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

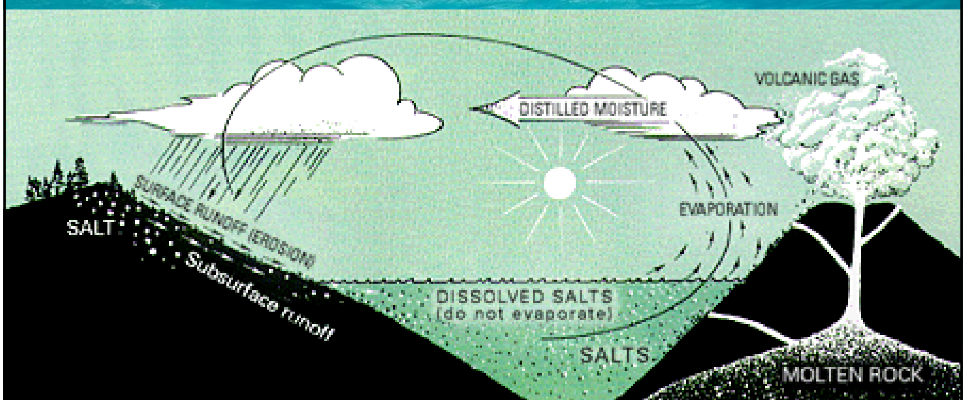
- It was plain by the end of the 19th century that seawater could not be produced by the partial evaporation of river water.
- At the end of that route lie only closed-basin lakes such as the Dead Sea and the great Salt Lake, which are highly alkaline compared with the oceans.
- In oceans there must 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

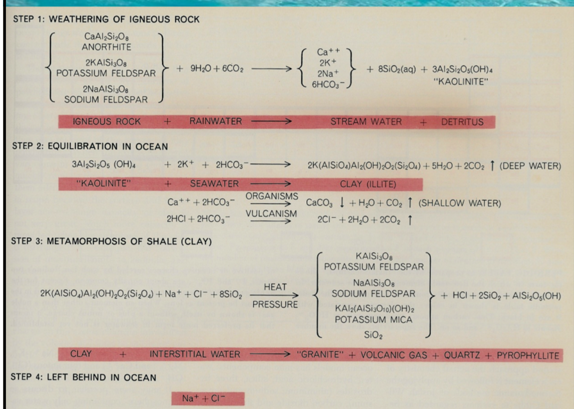
- Halley's theory is partly correct.
- In addition, sodium was leached out of the ocean floor when the oceans first formed.
- The presence of the other dominant ion of salt, chloride, results from "outgassing" of chloride (as hydrochloric acid) with other gases from Earth's interior via volcanoes and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



Why the sea is salt



- Step 1 yields a solution of alkali ions and bicarbonate (HCO_3^-) ions in which hydrated silica (SiO_2) and aluminosilicate detritus are suspended. In crystalline form the aluminosilicate would be **kaolinite**.
- In the ocean *(Step 2)* the "kaolinite" is complexed with potassium ions (K^+) to form illite clay. Marine organisms use the calcium ion (Ca^{2+}) to make calcium carbonate shells, which form sediments in shallow water. Hydrochloric acid (HCl), injected by undersea volcanoes, reacts with bicarbonate ions, returning some carbon dioxide to the atmosphere.
- In Step 3 clay is metamorphosed into "granite."
- Sodium chloride *(Step 4)* remains.

ONLY SALT REMAINS after the ocean "laboratory" has finished processing the complex of chemicals removed from igneous rock by rainwater containing dissolved carbon dioxide.

Salinidade

Salinidade - relação entre o conteúdo de sais dissolvidos em uma dada quantidade (unidade de massa) de água.

Operacionalmente, contudo, sua determinação não é simples, uma vez que:

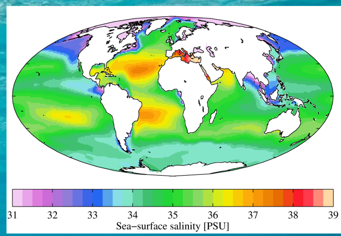
1. moléculas de água podem ficar retidas na estrutura cristalina dos sais durante a secagem e
2. a T°C necessária para que se evapore toda a água faz com que os carbonatos sejam convertidos em óxidos, os haletos (*) sejam parcialmente vaporizados e a matéria orgânica seja convertida em dióxido de carbono (CO_2)

Robert Boyle (1627-1691)
(evapora-se e mede-se o ratio)

* do nome grego *halos* - sal

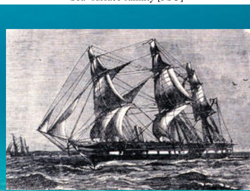
Salt content of open oceans

William Dittmar (1884) atesta que existe um rácio constante entre os diversos sais dissolvidos na água do mar, independente da salinidade e da localização geográfica da amostra.



Foi nesse período que se começou a pensar na determinação da salinidade das águas marinhas a partir da quantidade de algum dos iões presentes.

Salinidade média dos oceanos obtida pela 1ª vez por Dittmar in 1884 com analyses químicas de 77 amostras de água de diversos partes do globo



(Scientific expedition of the British corvette, H.M.S. Challenger)

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- Knudsen (1901) e seu grupo estabeleceram uma equação que relaciona a clorinidade (concentração de haletos totais) com a salinidade.

$$S(‰) = 0,030 + 1,805 \cdot Cl(‰)$$

em que $S(‰)$ é a salinidade e $Cl(‰)$ é a clorinidade, ambas em partes por mil (‰) que é equivalente a g/kg.

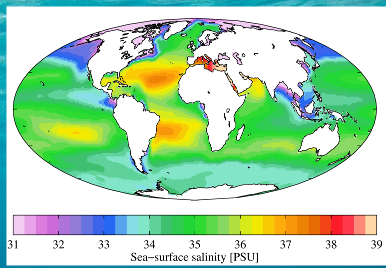
- Os halogenetos inorgânicos são sais que contém os íons F^-, Cl^-, Br^- ou I^-.

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)

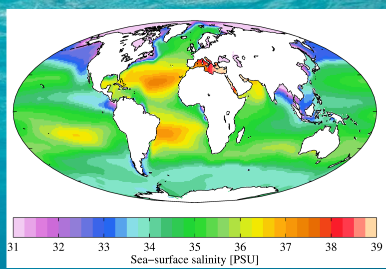
Throughout the world, the salinity of sea water averages about 35 psu.



Salt content of open oceans

Décadas passaram até que a imprecisão deste método foi substituida pelo surgimento dos primeiros condutivímetros permit issem novos avanços

Condutividade eléctrica da amostra de água do mar, quando comparada com a da "água de Copenhaga" (água padrão da IAPSO), cuja salinidade, clorinidade e condutividade são precisamente conhecidas.

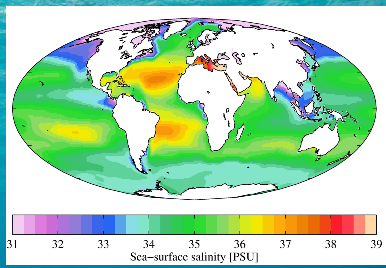


$$S(‰) = -0,08996 + 28,29720 \cdot {R_{15}}^1 + 12,80832 \cdot {R_{15}}^2 - 10,67869 \cdot {R_{15}}^3 + 5,98624 \cdot {R_{15}}^4 - 1,32311 \cdot {R_{15}}^5$$

Nesta equação, R_{15} é o rácio entre a condutividade da amostra e a condutividade da água padrão da IAPSO, ambas medidas a 15 °C.

Salt content of open oceans

Depois substituiu-se a água padrão da IAPSO por uma solução padrão de cloreto de potássio (KCl), com 32,4356 g desse sal para cada quilograma da solução, para ter sua condutividade comparada com a condutividade da amostra de água do mar.

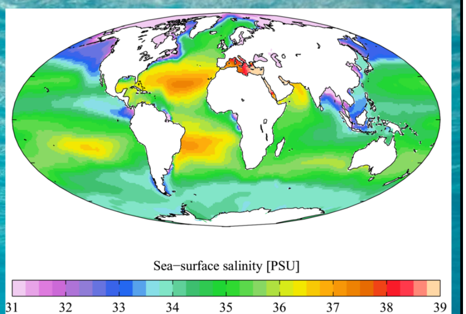


Escala de salinidade prática - PSU

$$S = 0,0080 - 0,1692 \cdot K_{15}^{0,5} + 25,3851 \cdot K_{15}^{1} + 14,0941 \cdot K_{15}^{1,5} - 7,0261 \cdot K_{15}^{2} + 2,7081 \cdot K_{15}^{2,5}$$

Onde K_{15} é o rácio entre a condutividade da amostra e a condutividade da solução padrão de cloreto de potássio, ambas medidas a 15 °C e 1 atm. Quando o rácio medido em K_{15} é exactamente 1, então $S = 35$ PSU, o valor médio da salinidade nas águas oceânicas.

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.

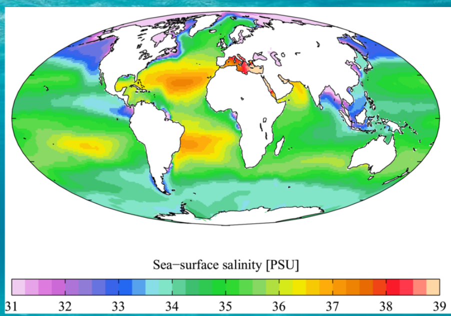
Within the North Atlantic, the saltiest part is the Sargasso Sea, an area of about 5 million km^2, located about 3,200 km west of the Canary Islands.

The saltiness of this sea is due in part to the high water temperature (up to 28° 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.

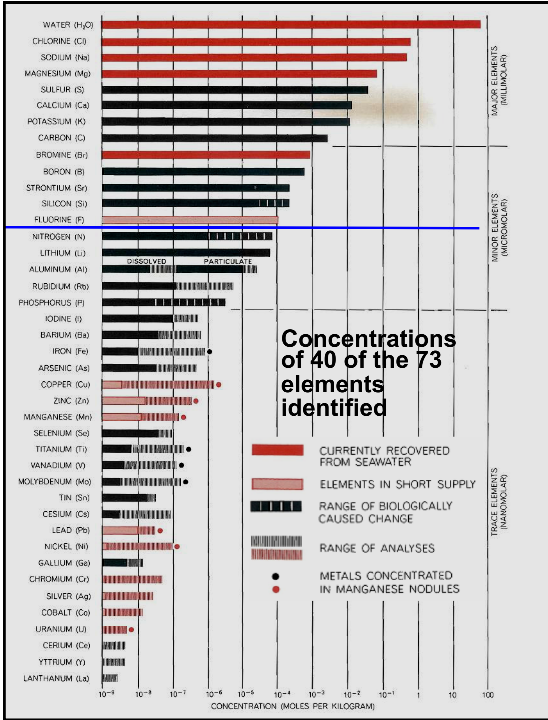
- Partly landlocked seas or coastal inlets that receive substantial runoff from precipitation falling on the land also may have low salinities.



- 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^-)

Table 2 Composition of artificial salt mixture

Five salts, six ions

(99% of the dissolved constituents of sea water)

Common names of salts	Chemical composition	100 kg kg
Sodium chloride (common salt)	NaCl	65.75
Magnesium sulphate (Epsom salt)	$MgSO_4 . 7H_2O$	16.25
Magnesium chloride	$MgCl_2 . 6H_2O$	13.00
Flake calcium chloride	$Ca\ Cl_2 . 2H_2O$	3.50
Potassium chloride	KCl	1.76

35.55 g desta mistura por litro de água-torneira resultará em água-do-mar artificial com salinidade aprox. de 30 psu

Sea Urchin Embryology

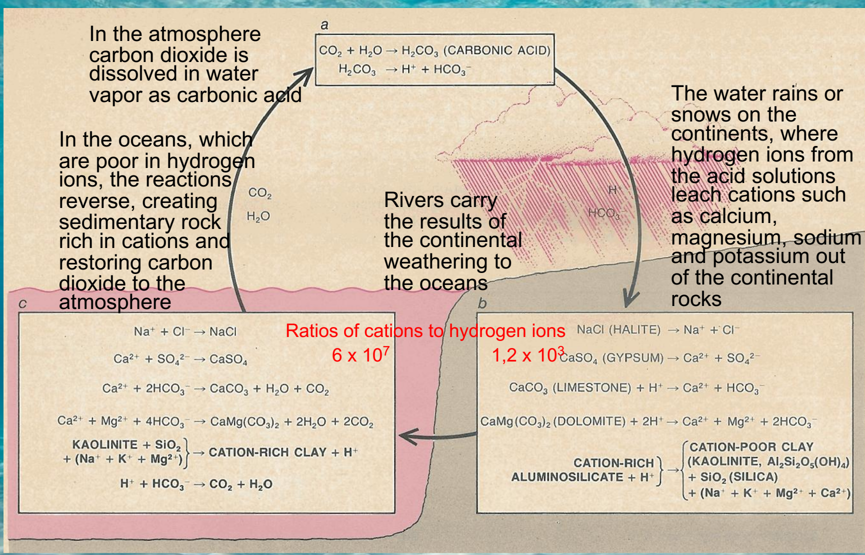
ARTIFICIAL SEA WATER

Six salts, seven ions

SALT	G/LITER	1 litre g
sodium chloride	24.6	23.51
magnesium sulfate * 7H2O	6.29	5.74
magnesium chloride * 6H2O	4.66	4.55
calcium chloride * 2H2O	1.36	1.19
potassium chloride	0.67	0.56
sodium bicarbonate	0.18	-----
Totals	37.76	35.55

use a pH meter to bring pH to 8.0

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

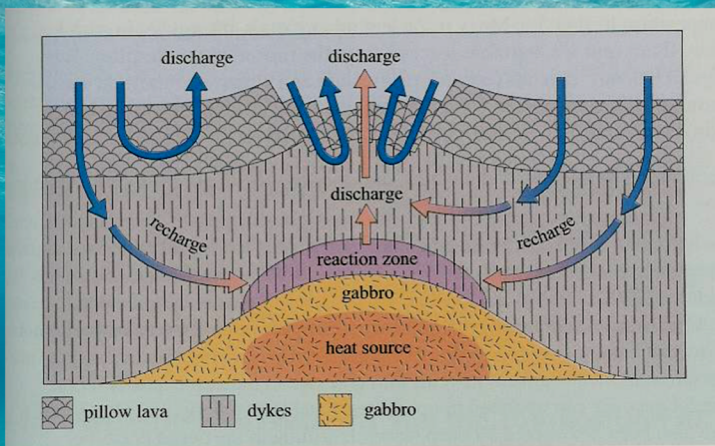
Hydrothermal vents

- 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

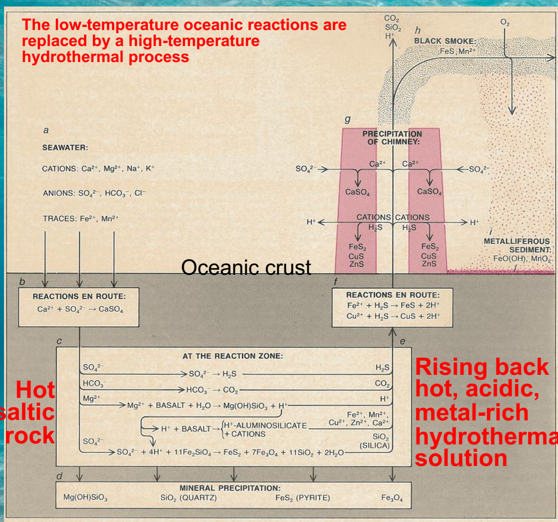


Schematic cross-section of oceanic crust at a mid-ocean ridge showing the flow paths of water through the recharge, reaction and discharge zones of the hydrothermal system.

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

SciAm 1983

Hydrothermal Reactions at the midocean ridges



Hot basaltic rock

Rising back hot, acidic, metal-rich hydrothermal solution

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

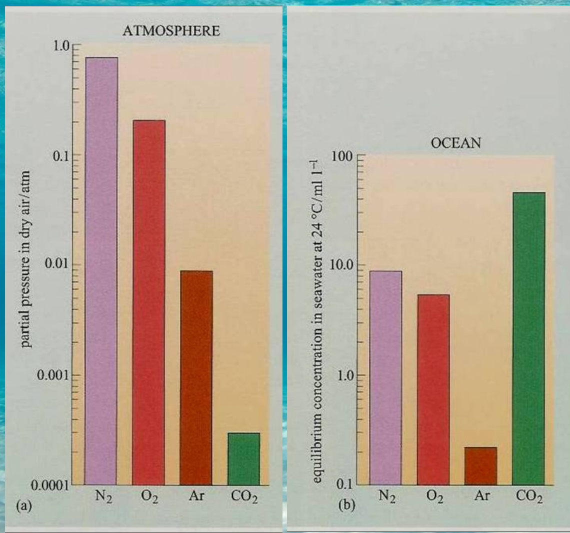
Submarine volcanism

- 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.

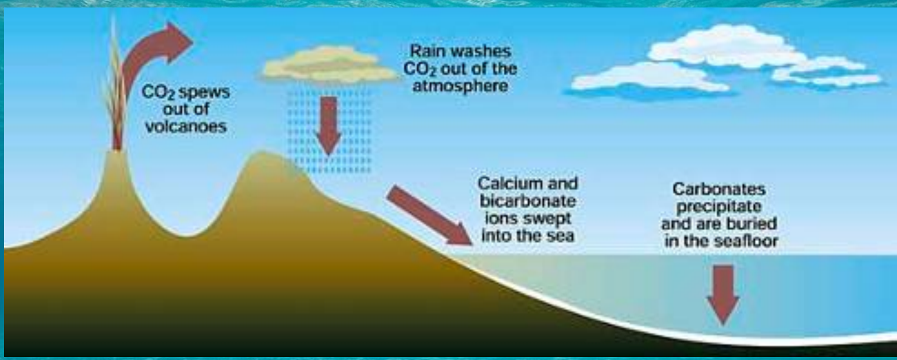
Carbon dioxide

- 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.

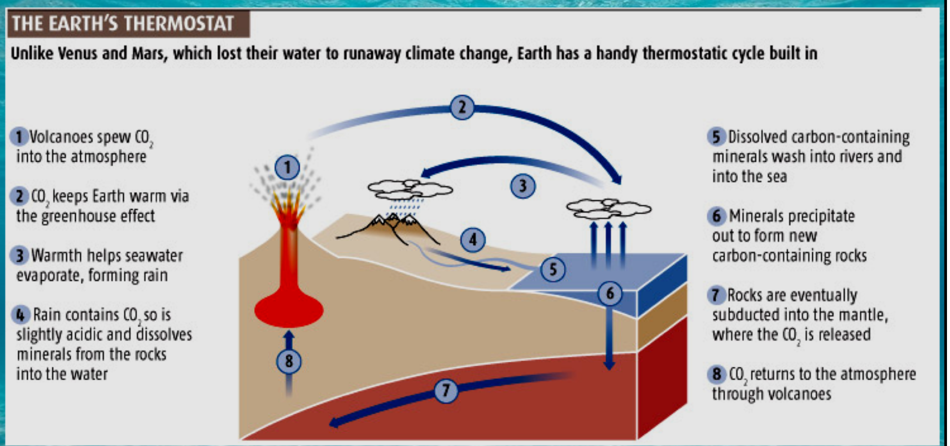
Form/Location	**Percentage**
CO_2 in the atmosphere	1.4%
CO_2/H_2CO_3 in the ocean	0.5%
HCO_3^- in the ocean	79.9%
CO_3^{--} in the ocean	9.6%
Organics on land	4.9%
Organics in the ocean	3.7%

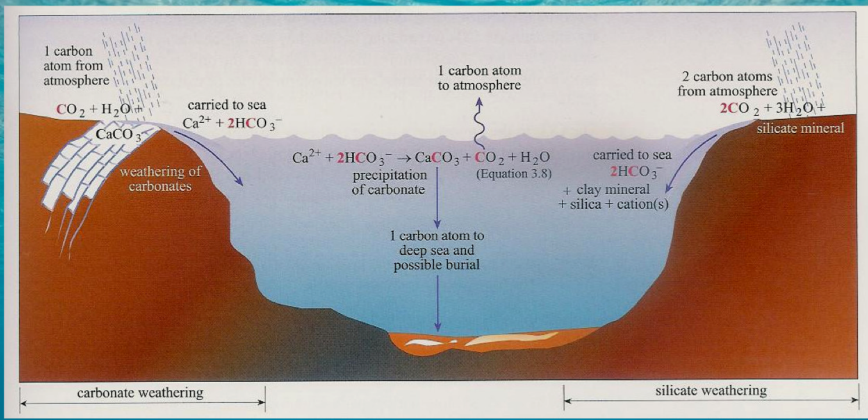
Cycle of carbon from volcanoes to the ocean floor



Are the oceans becoming more salty?

Are the oceans becoming more salty?





- 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.

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:

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

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The second reaction –

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

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

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(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.

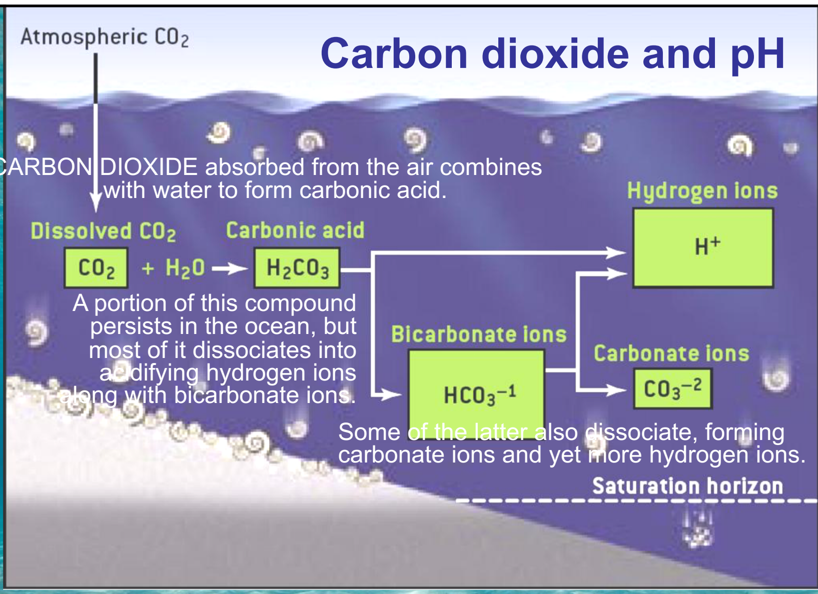
Carbon dioxide and pH

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.