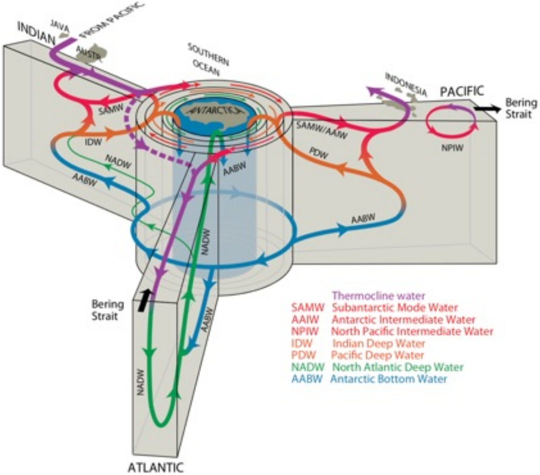
What are the drivers of the ocean CO_2 sink?

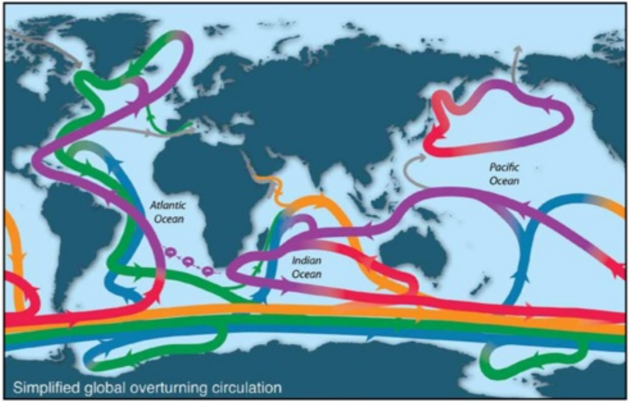
- Ocean Circulation
  - Transport of heat
  - Heat fluxes – cooling / warming of surface waters drives CO2 uptake / outgassing through impact on CO_2 solubility
  - Transport of recently ventilated waters high in anthropogenic carbon to depth
  - Transport of old waters high in remineralised carbon and nutrients to the surface



What are the drivers of the ocean CO_2 sink?

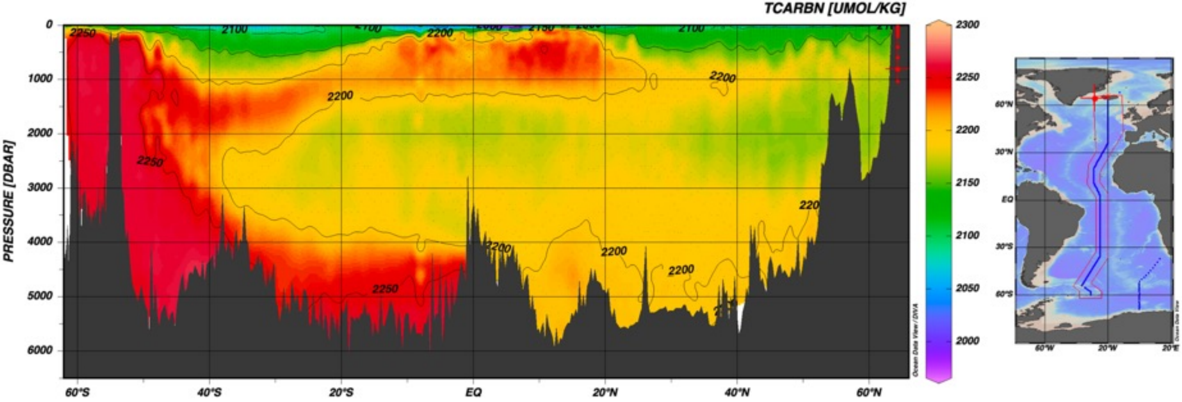
- Ocean Circulation





Talley 2013

Circulation apparent in DIC distribution

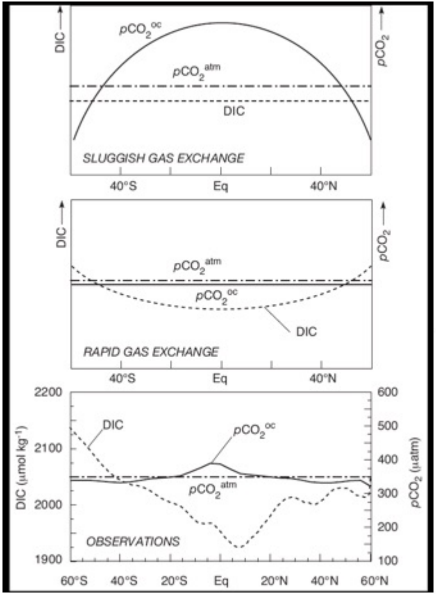


North-South distribution of pCO_2 and DIC

Very slow gas exchange (model), constant DIC

Rapid gas exchange (model), pCO_2water = pCO_2air

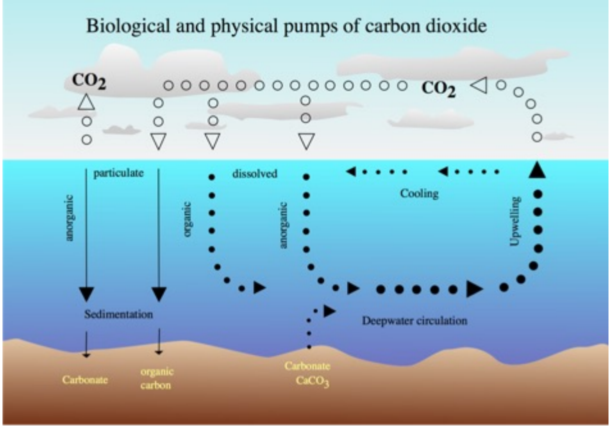
Observations:
-pCO_2water ≠ pCO_2air
-rather slow gas transfer



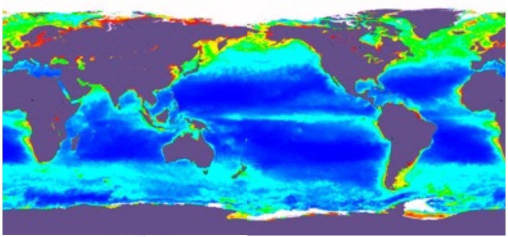
(Sarmiento and Gruber, 2006)

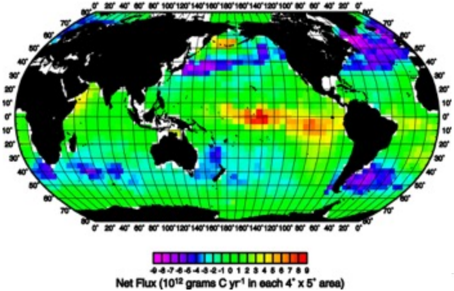
What are the drivers of the ocean CO_2 sink?

- Ocean Circulation
  - Transport of heat
  - Heat fluxes – cooling / warming of surface waters drives CO2 uptake / outgassing through impact on CO_2 solubility
  - Transport of recently ventilated waters high in anthropogenic carbon to depth
  - Transport of old waters high in remineralised carbon and nutrients to the surface
- Biological production and the drawdown in carbon concentrations associated with this
  - Nutrient supply that sustains biological production



Biological influence on air-sea flux.

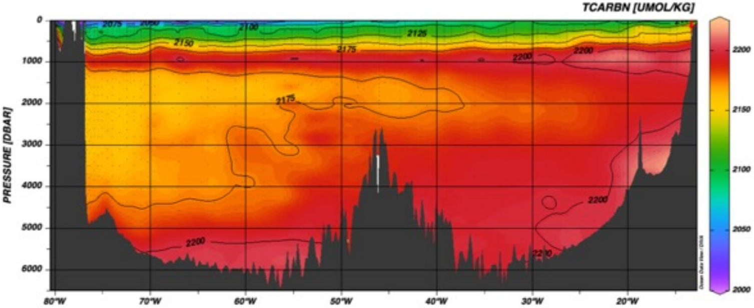




- Blooms of plankton fix carbon dioxide from the water and lower DIC, hence pCO_2.
- Particularly marked in the North Atlantic which has the most intense bloom of any major ocean region.
- In the equatorial Pacific, plankton blooms are suppressed by lack of iron – part of the explanation for high pCO_2there.
- In the equatorial Atlantic, upwelling is less intense and there is more iron from atmospheric dust.

Ocean carbon “pumps”

Deep water has higher (10-20%) total carbon content and nutrient concentrations than surface water. There are several processes contributing to this:



The "**Solubility pump**" tends to keep the deep sea higher in total inorganic carbon (DIC) compared to the warm surface ocean.

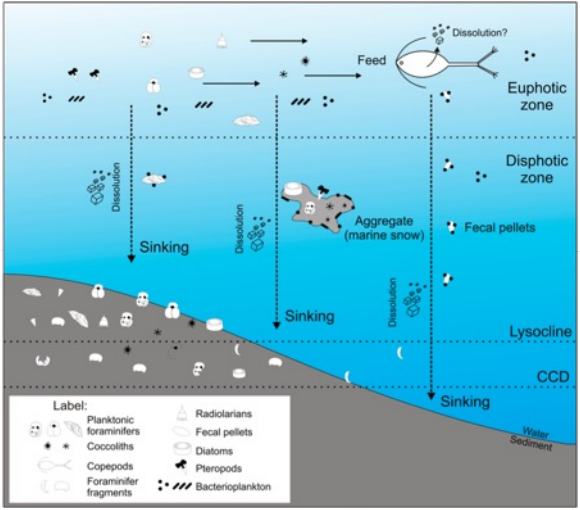
The “**Biological pump(s)**" – the flux of biological detritus from the surface to deep, enriches deep water concentrations. There are two distinct phases of the carbon in this material:

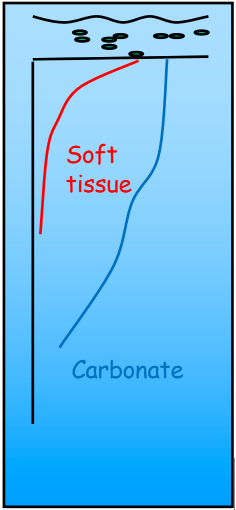
- The "soft tissue" pump enriches the deep sea in inorganic carbon and nutrients by transport of organic carbon compounds.
- The calcium carbonate pump enriches the deep sea in inorganic carbon and calcium.

Ocean biological "pumps"

Falling dead organisms, faecal pellets and detritus are "remineralised" at depth. Remineralization occurs

- By bacterial activity.
- By inorganic dissolution of carbonate below the lysocline.
- The different phases have different depth profiles for remineralisation.





Ocean biological soft tissue pump

This mechanism acts continually to reduce the partial pressure of CO_2 (pCO_2) in the surface ocean, and increase it at depth.

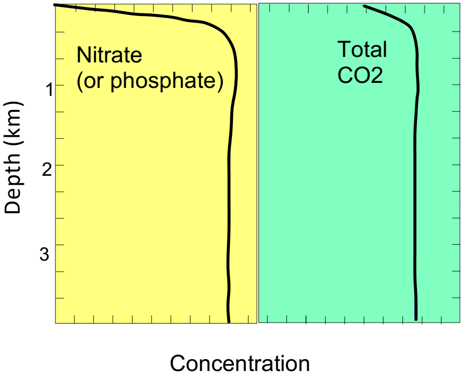
Over most of the ocean, upwelling water is depleted of inorganic carbon and nutrients (nitrate and phosphate) by plankton.

In the process they remove about 10% of the inorganic CO_2 in the water. Most of this goes to form organic matter via the reaction:

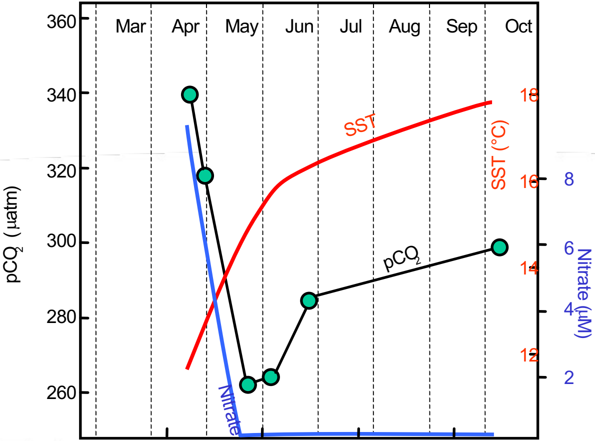
$$CO_2 + H_2O \Rightarrow CH_2O + O_2.$$

Because the *buffer factor* β ~10, this has a large effect on surface pCO_2, decreasing it by 2-3 times.

The reverse reaction occurs by (mostly bacterial) respiration at depth, and increases CO_2 concentration there.



Surface pCO$_2$, nutrient and surface temperature in the North Atlantic



Ocean biological carbonate pump

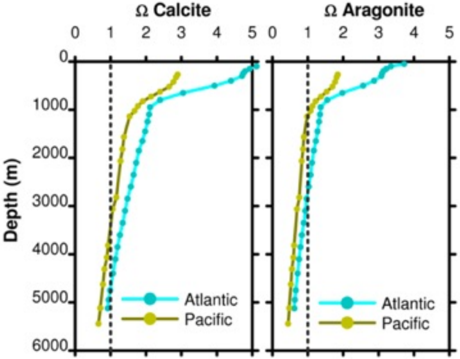
This mechanism also transfers carbon from the surface ocean to the deep sea.

Some of the carbon taken up by the biota in surface waters goes to form calcium carbonate.

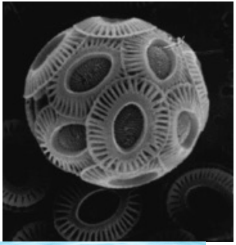
The $CaCO_3$ sinks to the deep sea, where some of it may re-dissolve and some become sedimented. The redissolution can only occur below the lysocline, which is shallower in the Pacific than the Atlantic.

In contrast to the soft tissue pump, this mechanism tends to *increase* surface ocean pCO_2 and therefore atmospheric CO_2 . The net reaction is:

$$Ca^{++} + 2HCO_3^- \Rightarrow H_2O + CO_2\Uparrow + CaCO_3\Downarrow$$



Biological carbonate pump – Coccolithophores: calcite precipitating plankton



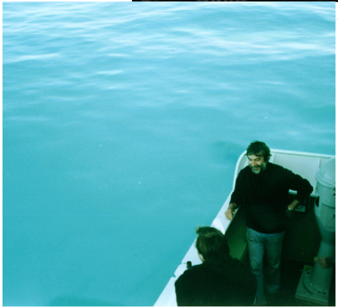
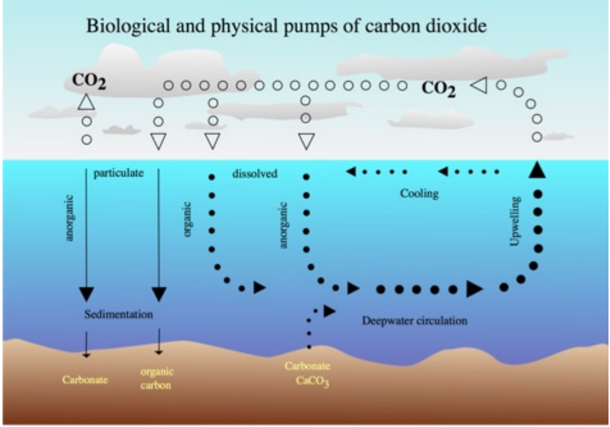


Photo: courtesy D. Purdie

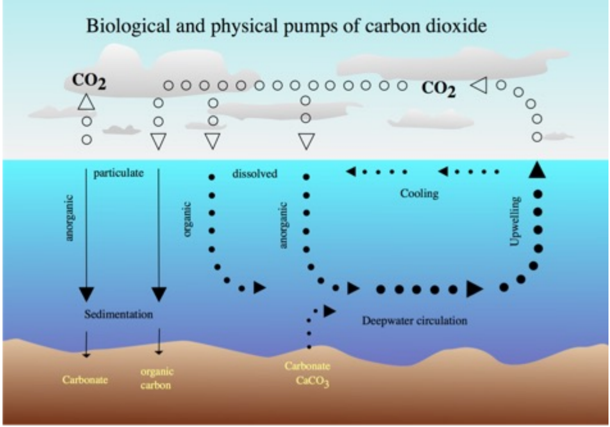
What are the drivers of the ocean CO_2 sink?

- Ocean Circulation
  - Transport of heat
  - Heat fluxes – cooling / warming of surface waters drives CO2 uptake / outgassing through impact on CO_2 solubility
  - Transport of recently ventilated waters high in anthropogenic carbon to depth
  - Transport of old waters high in remineralised carbon and nutrients to the surface
- Biological production and the drawdown in carbon concentrations associated with this
  - Nutrient supply that sustains biological production
- Wind regime – speed of air-sea CO_2 transfer related to wind strength



What are the drivers of the ocean CO_2 sink?

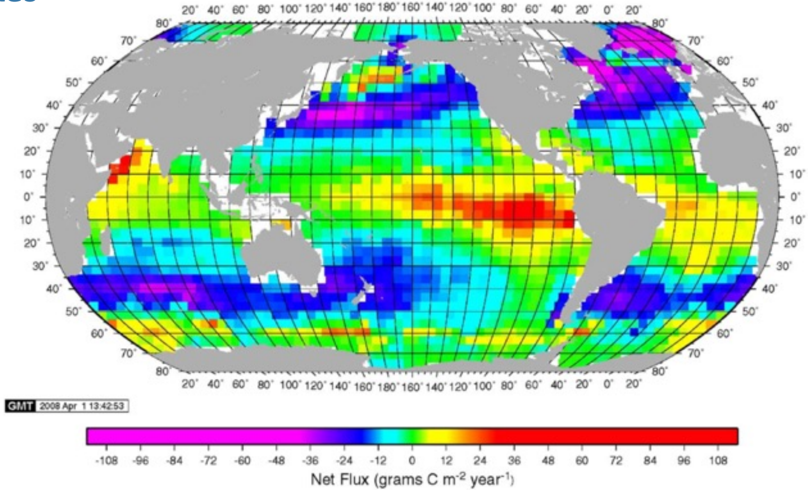
- Ocean Circulation
  - Transport of heat
  - Heat fluxes – cooling / warming of surface waters drives CO2 uptake / outgassing through impact on CO_2 solubility
  - Transport of recently ventilated waters high in anthropogenic carbon to depth
  - Transport of old waters high in remineralised carbon and nutrients to the surface
- Biological production and the drawdown in carbon concentrations associated with this
  - Nutrient supply that sustains biological production
- Wind regime – speed of air-sea CO_2 transfer related to wind strength



Ocean CO_2 sink currently a delicate balance between speed at which CO_2 enters the ocean, & speed at which it is removed from the surface -> substantial variability

Air-sea carbon dioxide fluxes

Annual flux of contemporary CO_2

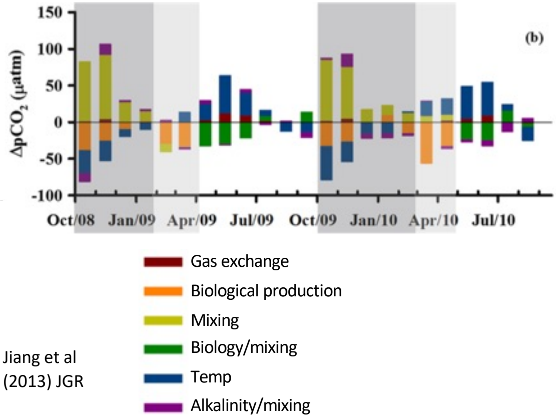


Takahashi et al (2009) DSR

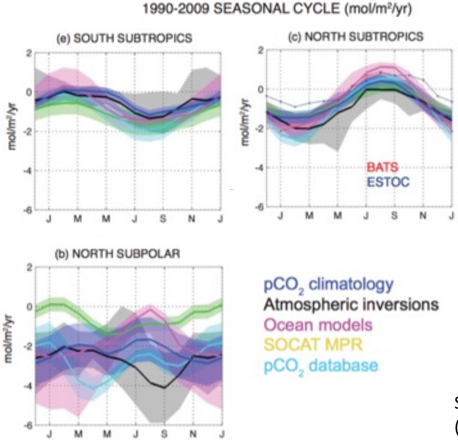
What are the drivers of the ocean CO_2 sink?

NORTH ATLANTIC

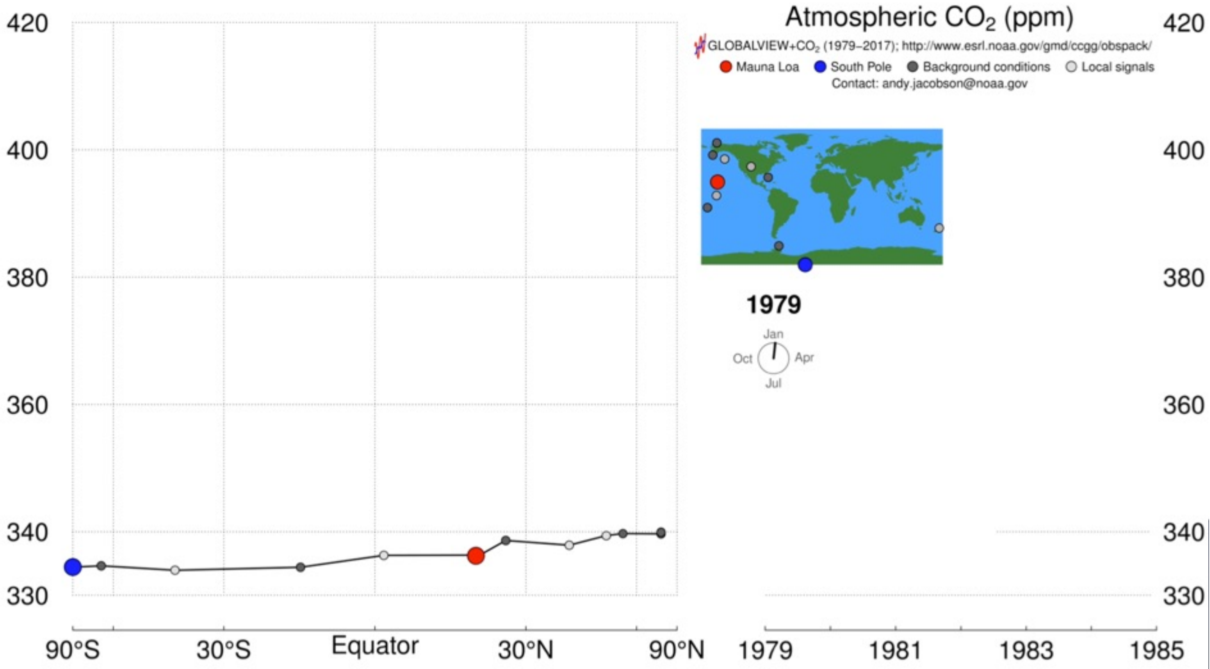
Variability in seasonal ΔpCO_2 amplitude, and continuing disagreement between different methods for constraining the seasonal CO_2 cycle



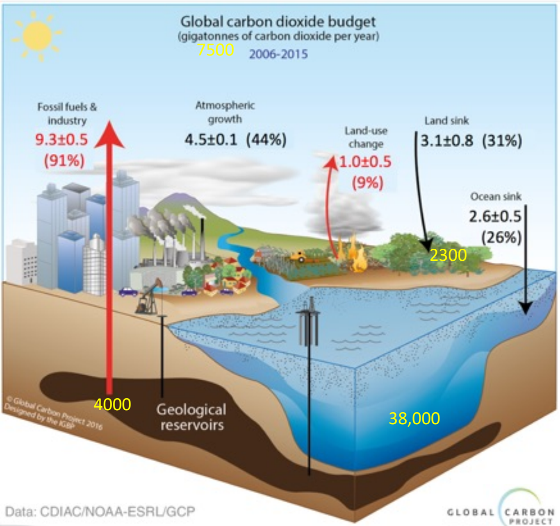
Jiang et al (2013) JGR



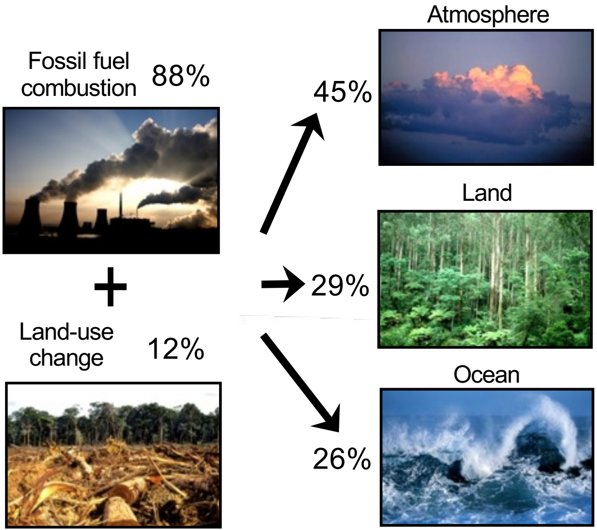
Schuster et al (2013) BG


Atmospheric CO$_2$ (ppm)
GLOBALVIEW+CO$_2$ (1979–2017); http://www.esrl.noaa.gov/gmd/ccgg/obspack/
● Mauna Loa ● South Pole ● Background conditions ○ Local signals
Contact: andy.jacobson@noaa.gov
1979
Jan
Apr
Jul
Oct
420
400
380
360
340
330
90°S
30°S
Equator
30°N
90°N
1979
1981
1983
1985

Carbon dioxide



Data: CDIAC/NOAA-ESRL/GCP



Fossil fuel combustion 88%

+

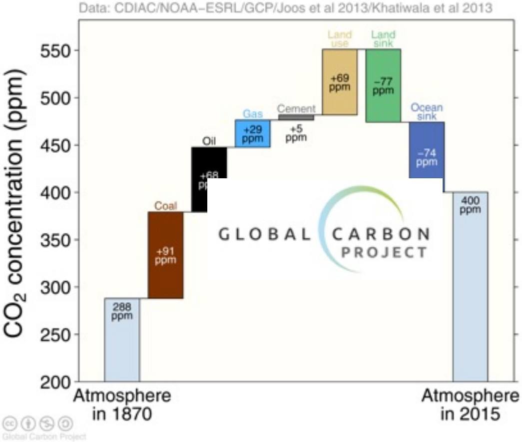
Land-use change 12%

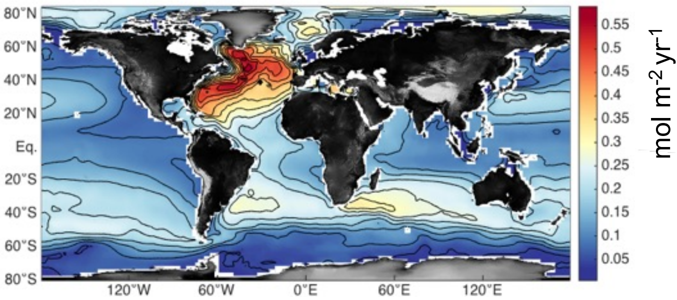
45% Atmosphere

29% Land

26% Ocean

Oceanic Anthropogenic Carbon dioxide



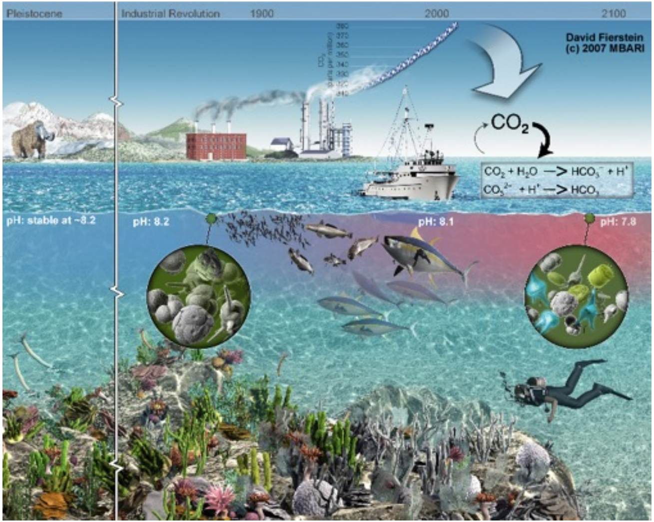


Column inventory of anthropogenic carbon

Brown et al., 2016

Le Quere et al., 2017

Oceanic consequences of atmospheric CO_2 increases

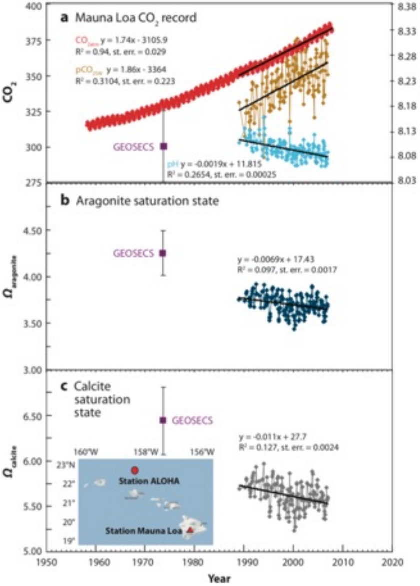


Ocean acidification

- CO_2 generates an acid in seawater (pH drop):

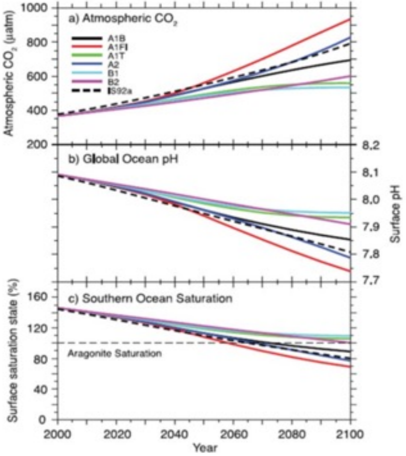
$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow$
$HCO_3^- +$ H^+

- surface ocean pH has already dropped by ~0.1



Doney et al 2009

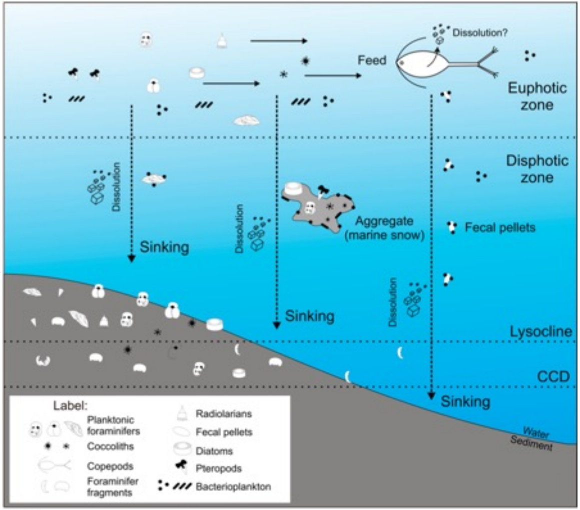
- pH expected to drop by additional 0.2-0.3 by 2100

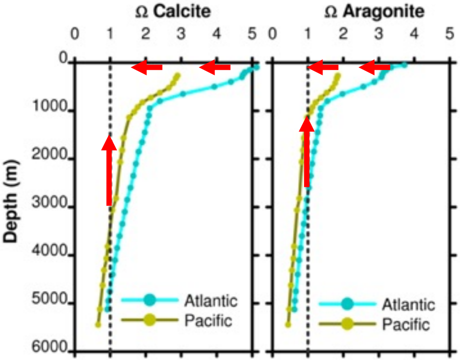


$CaCO_3$ dissolution $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + H^+$

- dissolves under high pressure, low temperature, acidic water
- *some* of the H^+ combines with CO_3^{2-} (buffering):
  - $CO_3^{2-} + H^+ \rightarrow HCO_3^-$
  - saturation state of $CaCO_3$ depends on $[Ca^{2+}]*[CO_3^{2-}]$
  - seawater is then less saturated as pH drops
- aragonite is more soluble than calcite
- organisms with aragonite shells (pteropods, corals) may have difficulty calcifying by 2100 (average surface pH 7.75-7.95)

$CaCO_3$ dissolution





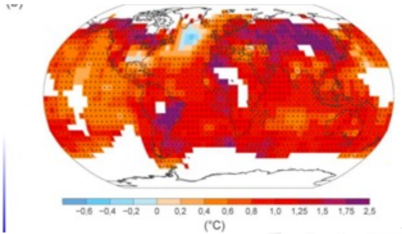
Aragonite saturation depth Ω = 1

Calcite saturation depth Ω = 1

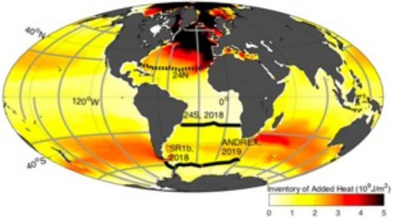
Saturation depths are shallowing

Monticello Petro et al (2018)

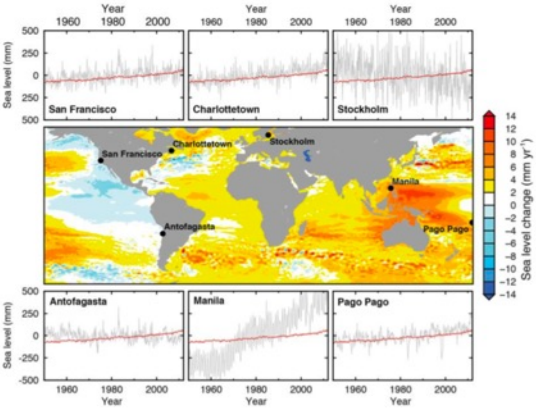
Additional Consequences



Observed air temperature changes 1902-2012



Anthropogenic heat uptake (column inventory) for last 50 years



Sea level change 1993-2012

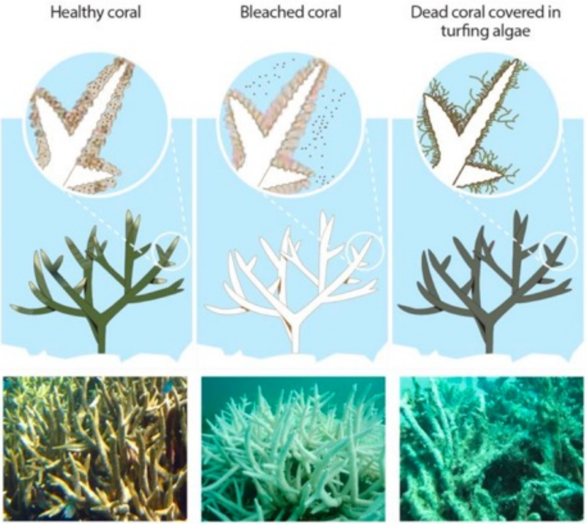
IPCC AR5

Coral bleaching

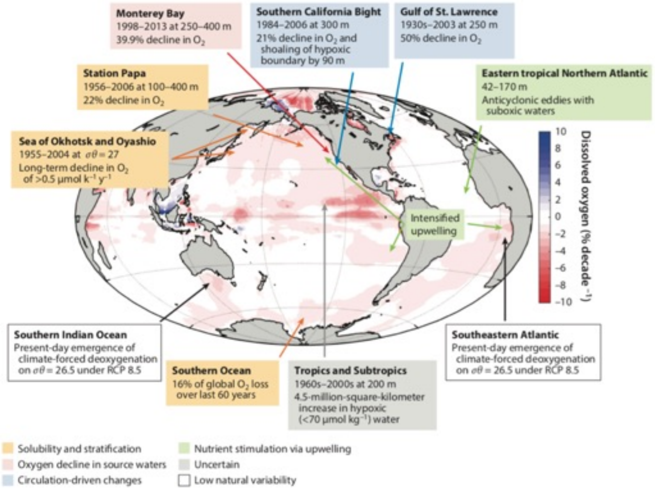
High temperatures cause coral to expel the algae living within, causing the coral to turn completely white.

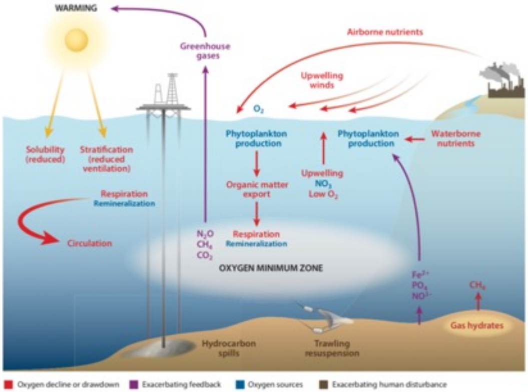
Corals can survive a bleaching event, but they are under more stress and are subject to mortality

Above-average sea water temperatures caused by global warming is the leading cause of coral bleaching



Deoxygenation

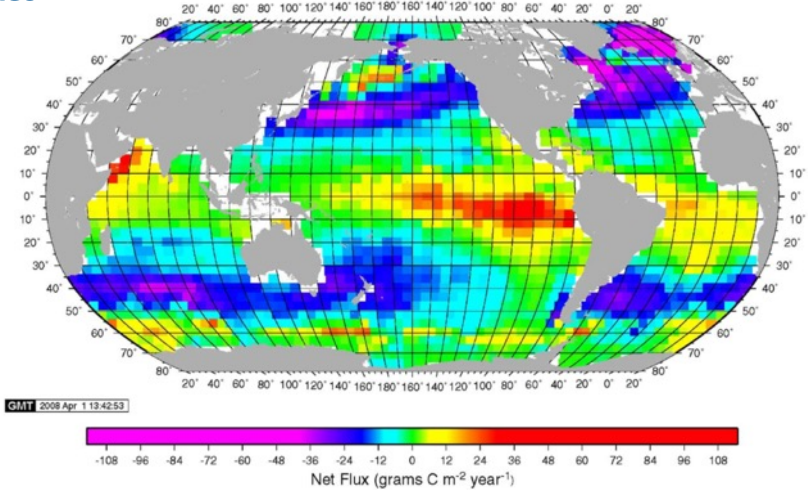




Levin, 2018

Air-sea carbon dioxide fluxes

Annual flux of contemporary CO_2



Takahashi et al (2009) DSR

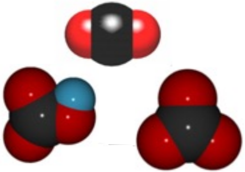
Carbon in seawater

inorganic	organic
~98% DIC	**~2% DOC**

- CO_2(g) has many possible transformations upon dissolution in H_2O

- Major dissolved forms:

DIC	CO_2*	$CO_{2(aq)}$	(*aqueous carbon dioxide* – a dissolved gas)	~1%
		H_2CO_3	(*carbonic acid* – trace amount)	Trace
		HCO_3^-	(*bicarbonate ion*)	~90%
		CO_3^{-2}	(*carbonate ion*)	~10%

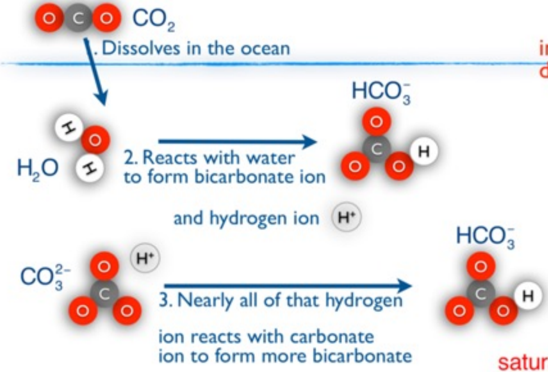


- Species interconvert readily

- Perturbations to one part of CO_2 system leads to redistribution of species

- Reactions not always intuitive!

EFFECT OF ADDING CO_2 TO SEAWATER



$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$$

increase in dissolved CO_2 ↑

↓ decreases carbonate

↑ increases bicarbonate

also hydrogen ion concentration increases

i.e., pH = –lg [H⁺] decreases

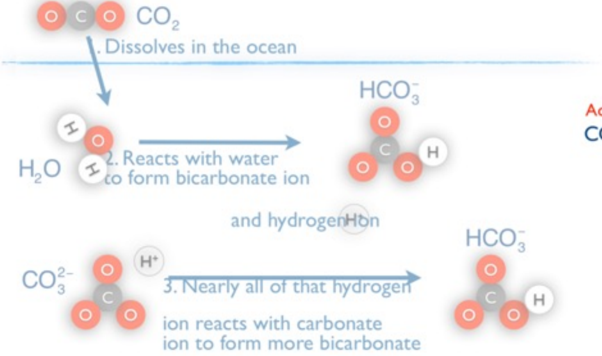
and saturation state of calcium carbonate decreases

saturation state $\Omega = \frac{[Ca^+][CO_3^{2-}]}{K_{sp}}$

(a measure of how "easy" it is to form a shell)

Slide courtesy A. Dickson

CARBON DIOXIDE EQUILIBRIA IN SEA WATER



CO_2

1. Dissolves in the ocean

H_2O

2. Reacts with water to form bicarbonate ion

HCO_3^-

and hydrogen ion

CO_3^{2-}

3. Nearly all of that hydrogen ion reacts with carbonate ion to form more bicarbonate

HCO_3^-

Gas solubility

$$CO_2(g) = CO_2(aq)$$

concentration of unionized CO_2 in sea water (mol kg^{-1})

$$K_0 = \frac{[CO_2]}{x(CO_2)\cdot p}$$

mole fraction of CO_2

equilibration pressure

Acid Dissociation

$$CO_2 + H_2O = H^+ + HCO_3^-$$

total hydrogen ion concentration

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^- \quad K_1/K_2 = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{2-}]}$$

Slide courtesy A. Dickson

CARBON DIOXIDE PARAMETERS IN SEA WATER

- Total Dissolved Inorganic Carbon

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

T, p independent

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

- Total Hydrogen Ion Concentration (pH)

$$pH = -\lg [H^+]$$

T, p dependent

UNITS: pH is dimensionless
But, total hydrogen ion concentration is in moles per kilogram of solution

These are the most commonly used analytical parameters; others exist – or could be imagined.

- Partial Pressure of CO_2
(in air that is in equilibrium with the water sample)

$$p(CO_2) = x(CO_2)\,p = [CO_2]/K_0$$

T, p dependent

UNITS: pressure units (usually μatm)

- Total Alkalinity

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

T, p independent

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

CARBON DIOXIDE PARAMETERS IN SEA WATER

- Total Dissolved Inorganic Carbon

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

T, p independent

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

- Total Hydrogen Ion Concentration (pH)

$$pH = -\lg [H^+]$$

T, p dependent

UNITS: pH is dimensionless
But, total hydrogen ion concentration is in moles per kilogram of solution

- Partial Pressure of CO_2
  (in air that is in equilibrium with the water sample)

$$p(CO_2) = x(CO_2)\,p = [CO_2] / K_0$$

UNITS: pressure units (usually μatm)

- Total Alkalinity

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

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

In a system at equilibrium, with both a gaseous and an aqueous phase, the state of the CO_2 system is described by a knowledge of the $p(CO_2)$ in the gas phase, and of the four concentrations: $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H^+]$, in the aqueous phase.

However, there are also three equilibrium relationships between these various concentrations:

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

Seawater Carbonate chemistry

$$CO_2(g) \xrightleftharpoons{K_0} CO_2^*(aq) \overset{K_1}{\rightleftharpoons} H^+(aq) + HCO_3^-(aq) \overset{K_2}{\rightleftharpoons} H^+(aq) + CO_3^{2-}(aq);$$

K0, K1 and K2 have been derived by many different sets of research across a range of salinities and temperatures using more real and synthetic seawater

- ***Carbon dioxide in seawater (K_0)***

$$\ln(K_0/k^\circ) = 93.4517\left(\frac{100}{T/\mathrm{K}}\right) - 60.249 + 23.3585\ln\left(\frac{T/K}{100}\right) + S\left[0.023517 - 0.023656\left(\frac{T/K}{100}\right) + 0.00047036\left(\frac{T/K}{100}\right)^2\right] \quad (1.57)$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Weiss*, 1974]

- ***Carbonic Acid (K_1, K_2)***

$$\log_{10}(K_1/k^\circ) = +\left(\frac{3670.7}{T/\mathrm{K}}\right) - 62.008 + 9.7944\ln(T/\mathrm{K}) - 0.0118S + 0.000116S^2 \quad (1.58)$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Mehrbach et al.*, 1973] as refit by *Dickson and Millero* [1987]

$$\log_{10}(K_2/k^\circ) = \left(\frac{1394.7}{T/\mathrm{K}}\right) + 4.777 - 0.0184S + 0.000118S^2 \quad (1.59)$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Mehrbach et al.*, 1973] as refit by *Dickson and Millero* [1987]

Carbon speciation for varying pH (total carbon constant)

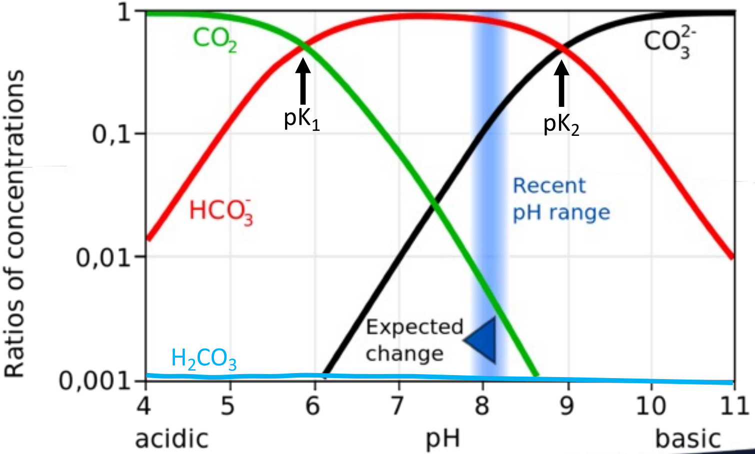
$$CO_2(g) \overset{K_0}{\rightleftharpoons} CO_2^*(aq) \overset{K_1}{\rightleftharpoons} H^+(aq) + HCO_3^-(aq) \overset{K_2}{\rightleftharpoons} H^+(aq) + CO_3^{2-}(aq);$$

$$K_1^* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$$

$pK_1 = -\log_{10}(K_1^*)$,
$pH = pK_1$ then $[CO_{2T}] = [HCO_3^-]$

$$K_2^* = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]}$$

$pK_2 = -\log_{10}(K_2^*)$, $pH = pK_2$
then $[HCO_3^-] = [CO_3^{2-}]$



Effects of pressure on carbon speciation

$$CO_2(g) \underset{}{\overset{K_0}{\rightleftharpoons}} CO_2^*(aq)$$

$$CO_2^*(aq) + H_2O(l) \overset{K_1}{\rightleftharpoons} H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \overset{K_2}{\rightleftharpoons} H^+(aq) + CO_3^{2-}(aq)$$

	1 atm	1000 atm
pK_1^*	5.89	5.55
pK_2^*	9.13	8.93

Decreasing pressure moves reactions to the left

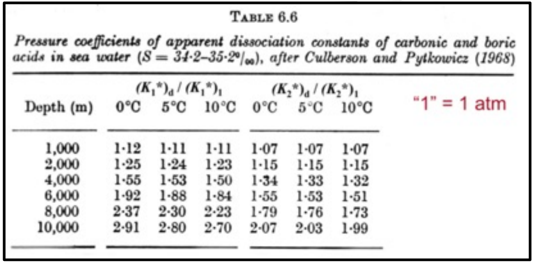


TABLE 6.6

Pressure coefficients of apparent dissociation constants of carbonic and boric acids in sea water (S = 34·2–35·2‰), after Culberson and Pytkowicz (1968)

Depth (m)	$(K_1^*)_d / (K_1^*)_1$ 0°C	5°C	10°C	$(K_2^*)_d / (K_2^*)_1$ 0°C	5°C	10°C
1,000	1·12	1·11	1·11	1·07	1·07	1·07
2,000	1·25	1·24	1·23	1·15	1·15	1·15
4,000	1·55	1·53	1·50	1·34	1·33	1·32
6,000	1·92	1·88	1·84	1·55	1·53	1·51
8,000	2·37	2·30	2·23	1·79	1·76	1·73
10,000	2·91	2·80	2·70	2·07	2·03	1·99

"1" = 1 atm

Therefore, as you raise a sample from depth to shallower levels:

- K_1 and K_2 decrease
- Reactions shift to the left
- pH increases
- CO2(g) release

How to measure the carbon system

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, alkalinity, pH and pCO_2

- **DIC** = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

  At seawater pH, >99% of CO2 species are HCO_3^- and CO_3^{2-}, so **DIC ~= $[HCO_3^-] + [CO_3^{2-}]$**

- **pCO_2 is the concentration ("partial pressure") in air**

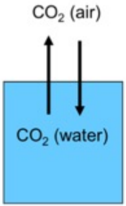
  $pCO_2 = [CO2_{(aq)}] / K_0$

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

  $CO_{2(aq)}$ is the concentration in seawater

  K_0 is the solubility coefficient
  - Decreases with increasing temperature (warmer = higher pCO_2)
  - Decreases with increasing salinity (saltier = higher pCO_2)

- $P_{CO2(air)} > P_{CO2(water)}$ Flux of CO_2 from air to water
- $P_{CO2(air)} = P_{CO2(water)}$ No net flux of CO_2 (equilibrium)
- $P_{CO2(air)} < P_{CO2(water)}$ Flux of CO_2 from water to air



How to measure the carbon system

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, alkalinity, pH and pCO_2

- **pH = -log $[H^+]$**

- The pH of seawater varies only between about 7.5 and 8.4 (i.e. slightly alkaline)
- Over geological time, pH is thought to be controlled by water / mineral equilibria
- Over shorter timescales (10^4 to 10^5 years) the CO_2 system (and its shifting equilibria) regulates seawater pH

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$$

- Temperature and pressure effects:

For temperatures T_1 and T_2:

$$pH_{T2} = pH_{T1} + 0.011(T_2 - T_1)$$

Increased T causes pH to increase

Increased P causes pH to decrease

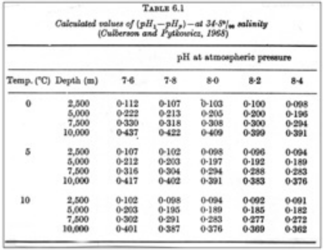


TABLE 6.1

Calculated values of $(pH_1 - pH_p)$—at 34·8‰ salinity (Culberson and Pytkowicz, 1968)

		pH at atmospheric pressure				
Temp. (°C)	Depth (m)	7·6	7·8	8·0	8·2	8·4
0	2,500	0·112	0·107	0·103	0·100	0·098
	5,000	0·222	0·213	0·205	0·200	0·196
	7,500	0·330	0·318	0·308	0·300	0·294
	10,000	0·437	0·422	0·409	0·399	0·391
5	2,500	0·107	0·102	0·098	0·096	0·094
	5,000	0·212	0·203	0·197	0·192	0·189
	7,500	0·316	0·304	0·294	0·288	0·283
	10,000	0·417	0·402	0·391	0·383	0·376
10	2,500	0·102	0·098	0·094	0·092	0·091
	5,000	0·203	0·195	0·189	0·185	0·182
	7,500	0·302	0·291	0·283	0·277	0·272
	10,000	0·401	0·387	0·376	0·369	0·362

How to measure the carbon system

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, alkalinity, pH and pCO_2

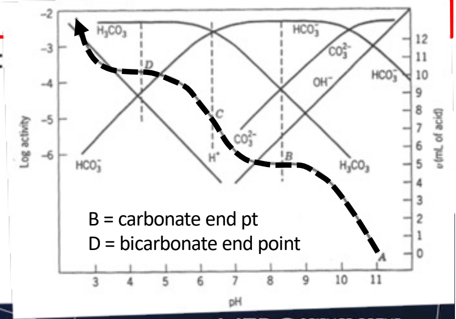
- **Alkalinity = the acid-buffering capacity of seawater**
  - Total Alkalinity (TA) represents ability of seawater to resist pH change upon addition of acid. For seawater we focus on its ability to absorb H^+

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

- End point of an alkalinity titration (using acid titrant) is when:

  Added $[H^+] = 2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] +$
  $3[BO_3^{-3}] + [OH^-] + [H^+ \text{acceptors}]$

- TA usually reported in meq/L or meq/kg (an "equivalent" is a mole of charge)



B = carbonate end pt
D = bicarbonate end point

How to measure the carbon system

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, alkalinity, pH and pCO_2

- **Alkalinity = the acid-buffering capacity of seawater**
  - Total Alkalinity (TA) represents ability of seawater to resist pH change upon addition of acid. For seawater we focus on its ability to absorb H^+

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

- End point of an alkalinity titration (using acid titrant) is when:

$$\text{Added } [H^+] = 2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] + [H^+\text{acceptors}]$$

- TA usually reported in meq/L or meq/kg (an "equivalent" is a mole of charge)

Carbonate alkalinity, CA = $2[CO_3^{2-}] + [HCO_3^-]$
Typically, HCO_3^- and CO_3^{-2} are present at ~1000x concentration of other proton acceptors • Hence: CA nearly equals TA

How to measure the carbon system

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, alkalinity, pH and pCO_2

- **Alkalinity = the acid-buffering capacity of seawater**

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

These components are derived from their own equilibrium equations, which have been characterized for a range of temperatures, and salinities

$$[\mathrm{B(OH)_4^-}] = B_T/(1+[\mathrm{H^+}]/K_B)$$

$$[\mathrm{OH^-}] = K_W/[\mathrm{H^+}]$$

$$[\mathrm{H_3PO_4}] = \frac{P_T[\mathrm{H^+}]^3}{[\mathrm{H^+}]^3 + K_{1P}[\mathrm{H^+}]^2 + K_{1P}K_{2P}[\mathrm{H^+}] + K_{1P}K_{2P}K_{3P}}$$

$$[\mathrm{H_2PO_4^-}] = \frac{P_T K_{1P}[\mathrm{H^+}]^2}{[\mathrm{H^+}]^3 + K_{1P}[\mathrm{H^+}]^2 + K_{1P}K_{2P}[\mathrm{H^+}] + K_{1P}K_{2P}K_{3P}}$$

$$[\mathrm{HPO_4^{2-}}] = \frac{P_T K_{1P}K_{2P}[\mathrm{H^+}]}{[\mathrm{H^+}]^3 + K_{1P}[\mathrm{H^+}]^2 + K_{1P}K_{2P}[\mathrm{H^+}] + K_{1P}K_{2P}K_{3P}}$$

$$[\mathrm{PO_4^{3-}}] = \frac{P_T K_{1P}K_{2P}K_{3P}}{[\mathrm{H^+}]^3 + K_{1P}[\mathrm{H^+}]^2 + K_{1P}K_{2P}[\mathrm{H^+}] + K_{1P}K_{2P}K_{3P}}$$

$$[\mathrm{SiO(OH)_3^-}] = Si_T/(1+[\mathrm{H^+}]/K_{Si})$$

$$[\mathrm{NH_3}] = NH_{3T}/(1+[\mathrm{H^+}]/K_{NH_3})$$

$$[\mathrm{HS^-}] = H_2S_T/(1+[\mathrm{H^+}]/K_{H_2S})$$

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

$$[\mathrm{HSO_4^-}] = S_T/(1+K_S/[\mathrm{H^+}]_F)$$

$$[\mathrm{HF}] = F_T/(1+K_F/[\mathrm{H^+}])$$

For e.g. phosphoric acid

Phosphoric Acid (K_{1P}, K_{2P}, K_{3P})

$$\ln(K_{1P}/k^\circ) = \frac{-4576.752}{(T/\mathrm{K})} + 115.525 - 18.453\ln(T/\mathrm{K}) + \left(\frac{-106.736}{(T/\mathrm{K})} + 0.69171\right)S^{0.5} + \left(-\frac{0.65643}{(T/\mathrm{K})} - 0.01844\right)S \tag{1.64}$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Millero*, 1995]

$$\ln(K_{2P}/k^\circ) = \frac{-8814.715}{(T/\mathrm{K})} + 172.0883 - 27.927\ln(T/\mathrm{K}) + \left(\frac{-160.340}{(T/\mathrm{K})} + 1.3566\right)S^{0.5} + \left(\frac{0.37335}{(T/\mathrm{K})} - 0.05778\right)S \tag{1.65}$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Millero*, 1995]

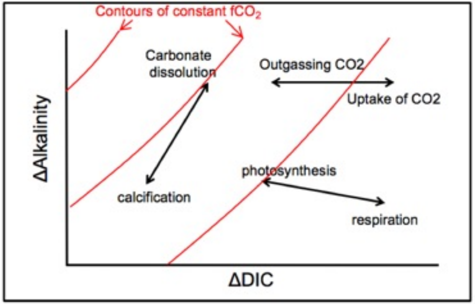
$$\ln(K_{3P}/k^\circ) = \frac{-3070.75}{(T/\mathrm{K})} - 18.141 + \left(\frac{17.27039}{(T/\mathrm{K})} + 2.81197\right)S^{0.5} + \left(\frac{-44.99486}{(T/\mathrm{K})} - 0.09984\right)S \tag{1.66}$$

where $k^\circ = 1$ mol kg-soln^{-1}

[*Millero*, 1995]

Processes affecting DIC and TA

	DIC	TA	[pH]	pCO_{2w}
Photosynthesis	-1	+0.14 = 16/117	+	-
Respiration	+1	-0.14 = 16/117	-	+
Calcification	-1	-2	/	+
Air-sea CO_2 input	+1	0	-	+
Warming	0	0	+	++



photosynthesis

$$117\,CO_2 + 16\,H^+ + 16NO_3^- + H_3PO_4 + 122\,H_2O \rightleftharpoons (CH_2O)_{117}(NH_3)_{16}(H_3PO_4) + 138\,O_2$$

respiration

calcification: $Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$

CO_2 system calculations

There are four parameters of the marine carbon system in seawater that can be measured:

DIC, carbonate alkalinity, pH and pCO_2

Any two of these properties can be used to determine the composition of the carbon system in seawater (*i.e.,* concentrations of $CO_2(aq)$, HCO_3^-, and CO_3^{2-}) and the other parameters not measured,

- Traditionally, alkalinity and pH or DIC were measured, and pCO_2 and DIC/pH calculated from them

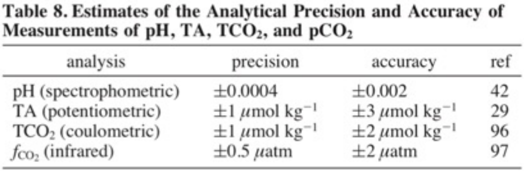


Table 8. Estimates of the Analytical Precision and Accuracy of Measurements of pH, TA, TCO_2, and pCO_2

analysis	precision	accuracy	ref
pH (spectrophotometric)	±0.0004	±0.002	42
TA (potentiometric)	±1 μmol kg^{-1}	±3 μmol kg^{-1}	29
TCO_2 (coulometric)	±1 μmol kg^{-1}	±2 μmol kg^{-1}	96
f_{CO_2} (infrared)	±0.5 μatm	±2 μatm	97

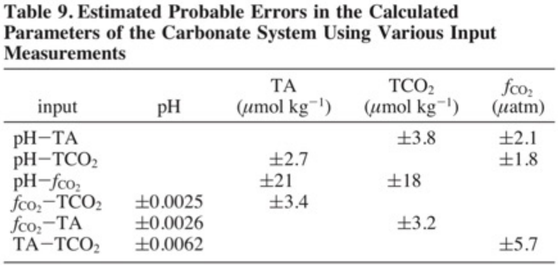


Table 9. Estimated Probable Errors in the Calculated Parameters of the Carbonate System Using Various Input Measurements

input	pH	TA (μmol kg^{-1})	TCO_2 (μmol kg^{-1})	f_{CO_2} (μatm)
pH−TA			±3.8	±2.1
pH−TCO_2		±2.7		±1.8
pH−f_{CO_2}		±21	±18	
f_{CO_2}−TCO_2	±0.0025	±3.4		
f_{CO_2}−TA	±0.0026		±3.2	
TA−TCO_2	±0.0062			±5.7

CO_2 system calculations

$$CO_2(g) \xrightleftharpoons{K_0} CO_2^*(aq)$$

$$CO_2^*(aq) + H_2O(l) \xrightleftharpoons{K_1} H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \xrightleftharpoons{K_2} H^+(aq) + CO_3^{2-}(aq)$$

Using **pH and pCO2**: $[CO_2^*] = pCO_2 K_0$

and $$K_1^* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$$

Combining gives: $$[HCO_3^-] = \frac{[CO_2^*]K_1}{[H^+]}$$

$$[CO_3^{2-}] = \left(\frac{[CO_2^*]K_1}{[H^+]}\right)\frac{K_2}{[H^+]}.$$

○ *(=measured)*

○ *(=derived)*

H_2O has very high unit activity (except at very high ionic strength) and is thus excluded from the equations

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

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

CO_2 system calculations

$$CO_2(g) \xrightleftharpoons{K_0} CO_2^*(aq)$$

$$CO_2^*(aq) + H_2O(l) \xrightleftharpoons{K_1} H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \xrightleftharpoons{K_2} H^+(aq) + CO_3^{2-}(aq)$$

Using **pH and pCO2**: $[CO_2^*] = \boxed{pCO_2} K_0$

and $$K_1^* = \frac{\boxed{\{H^+\}}[HCO_3^-]}{[CO_2]}$$

Combining gives: $$[HCO_3^-] = \frac{[CO_2^*]K_1}{\boxed{[H^+]}}$$

$$[CO_3^{2-}] = \left(\frac{[CO_2^*]K_1}{\boxed{[H^+]}}\right)\frac{K_2}{\boxed{[H^+]}}.$$

🟢 *(=measured)*

🔴 *(=derived)*

Then $\boxed{DIC}$ = $[CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$

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

H_2O has very high unit activity (except at very high ionic strength) and is thus excluded from the equations

Thus, to determine the total CO_2 system in seawater all we need is pH and pCO_2

But these are not necessarily the best parameters to use because small errors in these lead to larger errors in DIC and TA

CO_2 system calculations

So instead, could use carbonate alkalinity **CA and DIC**:

$$CO_2(g) \underset{}{\overset{K_0}{\rightleftharpoons}} CO_2^*(aq)$$

$$CO_2^*(aq) + H_2O(l) \overset{K_1}{\rightleftharpoons} H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \overset{K_2}{\rightleftharpoons} H^+(aq) + CO_3^{2-}(aq)$$

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

Solve iteratively for $[H^+]$...

Then:

$$[HCO_3^-] = \frac{DIC\, K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2},$$

$$[CO_3^{2-}] = \frac{DIC\, K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}.$$

$$[CO_2^*] = \frac{[H^+][HCO_3^-]}{K_1}$$

$$f(CO_2) = \frac{[CO_2^*]}{K_0}.$$

🟢 *(=measured)*

🔴 *(=derived)*

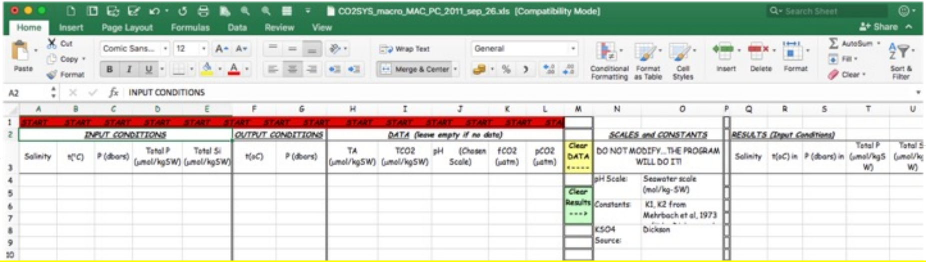
CO_2 system calculations

Many packages are available to calculate the carbonate system: We tend to use the CO2SYS program that is available as a standalone program (CO2calc), or in Excel, or in MATLAB code.

Biogeosciences, 12, 1483–1510, 2015
www.biogeosciences.net/12/1483/2015/
doi:10.5194/bg-12-1483-2015

Comparison of ten packages that compute ocean carbonate chemistry

J. C. Orr[1], J.-M. Epitalon[2], and J.-P. Gattuso[3,4]

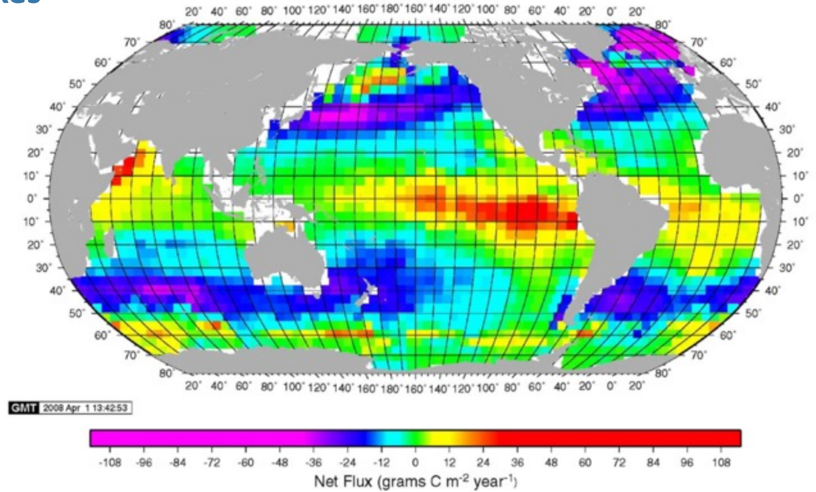


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1	START	START	START	START	START	START	START	START	START	START	START	START									
2	INPUT CONDITIONS					OUTPUT CONDITIONS		DATA (leave empty if no data)						SCALES and CONSTANTS			RESULTS (Input Conditions)				
3	Salinity	t(°C)	P (dbars)	Total P (μmol/kgSW)	Total Si (μmol/kgSW)	t(oC)	P (dbars)	TA (μmol/kgSW)	TCO2 (μmol/kgSW)	pH (Chosen Scale)	fCO2 (μatm)	pCO2 (μatm)	Clear DATA <-----	DO NOT MODIFY...THE PROGRAM WILL DO IT!			Salinity	t(oC) in	P (dbars) in	Total P (μmol/kgSW)	Total S (μmol/kg W)
4														pH Scale:	Seawater scale (mol/kg-SW)						
5													Clear Results --->								
6														Constants:	K1, K2 from Mehrbach et al, 1973						
7																					
8														KSO4	Dickson						
9														Source:							
10																					

- Data are inputted for sample salinity, temperature, pressure, phosphate, silicate, and two of the four carbon parameters
- Selections are made for different choices of dissociation constants, which will depend on application
- The full marine carbonate system will then be calculated

Air-sea carbon dioxide fluxes

Annual flux of contemporary CO_2



Takahashi et al (2009) DSR

Air-sea carbon dioxide fluxes

What sets the net air-sea flux?

The flux is set by patterns of sea-surface pCO_{2sw}, forced by:

Ocean circulation;

- Is surface water is cooling or heating?
- Is water being mixed up from depth?

Ocean biology;

- Is biological activity strong or weak?
- Is calcium carbonate being precipitated?

The rising concentration of atmospheric CO_2

- pCO_2 of air is rising and this tends to favour a flux from atmosphere into the ocean.

Air-sea carbon dioxide fluxes

$$CO_2 \text{ air-sea flux} = \overset{\text{Gas transfer velocity}}{K} \cdot \overset{\text{Solubility of } CO_2 \text{ gas in water}}{\alpha} \cdot (\overbrace{fCO_{2water} - fCO_{2air}}^{\text{Difference between fugacities of } CO_2 \text{ in surface seawater and air}})$$

pCO_2 : partial pressure of CO_2 (in µatm)

fCO_2 : fugacity of CO_2 (in µatm = 0.102315 Pa)

[~equivalent to pCO_2 but accounting for 'non-ideal' nature of CO_2 molecules]

$$fCO_2 = pCO_2 \exp\left(P_s \frac{B + 2\delta}{RT}\right)$$

where $R = 82.05746\ (\mathrm{cm^3\,atm\,mol^{-1}\,K^{-1}})$

P_s = sea level pressure

B and δ = virial coefficients for CO_2

Coefficient B ($\mathrm{cm^3\,mol^{-1}}$) is given by

$$B = -1636.75 + 12.0408T - 3.27957e^{-2}T^2 + 3.16528e^{-5}T^3$$

and δ ($\mathrm{cm^3\,mol^{-1}}$) by

$$\delta = 57.7 - 0.118T.$$

Essentially:

$fCO_2 = \gamma\ pCO_2 = \gamma\ P\ xCO_2$

γ, fugacity coefficient ~0.997)

Air-sea carbon dioxide fluxes

Gas transfer velocity

Solubility of CO_2 gas in water

Difference between fugacities of CO_2 in surface seawater and air

$$\text{CO}_2 \text{ air-sea flux } = K \bullet \alpha \bullet \overbrace{(fCO_{2water} - fCO_{2air})}$$

Gas transfer velocity: $K = 0.251\, u^2 (Sc / 660)^{-0.5}$

Wanninkhof (2014)

Where u = wind speed in m s^{-1}

Sc = Schmidt ‘piston velocity’ number, which varies with SST (°C)

$$Sc = 1923.6 + -125.06T + 4.3773T^2 + -0.085681T^3 + 0.00070284T^4$$

CO_2 solubility, α, is a function of temperature (°K) and salinity

$$\begin{aligned}\alpha &= -58.0931 + 90.5069(100/T) \\ &+ 22.2940 \ln(T/100) + \text{SSS}[0.027\,766 \\ &- 0.025\,888(T/100) + 0.005\,057\,8(T/100)^2]\end{aligned}$$

Air-sea carbon dioxide fluxes

Gas transfer velocity

The gas transfer velocity *K* (also called "piston velocity", or "coefficient of gas exchange") is a parameter which measures how easy it is for a gas to be transported across the interface.

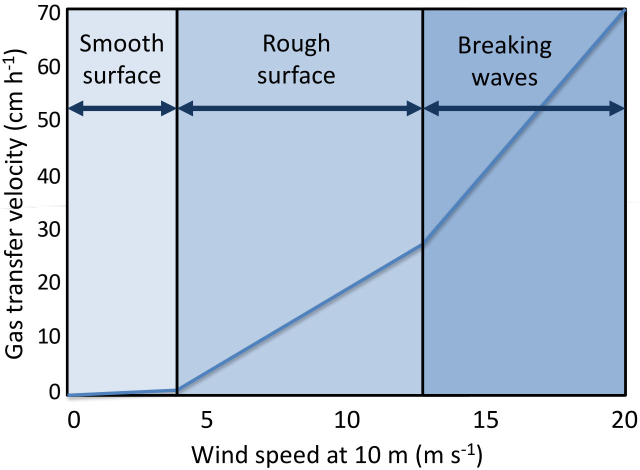
Called a velocity because it has these dimensions (LT^{-1}), it is not however the velocity of the molecules transferring.

A typical value of *K* in the ocean would be 3 metres per day, but it varies by more than an order of magnitude with weather conditions, being higher (easier transfer) in windy conditions and rough seas. (w*hy? more active turbulence, therefore a thinner film layer).*

Diffusivity is an inverse function of molecular weight, so transfer velocity decreases for higher molecular weight gases. The dependency is relatively weak however.

Air-sea carbon dioxide fluxes

Gas transfer velocity



CO_2 system calculations

$$CO_2 \text{ air-sea flux} = K \bullet \alpha \bullet (fCO_{2water} - fCO_{2air})$$

Calculate air-sea flux of CO_2 for local waters for 2018 atmospheric CO_2 of 405.35:

Salinity	Temp (°C)	Temp (°K)	Wind speed (ms^{-1}) u	pCO_{2sw}
32.3450012	19.6359997	292.786	7.40736	556.4
33.9990005	19.2959995	292.446	3.49792	793.6
34.3310013	18.8500004	292	3.90944	445.7
34.3400002	18.9179993	292.067999	4.73248	443.3
		273.15		
34.3170013	18.8829994	292.032999	4.52672	386.4
33.3139992	19.191	292.341	2.10904	469.5
32.598999	19.566	292.716	2.72632	468.3

$$K = 0.251\, u^2 \, (Sc / 660)^{-0.5}$$

$$Sc = 1923.6 + -125.06T + 4.3773T^2 +-0.085681T^3+ 0.00070284T^4$$

(T,°C)

$$\begin{aligned}\alpha &= -58.0931 + 90.5069(100/T) \\ &+ 22.2940 \ln(T/100) + \mathrm{SSS}[0.027\,766 \\ &- 0.025\,888(T/100) + 0.005\,057\,8(T/100)^2]\end{aligned}$$

(T,°K)