Departamento de Biologia Animal

A importância dos oceanos para a evolução da vida na Terra

Especificidades físico-químicas da água do mar.
Porque é salgada e alcalina a água dos mares e oceanos?

2.1. Salinidade
2.2. Origens da água e dos sais dos oceanos
2.3. Dióxido de carbono e pH

## Salt content of open oceans

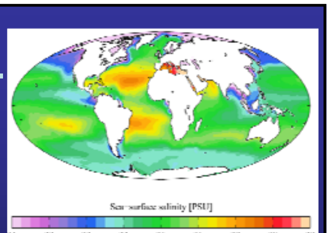
The salt content of the open oceans, free from land influences, is rarely less than 33 psu and seldom more than 38 psu.

psu = practical salinity unit (‰, ppt)

Throughout the world, the salinity of sea water averages about 35 psu.

This average salinity was obtained by William Dittmar in 1884 from chemical analyses of 77 sea water samples collected from many parts of the world during the scientific expedition of the British corvette, H.M.S. Challenger.

## The saltiest water...




The saltiest water (40 psu) occurs in the Red Sea and the Persian Gulf, where rates of evaporation are very high.

**Of the major oceans, which is the saltiest?**

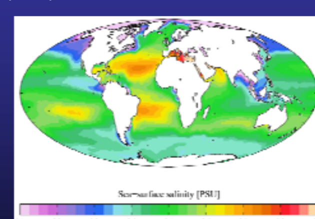
**the North Atlantic is the saltiest; its salinity averages about 37.9 psu.**

Within the North Atlantic, the saltiest part is the Sargasso Sea, an area of about 5 million km², located about 3,200 km west of the Canary Islands.

The saltiness of this sea is due in part to the high water temperature (up to 28º C) causing a high rate of evaporation and in part to its remoteness from land; because it is so far from land, it receives no fresh-water inflow.

## .. and the lowest salinities

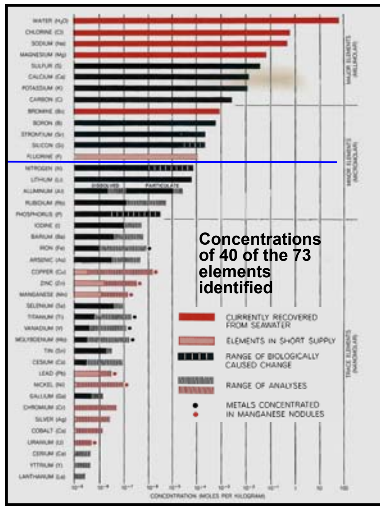
- Low salinities occur in polar seas where the salt water is diluted by melting ice and continued precipitation.
- Partly landlocked seas or coastal inlets that receive substantial runoff from precipitation falling on the land also may have low salinities.




- The Baltic Sea ranges in salinity from about 5 to 15 psu.
- The salinity of the Black Sea is less than 20 psu.

## What is in crude salt water?

- There are 11 major constituents.
- The most important (85,5 %) are the two that make up our purified table salt, sodium ($Na^+$) and chloride ($Cl^-$). It is these that make the sea taste salty.
- The other nine are found in smaller amounts. They are:
  – sulphate, magnesium, calcium, potassium bicarbonate, bromide, borate, strontium and fluoride.
- Together these 11 make up 99.9% of the dissolved constituents of sea water and represent about 3.5% of the sea by weight.
- All of the 11 major constituents dissolved in sea water are found in concentrations of over 1 part per million by weight.




## Composition of seawater

11 major constituents:

[99,9% of the dissolved constituents of sea water]

- chlorine ($Cl^-$)
- sodium ($Na^+$)
  NaCl = 85,5%
- sulphate ($SO_4^-$)
- magnesium ($Mg^{2+}$)
- calcium ($Ca^{2+}$)
- potassium ($K^+$)
- bicarbonate ($HCO_3^-$)
- bromide ($Br^-$)
- borate ($B(OH)_3^-$)
- strontium ($Sr^{2+}$)
- fluorine ($F^-$)

## Water, how old?

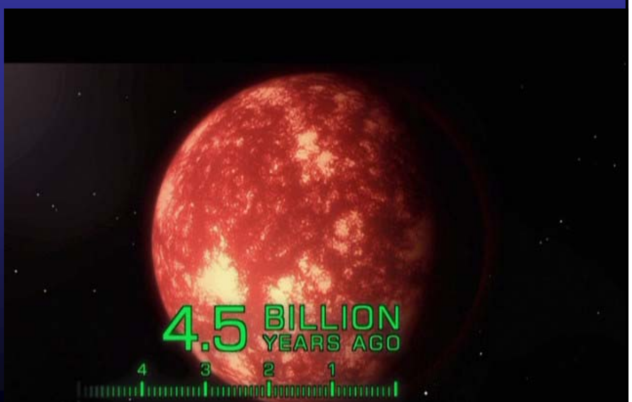
Oldest rocks sufficiently unaltered to retain cellular fossils preserving **Prokaryotic cells** (bacteria and cyanophytes) and **Stromatolites**?

African and Australian SEDIMENTS dated to **3.5 billion years old**

## Primordial rocks and primeval water

Primordial Rocks:

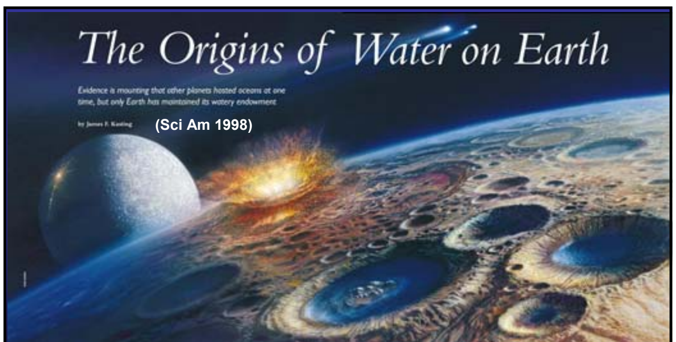
- Old pillow lavas, formed underwater in oceans approximately 3.9 billion years ago.
- However water was already around before.




## Origins of the hydrosphere

Until recently, there were competing views as to the origin of the Earth's water.

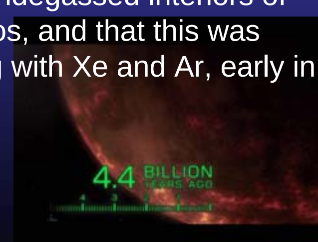
One was that the Earth accreted as a dry body and its water was subsequently added through cometary impact.




- **ICE-LADEN COMET** crashes into a primitive Earth, which is accumulating its secondary atmosphere (the original having been lost in the catastrophic impact that formed the moon) (believed to have occurred 4.527 ± 0.010 billion years ago)
- Earth appears moonlike, but its higher gravity allows it to retain most of the water vapor liberated by such impacts, unlike the newly formed moon in the background.
- A cooler sun illuminates **three additional comets hurtling toward Earth**, where they will also give up their water to the planet's steamy, nascent seas.

## Origins of the hydrosphere

The alternative view was that the Earth inherited its water from water-bearing minerals in the undegassed interiors of planetary embryos, and that this was outgassed, along with Xe and Ar, early in Earth history.



## THE ORIGIN OF THE SEA

Both the atmosphere and the oceans have accumulated gradually through geologic time from some process of **"degassing" of the Earth's interior**.

4.4 billion years ago, the earth was 100 million years old, while still bombarded by meteorites, most of the surface was solidifying into a crust of dark volcanic rock, and water was already forming.


- According to this hypothesis, the ocean had its origin from the prolonged escape of water vapor and other gases from the molten igneous rocks of the Earth to the clouds surrounding the cooling Earth.

## Origins of the hydrosphere

This debate was partially resolved with the measurement of the deuterium/hydrogen (*D/H*) ratio in three comets.

Using both
- spaceprobe measurements (the Giotto probe to comet Halley)
- and two ground-based measurements of radio and infrared emissions

All three measurements agree within experimental uncertainty and show that deuterium (heavy hydrogen) is twice as abundant relative to hydrogen in comets as it is in the terrestrial hydrosphere.

**Such a major distinction effectively rules out comets as a major source of the Earth's water.**

## Origins of the hydrosphere

Thus the preferred model for the evolution of the hydrosphere is that it degassed from the mantle, and that this material was ultimately derived from water-bearing grains that became incorporated into planetesimals and eventually into planetary embryos.

### Earth may have had water from day one

The planet's water came from the dust from which Earth was born – and not simply from comet or asteroid impacts, new calculations suggest

- by **David Shiga**
- 05 November 2010
- From issue 2785 of New Scientist magazine, page 12.

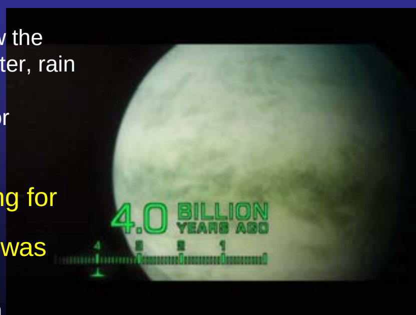
Older than the hills.

Now, it seems that water may after all have been present in Earth's building blocks. Simulations by Nora de Leeuw of University College London and colleagues suggest that the dust grains from which Earth formed had such a tenacious grip on water that they could have held onto the molecules despite the high temperatures.

The origin of the oceans has long been a mystery. Earth's birthplace in the dusty nebula around the young sun should have been hot enough to keep any water vaporised. So it seemed clear that the dust that coalesced to create Earth was bone dry, and that water somehow arrived later.

## THE ORIGIN OF THE SEA

- After the Earth's surface had cooled to a temperature below the boiling point of water, rain began to fall and continued to fall for centuries.




Continuous raining for millions of years, 90% of the earth was a vast ocean.

Panthalassa Ocean,
from Greek words Pan = all, Thalassa = oceans.

## THE ORIGIN OF THE SEA

**4.0 billion years ago → The Water World**

- As the water drained into the great hollows in the Earth's surface, the primeval ocean came into existence.

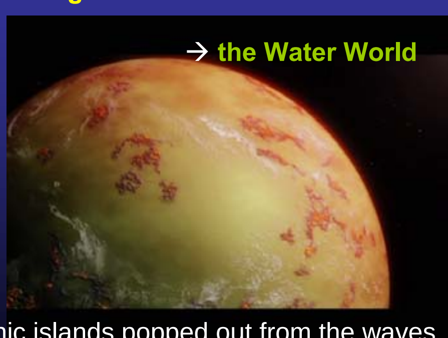
The forces of gravity prevented the water from leaving the planet.


## THE ORIGIN OF THE SEA

**4.0 billion years ago**

Huge green oceans **(iron rich)** dominated

→ **the Water World**



- Small volcanic islands popped out from the waves
- 93 ºC temp

When the earth was first created the **MOON** was much closer.
It fill the sky.
Its gravitational pull was much stronger

**Tsunamis have since ravaged the earth**

→ **the Water World**

and generated towering waves above 800 m that raced across the primeval oceans

→ the Water World

Other different physical parameters of primeval oceans and earth :

- A cooler sun illuminated the Earth
- Earth rotation was faster than at present.
  Thus shorter circadian periods and photoperiods

**3.5 billion years ago**

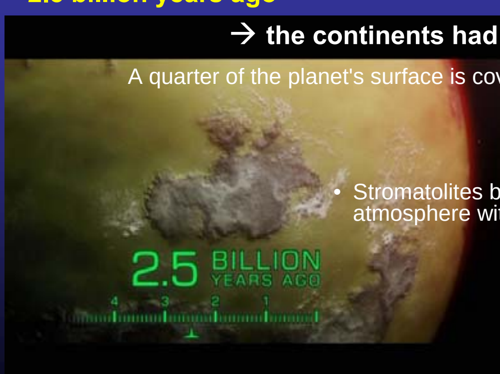
**→ granite and continents begun to grow**


- ***In the beginning***
  **the primeval seas must have been only slightly salty.**
- Ever since the first rains descended upon the young Earth and ran over the land breaking up rocks and transporting their minerals to the seas, **the ocean has become saltier.**

**2.5 billion years ago**

**→ the continents had arrived**

A quarter of the planet's surface is covered by land

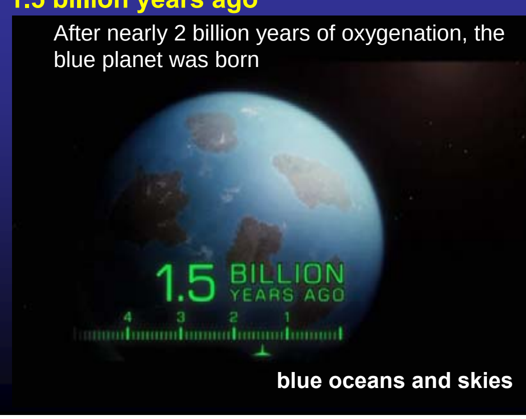



- Stromatolites begin filling the atmosphere with oxygen

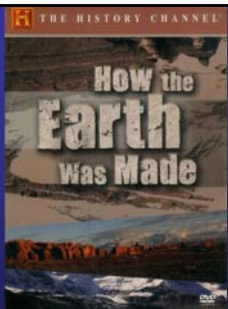
The dominance of the oceans was over.

**1.5 billion years ago**

After nearly 2 billion years of oxygenation, the blue planet was born




**blue oceans and skies**

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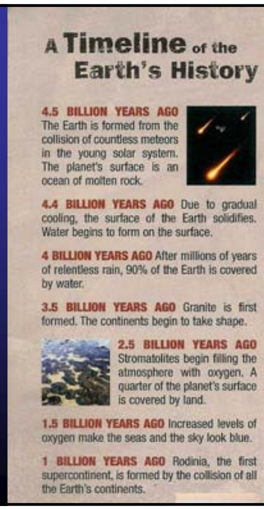


A Timeline of the Earth's History

**4.5 BILLION YEARS AGO** The Earth is formed from the collision of countless meteors in the young solar system. The planet's surface is an ocean of molten rock.

**4.4 BILLION YEARS AGO** Due to gradual cooling, the surface of the Earth solidifies. Water begins to form on the surface.

**4 BILLION YEARS AGO** After millions of years of relentless rain, 90% of the Earth is covered by water.

**3.5 BILLION YEARS AGO** Granite is first formed. The continents begin to take shape.

**2.5 BILLION YEARS AGO** Stromatolites begin filling the atmosphere with oxygen. A quarter of the planet's surface is covered by land.

**1.5 BILLION YEARS AGO** Increased levels of oxygen make the seas and the sky look blue.

**1 BILLION YEARS AGO** Rodinia, the first supercontinent, is formed by the collision of all the Earth's continents.

## The origins of sea salt

Scientific theories behind the origins of sea salt started with Sir Edmond Halley in 1715, who proposed that salt and other minerals were carried into the sea by rivers, having been leached out of the ground by rainfall runoff.

Upon reaching the ocean, these salts would be retained and concentrated as the process of evaporation (Hydrologic cycle) removed the water.

Halley noted that of the small number of lakes in the world without ocean outlets (such as the Dead Sea and the Caspian Sea), most have high salt content.

Halley termed this process "continental weathering“

[port. meteorização continental]

## Chemical composition of the ocean

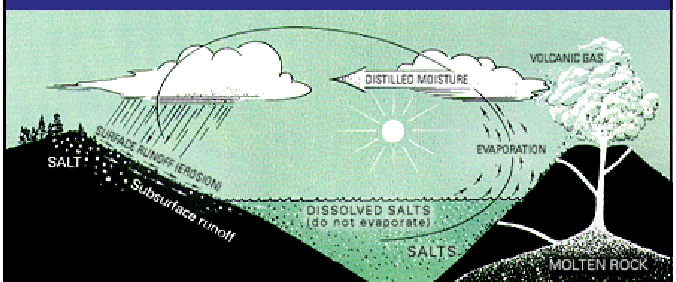
- It was plain by the end of the 19th century that seawater could not be produced by the partial evaporation of river water.
- At the end of that route lie only closed-basin lakes such as the Dead Sea and the great Salt Lake, which are highly alkaline compared with the oceans.
- In oceans there must be a reaction that converts bicarbonate back into carbon dioxide.
- What controls the pH of the oceans? Why is it consistently 7,5 to 8 or close to acid-alkaline neutrality?
- Might the chemical composition of the oceans come as much from hydrothermal reactions as it does from the products of weathering on the continents?

## Geochemical explanations

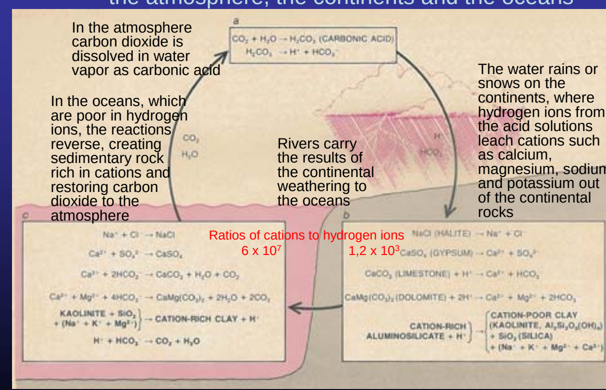
- Halley's theory is partly correct.
- In addition, sodium was leached out of the ocean floor when the oceans first formed.
- The presence of the other dominant ion of salt, chloride, results from "outgassing" of chloride (as hydrochloric acid) with other gases from Earth's interior via volcanoes and hydrothermal vents.
- The sodium and chloride ions subsequently became the most abundant constituents of sea salt.

**THE SALTS IN THE SEA COME FROM:**

- WEATHERING OF CONTINENTS
- HYDROTHERMAL VENTS
- SUBMARINE VOLCANOES




## Chemical balance between the atmosphere, the continents and the oceans



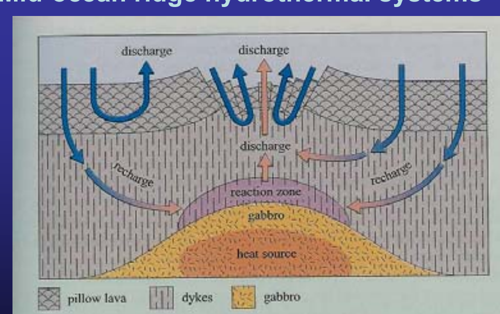

The result requires that an amount of carbon dioxide equal to its abundance in the atmosphere be consumed in about 4000 years.

Clearly there must be a reaction that converts bicarbonate back into carbon dioxide

## Hydrothermal vents

- Rivers are not the only source of dissolved salts.
- About twenty years ago, features on the crest of oceanic ridges were discovered that modified our view on how the sea became salty.
- These features, known as **hydrothermal vents**, represent places on the ocean floor where sea water that has seeped into the rocks of the oceanic crust, has become hotter, and has dissolved some of the minerals from the crust, now flows back into the ocean.
- With the hot water comes a large complement of dissolved minerals.
- **Estimates of the amount of hydrothermal fluids now flowing from these vents indicate that the entire volume of the oceans could seep through the oceanic crust in about 10 million years.**
- Thus, this process has a very important effect on salinity.

## Mid-ocean ridge hydrothermal systems

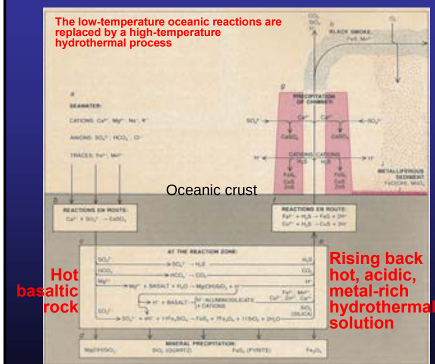



Schematic cross-section of oceanic crust at a mid-ocean ridge showing the flow paths of water through the recharge, reaction and discharge zones of the hydrothermal system.

Nick Rogers (2008). An Introduction to Our Dynamic Planet.

SciAm 1983

## Hydrothermal Reactions at the midocean ridges




The carbon dioxide emerging from the vents is mixing into the ocean. Eventually it reaches the surface, enters the atmosphere and closes the carbon dioxide cycle

- Ridge axis consume most of the magnesium and most of the sulfate that rivers introduce into the sea.
- Conversely, they release almost all the manganese, five to ten times more lithium and rubidium, and a third to a half as much potassium, calcium, barium and silica.

Hydrothermal reactions at the midocean ridges regenerate carbon dioxide to a far greater extent than the low-temperature oceanic process

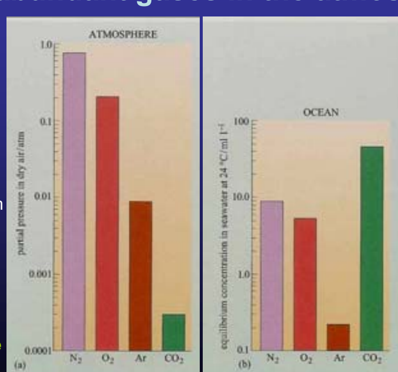
## Submarine volcanism

- A final process that provides salts to the oceans is submarine volcanism, the eruption of volcanoes under water.
- This is similar to the previous process in that seawater is reacting with hot rock and dissolving some of the mineral constituents.

## Concentration in seawater of the four most abundant gases in the atmosphere

The air we breathe is a cocktail of gases, the most important of which are:

- nitrogen 78%
- oxygen 21%
- argon 1%
- **carbon dioxide 0.03%**




However, in **seawater, carbon dioxide** is the most abundant dissolved gas followed by nitrogen, oxygen and argon.

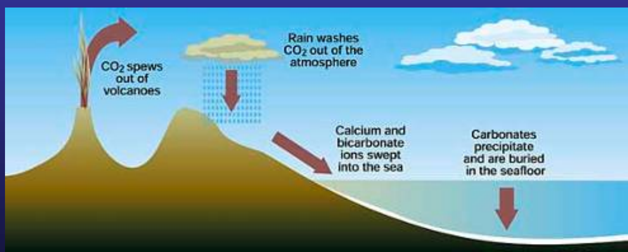
## Carbon dioxide

- Major sources of carbon dioxide are
  - respiration
  - decay
- Major sinks are
  - photosynthesis
  - construction of carbonate shells

**Fate of carbon dioxide in the ocean after 1000 years.**

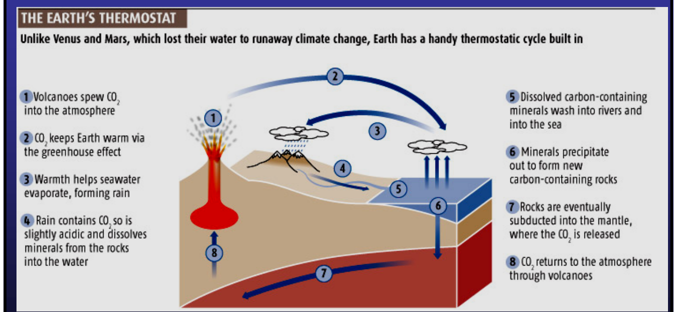
| Form/Location | Percentage |
|---|---|
| $CO_2$ in the atmosphere | 1.4% |
| $CO_2/H_2CO_3$ in the ocean | 0.5% |
| $HCO_3^-$ in the ocean | 79.9% |
| $CO_3^{--}$ in the ocean | 9.6% |
| Organics on land | 4.9% |
| Organics in the ocean | 3.7% |

## Cycle of carbon from volcanoes to the ocean floor




Are the oceans becoming more salty?

## Are the oceans becoming more salty?




## Q&A

**(a) What are the two main rock-weathering reactions involving dissolved $CO_2$?**

**A:** calcium carbonate ($CaCO_3$) and silicate ($NaAlSi_3O_8$) rocks

The first reaction - takes in one molecule of $CO_2$ for each molecule of $CaCO_3$ weathered but, because the precipitation of carbonate releases it again, there is no net drawdown of $CO_2$:

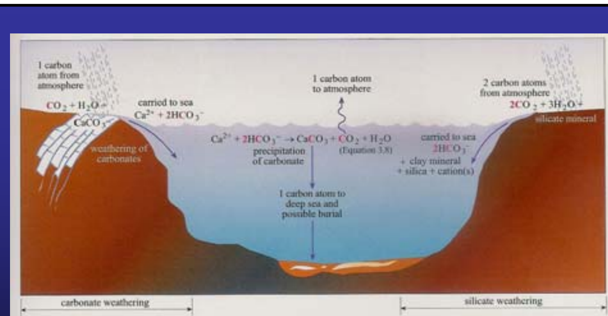
$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{from rainwater}}{CO_2 + H_2O} \underset{\text{carbonate precipitation}}{\overset{\text{carbonate dissolution}}{\rightleftharpoons}} \underset{\text{in solution in soil/stream water}}{Ca^{2+} + 2HCO_3^-}$$

The second reaction – silicate weathering [*meteorização de silicatos*] - removes two molecules of $CO_2$ from the atmosphere for every silicate molecule weathered:

$$\underset{\text{silicate rock}}{CaSiO_3} + \underset{\text{from rainwater}}{2CO_2 + 3H_2O} \rightarrow \underset{\text{stream/river water}}{Ca^{2+} + 2HCO_3^- + H_4SiO_4}$$

(b) Which of these is considered to lead to a net drawdown of $CO_2$ from the atmosphere when precipitation of carbonate occurs?

**A:** As the precipitation of carbonate releases one molecule of $CO_2$ into the atmosphere, a net drawdown of $CO_2$ from the atmosphere occurs when silicate rocks are weathered.




- In the weathering of ***carbonates***, one carbon comes from atmospheric $CO_2$ and one comes from the carbonate mineral itself.
- In ***silicate*** weathering, both carbon atoms come from the atmosphere
- Rock-weathering increases with rising temperatures, thus removing more $CO_2$ from the atmosphere.

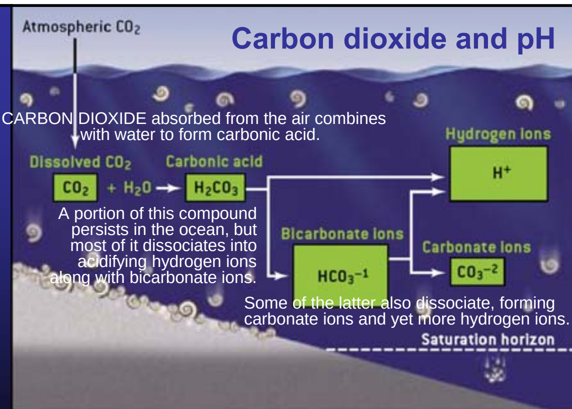
## Carbon dioxide and pH

Carbon dioxide controls the acidity of sea water

- A solution is acid if it has excess $H^+$ (hydrogen) ions and is a base if it has an excess of $OH^-$ (hydroxyl) ions
- pH measures how acidic or basic water is
  - pH of 0 to 7 is acidic
  - pH of 7 is neutral
  - pH of 7 to 14 is basic
- Seawater has a pH of 7.8 to 8.2.

The pH of pristine seawater measures from 8 to 8.3 meaning that the ocean is naturally somewhat alkaline.

## Carbon dioxide and pH



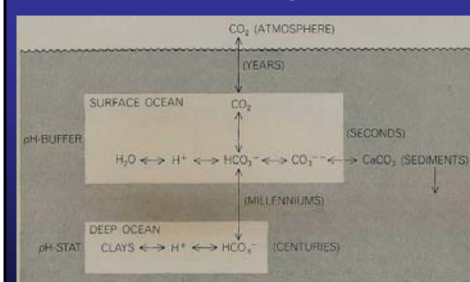

These chemical changes cause an upward shift in the "saturation horizons" for calcite and aragonite—the water levels deep in the sea below which shells of marine organisms made of these minerals dissolve.

## Carbon dioxide

### Solubility in seawater

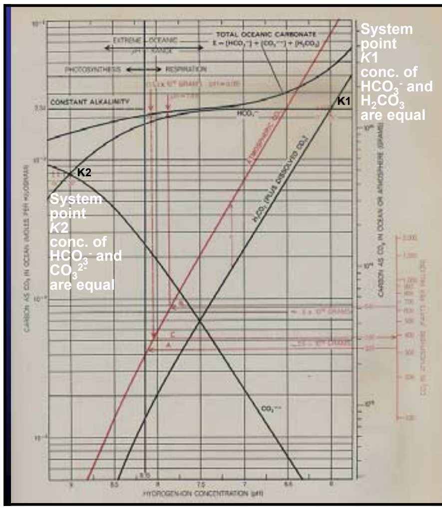
- **Solubility of $CO_2$ in seawater depends on temperature.** $CO_2$ is more soluble in cold waters and less soluble in warm waters
- Cold water under great pressure has a high saturation value for $CO_2$ and the additional $CO_2$ releases more $H^+$ ions making the water acid. In deep waters, this may results in dissolution of carbonate shells
- Warm, shallow water is under low pressure, contains less dissolved $CO_2$ and is less acidic. Carbonate sediments are stable and do not dissolve.
- Seawater has a relatively stable pH of about 8.3. This means it is slightly alkaline, a fact that is of importance if you set up your own aquarium. If you allow your aquarium water to become acid then the shells of animals like crabs or prawns, may start to soften and the animals undoubtedly suffer.

## Control of ocean pH




HYDROGEN-ION CONCENTRATION, or pH, of the ocean is controlled by two mechanisms, one that responds swiftly and one that takes centuries.

- The first, the "pH-buffer," operates near the surface and maintains equilibrium among carbon dioxide, bicarbonate ion ($HCO_3^-$), carbonate ion ($CO_3^{2-}$) and sediments.
- The slower mechanism, the "pH-stat," seems to exert ultimate control over pH; it involves the interaction of bicarbonate ions and protons ($H^+$) with clays. Clay will accept protons in exchange for sodium ions (primarily).



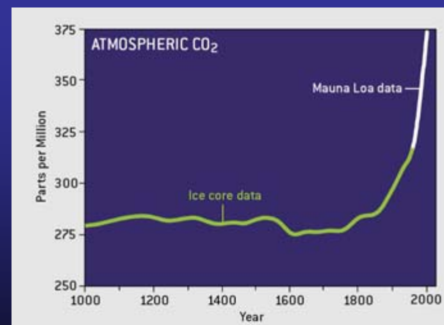

## OCEANIC CARBONATE SYSTEM

represented by a "Bjerrum diagram" that shows how carbonate in its several forms varies with the ocean's pH under constant carbonate alkalinity

The ocean's pH determines the relative proportions of the different DIC compounds

($H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$)

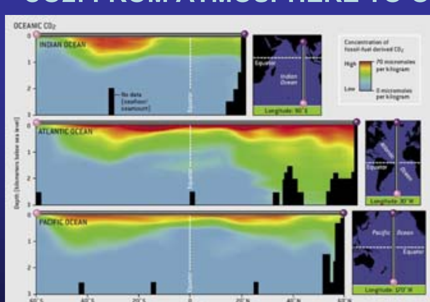
## CO2: FROM ATMOSPHERE TO OCEAN




The concentration of carbon dioxide in the atmosphere has mounted considerably over the past century or so.

This worrisome trend is well documented (*right*) by a combination of two techniques: the examination of air bubbles trapped in glacial ice (*green segment,* which shows 75-year averages) as well as direct measurements of the atmosphere (*white segment,* which reflects the annual average determined at a weather station situated atop Mauna Loa on the big island of Hawaii).

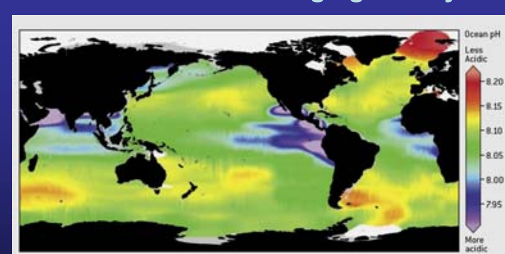
## CO2: FROM ATMOSPHERE TO OCEAN




The absorption of carbon dioxide has already caused the pH of modern surface waters to be about 0.1 lower (less alkaline) than it was in preindustrial times.

- Large as it is, the increasing concentration of carbon dioxide in the atmosphere would have been even greater had not much of it been absorbed by the sea, a phenomenon that detailed oceanographic surveys have now documented. About a third of the carbon dioxide ($CO_2$) released by the burning of fossil fuels currently ends up in the ocean.
- The cross sections show where about half of this fossil-fuel effluent now resides—in the upper portions of the world's oceans.
- The ocean has absorbed fully half of all the fossil carbon released to the atmosphere since the beginning of the Industrial Revolution.

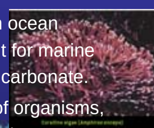
## The Ocean's Changing Acidity

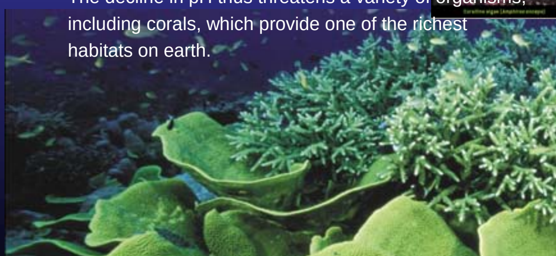


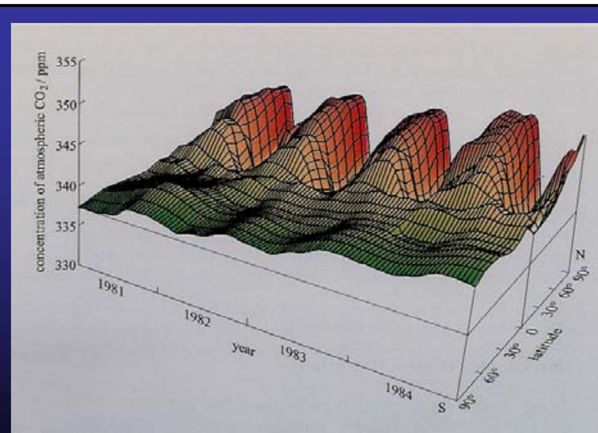

Measurements taken in the top 50 meters of the ocean reveal that pH varies considerably from place to place. Scientists expect oceanic pH to decrease in the years ahead.

Areas of relatively low pH arise mostly through the natural upwelling of deeper waters. Those zones, such as in the east equatorial Pacific, might be good places for scientists to study the effects expected to prevail over wider areas in the future.

- Absorbed $CO_2$ forms carbonic acid in seawater, lowering the prevailing pH level and changing the balance of carbonate and bicarbonate ions.
- The shift toward acidity, and the changes in ocean chemistry that ensue, makes it more difficult for marine creatures to build hard parts out of calcium carbonate.
- The decline in pH thus threatens a variety of organisms, including corals, which provide one of the richest habitats on earth.



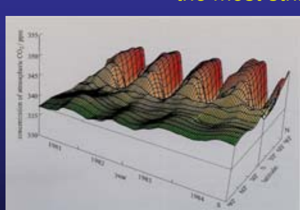





Sea-level seasonal fluctuations in atmospheric concentrations of $CO_2$ from 1981 to 1984, as a function of 10º latitude bands

## Questions

Apart from the peaks and troughs, what are the most striking aspects of this diagram?



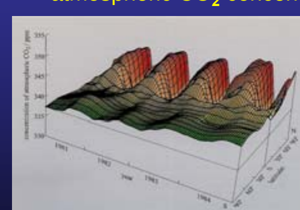
Sea-level seasonal fluctuations in atmospheric concentrations of $CO_2$ from 1981 to 1984, as a function of 10º latitude bands

The seasonal oscillations are marked in the Northern Hemisphere, but extremely damped in the Southern Hemisphere.

- The lows in the Northern Hemisphere correspond to (small) highs in the Southern Hemisphere

## Questions

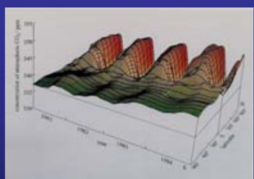
What is the reason for the seasonal fluctuations in atmospheric $CO_2$ concentration?



Sea-level seasonal fluctuations in atmospheric concentrations of $CO_2$ from 1981 to 1984, as a function of 10º latitude bands

- The fluctuations in atmospheric $CO_2$ concentration are a result of the uptake of $CO_2$ by plants during photosynthesis in spring and summer, i.e. removal of carbon from the atmosphere and its fixation in living plant material.
- Note that it is the lows that correspond to spring and summer, and the highs that correspond to winter.

## Questions



Sea-level seasonal fluctuations in atmospheric concentrations of $CO_2$ from 1981 to 1984, as a function of 10º latitude bands

**By reference to any global map, suggest why this pattern is dampened in the Southern Hemisphere?**

- The pattern is dampened in the Southern Hemisphere because primary productivity per unit area in the ocean is much less than on land and the Southern Hemisphere is largely ocean.