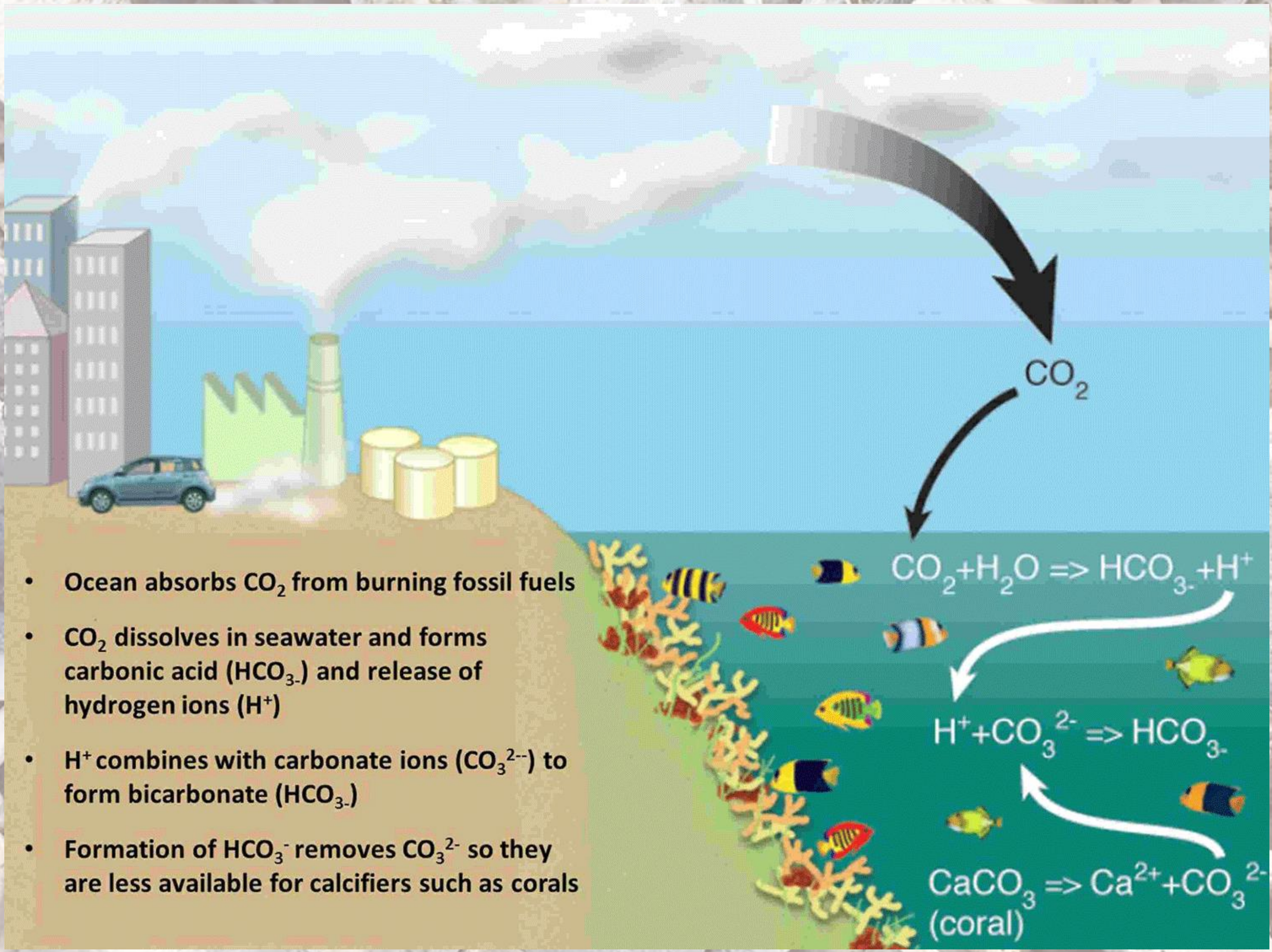
WHAT IS OA?



- Ocean absorbs CO_2 from burning fossil fuels
- CO_2 dissolves in seawater and forms carbonic acid (HCO_{3-}) and release of hydrogen ions (H^+)
- H^+ combines with carbonate ions (CO_3^{2--}) to form bicarbonate (HCO_{3-})
- Formation of HCO_3^- removes CO_3^{2-} so they are less available for calcifiers such as corals

CO_2
$CO_2 + H_2O \Rightarrow HCO_{3-} + H^+$
$H^+ + CO_3^{2-} \Rightarrow HCO_{3-}$
$CaCO_3 \Rightarrow Ca^{2+} + CO_3^{2-}$
(coral)

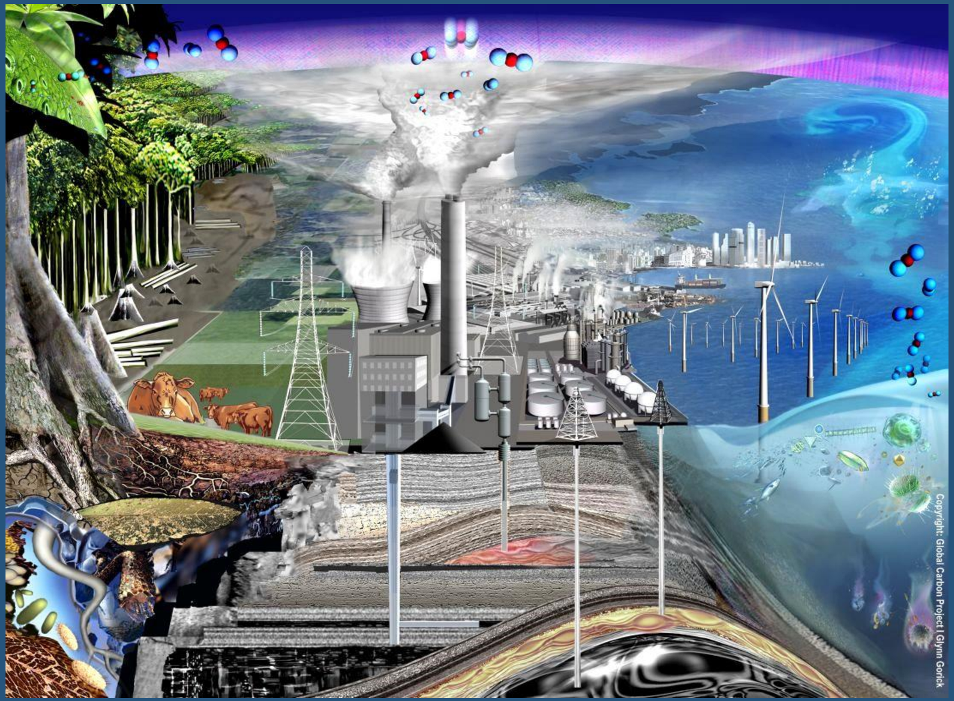
Summary of OA Science

- Well documented, progressive increase in the acidity of the ocean
- Acidity *increases* as the pH *decreases*
- OA is also changing seawater carbonate chemistry. The concentrations of *dissolved* CO_2, hydrogen ions, and bicarbonate ions are increasing, and the concentration of carbonate ions is decreasing

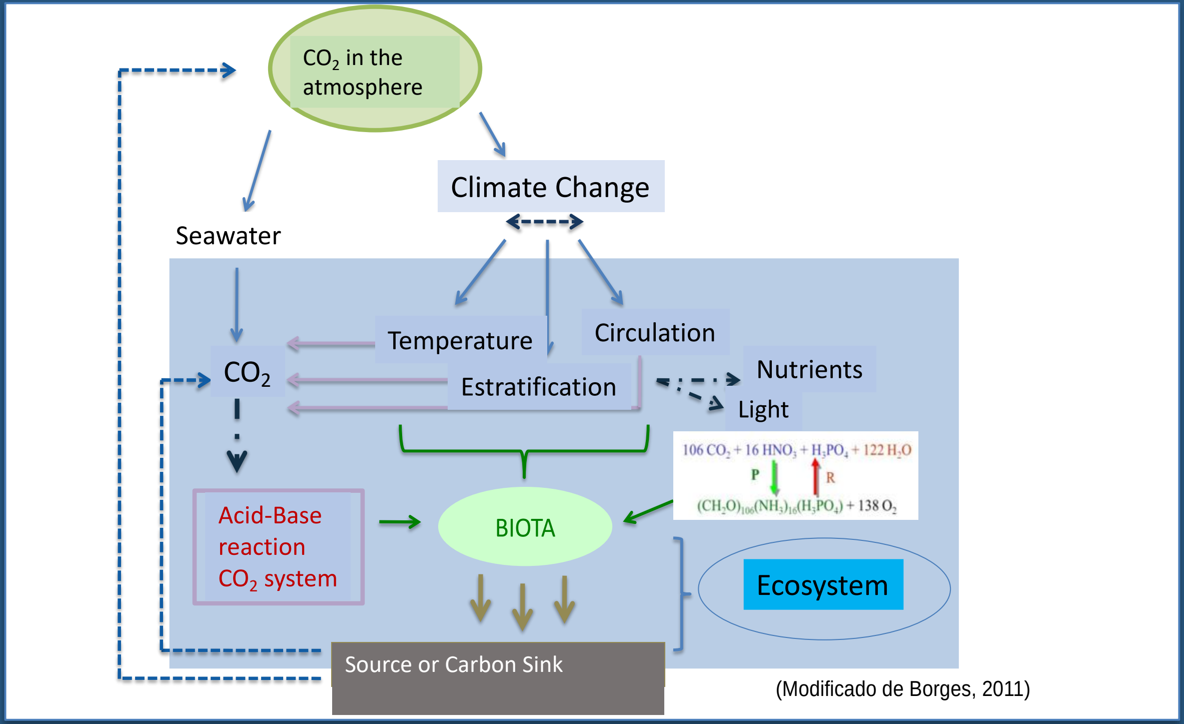
- Changes in pH and carbonate chemistry force marine organisms to spend more energy forming shells etc.
- Current rate of these chemistry changes are unprecedented (nothing like this in 300 million years)
- OA is one more stressor (cumulates with higher temperatures and deoxygenation)

OA BASICS

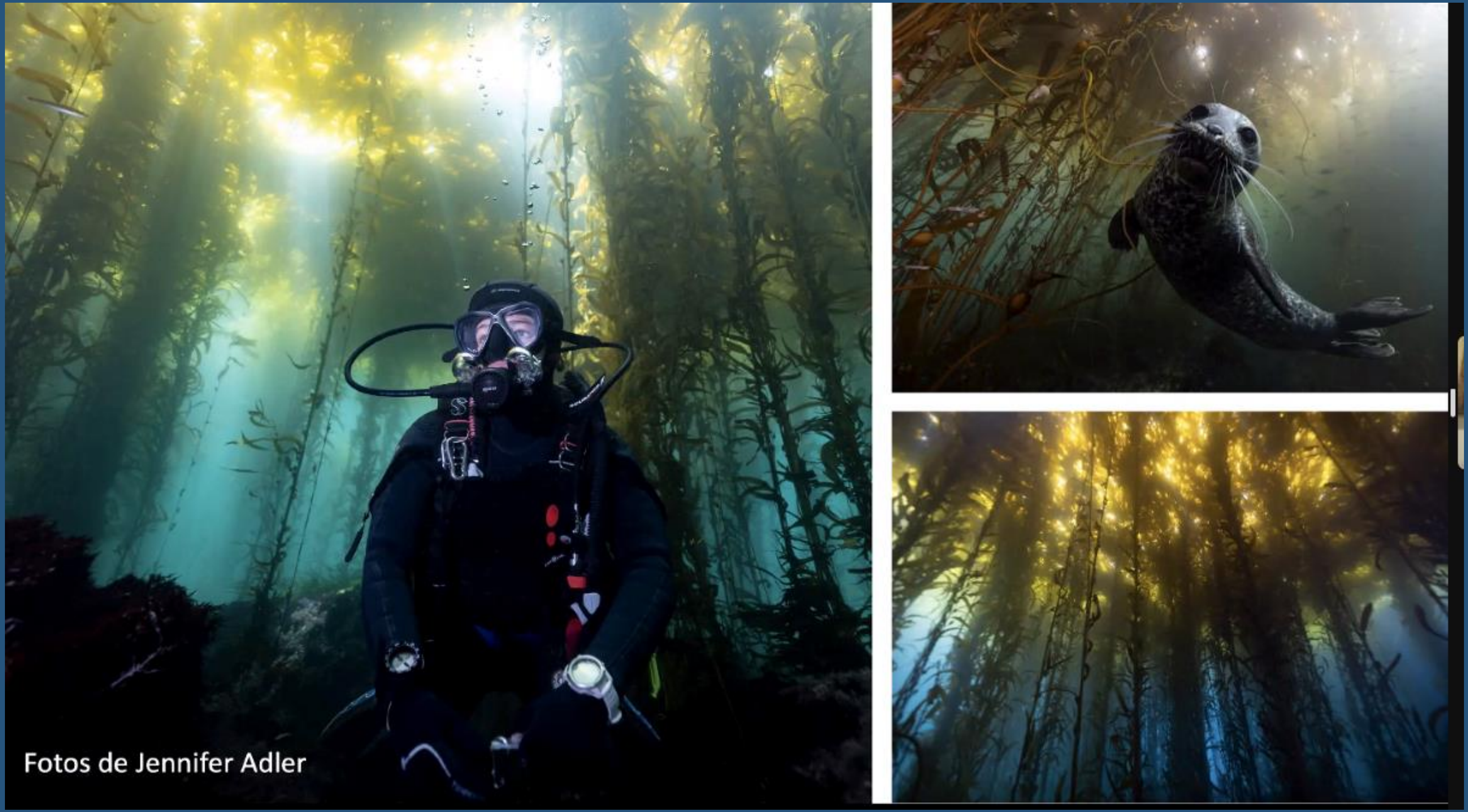
The Carbon Cycle

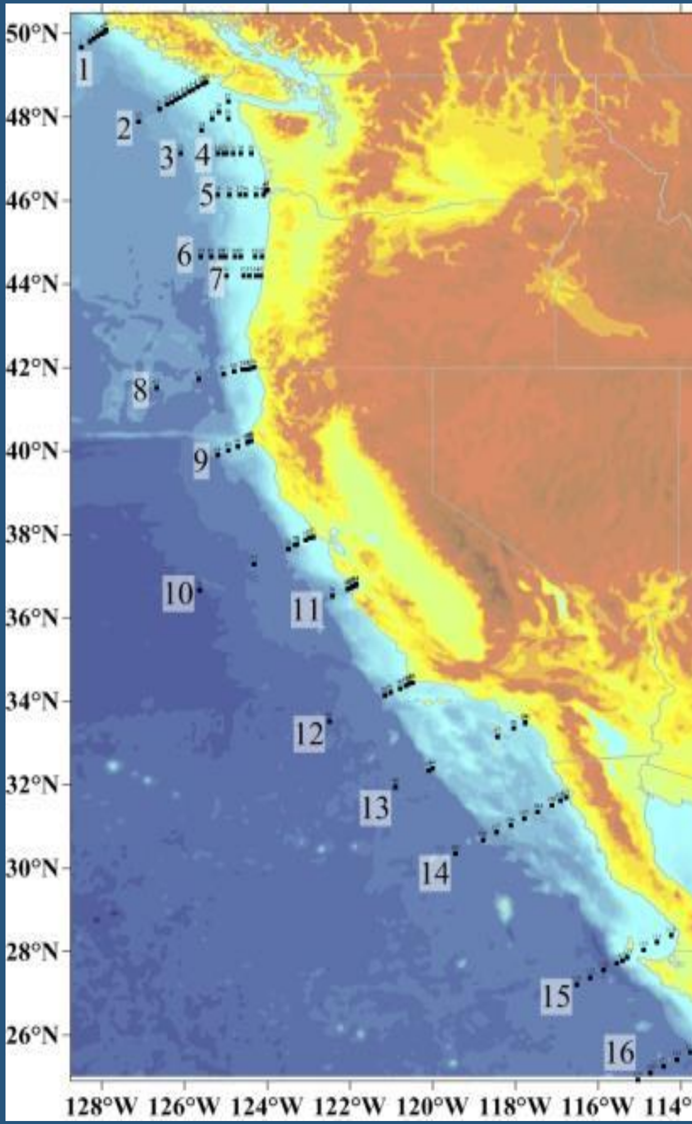


The ocean offers us ecosystem services



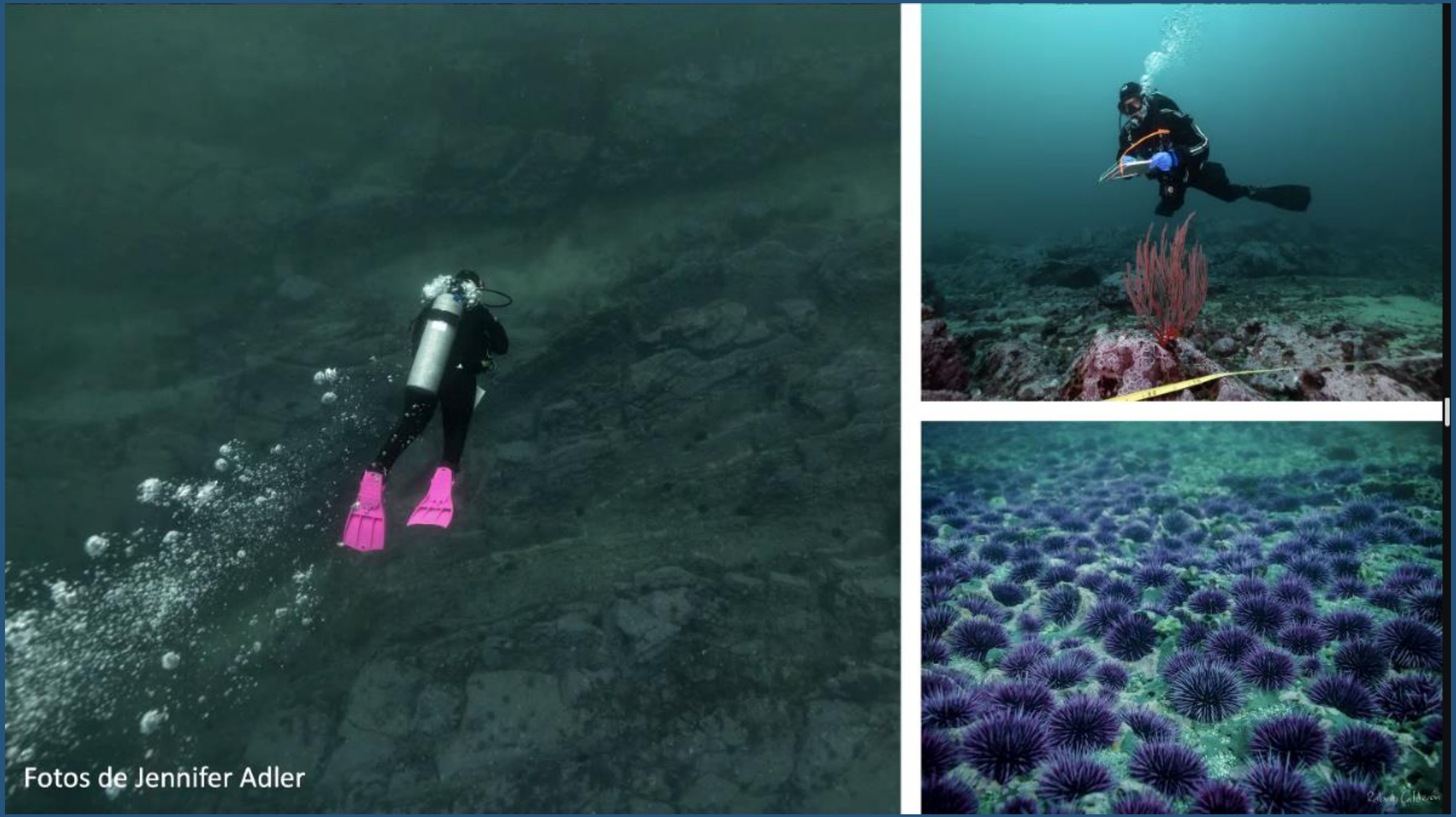
In 2007 Coastal of Baja California Mexico use to see like this photo





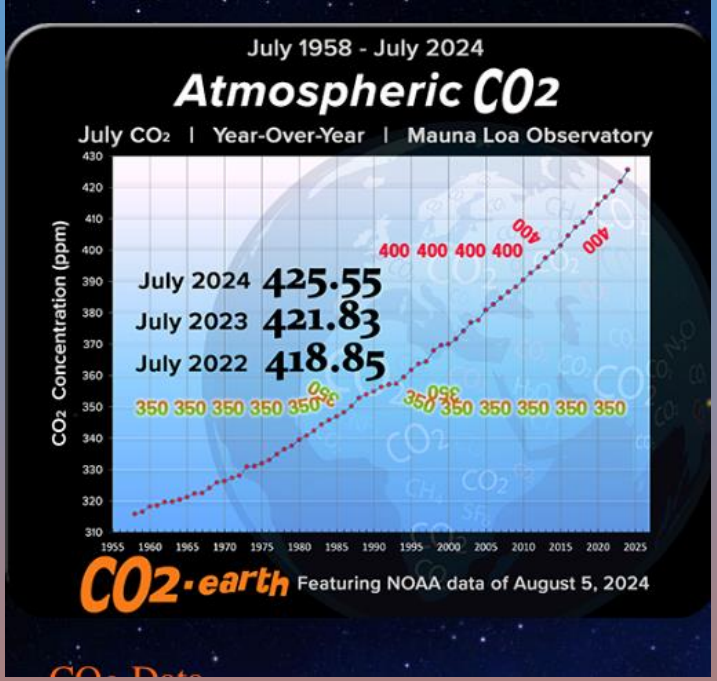
Dra. Fiorenza Michelli

The same environment after 2014



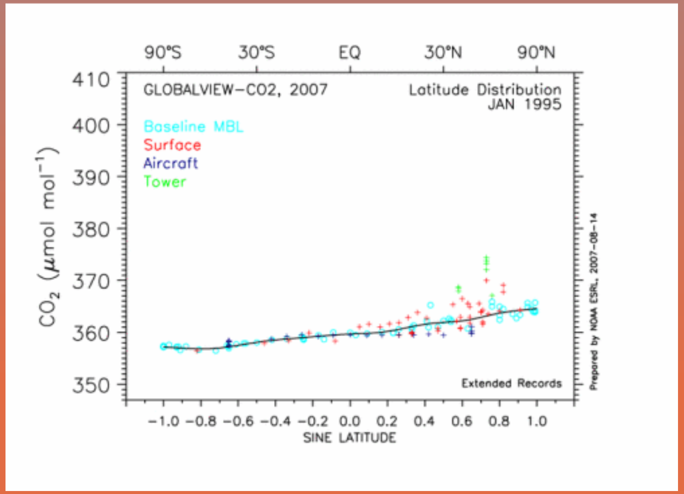
Marine forests, between collapse and reforestation plans
Giant algae create marine forests on the northeastern Pacific coasts, but in Baja California these ecosystems are threatened due to heat waves and purple urchin infestations.

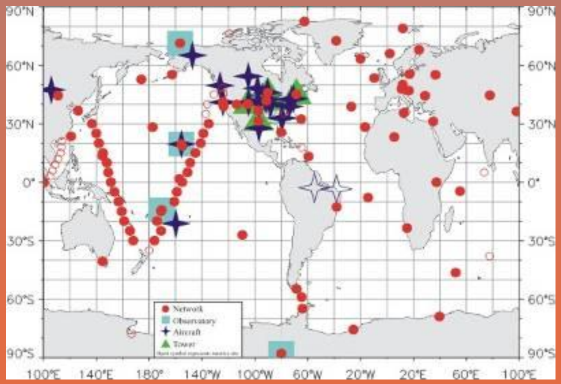
- Atmospheric CO_2 has risen by about 40% above pre-industrial levels.
- The ocean absorbs about 1/3 of human-caused emissions of CO_2 annually, thereby making seawater more acidic (decreasing pH).



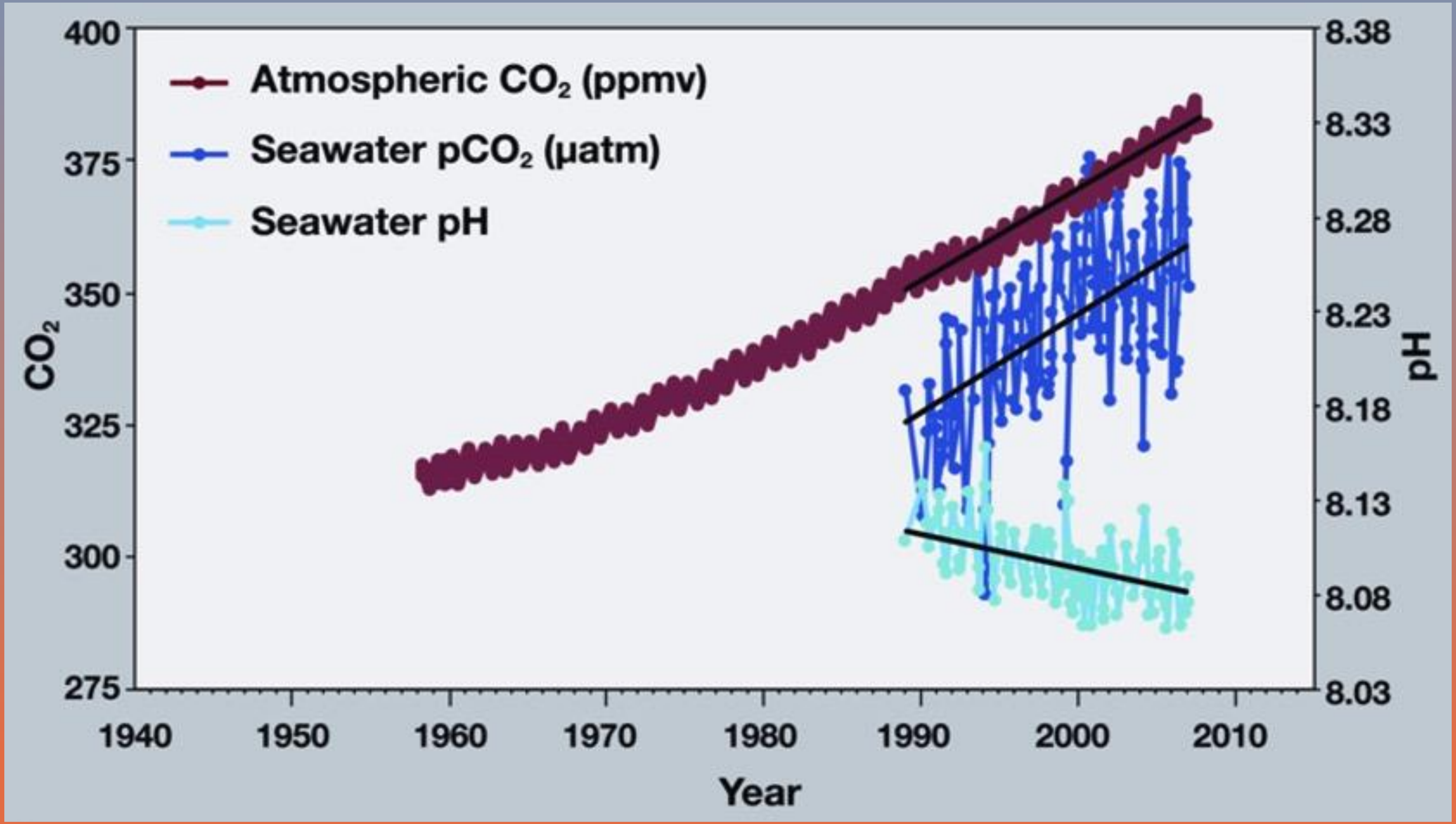
26%

$8.8 \pm 1.8\ GtCO_2/yr$





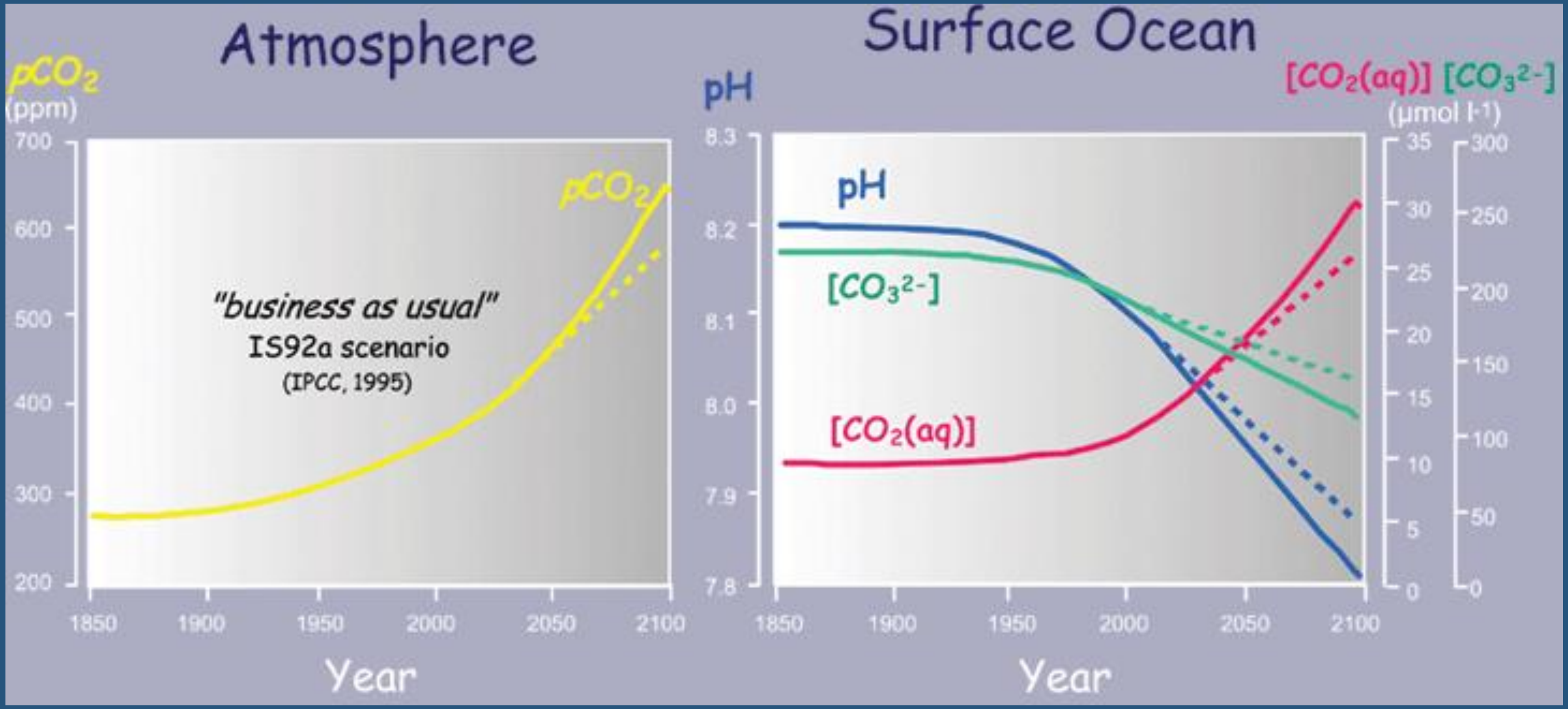
Change in Ocean pH mirrors CO_2 Concentrations (pCO_2)



pCO_2 (CO_2 partial pressure) is commonly referred to as CO_2 concentration in seawater

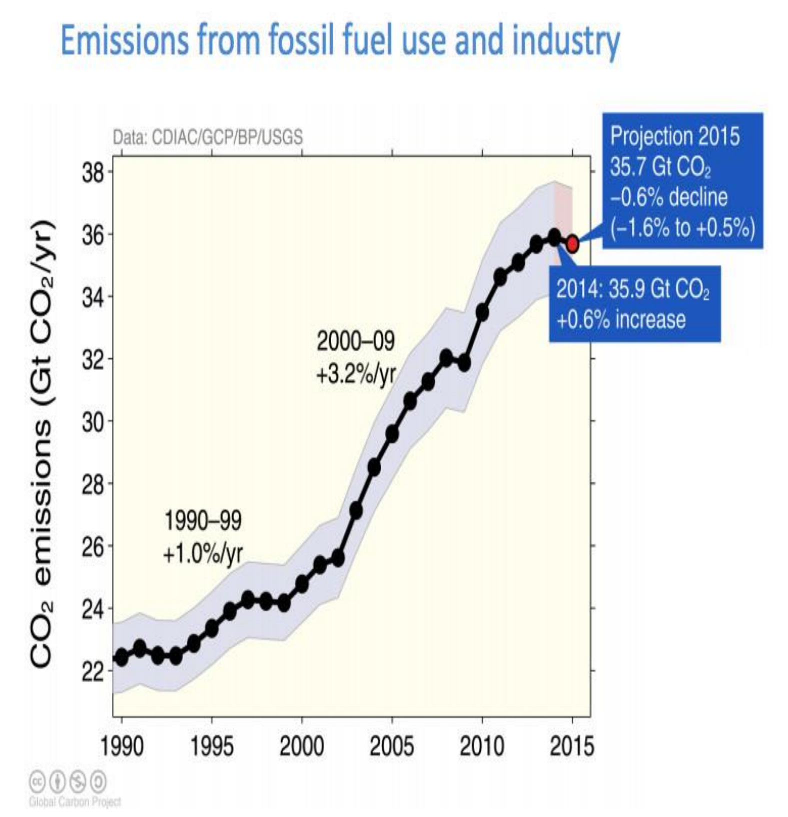
Image courtesy of NOAA. Modified after R. A. Feely, Bulletin of the American Meteorological Society, July 2008.

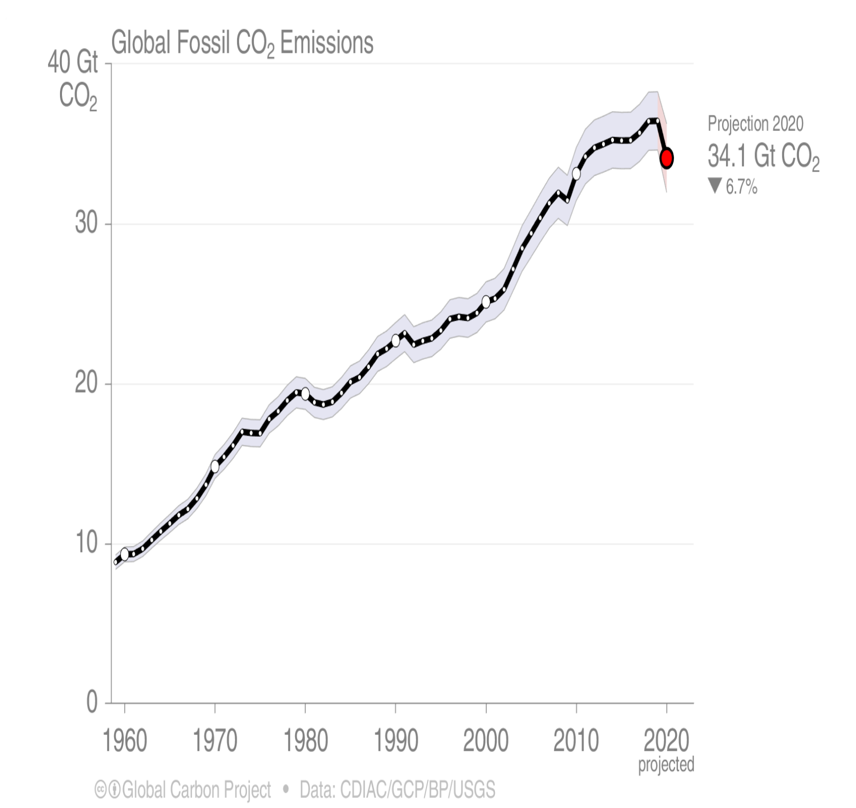
Projections show that continued emissions could drop ocean pH another 0.5 pH units to 7.7 by 2100. A decrease of 60% for $CaCO_3$ concentration is espected.

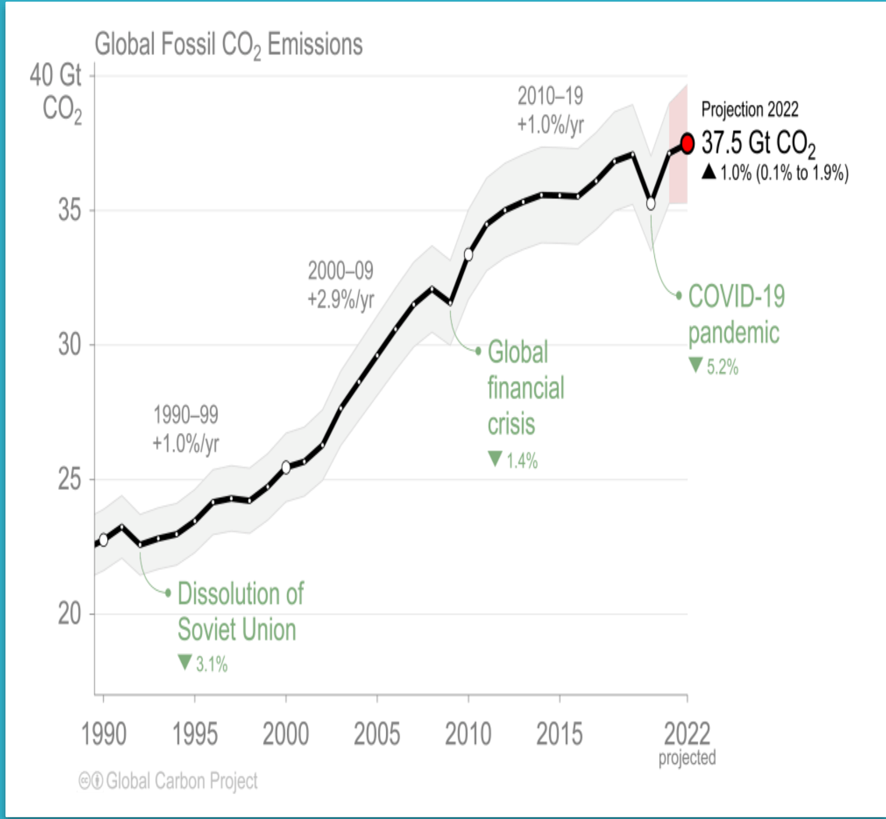


Tomado de Wolf-gladrow et al., 1999.

Fossil Fuel Emissions: Actual vs. IPCC Scenarios







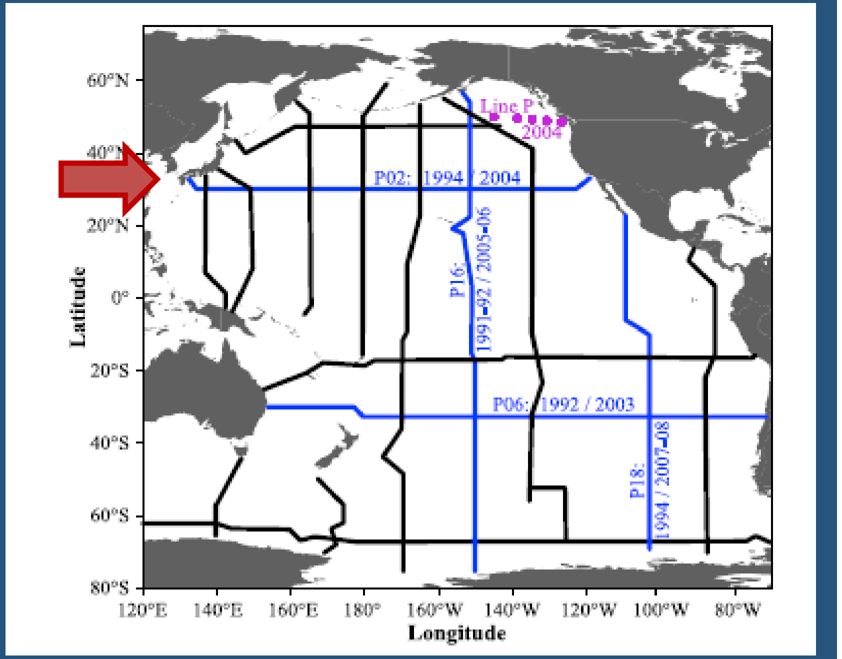
Updated from Raupach et al. 2007, PNAS; Data: Gregg Marland, Thomas Boden-CDIAC 2010; International Monetary Fund 2010

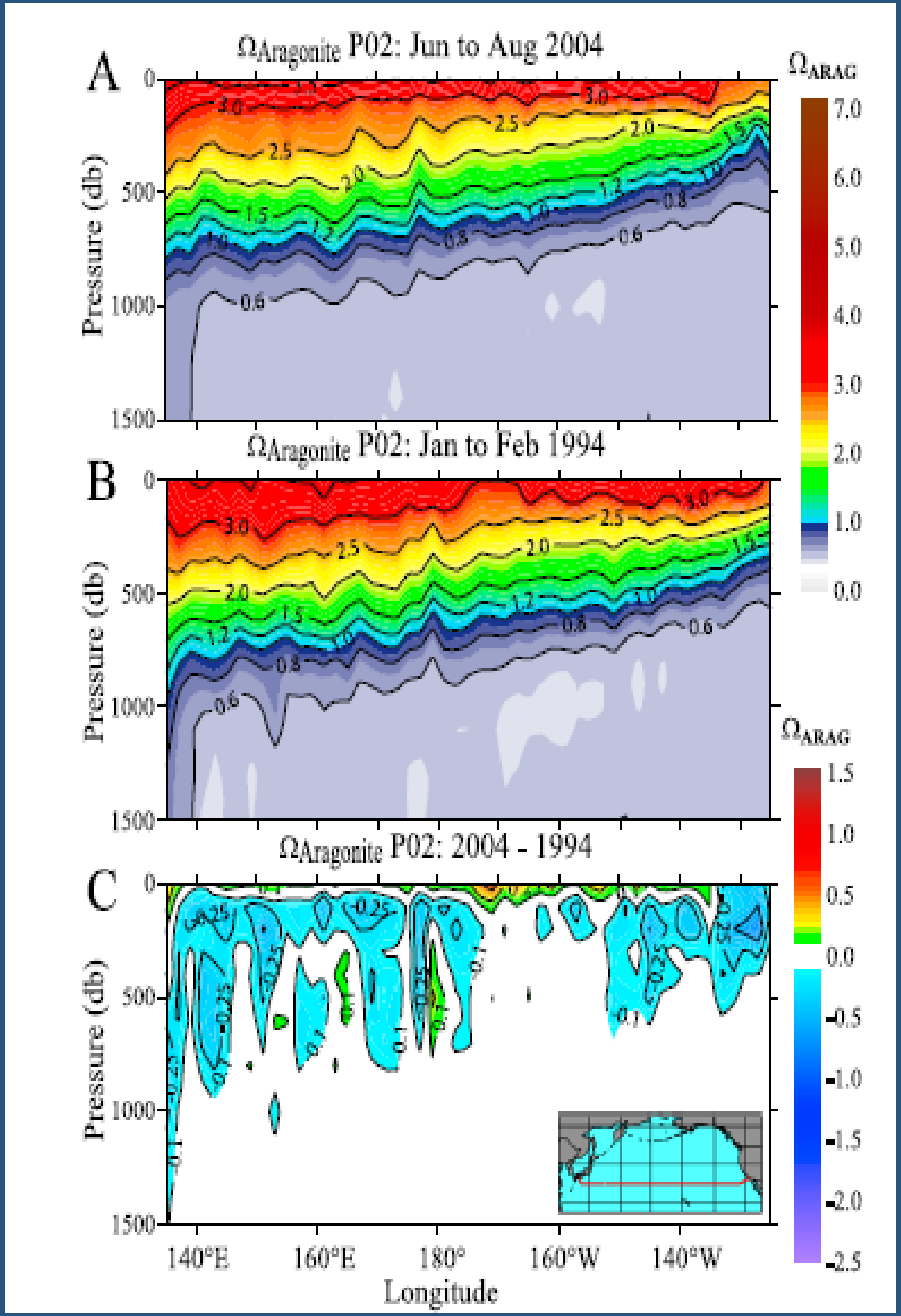
https://www.brusselstimes.com/320490/global-co2-emissions-to-break-new-records-in-2022

Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean

Richard A. Feely,[1] Christopher L. Sabine,[1] Robert H. Byrne,[2] Frank J. Millero,[3] Andrew G. Dickson,[4] Rik Wanninkhof,[5] Akihiko Murata,[6] Lisa A. Miller,[7] and Dana Greeley[1]

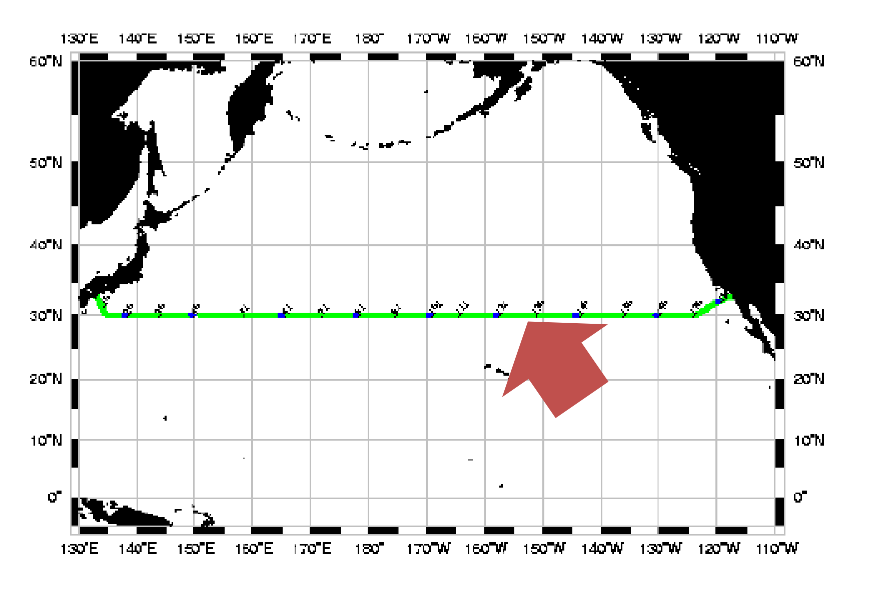
GLOBAL BIOGEOCHEMICAL CYCLES,



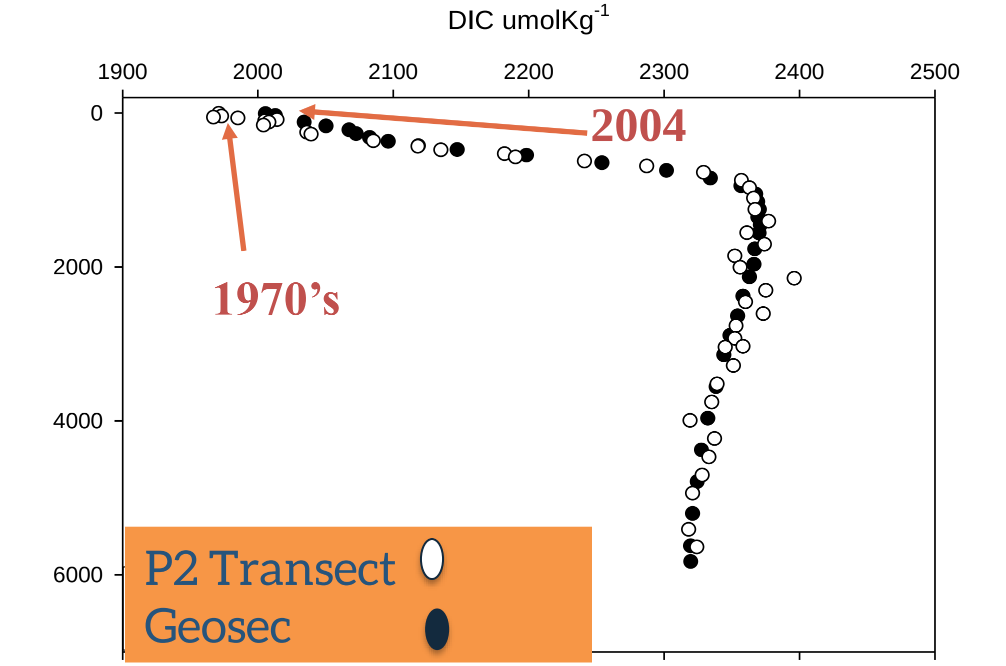


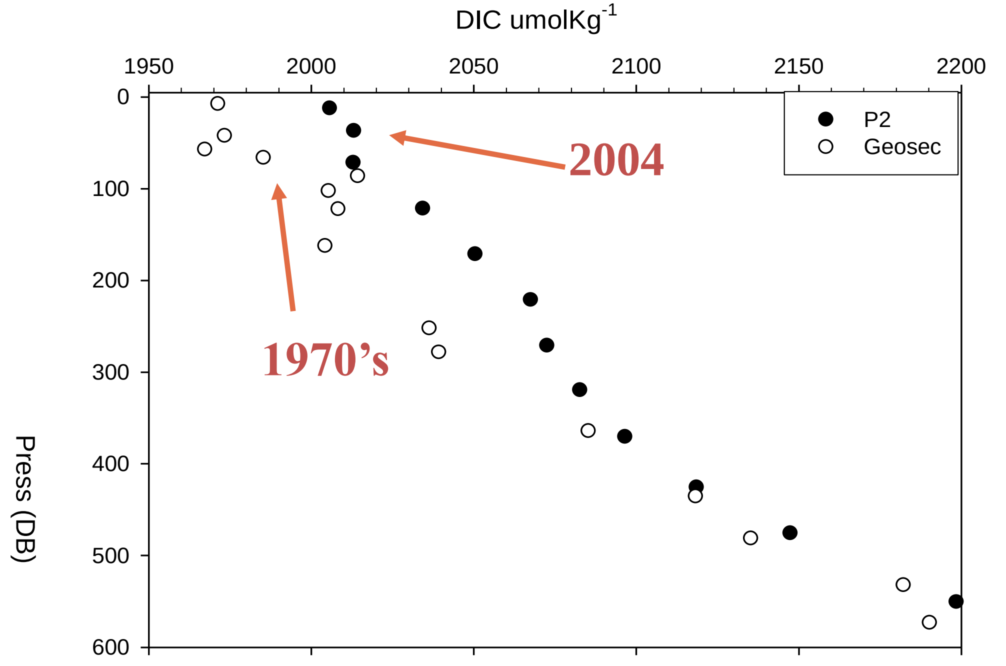
The saturation horizon
It's getting shallower
From 1 to 2m per year.

"See to be believe"



R/V *Roger Revelle* is operated by Scripps Institution of Oceanography





“¿Why is important understand the CO_2 System ?

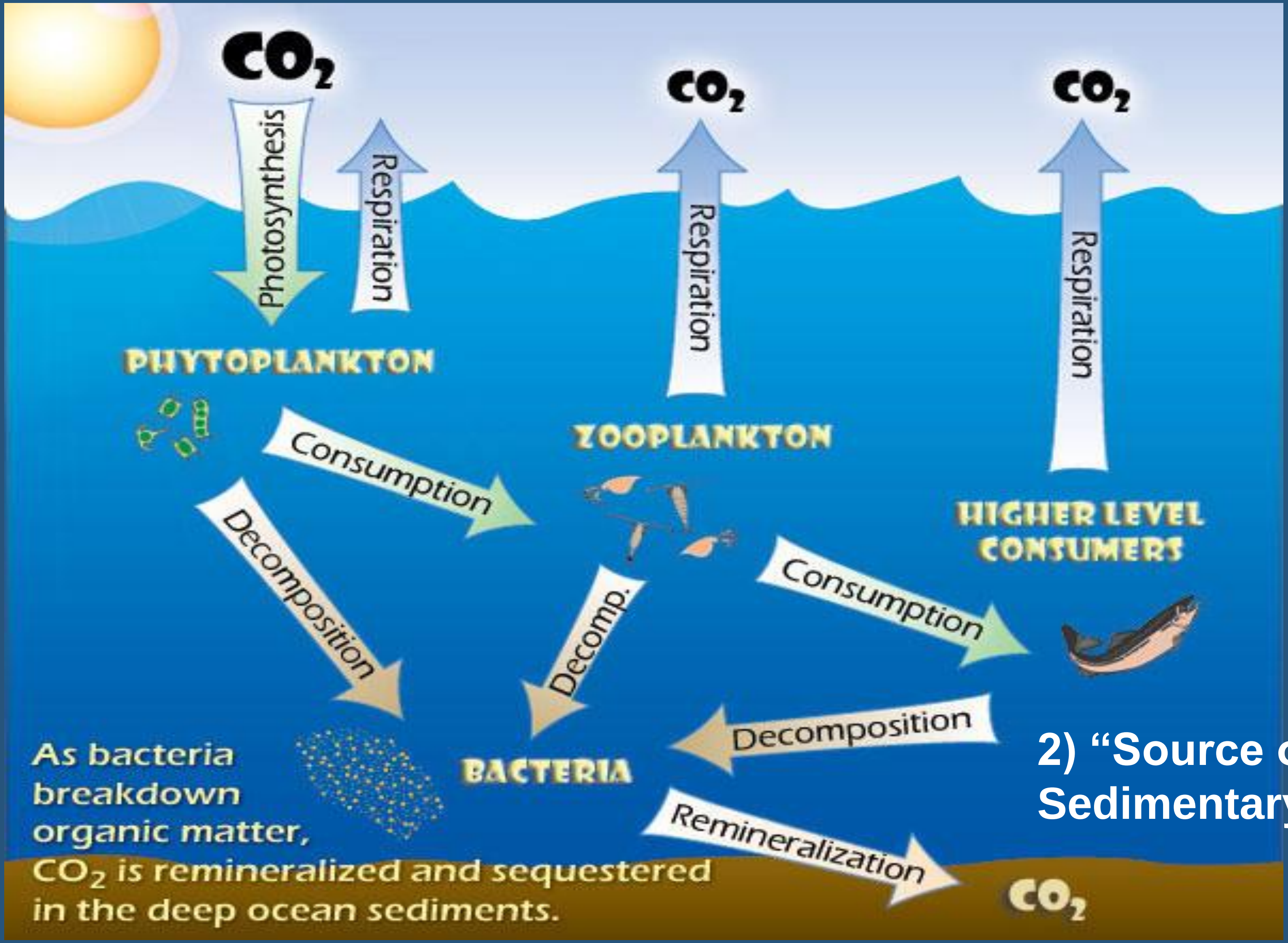
- CO_2 controls the fraction of incoming radiation that remains trapped in the atmosphere (greenhouse effect), which controls the planetary climate.

- CO_2 is the raw material used to build organic matter.

- CO_2 controls the pH of the oceans

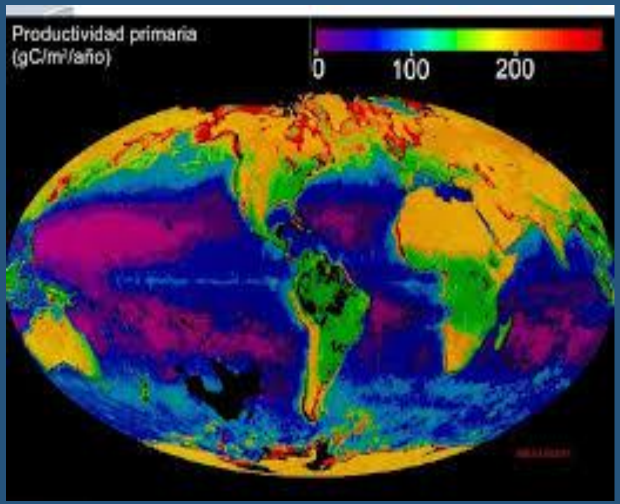
- The distribution of CO_2 species affects the preservation of $CaCO_3$ deposited on the seabed

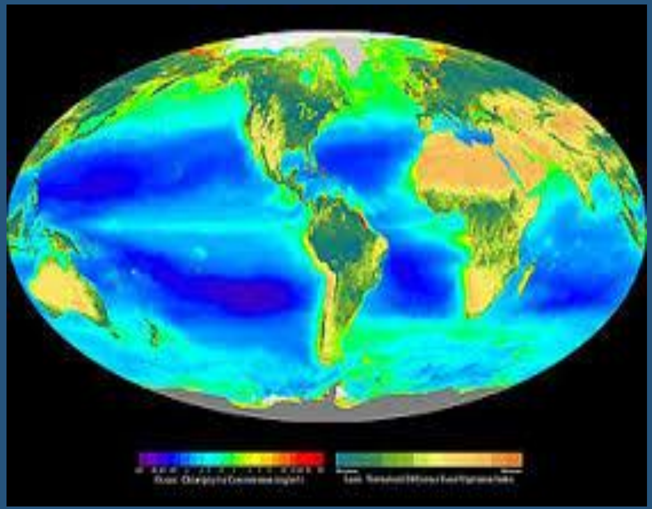
Controls the amount of CO_2 in the atmosphere

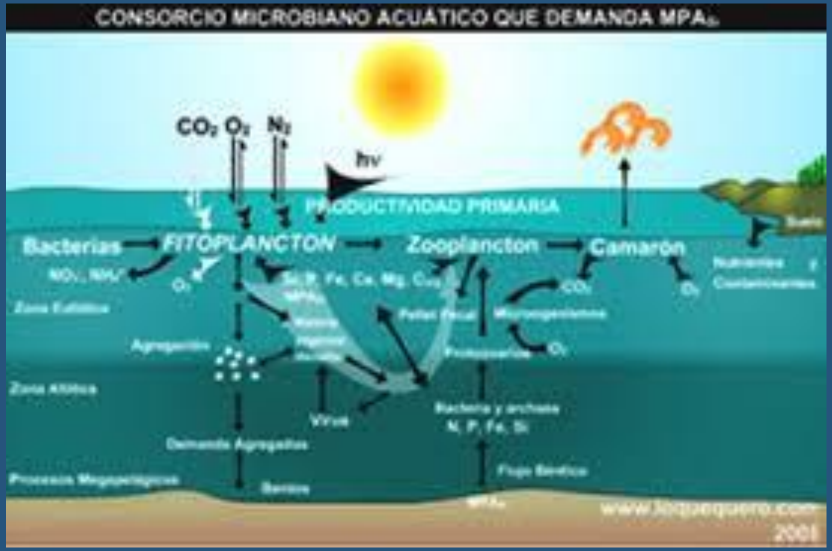


2) “Source of material Sedimentary”

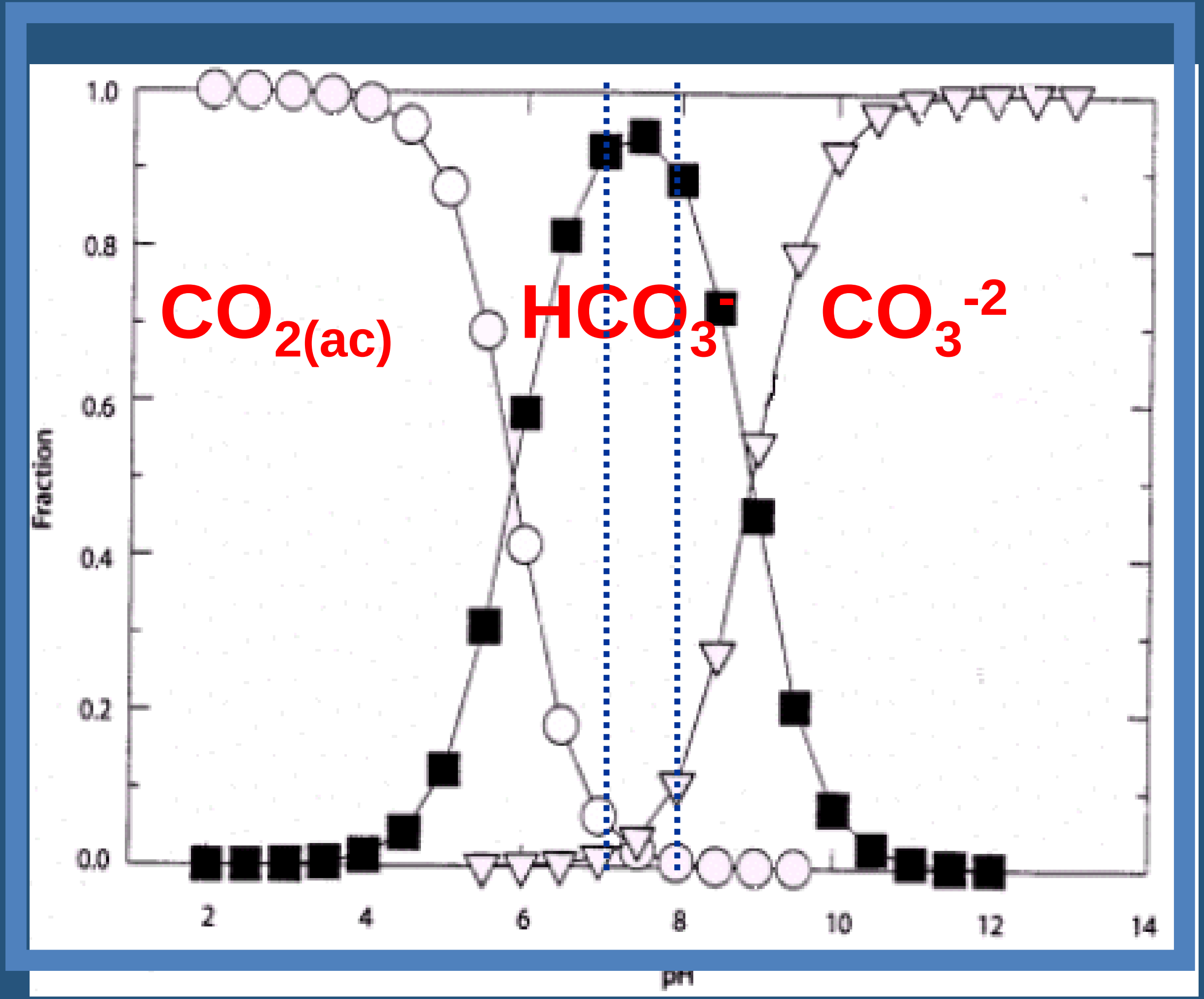
Carbon Source for Primary Organic Productivity





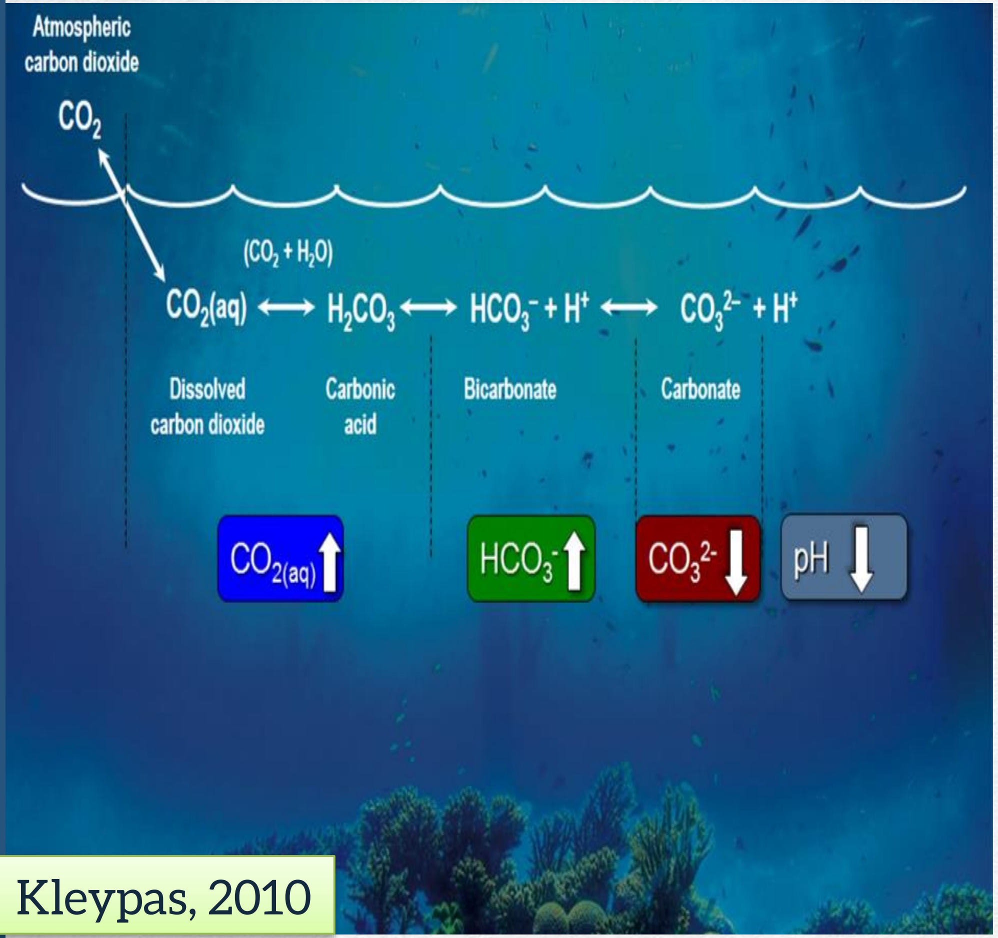


“Regulates pH”

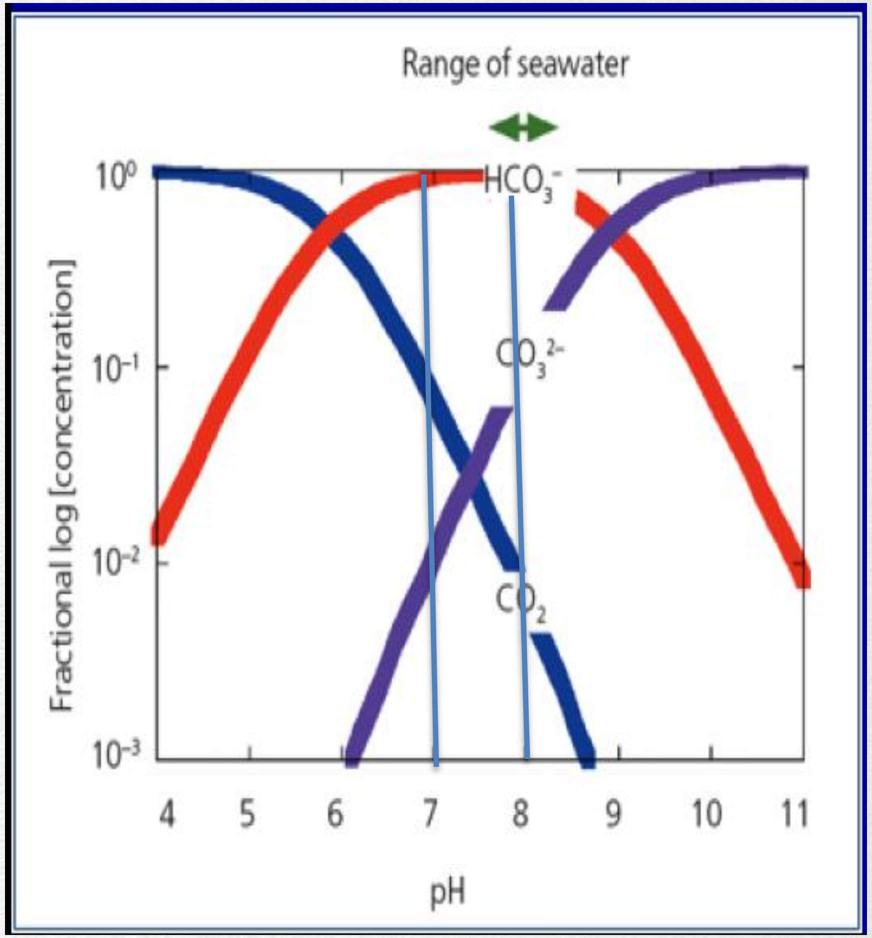


Tomado de Millero et al., 1994

Therefore the term "ocean acidification" is the decrease in pH in seawater due to the dissolution of anthropogenic CO_2.



Kleypas, 2010



To study the Ocean Acidification "OA" several "Tools" are required:

1. Understanding acid-base reactions in seawater "Especially CO_2"
2. Understand which CO_2 parameters (pH, Total Alkalinity, Dissolved Inorganic Carbon, pCO_2) are normally measured in seawater and how.
3. Have access to a computing tool to perform CO_2 system calculations such as CO2Sys or CO_2 Cal.
4. Have access to analytical equipment (and training) to perform measurements of carbon variables.

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Part 1: Seawater carbonate chemistry

Available in the web

1 The carbon dioxide system in seawater: equilibrium chemistry and measurements

Andrew G. Dickson
Scripps Institution of Oceanography, University of California, USA

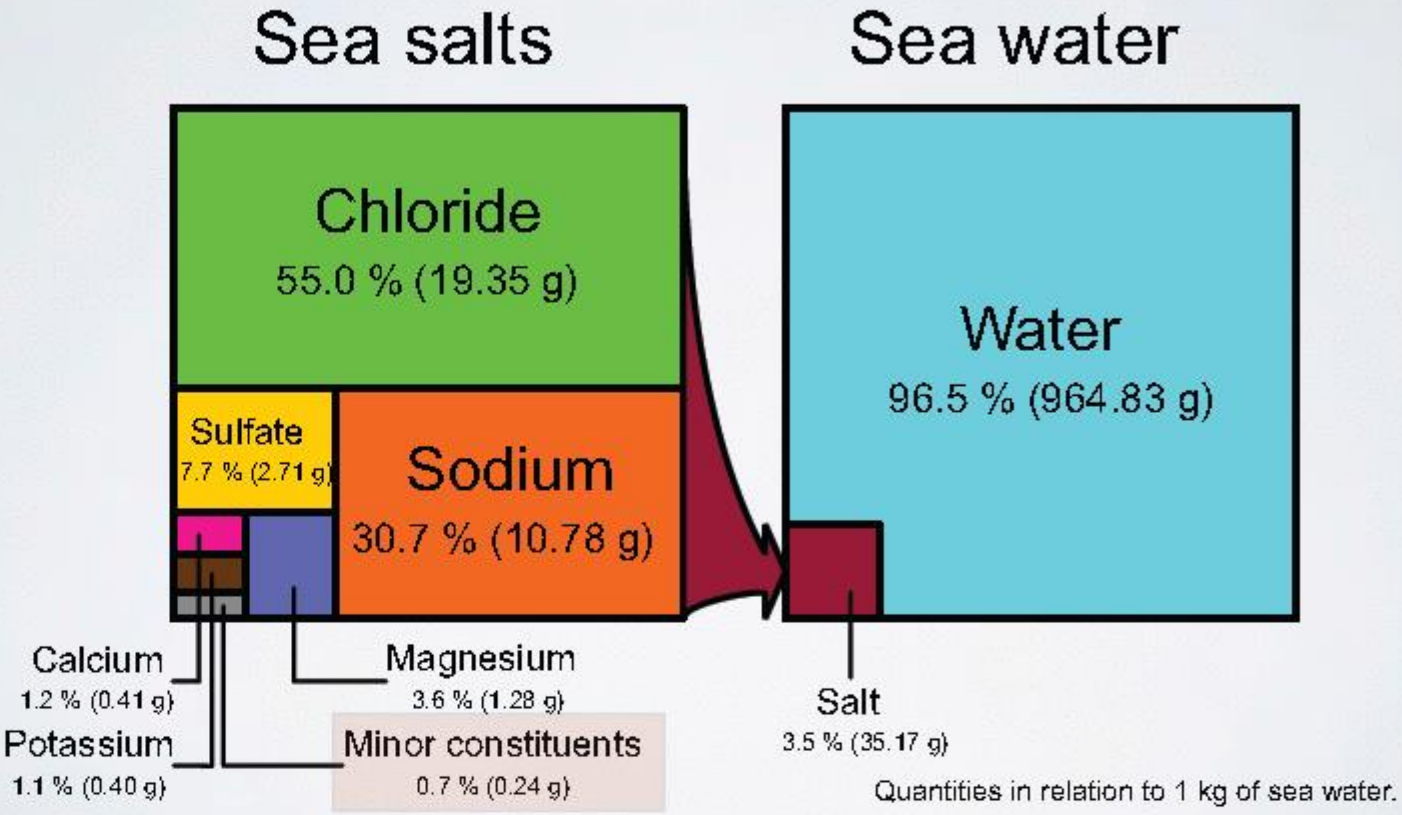
1.1 Introduction

The world's oceans can be thought of as a dilute solution of sodium bicarbonate (toget
species at still lower concentrations) in a saltwater background. In the surface water
for example, the concentration of total dissolved inorganic carbon (the sum of the co
coexisting species: bicarbonate ion, carbonate ion, and unionised dissolved carbon d
mmol kg^{-1}. About 90% of this is present as bicarbonate ion, the proportion of carbon
of 10 less (~10%), and that of unionised carbon dioxide yet another factor of 10 less (
equilibria between these various species (see below), seawater is buffered (weakly) w
hydrogen ion (present at much lower concentrations: <10^{-8} µmol kg^{-1}).

Over the past twenty years, accurate measurement of the seawater carbon dioxide sy
priority for scientists who have worked to understand just how much of the carbon d
man's activities has ended up in the ocean, where it is distributed, and how it has ch
the oceans. The chemical changes associated with the increase of CO_2 in the oceans
ocean acidification. As we work to design suitable experiments to understand the b
consequences of such changes, it is important that the chemistry of CO_2 be well char
laboratory experiments and field observations that are undertaken. Achieving this re
of the basic solution chemistry underlying ocean acidification, as well as of the relati

INTRODUCTION TO CO_2 EQUILIBRIA IN SEA WATER

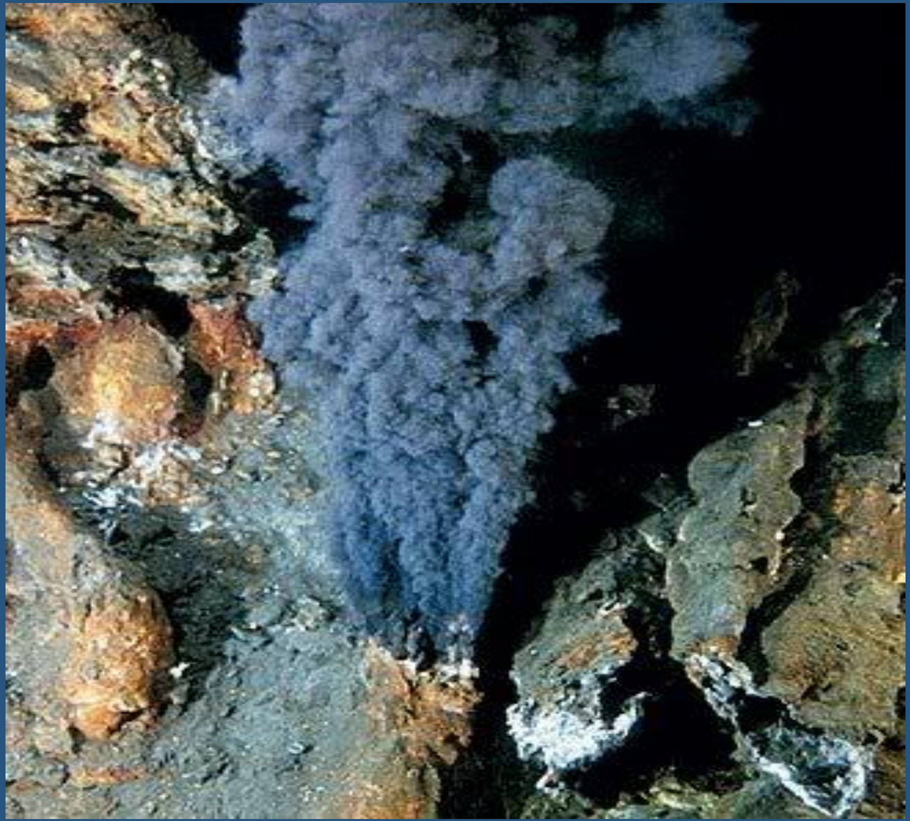
COMPOSITION OF SEA WATER ($S = 35$)



Why is salty?

“Not salinity changes since 200 millions of years ”

Hydrothermalism and volcanism



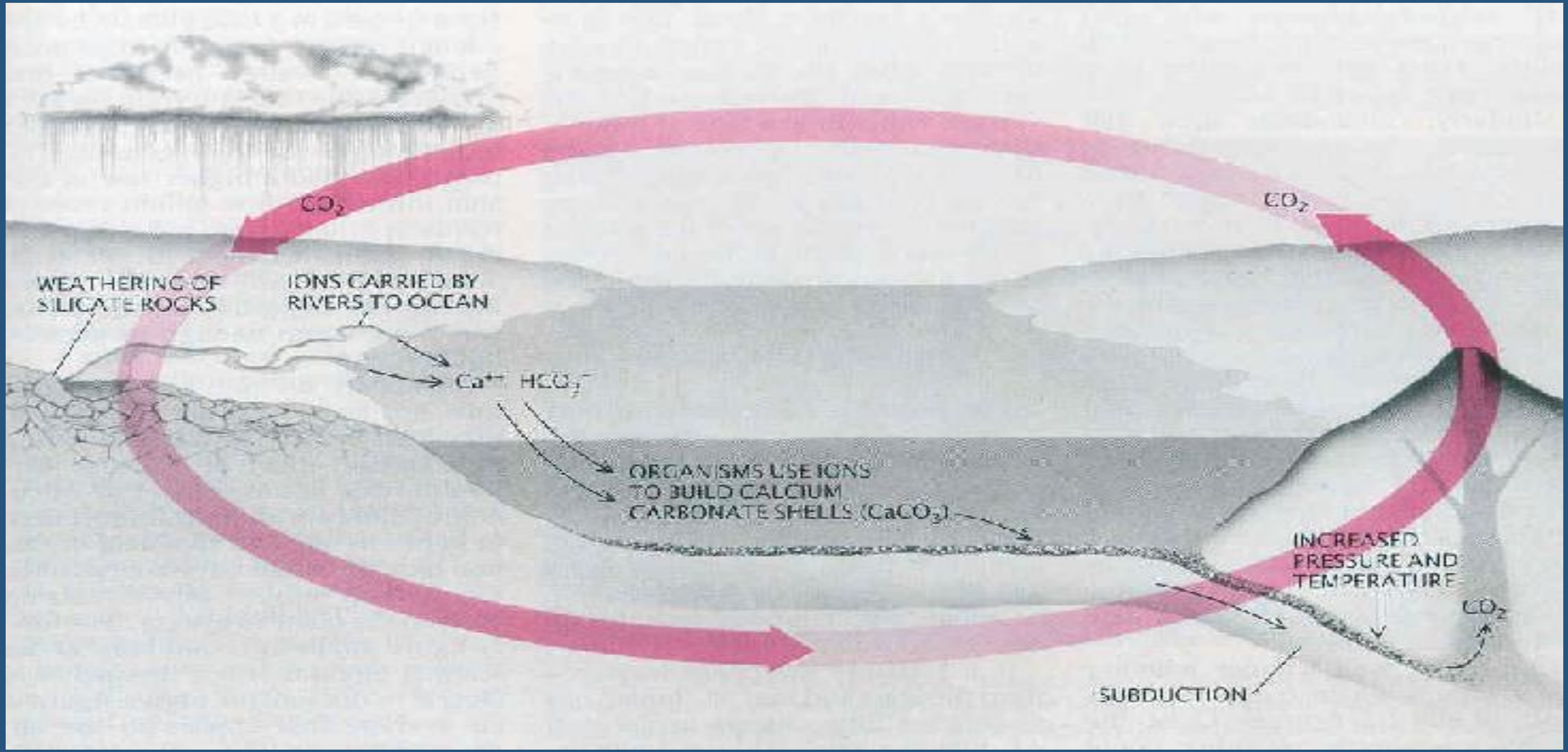
“Rivers?”

Rocks Iweathering:

1) $CaCO_3$ + $CO_2 + H_20 \rightarrow Ca^{+2} + 2HCO_3^-$

.

$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4SiO_2$



Acid-base species comprise a subset of the "minor constituents" present in seawater

HCO_3^- $SiO(OH)_3^-$ H^+

H_2O

CO_3^{2-} CO_2 H_3PO_4 $H_2PO_4^-$

NH_4^+ organic acids

OH^- $B(OH)_3$

organic bases HF PO_4^{3-}

NH_3

HPO_4^{2-} $Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; *t* = 18 °C

Acid-base species comprise a subset of the "minor constituents" present in seawater

HCO_3^-

$SiO(OH)_3^-$

H^+ — 10^{-2} µmol kg^{-1}

CO_2

H_2O — 54 mol kg^{-1}

CO_3^{2-}

H_3PO_4

$H_2PO_4^-$

NH_4^+

organic acids

OH^- — 3.2 µmol kg^{-1}

$B(OH)_3$

organic bases

HF

NH_3

PO_4^{3-}

HPO_4^{2-}

$Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; t = 18 °C

Acid-base species comprise a subset of the "minor constituents" present in seawater

1903 µmol kg^{-1}

HCO_3^- $SiO(OH)_3^-$ H^+

H_2O

CO_2 15 µmol kg^{-1}

CO_3^{2-} H_3PO_4 $H_2PO_4^-$

NH_4^+

159 µmol kg^{-1}

organic acids

OH^- $B(OH)_3$

organic bases HF NH_3 PO_4^{3-}

HPO_4^{2-} $Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; t = 18 °C

Acid-base species comprise a subset of the "minor constituents" present in seawater

HCO_3^-

$SiO(OH)_3^-$

H^+

H_2O

CO_2

CO_3^{2-}

H_3PO_4

$H_2PO_4^-$

NH_4^+

organic acids

OH^-

344 μmol kg^{-1} → $B(OH)_3$

organic bases

HF

NH_3

PO_4^{3-}

HPO_4^{2-}

$Si(OH)_4$

$B(OH)_4^-$ ← 72 μmol kg^{-1}

other acid/base species

Average ocean water; pH = 8; t = 18 °C

Acid-base species comprise a subset of the "minor constituents" present in seawater

HCO_3^-

$SiO(OH)_3^-$ ← 3 µmol kg⁻¹

CO_2

H_2O

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

OH^-

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

97 µmol kg⁻¹ → $Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; t = 18 °C

Acid-base species comprise a subset of the "minor constituents" present in seawater

HCO_3^- $SiO(OH)_3^-$ H^+

H_2O 2.10^{-2} μmol kg^{-1} → $H_2PO_4^-$

CO_3^{2-} CO_2

NH_4^+ 10^{-8} μmol kg^{-1} → H_3PO_4

organic acids

OH^- $B(OH)_3$

organic bases HF

NH_3 0.2 μmol kg^{-1} → PO_4^{3-}

1.8 μmol kg^{-1} → HPO_4^{2-} $Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Carbon Chemistry in the Ocean and the challenge

$CO_{2(gas)}$

"1 Atmosphere-Ocean Rx"

"2 Acido-Base Rx"

$CO_2 + H_2O \leftrightarrow H_2CO_3$ — 22 ∝mol kg^{-1}

Acido Carbónico

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ — 2023 ∝mol kg^{-1}

Bicarbonato

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ — 125 ∝mol kg^{-1}

Carbonato

TCO_2 or DIC — 2170 ∝mol kg^{-1}

"3 Oxido-Red"

CO2+H2O ←→ O2+CH2O

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

"4 Precipitation-Dissolution Rx"

To study the Ocean Acidification "OA" several "Tools" are required:

1. Understanding acid-base reactions in seawater "Especially CO_2"
2. Understand which CO_2 parameters (pH, Total Alkalinity, Dissolved Inorganic Carbon, pCO_2) are normally measured in seawater and how.
3. Have access to a computing tool to perform CO_2 system calculations such as CO2Sys or CO_2 Cal.
4. Have access to analytical equipment (and training) to perform measurements of carbon variables.

We need at least two parameters of the CO_2 system to be able to estimate the other two and the different CO_2 species from the system

- Disolved Inorganic Carbon
- pH
- pCO_2
- Total Alcalinity

temperature, salinity, pressure is needed

Options: silicate and phosphate.

Dissolved Inorganic Carbon

DIC or TCO_2 = $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$

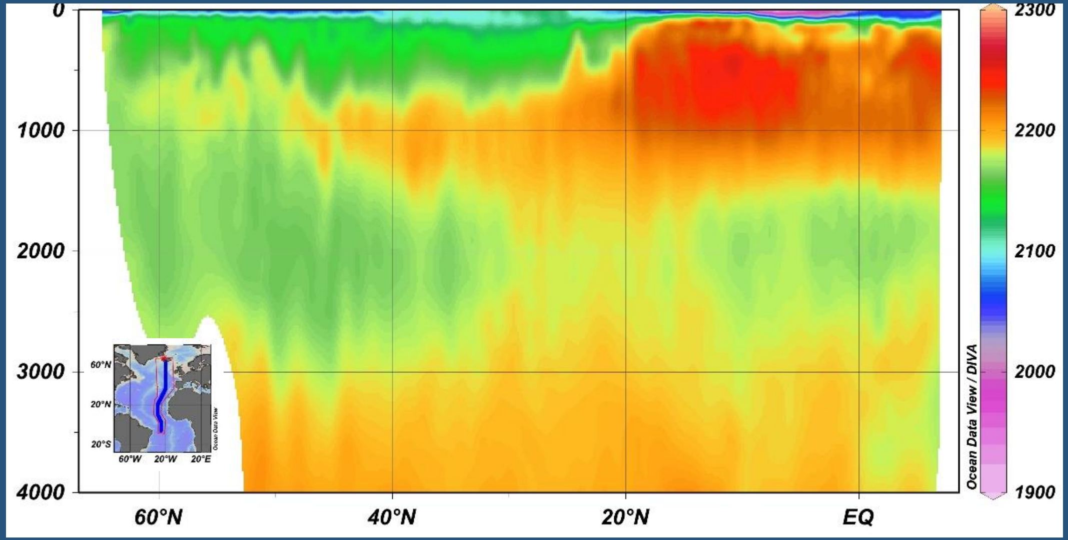
Sample (volume or mass)
+
H3PO4

==➔ **CO_2 (ac)**

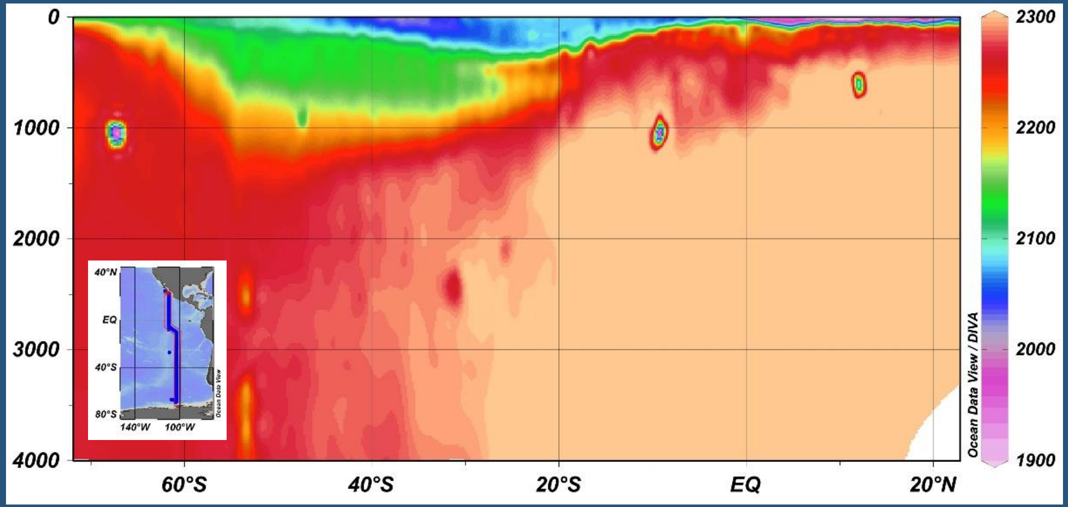
Determination by coulometry
(precision 1 µmol/kg)

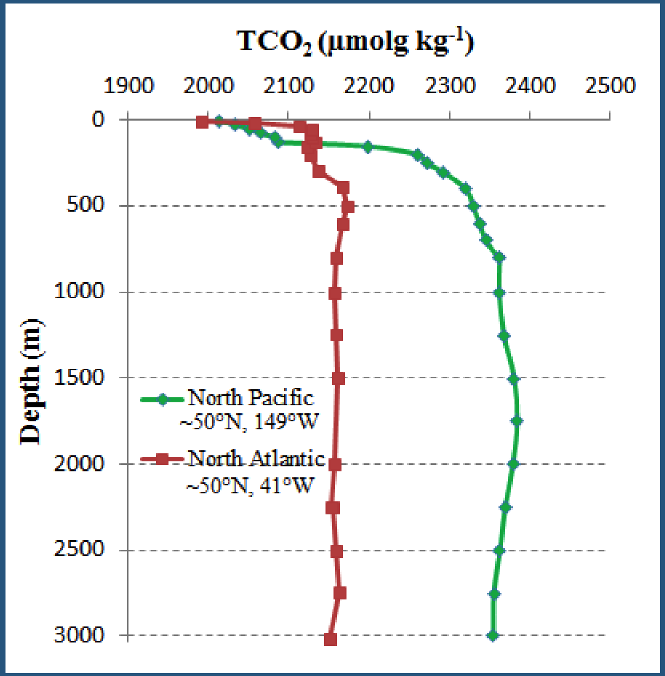
Total CO_2 or Dissolved Inorganic Carbon

Atlantic Ocean



Pacífic Ocean





pH Sensors

- **Potentiometric**

- **Spectrophotometric**

Potentiometric determination (precision 0.005 pH units)

Spectrophotometric determination (precision 0.001 pH units)

pH: Scales (1) National Bureau Standars (NBS) (2) Total Protons (H_{tot}) (3) Seawater (SWS)

pH= -Log [H^+]

pH scales related by the follow equations:

$$-pH_{NBS} \quad aH = 10$$

The reference state for the NBS/IUPAC scale is the infinitely dilute solution, which is very useful in very dilute natural waters, such as rivers and lakes. However, this scale is not recommended for seawater, due to its high ionic strength (Dickson, 1984; Millero et al., 1993). Preferable scale based on proton concentration.

pH: (2)Total Protons (H_{tot})

Total pH scale, pH_T, 1973 (modified by Dickson 1990)

It takes into account

1) the free protons +
2) contribution from the association of the SO_4^{2-} ion with H^+ to form HSO_4-

$$pH_T = -\log[H^+]_T$$

$$HSO_4^- = H^+ + SO_4^{2-}$$

$$K'_S = [H^+]_F[SO_4^{2-}] / [HSO_4^-]$$

$$[H^+]_T = [H^+]_F(1 + [SO_4^{2-}]/K'_S)$$

pH: (3) Seawater (SWS)

Seawater pH scale, pHSWS, 1979

It takes into account

1) the free protons +
2) contribution from the association of the SO_4^{2-} ion with H^+ to form HSO_4^-
3) In addition to sulfates, it includes contributions from the fluoride ion.

$$pH_{SWS} = -\log[H^+]_{SWS} = -\log([H^+]_F(1 + [SO_4^{2-}]/K'_S + [F^-]/K'_F))$$

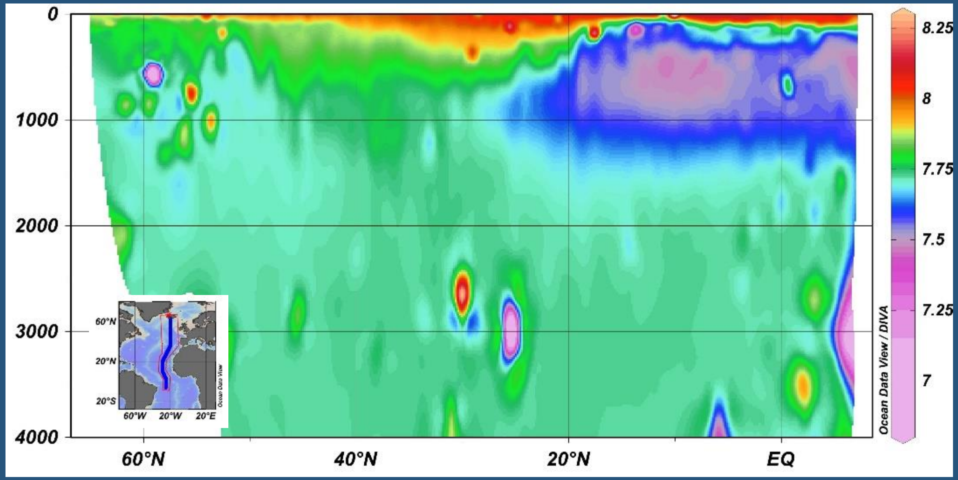
As a comparison important!!

To 20 deg C, Salinity 35, and 1 atm, pH values in protons total escale are aproximates:

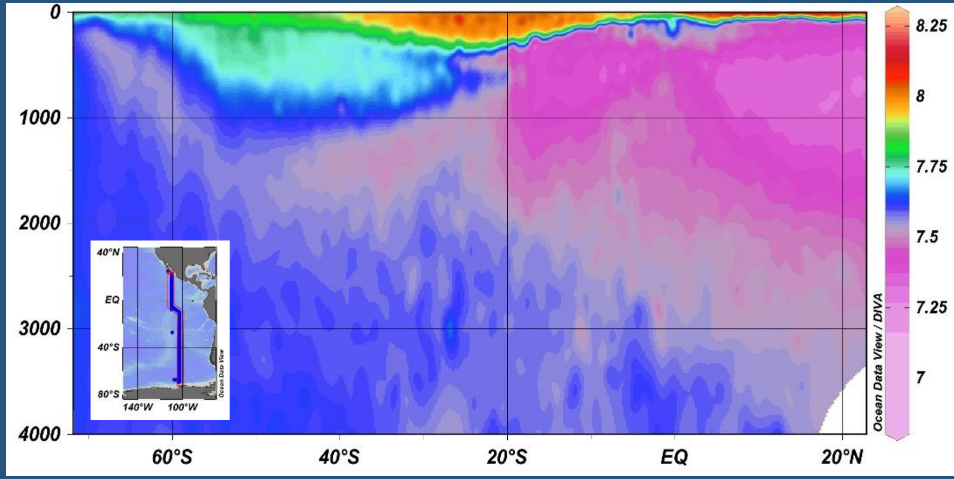
.01 units higher in seawater scale

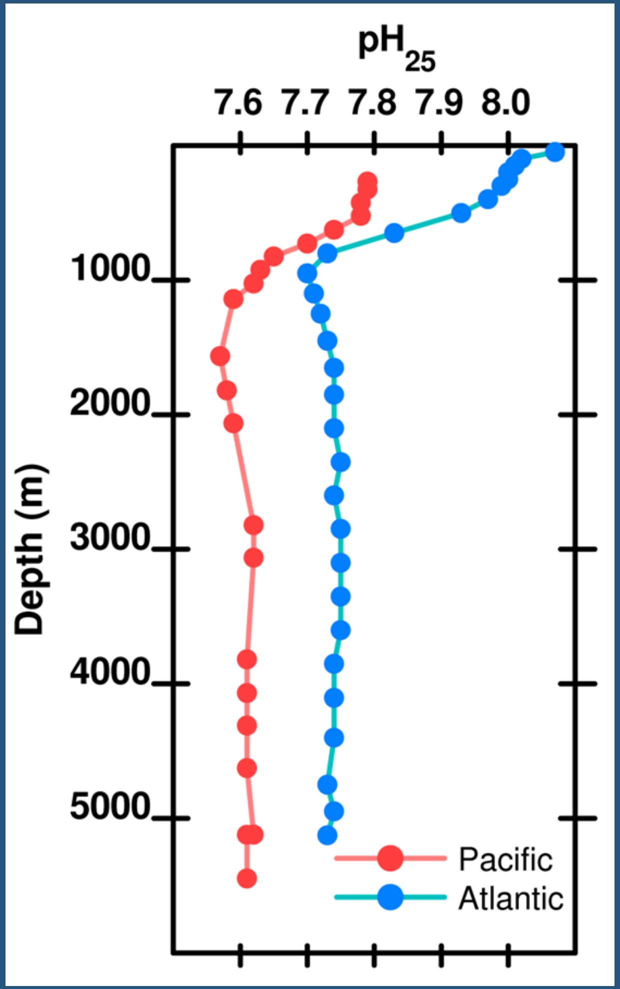
.13 units lower in NBS pH escale

Atlantic Ocean

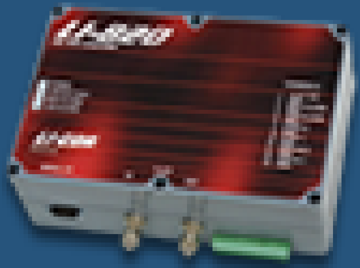


Pacífic Ocean





Partial Pressure of CO_2



¿What is pCO2?

Pressure exerted by CO_2 on an inert gas (e.g. N_2) in equilibrium with a solution.

$pCO_2 = xCO_2 (Pair - pH_2O)$

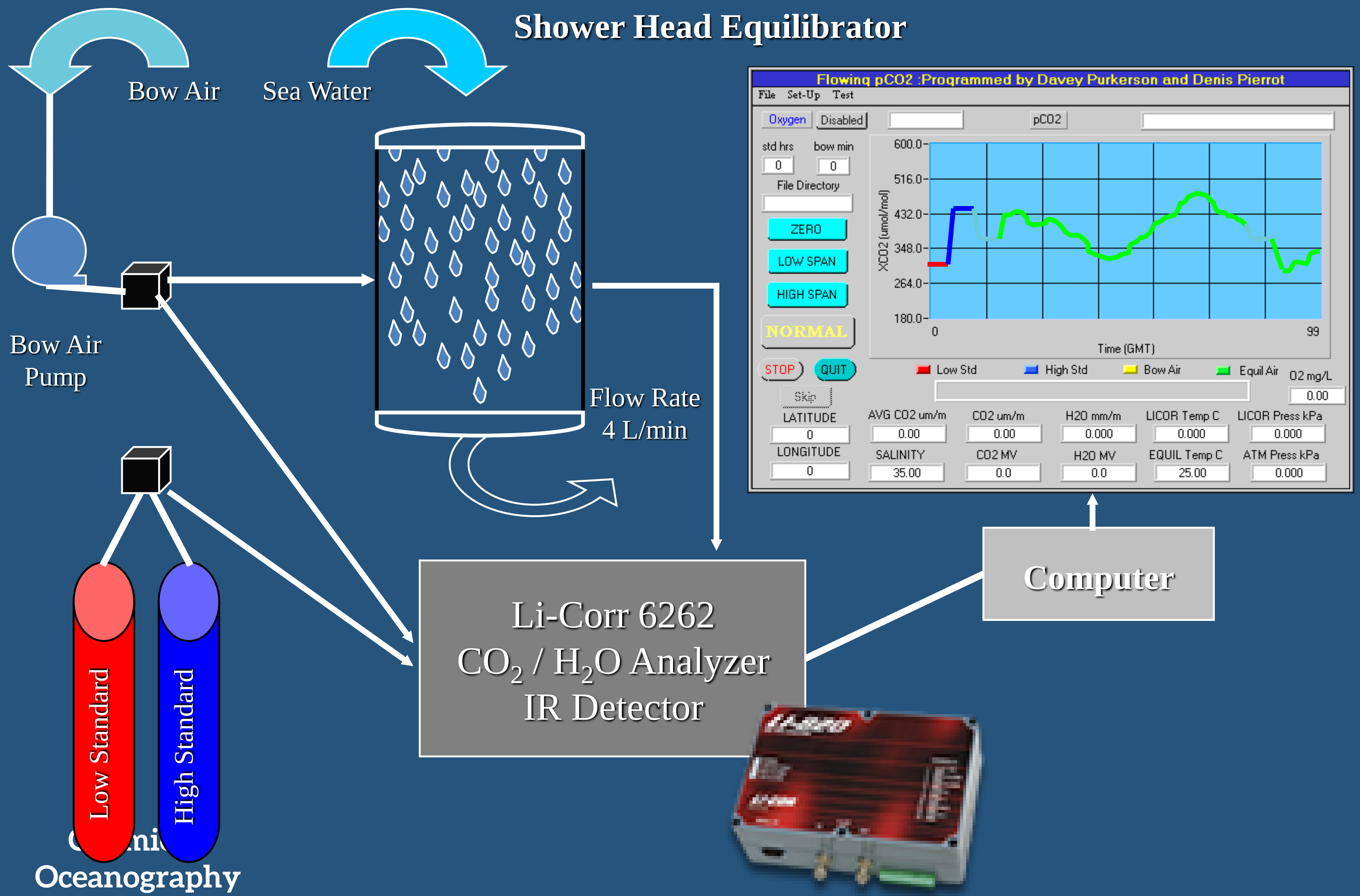
xCO_2: molar fraction (ppm, in dry air)
pH_20 : water vapor pressure

$pCO_2 \approx fCO_2$

Determination by infrared absorption spectroscopy (IR sensor)
(precision 1µatm)

Spectrophotometric determination (precision 2-5µatm)

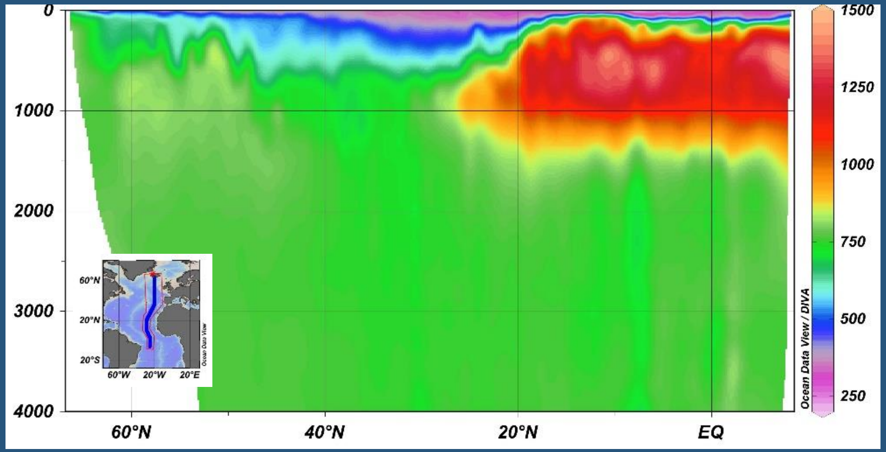
Flowing pCO_2 System



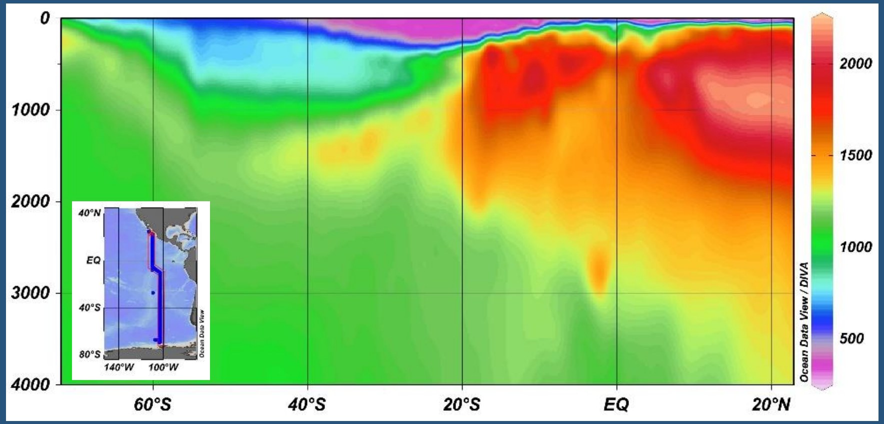
Oceanography

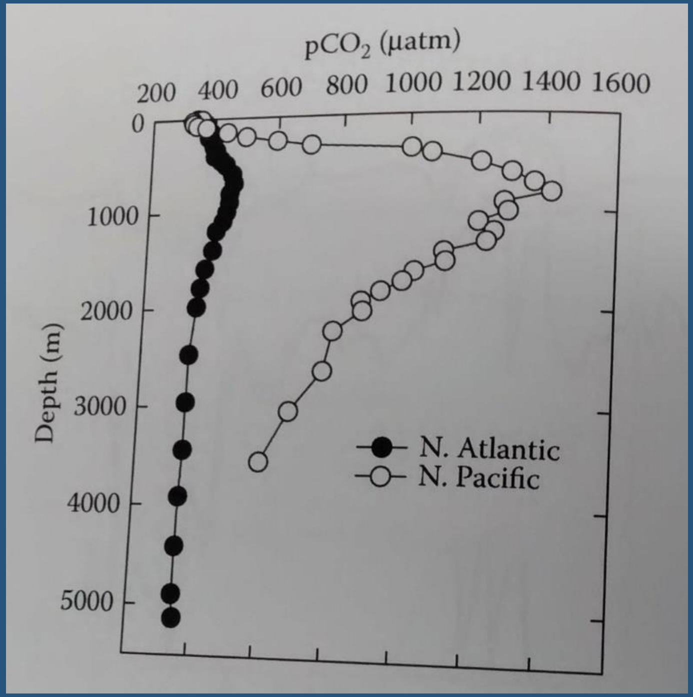
Parámetros del sistema del carbono: pCO_2

Atlántic Ocean

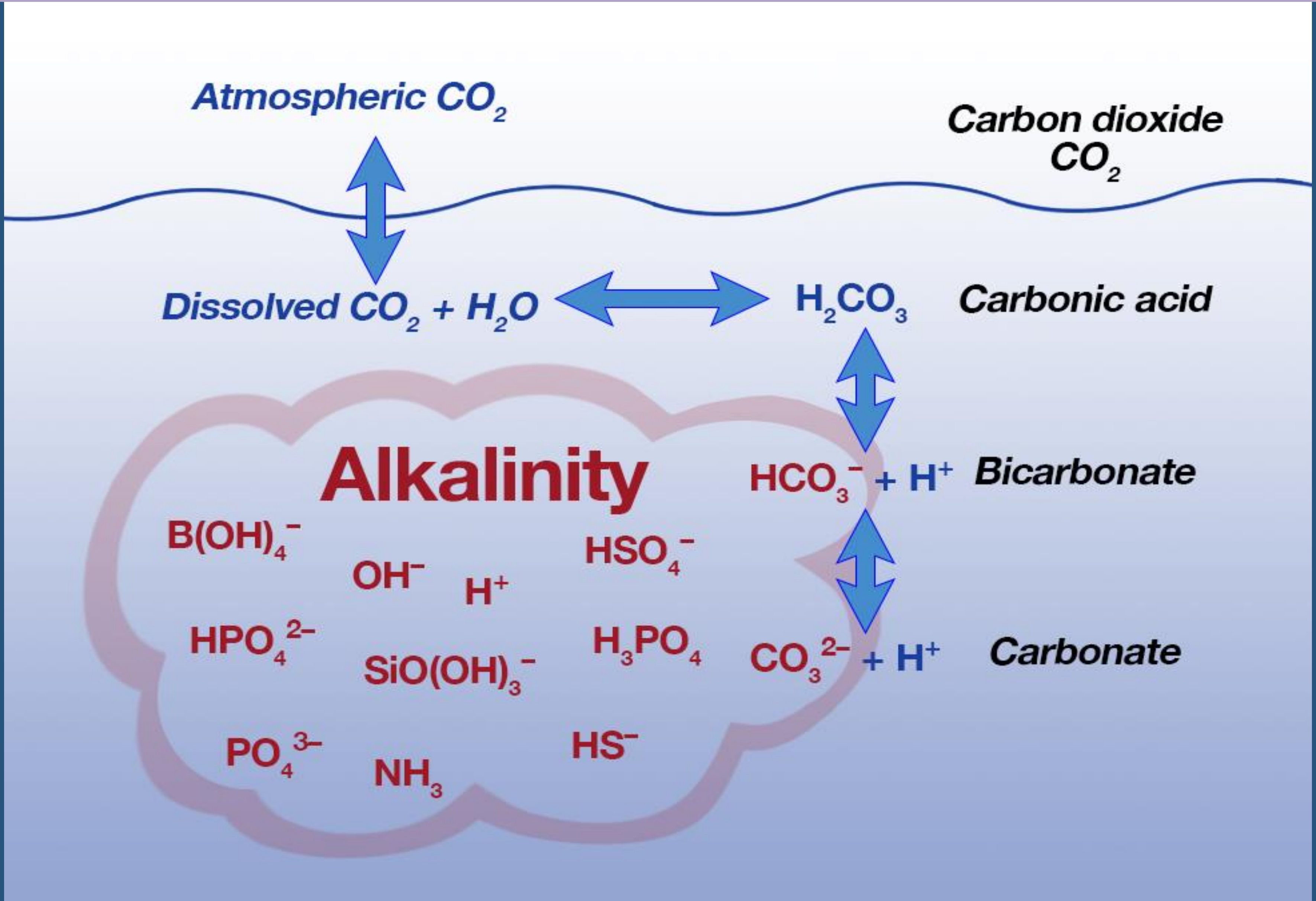


Pacífic Ocean

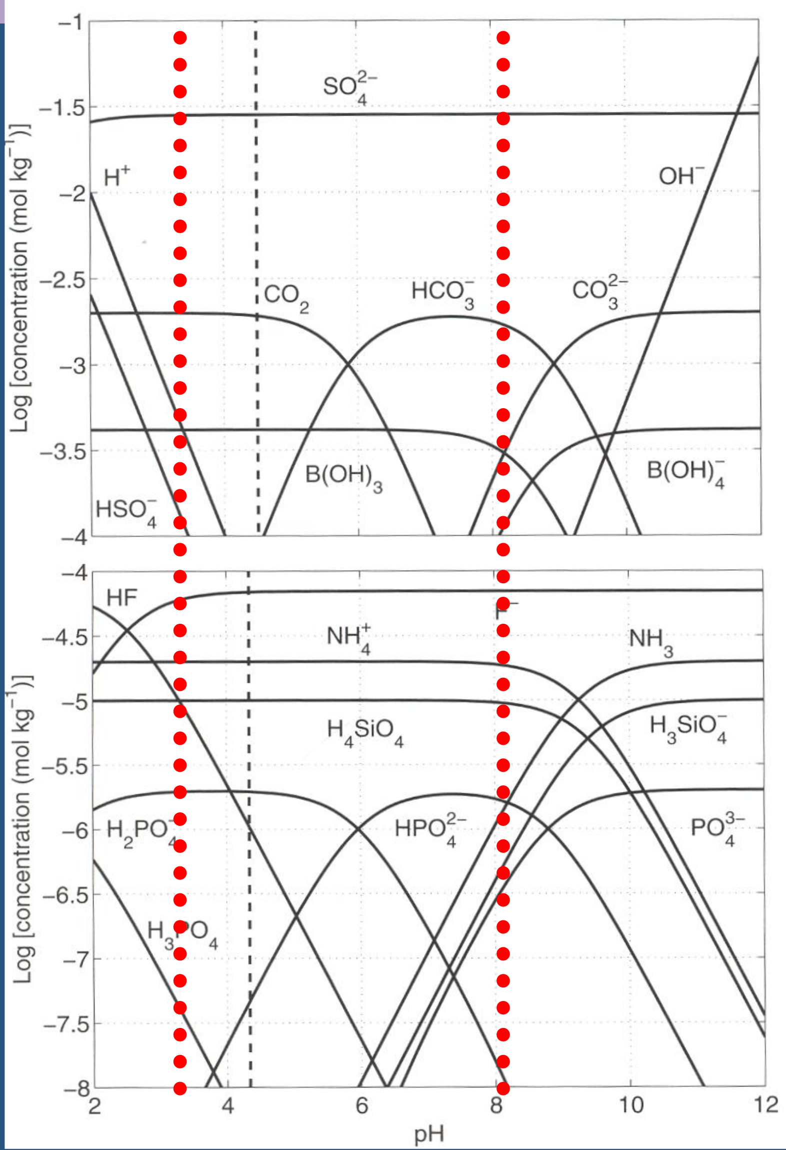




Total Alkalinity

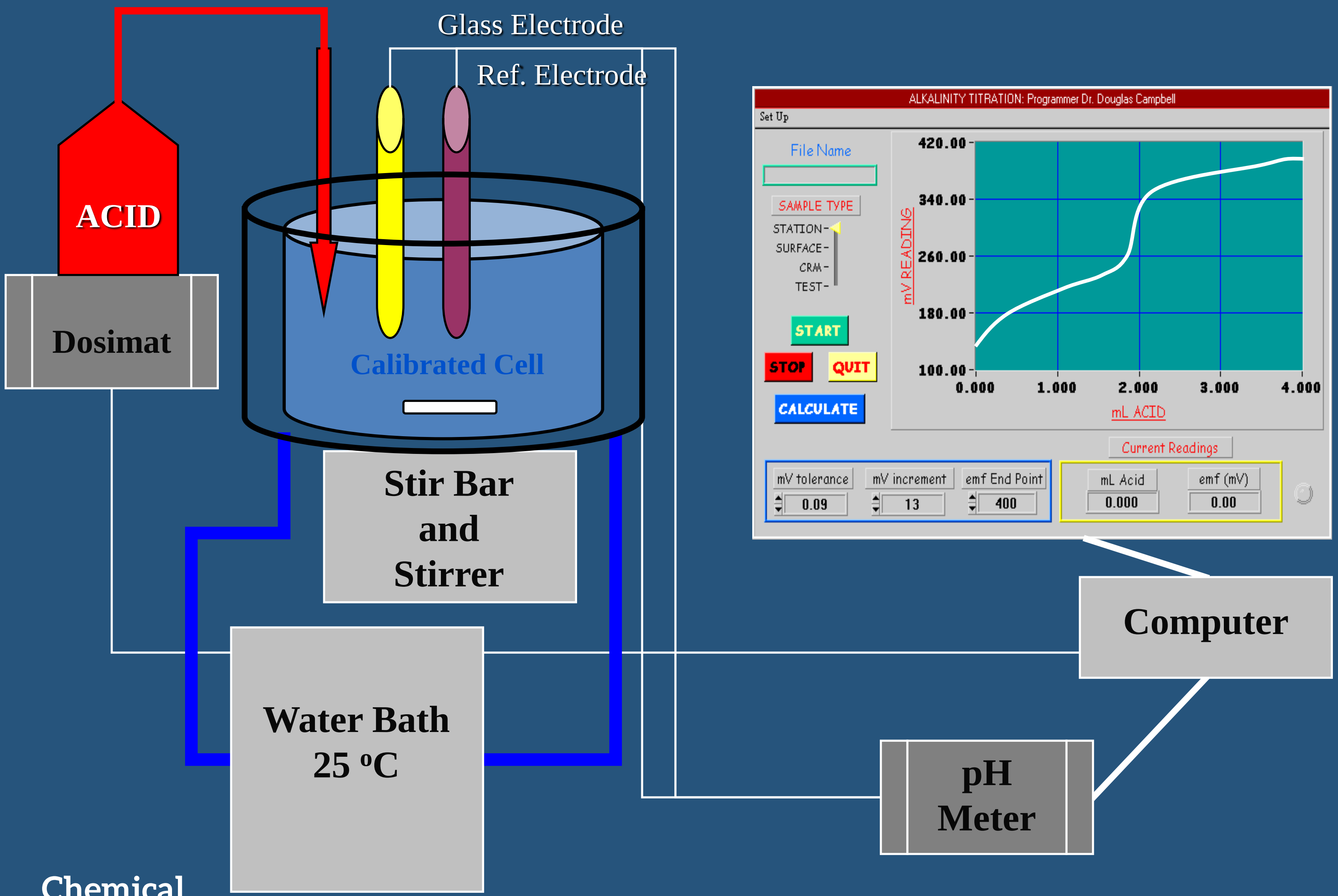


Alcalinidad Total



"The total alkalinity of natural waters is thus defined as the number of hydrogen ions equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K>10^{-4.5}$, at 25ºC and zero ionic strength) over proton donors (acids with $K>10^{-4.5}$) in one kilogram of sample" *Dickson, 1994*

Total Alkalinity System

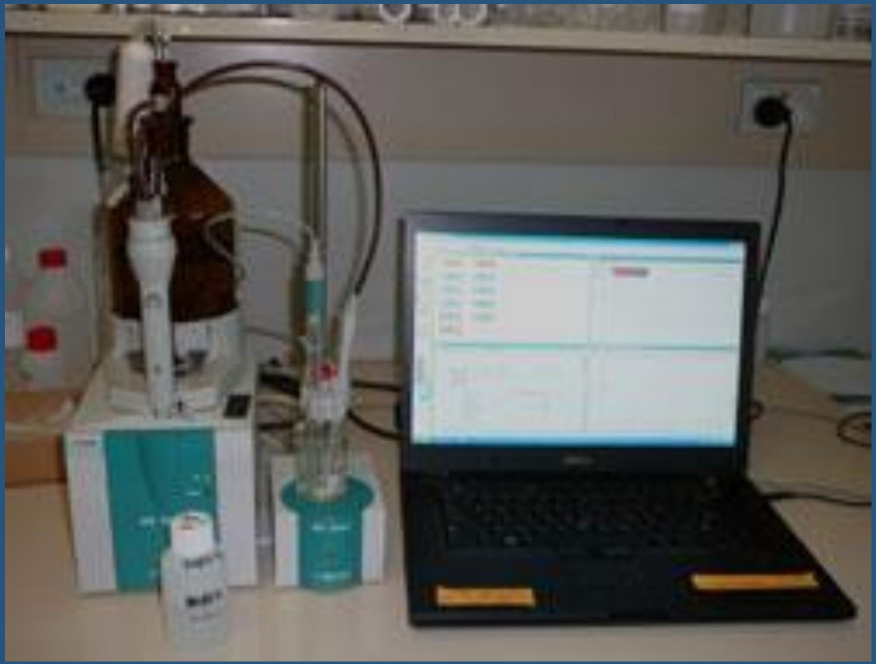


Chemical Oceanography

Total Alkalinity

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] +$$
$$+ [\text{Nutrients}] + [\text{Extra-Bases}]$$

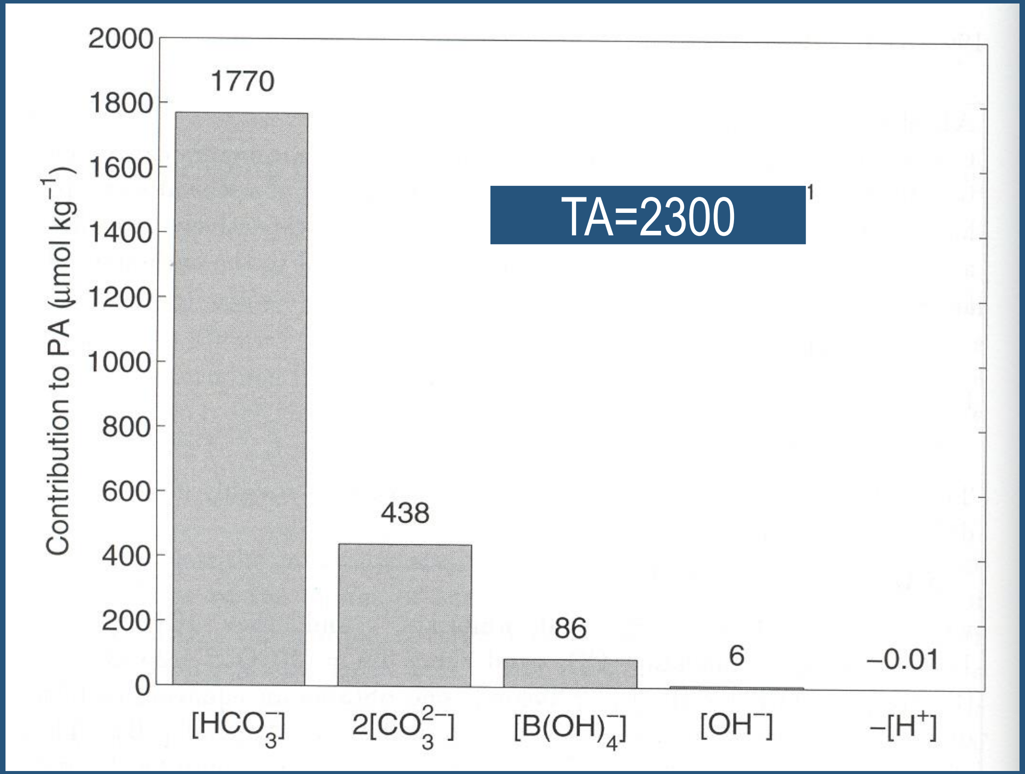
Known volume of seawater is acidified with a 0.1 N HCl solution to pH between 3.8 and 4.2.



Total Alkalinity

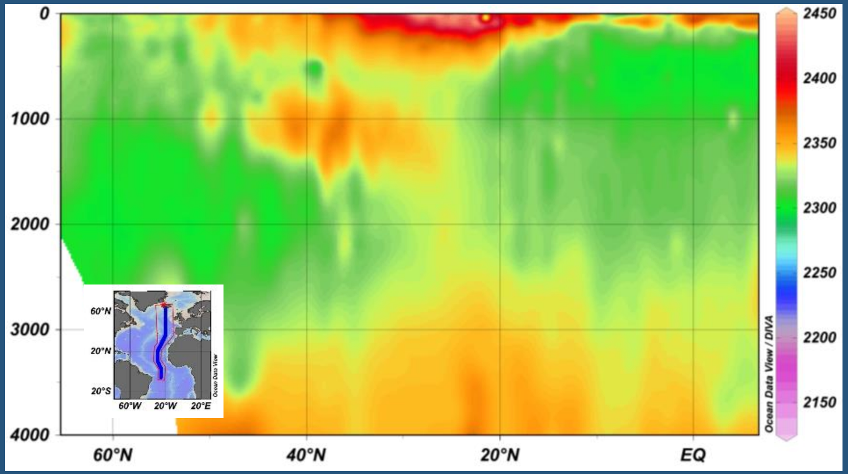
$TA = [HCO_3^-] + 2 \cdot [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H_3O^+]$

$TA = [HCO_3^-] + 2 \cdot [CO_3^{2-}]$ 96% of TA

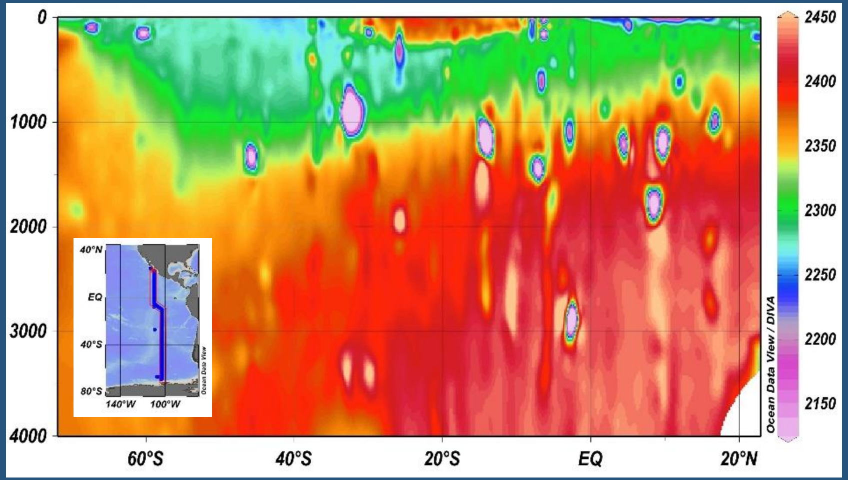


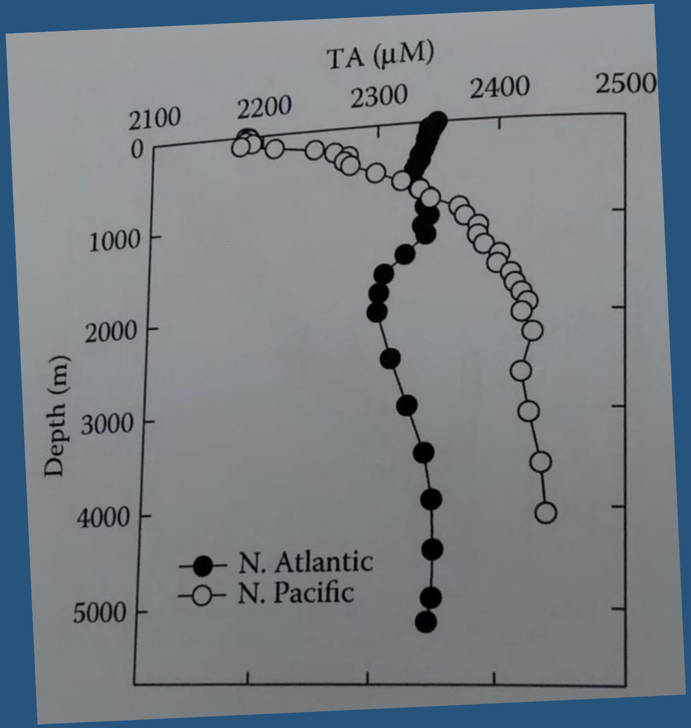
Total Alkalinity

Atlantic Ocean



Pacífico Ocean





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)

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

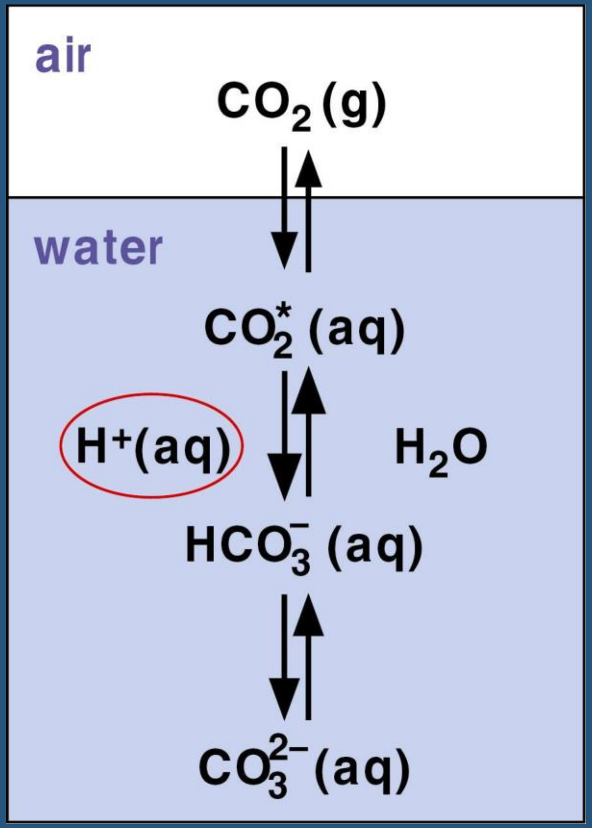
Why are the concentrations of these species not affected by CO_2 dissolution In surface waters?

How does the Thermodynamics of CO_2 in seawater help us?

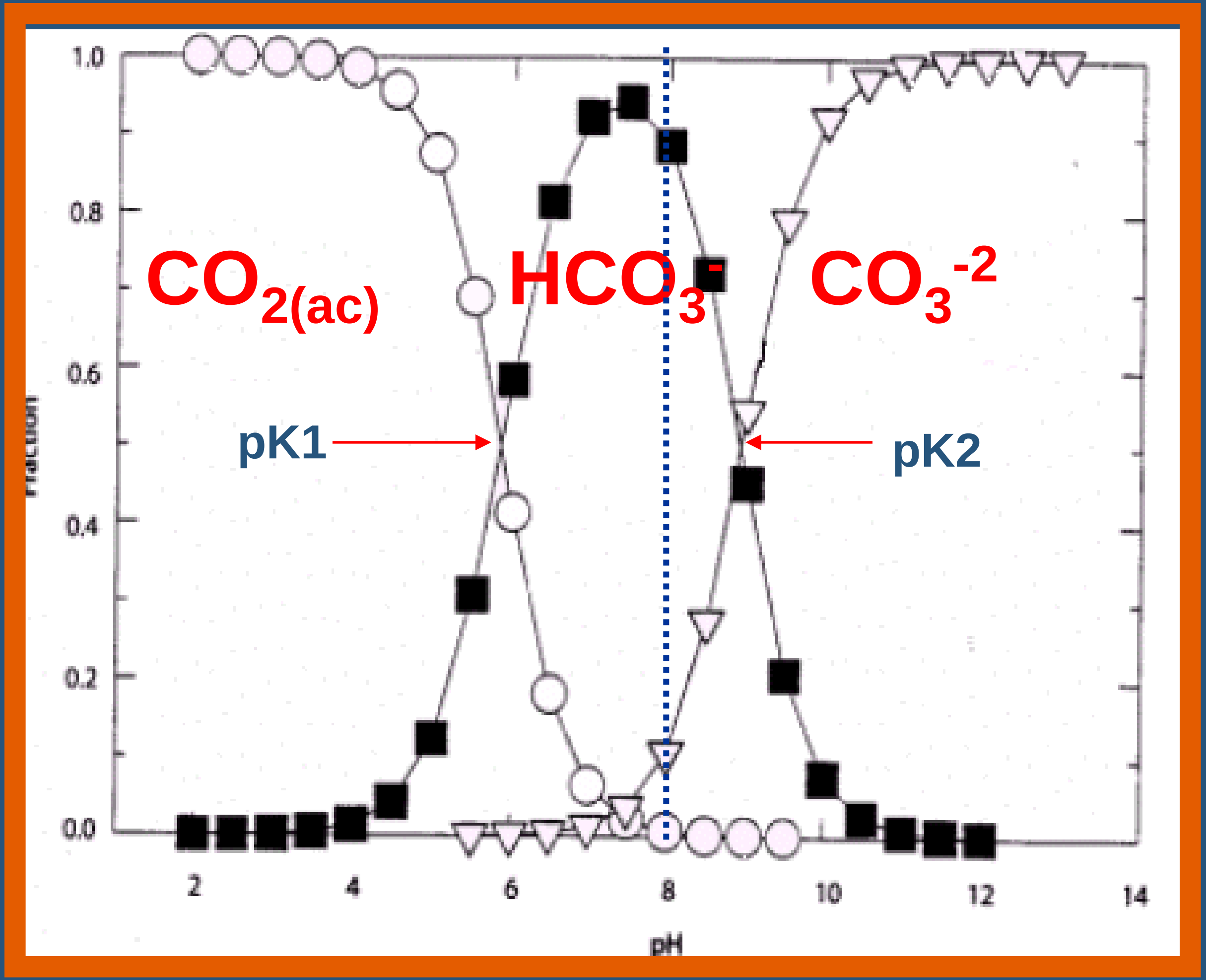
$K_0 = [CO_2]/p(CO_2)$
$K_1 = [H^+][HCO_3]/[CO_2]$
$K_2 = [H^+][CO_3]/[HCO_3]$
: T, S, P

CO_2 system parameters :

pH,
Total alkalinity (T*A*)
Dissolved inorganic carbon (DIC)
Partial Pressure of CO_2 (pCO_2)



“pK’s”



Millero et al., 1994

$K1 = [H+][HCO3]/[CO2]$
$K2 = [H+][CO3]/[HCO3]$

“K” Values depend of S, T, P.

Valores de K'

The values here are for S = 35, T = 25°C and P = 1 atm.

Constant	Apparent Seawater Constant (K')
K'_H	$10^{-1.53}$
K'_1	$10^{-6.00}$
K'_2	$10^{-9.10}$
K'_w	$10^{-13.9}$

Resume to this point:

- The CO_2 system in the seawater
- Components of the CO_2 system: pH, DIC, pCO_2 and alkalinity.
- At least to measure two of the four
- Use the CO2Sys program to estimate the differents species from the carbon system
- “Next” process to control the differents variables

Any pair of parameters describing the CO_2 system in a seawater sample can be used.

- Mathematically all combinations should be equivalent.
- In practice this is not the case. Each of the terms has associated uncertainties. The uncertainties propagated through the calculations result in uncertainties in several calculated values.
- In addition the uncertainties of the measured CO_2 system parameters have uncertainties in several of their equilibrium constants and in the total concentrations of the acid-base systems.
- In addition the components of the alkalinity equation may be incomplete.

Estimated uncertainties for measurement techniques on discrete samples†

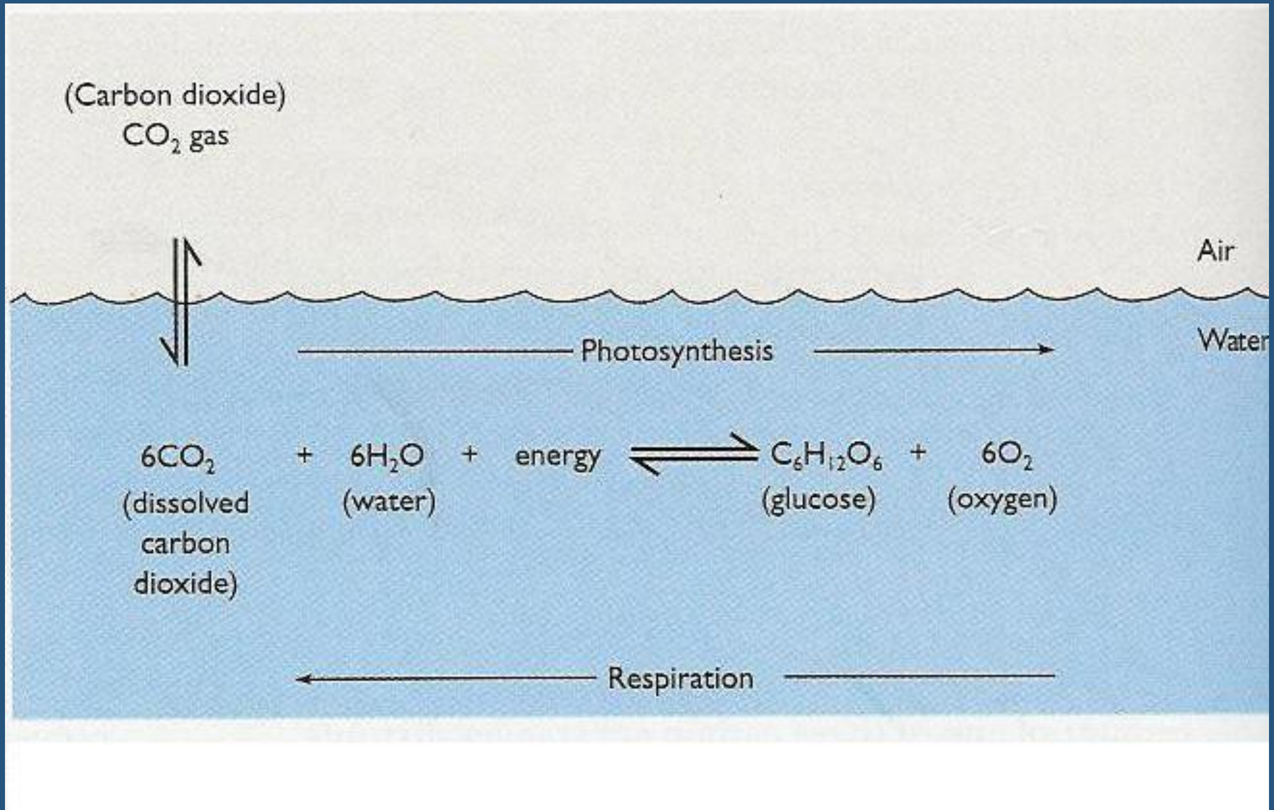
Parameter	State-of-the-art laboratory	State-of-the-art at-sea (suitable RMs)	Other techniques (suitable RMs)	Techniques not using RMs
Total alkalinity	1.2 μmol kg	2–3 μmol kg	4–10 μmol kg	?
Total carbon	1.0 μmol kg	2–3 μmol kg	4–10 μmol kg	?
pH	0.003	~0.005	0.01–0.02	?
p	1.0 μatm	~2 μatm	5–10 μatm	?

† Based on measuring surface oceanic CO_2 levels

CO_2 FACTS

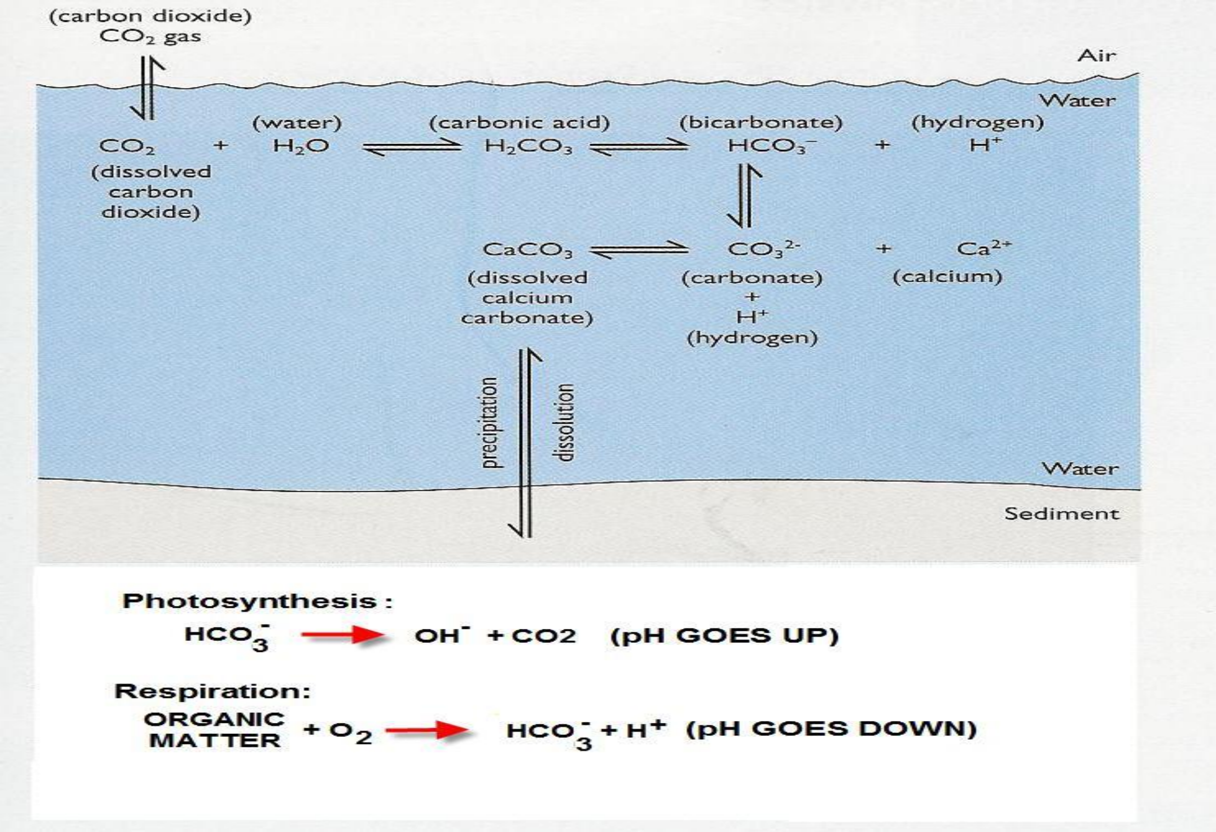
Photosynthesis ↓ use CO_2

Respiration increase ↑ CO_2



CO_2 FACTS

Photosynthesis change pH in the seawater



Controls on Ocean Distributions

A) Fotosíntesis/Respiración

Organic matter (approximated as CH_2O for this example) is produced and consumed as follows:

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O$$

Then:

$$CO_2 + H_2O \rightarrow H_2CO_3^*$$
$$H_2CO_3^* \rightarrow H^+ + HCO_3^-$$
$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

As CO_2 is produced during respiration we should observe:

$$pH \downarrow \; DIC \uparrow \; Alk \leftrightarrow \; P_{CO2} \uparrow$$

The trends will be the opposite for photosynthesis.

B) $CaCO_3$ dissolution/precipitation

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

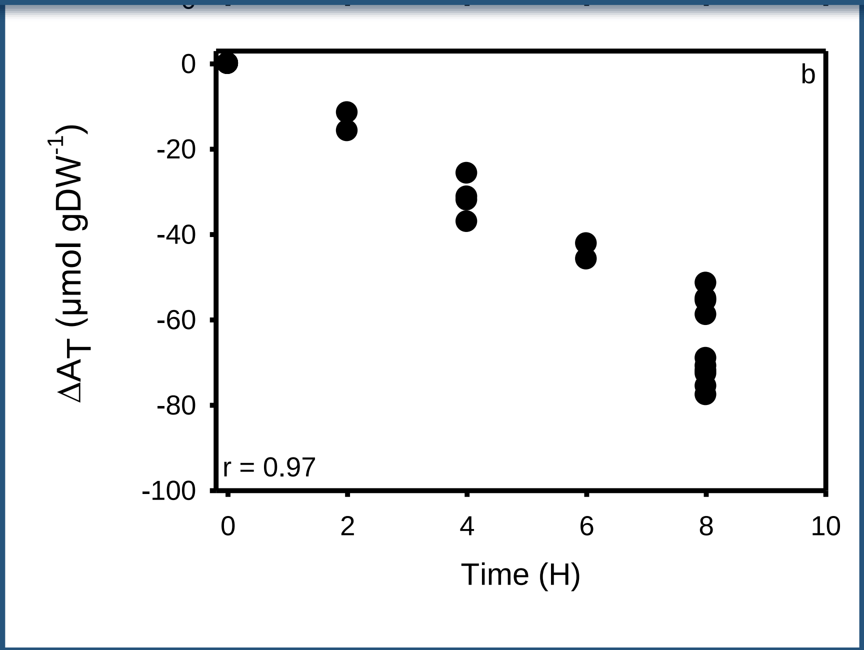
Also written as:

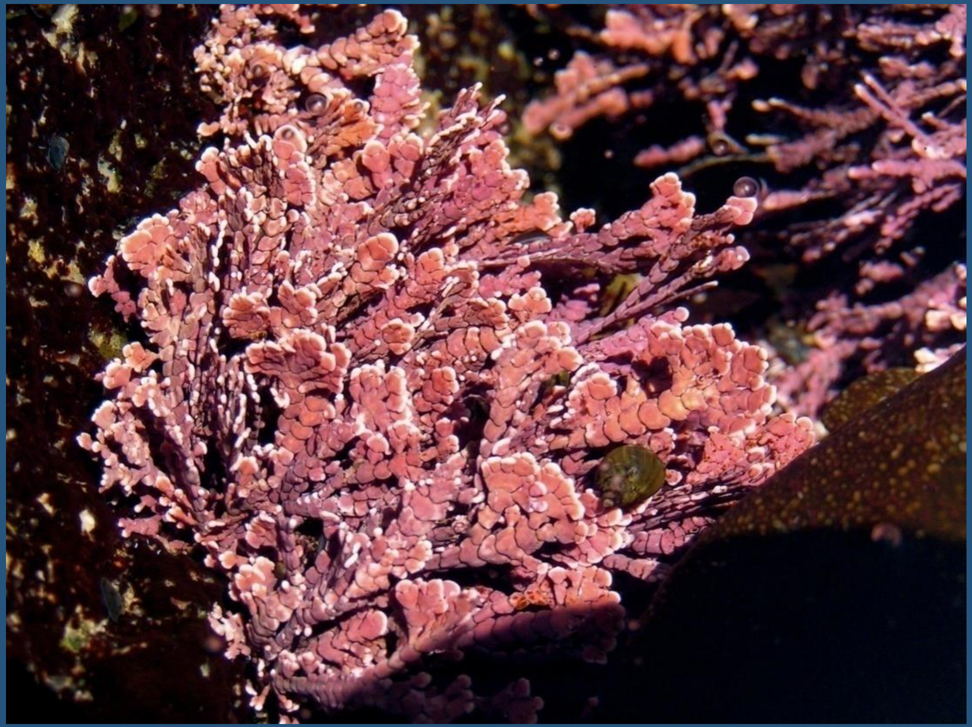
$$CaCO_3(s) + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2\,HCO_3^-$$

As $CaCO_3$(s) dissolves, CO_3^{2-} is added to solution. We should observe:

$$DIC \uparrow \; Alk \uparrow$$

Calcification Rates and Acquisition of Inorganic Carbon In Geniculate Coralline Algae Distributed in the Coast Of Baja California Mexico





Changes in total alkalinity in 8h incubations with constant aeration. a, control method; filtered seawater with constant aeration; b, lineal decrement of total alkalinity normalized by dry weight in *Bossiella orbigniana.*

"The State of Saturation "The Magic Number"

$\Omega aragonita = [Ca^{+2}]\,[CO_3^{-2}]/\mathit{Kps\ arag}$

$\Omega calcita = [Ca^{+2}]\,[CO_3^{-2}]/\mathit{Kps\ cal}$

$\Omega >> 1$ Organisms can build their shells "more easily"

$\Omega > 1$ Organisms can build shell

$\Omega < 1$ The shells "dissolve"

Adult Oyster Shell
—Formed from Calcite--Difficult to dissolve

Oyster larvae shell
—Formed from Aragonite—-Easy to dissolve

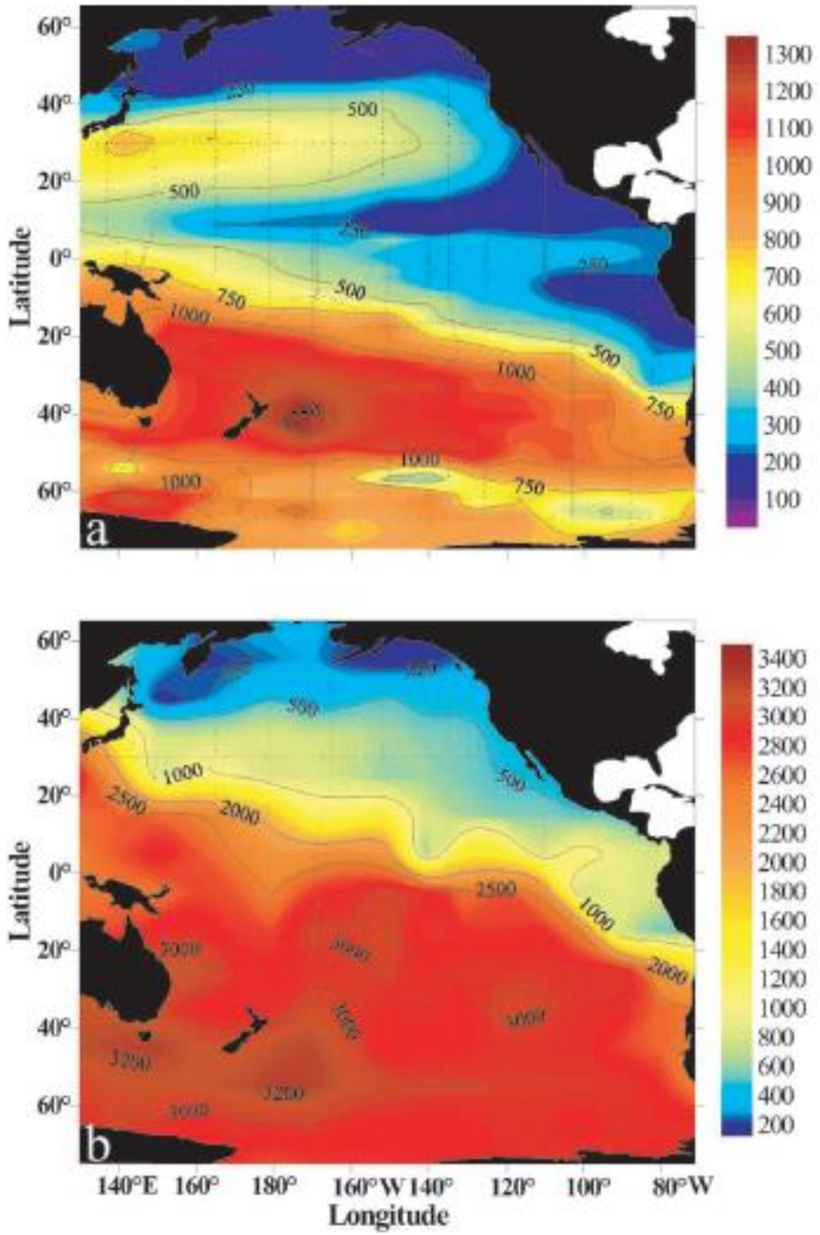


Figure 4. Saturation depth in meters for (a) aragonite and (b) calcite estimated from water column DIC and TA concentrations.

Aragonite

Both are $CaCO_3$

Calcite

To study the Ocean Acidification "OA" several "Tools" are required:

1. Understanding acid-base reactions in seawater "Especially CO_2"
2. Understand which CO_2 parameters (pH, Total Alkalinity, Dissolved Inorganic Carbon, pCO_2) are normally measured in seawater and how.
3. Have access to a computing tool to perform CO_2 system calculations such as CO2Sys or CO_2 Cal.
4. Have access to analytical equipment (and training) to perform measurements of carbon variables.