Carbon dioxide, Alkalinity and pH

OCN 633, Fall 2013

Eric Heinen De Carlo

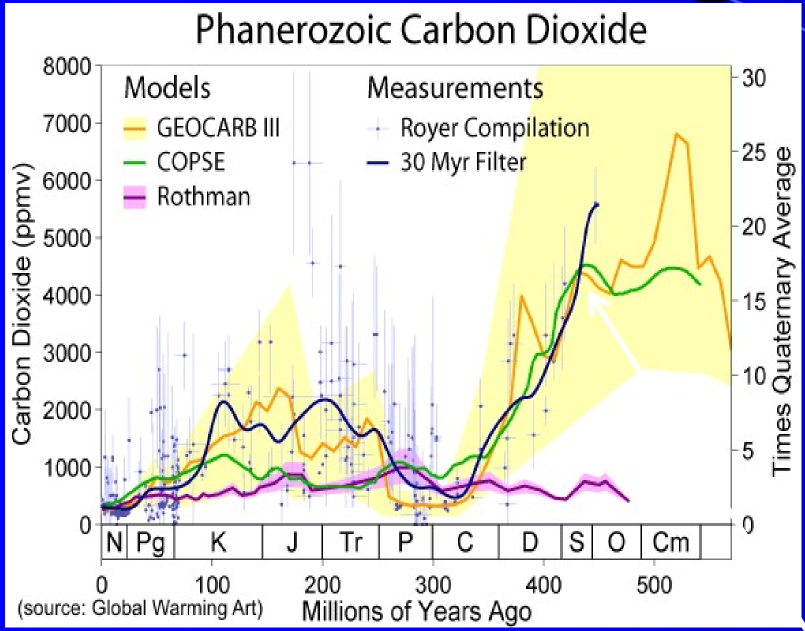
Why is it important to understand the CO_2 system?

- CO_2 is the raw material for organic matter
- CO_2 affects/controls the pH of the oceans
- CO_2 controls the fraction of inbound radiation that remains trapped in the atmosphere ➔ controls planetary climate (e.g., Venus, runaway greenhouse effect)
- Distribution of CO_2 species affects preservation of $CaCO_3$ in the water column and on sea floor

Current Status of CO_2

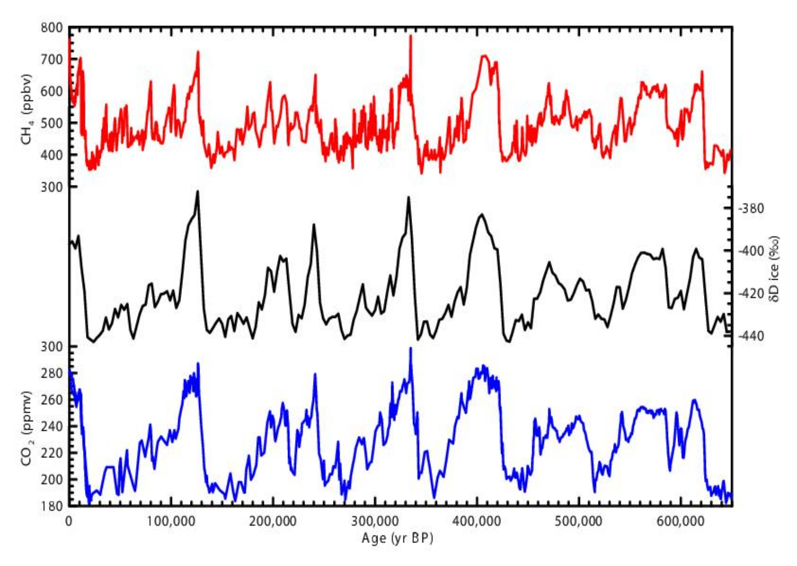
- There is ~53X more CO_2 in the ocean than in the atmosphere
- Humans currently add considerably to the CO_2 inventory of the atmosphere
- CO_2 input is mainly through oxidation of "buried" organic matter (i.e., oil and coal) with some additional fraction from "land use" changes and cement production

Geologic CO_2 records



(source: Global Warming Art)

Berner and Kothavala 2001; Bergmann et al. 2004; Rothman, 2001, Royer et al., 2004

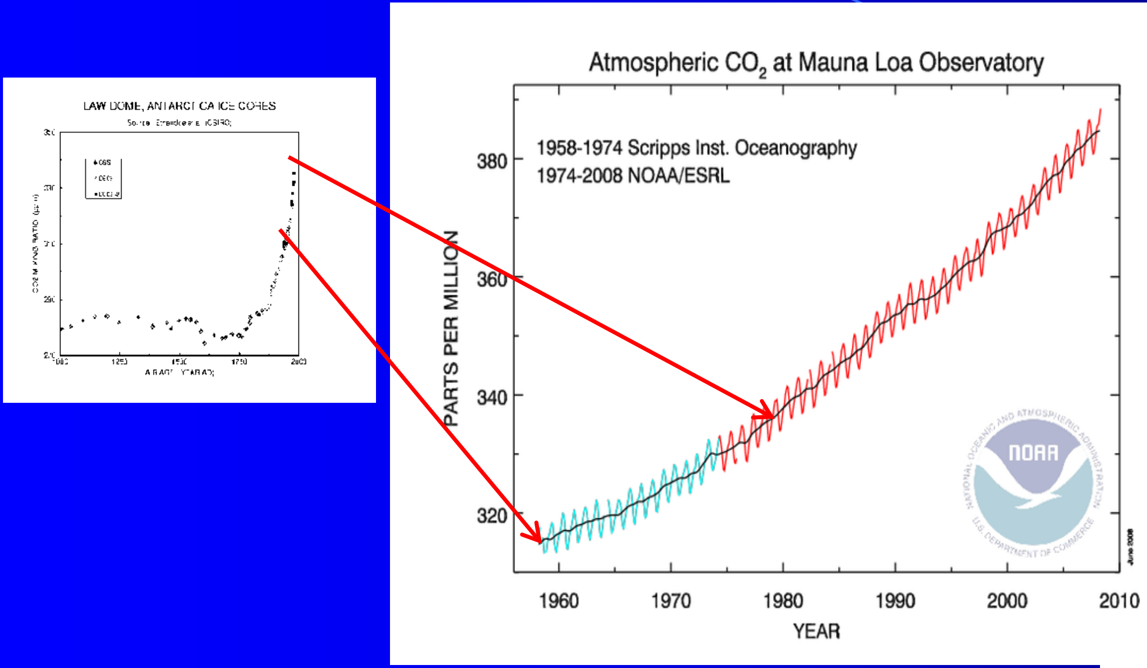


Modified after Siegenthaler et al., 2005 and Spahni et al. 2005

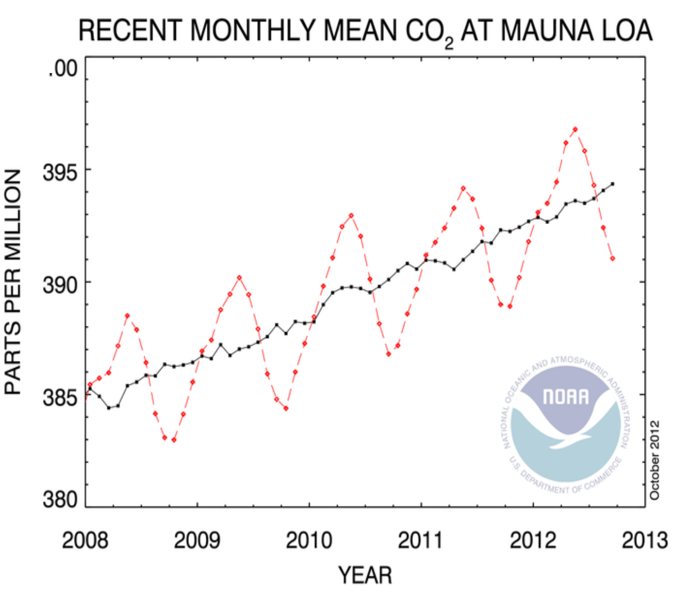
Historically pCO_2 was **much higher** (e.g., in the early Phanerozoic) but development of *Cooksonia* and other vascular plants in the Silurian ~425 Mya caused large decreases in the atmospheric concentration)

BUT OVER THE LAST ~1 Ma (at least until ~1850) pCO_2 ranged only from ~180 to ~280 ppmv

The Anthropocene… a new world!



Recent data:
Aug 2013 = 395 ppm
Aug 2012 = 392 ppm
Aug 2011 = 390 ppm
Sept 2003 = 373 ppm
at Mauna Loa obsv.



The concentration of CO$_2$ at Mauna Loa in early 2012 peaked at ~397 ppmv (for an annualized average ~395ppmv).

This is more than 100 ppm higher than during recent interglacial cycle peaks!

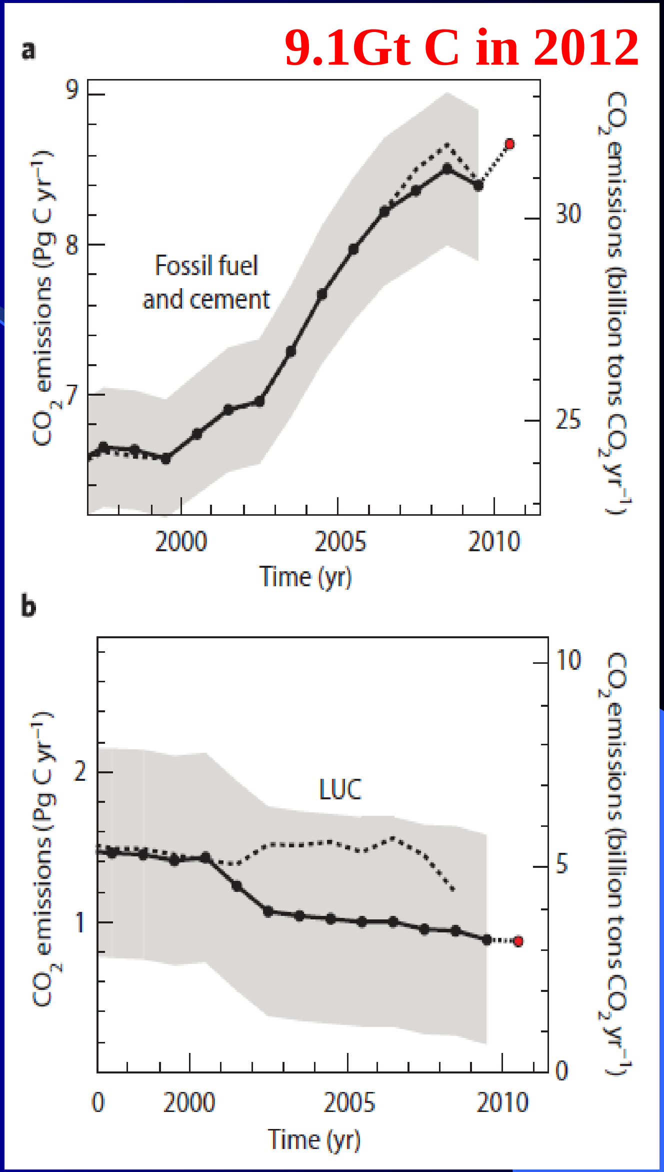
CO_2 Emissions

Globally, fossil fuel burning released ~32 Pg CO_2/yr in 2012 (fairly large uncertainty)

Land use change added ~3 Pg/yr

This CO_2 is partitioned between global reservoirs: **atmosphere, land, and ocean**

- **Good news: Partitioning reduces atm.CO_2 contents, tempering the greenhouse effect and global warming**
- **Bad news: Invasion of CO_2 into the ocean is causes acidification, and will continue as emissions increase over the next century (but there is some good news on LUC)**



9.1Gt C in 2012

Friedlingstein et al. (2010)
Nature Geosciences

Trends and Changes in CO_2 Emissions

Since 1750 roughly >400 Pg of carbon have been released to the atmosphere by human activity. **Half of that since mid-1970's.**

- CO_2 emissions increased about 1% per year in 1990's but grew ~3.4% per year from 2000-2008
- Emissions in 2009 dropped /global economic slump (but less than expected) but were still the 2nd highest in human history (30.8 X 10^9 tons/yr) to date…
- Large regional differences: Europe, Japan and N. America had the largest decreases in emissions (-6.9% US to -11.8% Japan) in 2009
- Emerging economies had increases (e.g., China, India, Korea)

Data for 2008+ from Friedlingstein et al., Nature Geosciences (2010)

Distribution of CO_2

CO_2 emissions are partitioned between reservoirs:

Atmosphere	~45%
Land	~29%
Ocean	~26%

Note: There is ~53X more C in the ocean (as DIC, DOC, POC) than in the atmosphere (as CO_2)

When pCO_2 (atm) was < pCO_2 (oce)

➔ gas transfer was **from the ocean to the atmosphere**

Currently atmospheric pCO_2 exceeds oceanic pCO_2 in many regions of the open ocean

➔ **Currently the open ocean is largely a SINK of CO_2**

Conditions in the coastal ocean vary…

Current Status of CO_2 (cont.)

- If added CO_2 remains in atmosphere → greenhouse effect will be greater than if input is to a different reservoir (e.g., biosphere, oceans)
- Greater amounts, however, may be going into the biosphere than previously thought…

The correlation between temperature and atmospheric CO_2 is less than perfect from 1880 to 2080… yet, overall trend is unmistakable

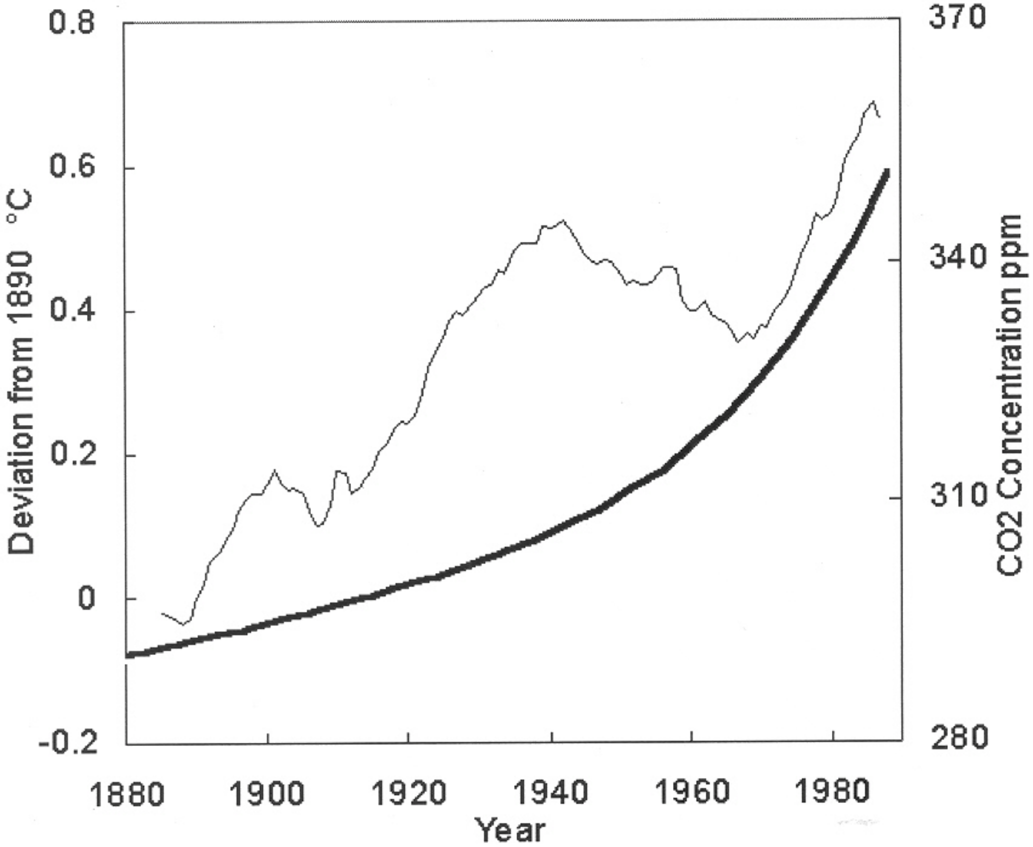
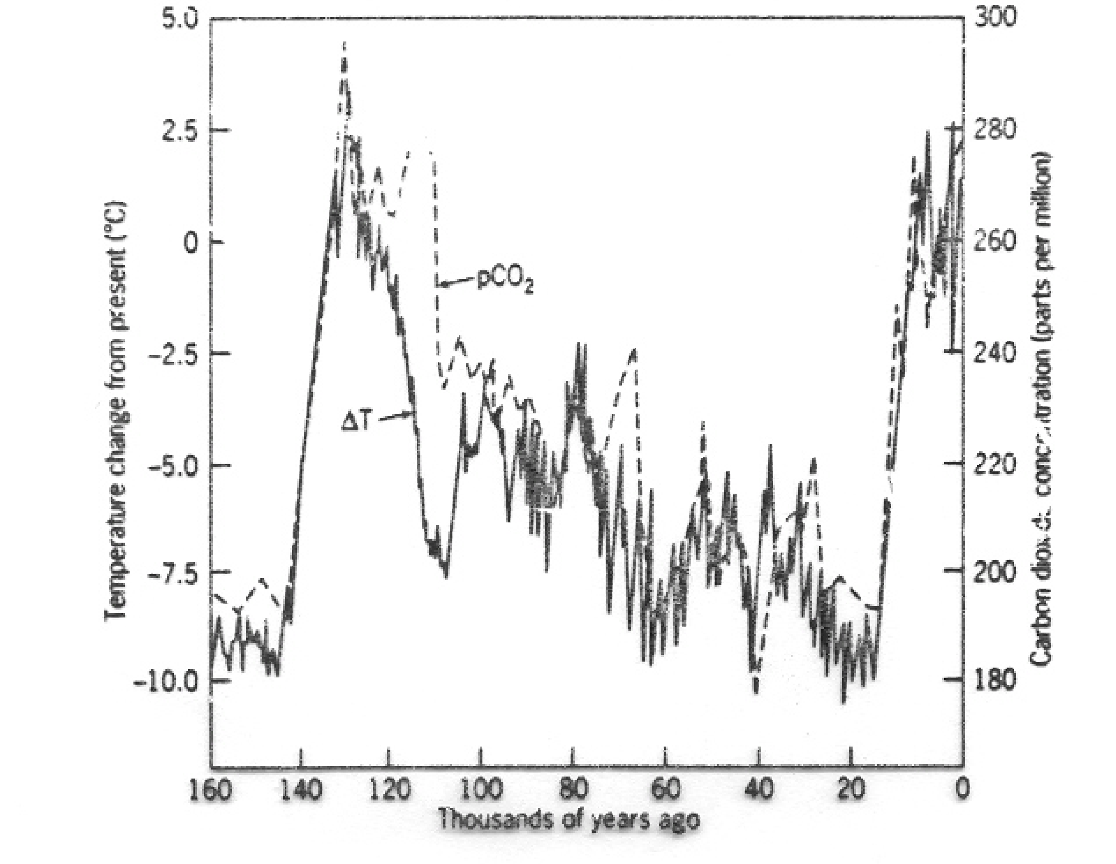


Figure 12: Eleven-year moving average of global surface temperature, as estimated by NASA GISS (23, 33, and 34), plotted as deviation from 1890 (left axis and light line), as compared with atmospheric CO2 (right axis and dark line) (2). Approximately 82% of the increase in CO2 occurred after the temperature maximum in 1940, as is shown in figure 1.

Longer range T correlation



Atmospheric temperature and CO_2 correlate much better on time scales of tens to hundreds of thousands of years

Hydrolysis of CO_2

- CO_2 has multiple possible transformations upon interaction with H_2O
- Forms include: $CO_{2(g)}$, $CO_{2(aq)}$, H_2CO_3, HCO_3^- and CO_3^{-2}
- Species interconvert readily
- Perturbations to one part of CO_2 system ➔ redistribution of other species
- Reactions not always intuitive ➔ worth explaining before discussing **Alkalinity**

Equations for CO_2 hydrolysis

We can describe the equilibrium of gaseous and aqueous CO_2 as:

$CO_{2(g)} \leftarrow\rightarrow CO_{2(aq)}$ $K_H = [CO_2]/pCO_2$

Subsequent hydration and dissociation reactions are described as:

$CO_{2(aq)} + H_2O \leftarrow\rightarrow H_2CO_3$ $K_0 = [H_2CO_3]/[CO_2] = 10^{-1.53}$

$H_2CO_3 \leftarrow\rightarrow HCO_3^- + H^+$ $K_3 = [HCO_3^-][H^+]/[H_2CO_3] = 10^{-6.0}$

$HCO_3^- \leftarrow\rightarrow CO_3^{-2} + H^+$ $K_2 = [CO_3^{-2}][H^+]/HCO_3^-] = 10^{-9.1}$

Notice that we have not yet specified a K_1…

Shifts in equilibrium

- addition of H^+ to a solution of HCO_3^- or CO_3^{-2} will drive each of the reactions backwards to H_2CO_3 or HCO_3^- because:

$$K_2 = [CO_3^{-2}][H^+]/HCO_3^-] = 10^{-9.1}$$

- if you increase $[H^+]$, then $[CO_3^{-2}]/HCO_3^-]$ must decrease if K_2 is to remain constant…
- this can only be achieved (without adding anything to the system) by converting some CO_3^{-2} to HCO_3^-

Species distribution as a f(pH)

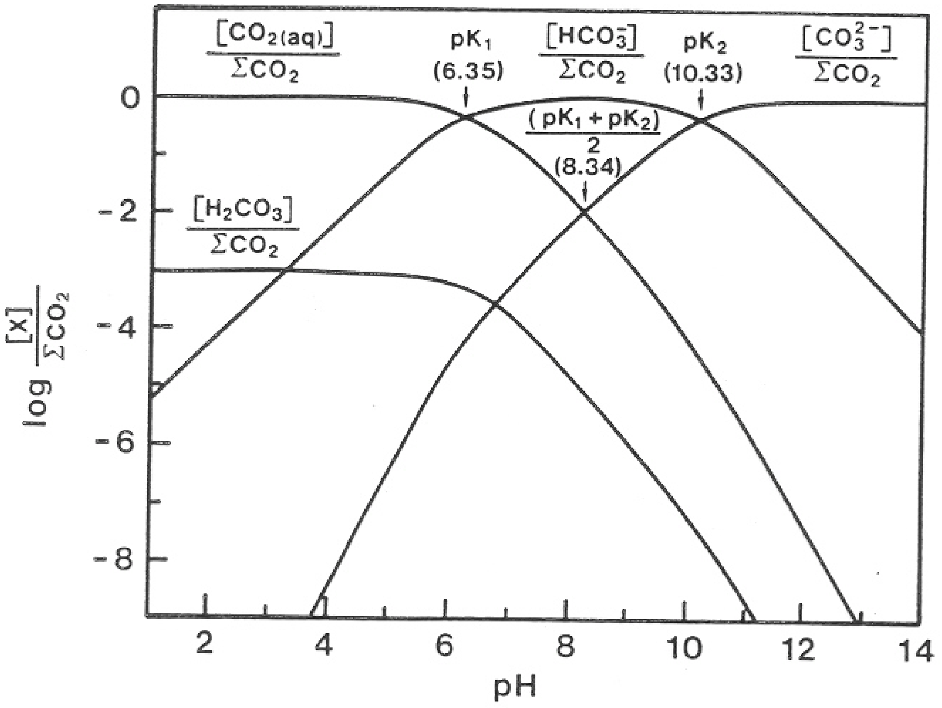


Figure 1.1. A Bjerrum diagram for the relative proportions of carbonic acid system chemical species as a function of pH, for the case where all activity coefficients are equal to 1. pK's are values at 25°C.

From Morse and Mackenzie, Geochemistry of Sedimentary Carbonates, 1990

Note: there is extremely little H_2CO_3 in SW because at the pH of SW it ionizes nearly completely

Bjerrum Plots

- Where lines cross on Bjerrum plots, concentrations of the relevant species are equal…
- Bjerrum plots use p functions (-log [x])
- Distribution is intuitive if you think in terms of pK's
- Note that values in prior diagram are for DI water at 25°C… NOT SEAWATER (see Stumm and Morgan, 1981, p177 for SW values)
- pK values depend on temperature and ionic strength
- at higher pH, the ability of a solution to absorb H^+ is greater because HCO_3^- is driven to CO_3^{-2}

Total CO_2 (DIC, C_T)

$$\text{Total } CO_2 = CO_{2(aq)} + H_2CO_3 + HCO_3^- + CO_3^{-2}$$

- at SW pH, >99% of CO_2 species are HCO_3^- and CO_3^{-2} (and most of that is HCO_3^-) so can simplify

$$\text{Total } CO_2 \approx HCO_3^- + CO_3^{-2}$$

- this is also known as total DIC or C_T
- relevant equilibria can be combined into a series of equations that allow us to relate the **activity** of any of the parameters…

Total CO_2 (2)

$$\{CO_2\} = pCO_2\, K_H$$

- the equation involving H_2CO_3 is usually eliminated by combining the solvation and first ionization, hence:

$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$ $\qquad K_1 = \{HCO_3^-\}\{H^+\}/\{CO_2\}$

$$\{HCO_3^-\} = K_1\, K_H\, pCO_2 /\{H^+\}$$

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

$$\{CO_3^{-2}\} = K_2\, K_1\, K_H\, pCO_2 /\{H^+\}^2$$

Total CO_2 (3)

- we replace thermodynamic activities with concentrations by using activity coefficients.
- this leads to another set of equations…

$$[CO_2] = pCO_2\,K_H/\gamma_{(CO_2)}$$

$$[HCO_3^-] = K_1K_H\,pCO_2/\{H^+\}\,\gamma_{(HCO_3^-)}$$

$$[CO_3^{-2}] = K_2K_1K_H\,pCO_2/\{H^+\}^2\,\gamma_{(CO_3^{-2})}$$

- These relationships allow us to determine concentrations of each of the species in terms of only the pH and the pCO_2 of the solution

Total CO_2 (4)

- At the surface of the ocean (mixed layer), the pCO_2 should be equal to that of the atmosphere (assuming equilibrium between the two reservoirs… but this is often not the case)
- Any seawater sample collected within the mixed layer should have the same in-situ pCO_2

Total CO_2 (5)

- Examine concept of total CO_2 again…which we refer to as Total Inorganic Carbon (TIC)

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

- But HCO_3^- + CO_3^{-2} account for >99% of the total CO_2 so we approximate to…

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

Total CO_2 (6)

- In seawater measurable carbonate parameters are:

  Total CO_2, pCO_2, pH (and Total Alk)

- We can use the equations developed earlier to susbtitute for HCO_3^- and CO_3^{-2}

Total CO_2 (7)

$$\text{Total } CO_2 = K_1 K_H\, pCO_2 / \{H^+\}\, \gamma_{(HCO_3^-)} + K_2 K_1 K_H\, pCO_2 / \{H^+\}^2\, \gamma_{(CO_3^{-2})}$$

- 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 C_T and A_T

Seawater pH

- 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), however, the CO_2 system (its shifting equilibria) regulates seawater pH

Alkalinity

- What is it and why do we care?
- Alkalinity can be defined in a variety of ways but it fundamentally begins with charge balance between major seawater cations and anions
- Different definitions can be applied to various situations…

Definitions of Alkalinity (1)

The buffer capacity of seawater

- Total Alkalinity (TA) represents ability of seawater to resist pH change upon addition of acid.
- Concept of “buffer” from chemistry: substance that resists pH change upon addition of acid or base
- For seawater we focus on ability to absorb H^+

Definitions of Alkalinity (2)

- HISTORICAL DEFINITION:

  Number of equivalents of strong acid needed to bring 1L of seawater to a given pH (formation of H_2CO_3 from CO_3^{-2})

Definitions of Alkalinity (3)

- A MORE RIGOROUS DEFINITION:

  alkalinity of a solution is the excess of the bases (proton acceptors) over the acids (proton donors)

  → this is the concentration of negative charge capable of reacting with added H^+

Bases in seawater

- Bases in seawater that accept protons
  - **carbonate species**
  - **boric acid species**
  - **hydroxide ion**
- Define alkalinity on basis of above species
- Calculate alkalinity by subtracting protons and other acids from the sum of bases of weak acids

Alkalinity titrations

TA= $2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] - [H^+]$ +[mystery organic H^+acceptors]

- End point of alkalinity is when: $[H^+]$ = $2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-]$ + [mystery organic H^+acceptors]
- TA usually reported in meq/L or meq/kg

Alkalinity titrations (2)

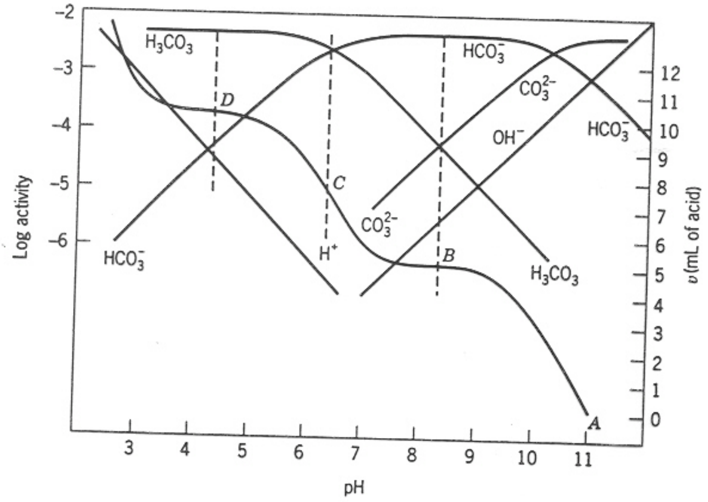


FIGURE 15.5. Titration curve (heavy line *ABCD*) for 5 mM Na_2CO_3 with acid. Also shown is the concurrent DIC speciation, with concentrations given as the log of their ion activities. *B* is the carbonate end point, *A* and *C* are regions of strong buffering, and *D* is the bicarbonate end point.

- carbonate species control pH near their pK’s because they buffer the solution upon addition of acid
- other bases (NH_3, $Si(OH)_3^-$, PO_4^{3-}) also contribute to TA but are much less abundant

TA is an important property affected by chemical and biological processes

- Because HCO_3^- and CO_3^{-2} are major anions of weak acids in seawater, any changes in total positive charge can cause shifts in their relative abundances
- Precipitation of $CaCO_3$ decreases TA
- TA is then a measure of the extent of calcification and other processes involving CO_2 (with caveats)
- Photosynthesis/respiration of biological communities changes DIC but not TA (again with caveats)
- Can calculate DIC from TA and pH

Carbonate Alkalinity

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

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

Charge Balance Alkalinity

Sum of cationic charges- Sum of anionic charges

- Ratio of HCO_3^- and CO_3^{-2} can adjust to maintain charge balance, but also adjusts with pH
- Shortfall of anions in Table 15.2 is made up by HCO_3^- and CO_3^{-2}

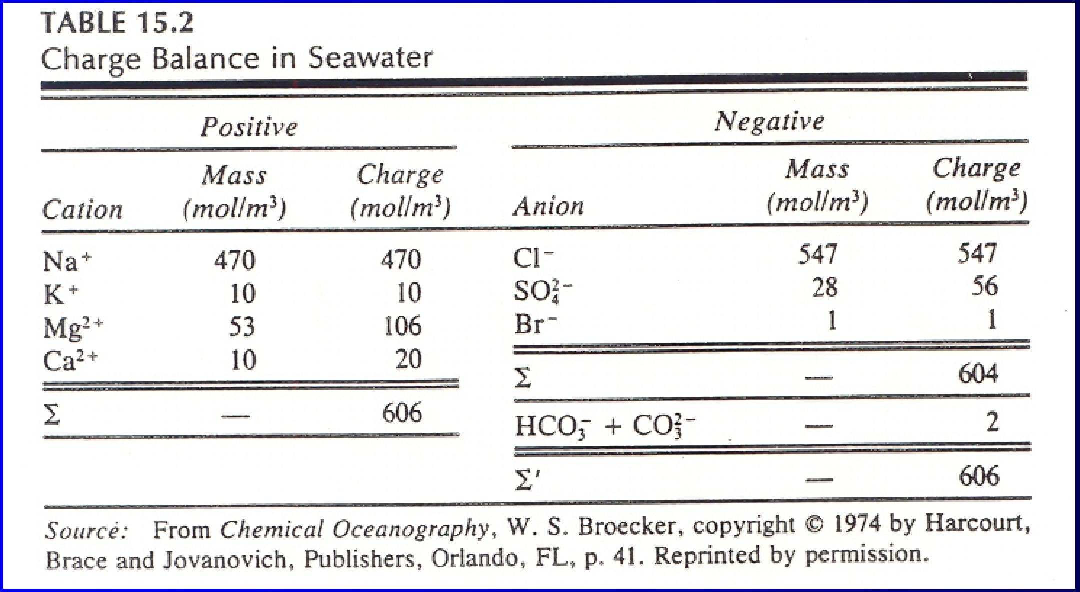


TABLE 15.2
Charge Balance in Seawater

Positive

Cation	*Mass (mol/m³)*	*Charge (mol/m³)*
Na^+	470	470
K^+	10	10
Mg^{2+}	53	106
Ca^{2+}	10	20
Σ	—	606

Negative

Anion	*Mass (mol/m³)*	*Charge (mol/m³)*
Cl^-	547	547
SO_4^{2-}	28	56
Br^-	1	1
Σ	—	604
$HCO_3^- + CO_3^{2-}$	—	2
Σ′	—	606

Source: From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich, Publishers, Orlando, FL, p. 41. Reprinted by permission.

Calculations

- Any two of the four properties: DIC, TA, pCO_2, pH can be used to calculate the other properties of the marine CO_2-carbonic acid system…
- Which two are measured depends on your “tools”
- Use of DIC and TA generally provides best constraint on system and improves accuracy of calculations

Equations for calculations

Combine equations for DIC and TA to derive:

$$[HCO_3^-] = 2[DIC] - [TA]$$

by reversing the substitution scheme we get…

$$[CO_3^{-2}] = [TA] - [DIC]$$

- We can therefore estimate the variations in carbonate or bicarbonate ion by measuring DIC and TA (or pH and pCO_2)

Distribution of CO_2 and Alk.

- Alkalinity is a conservative property in seawater (but not on coral reefs) because it is calculated as the difference between two conservative properties
- GEOSECS data from Atlantic show that, although alk. is generally conservative, there are some distinctive trends in its relationship with SAL (water masses)

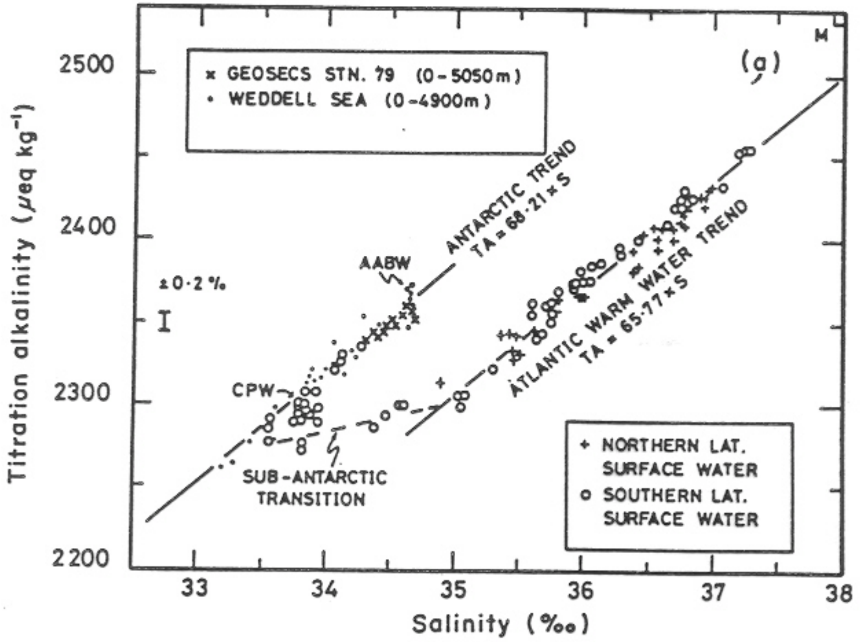


Figure 8.3 The alkalinity–salinity relationship for the Atlantic Ocean (from Campbell 1983, after Takahasi *et al*. 1980). Data are from GEOSECS stations (40°N–60°S) for water depths less than 50 m.

What processes affect Alk?

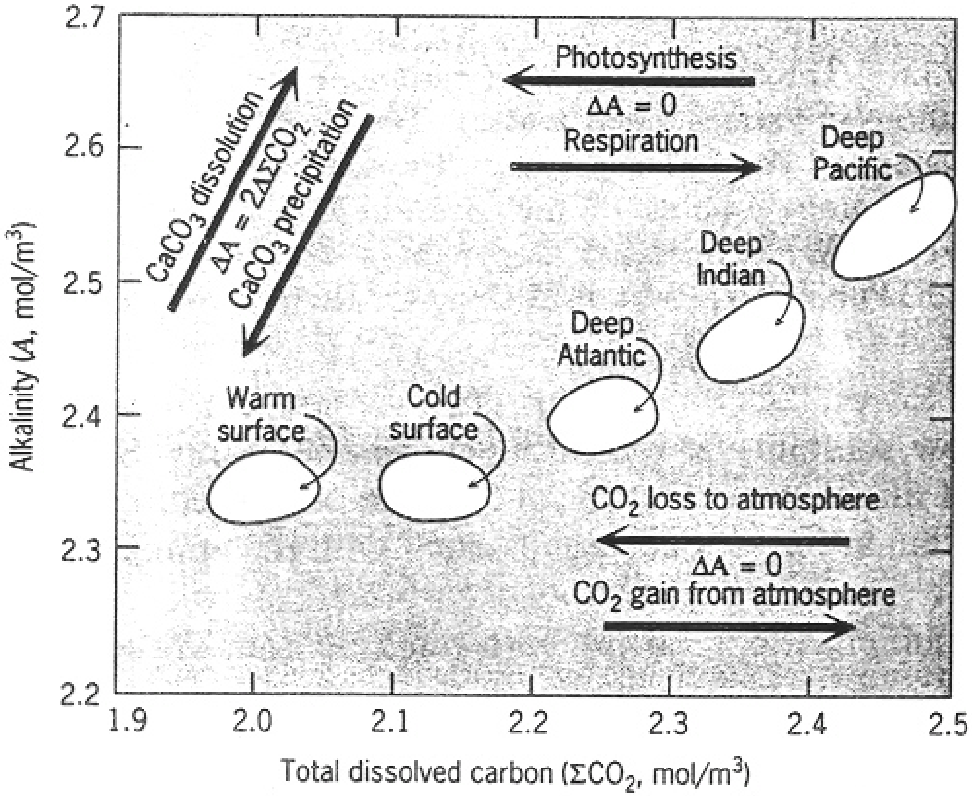


FIGURE 15.7. Relationship between the total dissolved inorganic carbon content and the alkalinity of waters from various parts of the ocean. The arrows indicate the effects of various processes occurring within the sea. *Source:* From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich Publishers, Orlando, FL, pp. 14–15. Reprinted by permission.

Equilibrium with atmosphere

At surface ocean equilibrium (should) exist between atmosphere and surface waters

- decreasing CO_2 in seawater through photosynthesis will cause increase in pH
- loss of CO_2 to atmosphere from upwelled cold, high pCO_2 water has same effect
- This is because we take protons out of system when they are used to make CO_2 from HCO_3^-
- Yet, the TA does not change because the decrease in pCO_2 and loss of DIC does not affect the components of TA (same + and – charges are present)

Calcification

- Removal of CO_2 from surface ocean to produce organic matter often also removes $CaCO_3$ to form shells
- Hence, calcification alters both alkalinity and the CO_2 system
- because calcification removes Ca^{2+} and, because alkalinity is charge dependent, removal of + charges causes reduction of TA
- Amount of TA reduced by calcification is 2X the effect on carbon content because of charge removal

De-Calcification

- Dissolution of $CaCO_3$ in deep water will be discussed in OCN 623 lectures…
- BUT… remineralization of organic matter produces CO_2 that reacts with CO_3^{-2}

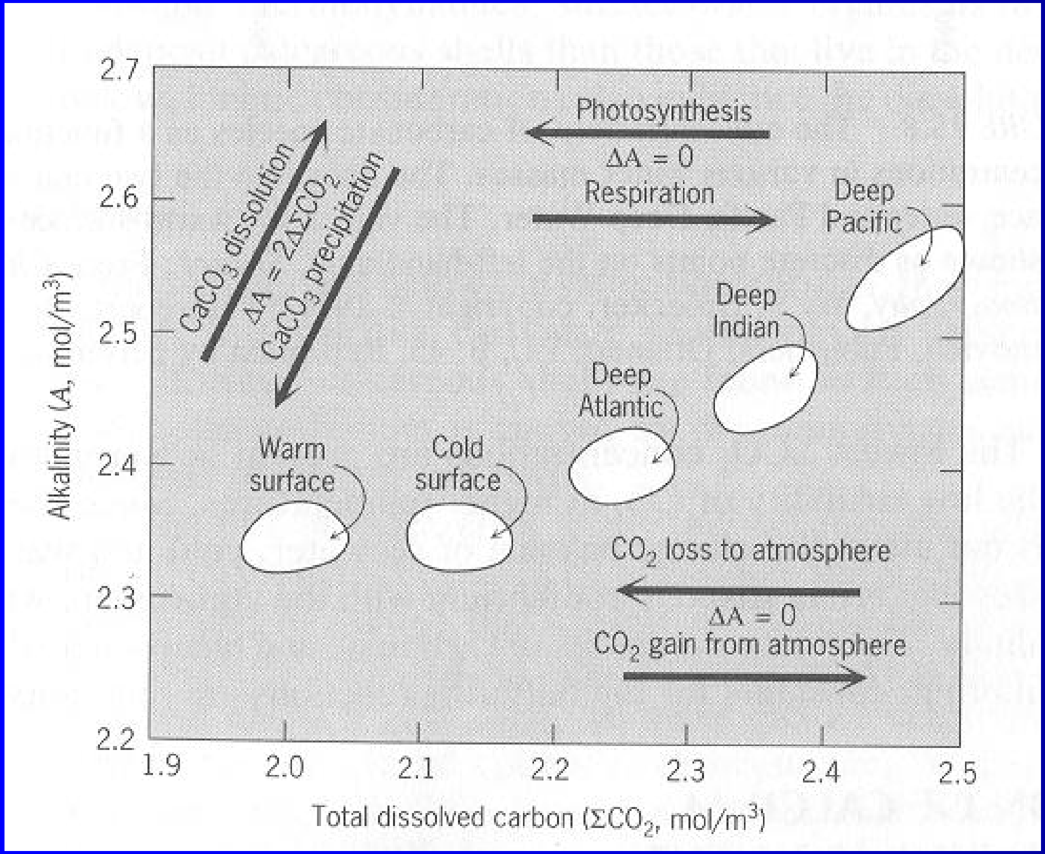
$$CO_2 + CO_3^{-2} + H_2O \leftarrow \rightarrow 2HCO_3^-$$

- in the deep ocean, the decrease in $[CO_3^{-2}]$ from this reaction has a marked effect on $CaCO_3$ solubility

$CaCO_3 \leftarrow\rightarrow Ca^{2+} + CO_3^{=}$

$CH_2O + O_2 \leftarrow\rightarrow CO_2 + H_2O$

$CO_2 + CO_3^{=} + H_2O \leftarrow\rightarrow 2HCO_3^{-}$



DISSOLUTION→ CHANGE IN DIC & ALKALINITY

REMIN. of O.M. → NO CHANGE IN ALKALINITY, BUT INCREASES DIC (unless it is by sulfate reduction)

Geographical Distribution of CO_2 Parameters

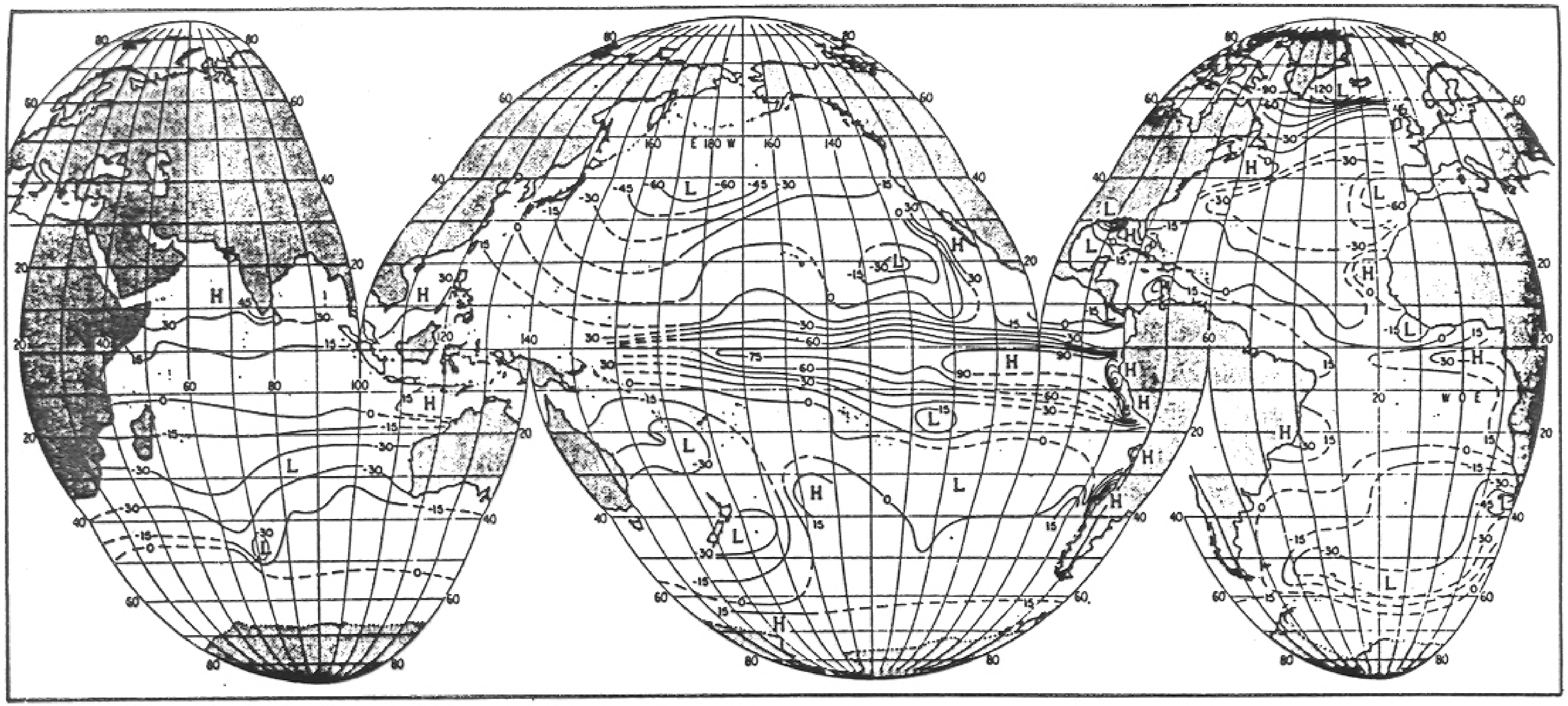


Figure 8.4 The distribution of P_{CO_2} in the World Ocean expressed as the departure in ppm from equilibrium with atmospheric CO_2 (from Keeling 1968). Most data represent summer conditions. The distribution shows a number of highs (H; positive values which imply evasion of CO_2 from the ocean to the air) and lows (L; negative values which imply invasion of CO_2 from the atmosphere to the ocean). More recently, other authors have presented data on the distribution of the sea/air CO_2 partial pressure difference (ΔP_{CO_2}). Positive values indicate that the ocean is a source of CO_2, and include the equatorial waters of the Pacific and the Atlantic. These areas are strong CO_2 sources as a result of the upwelling of deep CO_2-rich waters and surface warming; a combined effect which overcomes the P_{CO_2} lowering caused by photosynthesis, although the 'source' can disappear in the equatorial Pacific during El Niño events. Negative values indicate that the ocean is a sink for CO_2, and include the northern North Atlantic and the Southern Ocean which act as sinks due to the combined effects of water cooling and photosynthesis (see, e.g., Takahashi 1989; *Oceanus* 32 (No. 2), 22–29).

Geographical Distribution of CO_2 Parameters

- Last figure shows departures from atm. values

- High values at equator are from upwelling and subsequent gas evasion to atmosphere
- Low values → high bioproductivity
- Low values where cooling of ocean increases solubility of gas and causes gas infusion to surface ocean

Vertical Profiles

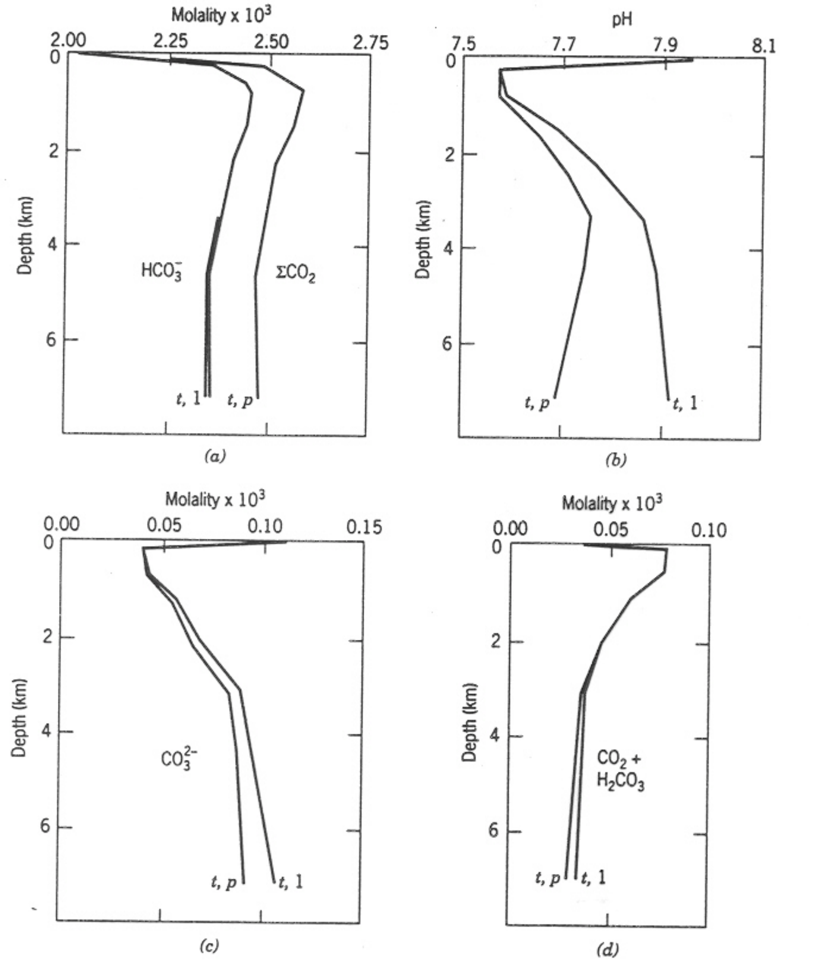


FIGURE 15.6. Vertical concentration profiles of *(a)* bicarbonate and ΣCO_2, *(b)* pH *(c)* carbonate, and *(d)* carbon dioxide + carbonic acid concentrations. Curves labe *t,p* have been corrected for the effects of in situ temperature and pressure on equilibrium speciation. Curves labeled *t,*1 have been corrected for the in situ temperature effect, but not for that caused by pressure. *Source:* From C. Culbersc and R. M. Pytkowicz, reprinted with permission from *Limnology and Oceanograp* vol. 13, p. 414, copyright © 1968 by the American Society of Limnology and Oceanography, Seattle, WA.

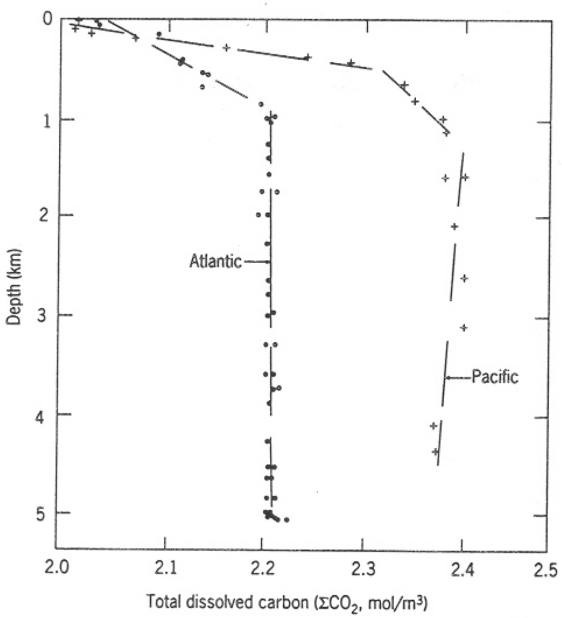


FIGURE 15.4. Variation of total dissolved inorganic carbon concentrations with depth in the Atlantic (36°N 68°W) and in the Pacific (28°N 122°W). *Source:* From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich, Publishers, Orlando, FL, p. 39. Data from Dr. R. Weiss, Scripps Institute of Oceanography, La Jolla, CA. Reprinted by permission.

Laboratory Definition of Alk.

- The titration alkalinity is defined as the number of equivalents of strong acid needed to titrate one kilogram of seawater to the HCO_3^- end point (Edmond, 1970)

Gran Titrations

- Involves stepwise addition of HCl in the pH range 3.7-3.0
- From data, F values are calculated (correspond to the increase in H+ after the 2nd equivalence point of H_2CO_3)
- A linear relationship is assumed and a regression line is used to determine the volume of acid that would correspond to the 2nd equivalence point
- Alk is then calculated from the amount of acid needed to reach the 2nd equivalence point and the actual volume of solution titrated

Gran Titrations II

- Gran titrations are tedious… require lots of time between sequential additions of acid
- Computer controlled autotitrators are really helpful, especially in dispensing small volumes of titrant
- Computer adds HCl until pH drops below 3.7, then records pH and volume of acid added
- Computer records mV and (total) volume for each increment
- From the above… calculate points along the F_2 line

Gran Titrations III

$$F_2 = (V_{sample} + V_{acid})10^{-pH}/N$$

V_{sample} = volume of sample (in L)

V_{acid} = volume of titrant (in L)

N = normality of titrant

- From set of points compute V_2, the volume of HCl needed to give $F_2 = 0$
- Requires using a regression of F_2 versus volume of acid
- Finally… TA = V_2 /sample volume