Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

Reading: Libes, Chapter 15, pp. 383 – 394

(Remainder of chapter: "Biogenic production, carbonate saturation and sediment distributions")

Outline

1. CO_2 speciation
2. pH
3. Alkalinity
4. Calculation of composition of marine CO_2 system
5. Oceanographic applications
6. Global CO_2

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

CO_2 Speciation

- CO_2(g) has many possible transformations upon dissolution in H_2O
- Major dissolved forms:
  - $CO_{2(aq)}$ (*aqueous carbon dioxide* – a dissolved gas)
  - H_2CO_3 (*carbonic acid* – trace amount)
  - HCO_3^- (*bicarbonate ion*)
  - CO_3^{-2} (*carbonate ion*)
- Species interconvert readily
- Perturbations to one part of CO_2 system leads to redistribution of species
- Reactions not always intuitive!

Equations for CO_2 Speciation

The equilibrium of gaseous and aqueous CO_2:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

Subsequent hydration and dissociation reactions:

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

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

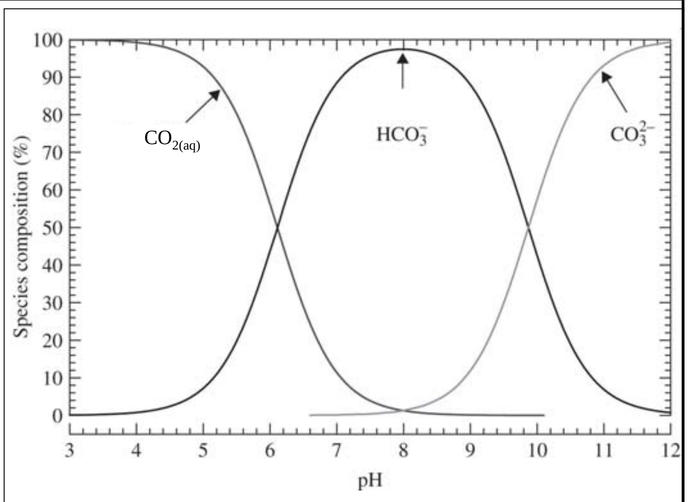
$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

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

Asterisk (*) indicates a "stoichiometric" constant

Hint: when pH is between 7.5 and 8.5:

$$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$$



Seawater values shown --- freshwater curves are shifted left

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

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

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

aob.oxfordjournals.org

How to Calculate K_1^* and K_2^*

pK = - log K

Millero et al. (2006) Mar. Chem. *100*, 80-94

For: S = 0 – 50, T = 0 – 50°C

At S = 35 and T = 25°C:

pK_1^* = 5.8401 pK_2^* = 8.9636

Effects of Pressure

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

Decreased pressure shifts reactions to left

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

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)

	$(K_1^*)_d / (K_1^*)_1$			$(K_2^*)_d / (K_2^*)_1$		
Depth (m)	0°C	5°C	10°C	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

As you raise a sample from depth:

- Ks' decrease
- Reactions shift to left
- pH increases
- $CO_{2(g)}$ release

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

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

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

Total CO_2 (ΣCO_2)

Total $CO_2 \equiv [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}]$

- At seawater pH, >99% of CO_2 species are HCO_3^- and CO_3^{-2}, so we can simplify:

Total $CO_2 \equiv [HCO_3^-] + [CO_3^{-2}]$

- This is also known as *dissolved inorganic carbon (DIC)*
- Equilibrium equations can be combined to allow us to calculate the concentration of any of the CO_2 species

$CaCO_3$ Precipitation/Dissolution

A tricky subject when discussing "CO_2"
(or, more properly, P_{CO2})

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

Does this reduce the CO_2 (P_{CO2}) level of the seawater?

No! Lost CO_3^{2-} will be replaced:

$$HCO_3^- \rightarrow CO_3^{2-} + H^+$$

But this H^+ release causes:

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

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

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

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

Thus, $CaCO_3$ precipitation causes a decrease in Total CO_2, but an <u>increase</u> in P_{CO2}

Hint: when pH is between 7.5 and 8.5:

$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$

Seawater pH

- 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 time scales (10^4 to 10^5 yrs) the CO_2 system (and its shifting equilibria) regulates seawater pH

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

Seawater pH – T and P Effects

For temperatures T_1 and T_2:

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

Increased T causes pH to increase

TABLE 6.1

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

Temp. (°C)	Depth (m)	pH at atmospheric pressure 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

"1" = 1 atm

Increased P causes pH to decrease

Definitions of Alkalinity

- GENERAL DEFINITION: The acid-buffering capacity of seawater
- *Total Alkalinity (TA)* represents ability of seawater to resist pH change upon addition of acid
- Remember the concept of a "buffer" (from basic chemistry): a substance that resists pH change upon addition of acid or base
- For seawater we focus on its ability to absorb H^+

Total Alkalinity (TA)

$$TA \equiv 2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] + [\text{organic/inorganic } H^+ \text{ acceptors}] - [H^+]$$

- End point of an alkalinity titration (using acid titrant) is when: $[H^+] = 2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] + [H^+\text{acceptors}]$
- TA usually reported in meq/L or meq/kg (an "equivalent" is a mole of charge)

Carbonate Alkalinity (CA)

$$CA \equiv 2[CO_3^{-2}] + [HCO_3^-]$$

- Typically, HCO_3^- and CO_3^{-2} are present at ~1000x conc of other proton acceptors
- Hence: CA nearly equals TA

Calculations

- Any two of the four CO_2 properties (ΣCO_2, P_{CO2}, pH, and carbonate alkalinity) can be used to determine the CO_2 system
- Traditionally, pH and alkalinity were measured
- Now we can also use ΣCO_2 and P_{CO2} to better constrain calculations, improving accuracy

Example Calculation #1

Use ΣCO_2 and Carbonate Alkalinity data to calculate the concentrations of each inorganic carbon species ($CO_{2(aq)}$, HCO_3^-, and CO_3^{2-}) (*assuming $CO_{2(aq)}$ is neglibible*) – two equations & two unknowns:

$$CA \equiv 2[CO_3^{-2}] + [HCO_3^-]$$

$$[HCO_3^-] = CA - 2[CO_3^{-2}]$$

$$\Sigma CO_2 \equiv [HCO_3^-] + [CO_3^{-2}]$$

$$= CA - 2[CO_3^{-2}] + [CO_3^{-2}]$$

$$= CA - [CO_3^{-2}]$$

$$[CO_3^{-2}] = CA - \Sigma CO_2$$

$$[HCO_3^-] = CA - 2(CA - \Sigma CO_2)$$

$$= 2\Sigma CO_2 - CA$$

Example Calculation # 2

Calculate the concentration (in mM) of each inorganic carbon species ($CO_{2(aq)}$, HCO_3^-, and CO_3^{2-}) if:

ΣCO_2 = 2.3 mM, pH = 8.0, T = 10°C, P = 1 atm, S = 35

At T = 10ºC, S = 35 :

$pK_1^* = 6.08$	$K_1^* = 10^{-6.08} = 8.318 \times 10^{-7}$
$pK_2^* = 9.28$	$K_2^* = 10^{-9.28} = 5.248 \times 10^{-10}$
pH = 8.0	$\{H^+\} = 10^{-8.0}$

From the definition of stoichiometric equilibrium constants:

$$[CO_2] = \frac{\{H^+\}[HCO_3^-]}{K_1^*} = 0.01202\ [HCO_3^-]$$

$$[CO_3^{2-}] = \frac{K_2^*[HCO_3^-]}{\{H^+\}} = 0.05248\ [HCO_3^-]$$

From the definition of ΣCO_2:

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

$$\therefore\ 2.3 = (0.01202 \times [HCO_3^-]) + [HCO_3^-] + (0.05248 \times [HCO_3^-])$$

$$2.3 = 1.0645 \times [HCO_3^-]$$

$$\therefore\ [HCO_3^-] = 2.16\text{ mM}$$

$$[CO_2] = (0.01202)(2.16) = 0.026\text{ mM}$$

$$[CO_3^{2-}] = (0.05248)(2.16) = 0.113\text{ mM}$$

What processes affect Alk and ΣCO_2?

- CO_2 exchange between the atmosphere and surface seawater changes ΣCO_2, but doesn't affect Alk
- Photosynthesis / respiration also changes ΣCO_2, but doesn't affect Alk (loss of HCO_3^- is balanced by loss of H^+)

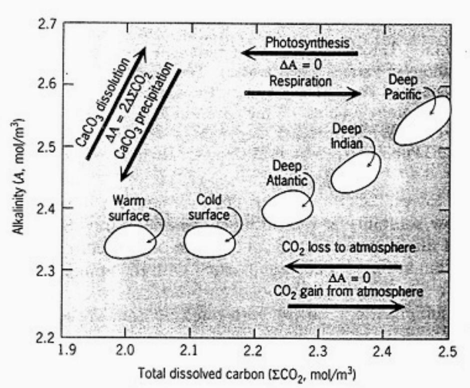


FIGURE 15.7. Relationship between the total dissolved inorganic carbon content and the alkalinity of waters from various parts of the ocean. The arrows indicate the effects of various processes occurring within the sea.

- $CaCO_3$ dissolution / precipitation changes both ΣCO_2 and Alk

Calcification

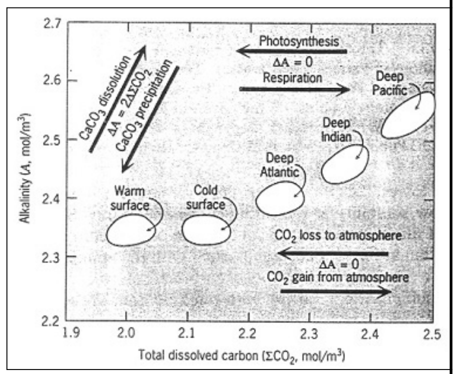
Effects on Alk-pH-ΣCO_2

- Surface-ocean plankton remove CO_3^{2-} and Ca^{2+} from seawater to form $CaCO_3$ tests (*calcification*):

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

- Calcification alters both Alk and ΣCO_2, but not pH

- Amount of Alk decrease is 2x the effect on ΣCO_2 because of double negative charge of CO_3^{2-}



$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$

Processes Affecting Alkalinity

TABLE 4.5 PROCESSES AFFECTING ALKALINITY

Process	Alkalinity Change for Forward Reaction
Photosynthesis and Respiration:	
(1*a*) $nCO_2 + nH_2O \underset{\text{respir.}}{\overset{\text{photos.}}{\rightleftharpoons}} (CH_2O)_n + nO_2$	No change
(1*b*) $106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \underset{\text{respir.}}{\overset{\text{photos.}}{\rightleftharpoons}} \underbrace{\{C_{106}H_{263}O_{110}N_{16}P_1\}}_{\text{"algae"}} + 138O_2$	Increase
(1*c*) $106CO_2 + 16NH_4^+ + HPO_4^{2-} + 108H_2O \underset{\text{respir.}}{\overset{\text{photos.}}{\rightleftharpoons}} \{C_{106}H_{263}O_{110}N_{16}P_1\} + 107O_2 + 14H^+$	Decrease
Nitrification:	
(2) $NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$	Decrease
Denitrification:	
(3) $5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 5CO_2 + 2N_2 + 7H_2O$	Increase
Sulfide Oxidation:	
(4*a*) $HS^- + 2O_2 \longrightarrow SO_4^{2-} + H^+$	Decrease
(4*b*) $FeS_2(s) + \frac{15}{4}O_2 + 3\frac{1}{2}H_2O \longrightarrow Fe(OH)_3(s) + 4H^+ + 2SO_4^{2-}$ pyrite	Decrease
Sulfate Reduction:	
(5) $SO_4^{2-} + 2CH_2O + H^+ \longrightarrow 2CO_2 + HS^- + H_2O$	Increase

Vertical ΣCO_2 and Alkalinity Profiles

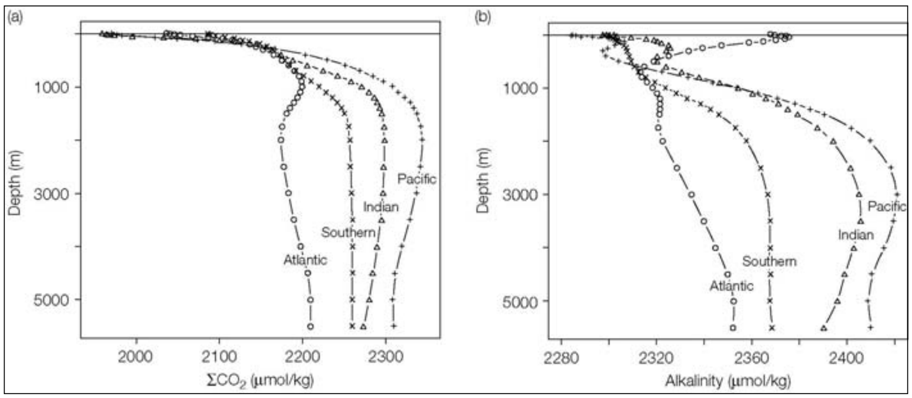


Figure 15.10

Current Status of Global CO_2

- CO_2 input to atmosphere is primarily through oxidation of fossil organic matter (*i.e.*, oil, coal and natural gas) and cement production
- We are currently adding considerably to the CO_2 inventory of the atmosphere and the oceans, while stimulating terrestrial biomass production
- There is ~53x as much CO_2 in the ocean as in the atmosphere

Fate of Anthropogenic CO_2 Emissions (2010)

9.1±0.5 PgC y^{-1}

+

0.9±0.7 PgC y^{-1}

5.0±0.2 PgC y^{-1}
50%

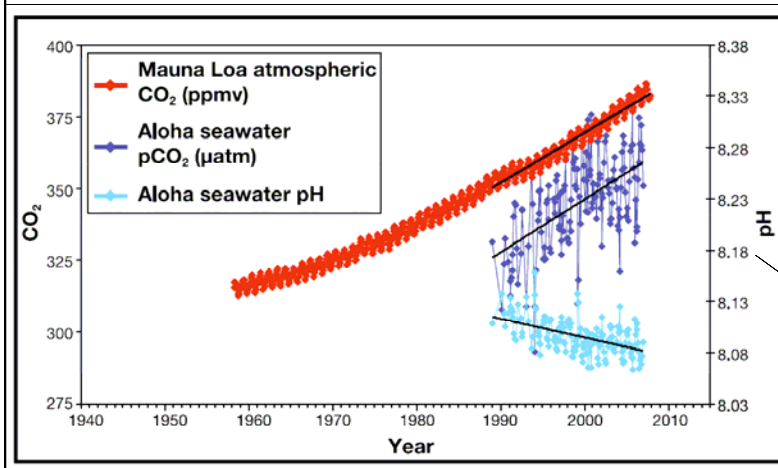
2.6±1.0 PgC y^{-1}
26%
Calculated as the residual of all other flux components

24%
2.4±0.5 PgC y^{-1}
Average of 5 models

Global Carbon Project 2010; Updated from Le Quéré et al. 2009, Nature Geoscience; Canadell et al. 2007, PNAS

Ocean CO_2 Increase Tracks Atmosphere

"Ocean Acidification"

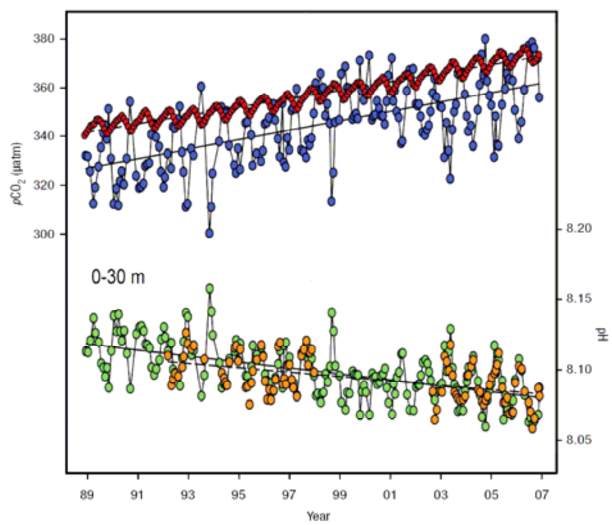


Pre-industrial (1700s) pH

Time series of atmospheric CO_2 at Mauna Loa and surface ocean pH and pCO_2 at Ocean Station Aloha in the subtropical North Pacific Ocean. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL; HOTS/Aloha data: Dr. David Karl, University of Hawaii (modified after Feely, 2008).

In More Detail...

Figure 1. Ocean carbon dioxide and pH measurements near Hawaii at Station ALOHA 1988-2007



This figure demonstrates that as carbon dioxide in the air and ocean increases over time, the pH in the seawater decreases (Dore et al., 2009). Top: Calculated partial pressure of carbon dioxide in seawater (blue ●), and in air at nearby Mauna Loa (red ●). Bottom: Direct measurement of pH in surface seawater (orange ●) compared with calculated pH (green ●)*. Scientists measure "partial pressure" of carbon dioxide (pCO_2), the pressure that carbon dioxide gas exerts if it were alone in a container instead of being a component of the mixture of gases in the atmosphere or ocean, in units called microatmospheres.*

Ocean Acidification: Starting with the Science. 2011. National Research Council

Ocean pH

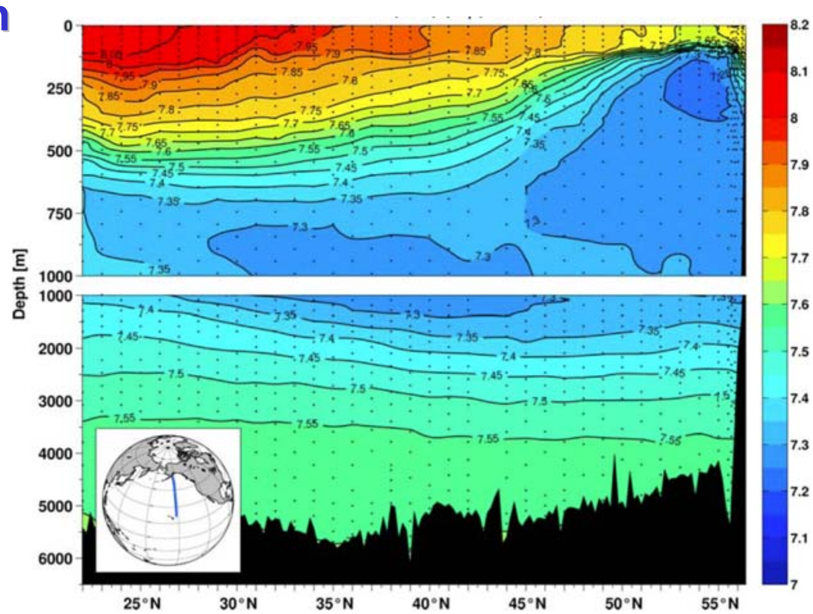
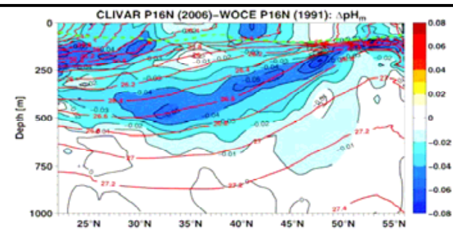


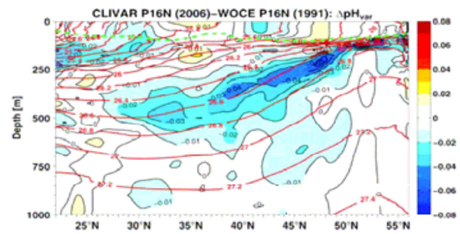
Figure 1. North Pacific Ocean pH along 152°W in 2006 (pH_T, 25°C).

Byrne et al. 2010, *Geophys. Res. Lett. 37*

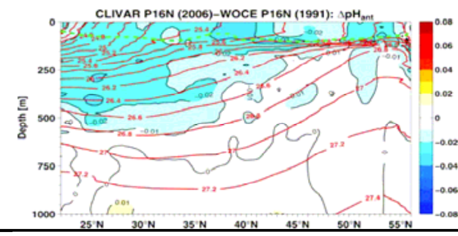
Change in seawater pH between 1991 and 2006



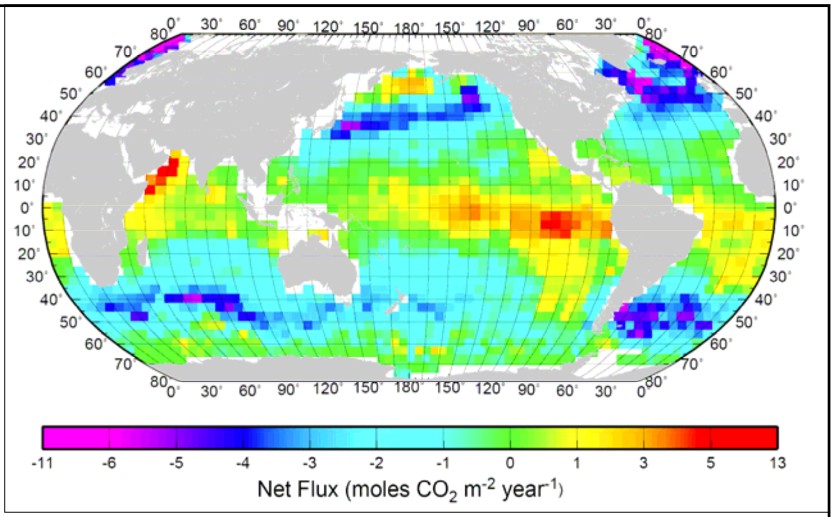
Change in seawater pH attributed to natural interdecadal/interannual DIC variability between 1991 and 2006 (due mostly to slowdown in downwelling, with more respiration at given depths)



Change in seawater pH attributed to the uptake of anthropogenic carbon between 1991 and 2006



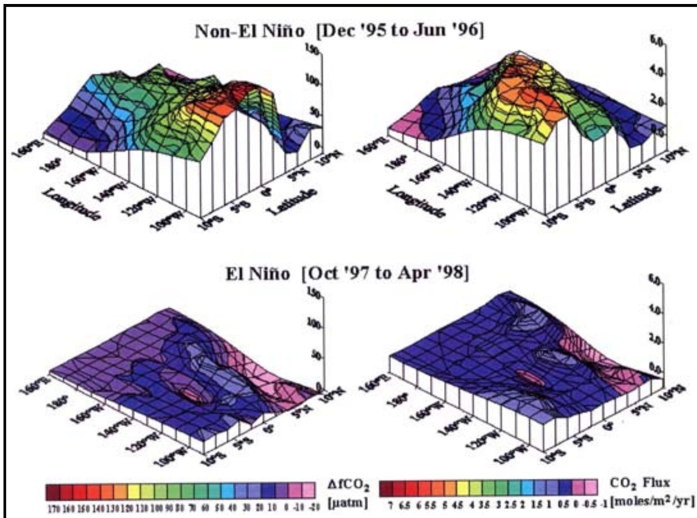
Global Oceanic CO_2 Flux



- High values at equator (esp. in the Pacific) and along west coasts are from *upwelling* and subsequent *gas evasion to atmosphere*
- Low values where there is high bioproductivity
- Low values where cooling of ocean increases solubility of gas and causes *gas infusion to surface ocean*

Sabine et al. 2009

El Niño Effects on CO_2 Exchange



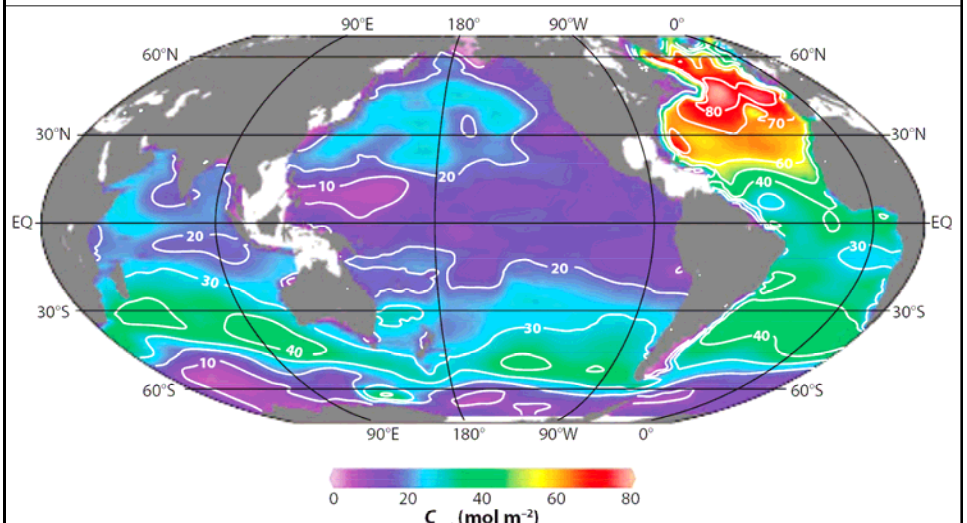
f = fugacity = partial pressure

Intra-annual variability of CO_2 fluxes are primarily affected by:

- Changes in upwelling rates of CO_2-enriched waters from the Equatorial Undercurrent
- Advection of CO_2-depleted waters from the western equatorial Pacific

Both processes are strongly affected by El Niño

Ocean Water-column Anthropogenic Carbon (C_{ant})



Sabine & Tanhua. 2010. Ann. Rev. Mar. Sci.

Homework

Due: Thurs, February 16, 2012

Consider a seawater with these characteristics:

S = 35 ΣCO_2 = 2.2 mM Carbonate alkalinity = 2.1 meq L^{-1}

T = 25°C

1) What is the pCO_2 of this seawater, assuming the Bunsen Coefficient for dissolved carbon dioxide (β_{CO2}) is 30 mmol L^{-1} atm^{-1}?

2) Is this seawater under- or super-saturated with respect to atmospheric CO_2? What is the basis for your answer?

Show All Calculations! State All Assumptions!