Major Ions, Conservative Elements and Dissolved Gases in Seawater

الايونات الرئيسية – العناصر المحافظة – الغازات المذابة في مياه البحر

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Identification

Major ions are defined as those elements whose concentration is greater than 1 ppm. One reason this definition is used is because Salinity is reported to ± 0.001 or 1 ppm. Thus, the major ions are those ions that contribute significantly to the salinity. According to this definition there are **11 major ions**, all other elements in seawater are present in concentrations less than 1ppm (<1mg/kg) and are called minor or trace constituents. At a salinity of S = 35.000 seawater has the following composition.

Ion	Formula	g/Kg	mmol/Kg
Sodium	Na^{+}	10.781	468.96
Magnesium	Mg^{2+}	1.284	52.83
Calcium	Ca^{2+}	0.4119	10.28
Potassium	K^{+}	0.399	10.21
Strontium	Sr^{2+}	0.00794	0.0906
Chloride	Cl^{-}	19.353	545.88
Sulfate	SO_4^{2-}	2.712	28.23
Bicarbonate	HCO_3^{-}	0.126	2.06
Bromide	Br^{-}	0.067	0.844
Borate	$H_3BO_4^{-}$	0.0257	0.416
Fluoride	F^{-}	0.00130	0.068
Totals	11	35.169	1119.87

The abundance and distribution of elements in the ocean is a function of their solubility in seawater and their reactivity or their degree of involvement in biological and chemical processes and oceanic circulation.

In order to efficiently summarize the major processes controlling the composition and distribution of elements in the ocean we will classify (group) the elements according to their distribution in seawater. We can broadly classify the elements in seawater into 4 groups: **conservative elements, dissolved gases, recycled elements and scavenged elements.**

The **conservative elements**: These include most of the major ions in seawater and a few other elements and complexes (Li^+, Rb^+, Cs^+, $MoO4^{2-}$ and $UO2(CO3)_3^{4-}$). The solubility of the minerals providing these elements is high (we can dissolve a lot of NaCl, KCl, $MgSO_4$ and $CaSO_4$ in seawater). Other non-major elements in this group interact only weakly with biological or other particles and are relatively soluble. The concentration of these elements **normalized to salinity** is constant with depth and in the different oceans. In other words, they are uniformly distributed. The ratio of one conservative element to another will also be constant. One way to establish if an element of unknown reactivity is conservative is to plot it versus another conservative element or against potential temperature or salinity.

Na, K, SO4, Br, B and F have constant ratios to Cl and each other, everywhere in the ocean. These elements are conservative.

Until recently, Mg was thought to be conservative. Recently, local Mg anomalies were found in deep waters located over mid-ocean ridges. Mg is known to be totally removed in high temperature hydrothermal vent solutions.

Dissolved Inorganic Carbon, DIC (H_2CO_3 + HCO_3^- + CO_3^{2-}) varies by ~ 20% due to vertical transport and remineralization of both $CaCO_3$ and organic matter.

SO_4^{2-} is conservative in oxic oceans but not in anoxic basins or within sediments. Sulfate is used by sulfate reducing bacteria to form HS^- or H_2S

Gases and Gas Exchange

There are several reasons for studying gas exchange, important ones are:

A. The ocean is a sink for anthropogenic CO_2 and one of the major transfer modes of CO_2 to the ocean from the atmosphere is by gas exchange.
B. Oxygen is a chemical tracer for photosynthesis. The gas exchange flux of O_2 is an important parameter for calculating net biological production.
C. Gas exchange is the process by which O_2 is transported into the ocean and is thus a control on aerobic respiration.
D. Some gases can act as tracers for ocean circulation (CFCs, SF_6).

Fundamental Properties of Gases

The relative composition of the main gases in the atmosphere (ratio of one gas to another) is nearly constant horizontally and vertically to almost 95 km (the atmosphere is well mixed). Atmospheric water (H_2O) is highly variable. Some trace gases involved in photochemical reactions can also be highly variable.

Composition of the Atmosphere

More than 95% of all gases except radon reside in the atmosphere. The atmosphere controls the oceans gas contents for all gases except radon, CO_2 and H_2O, which are more abundant in seawater.

	Gas	Mole Fraction in Dry Air (f_G)	Henry's Law Constant (mol/kg at 35‰ , 760 mm Hg)	
			K_H (10^{-3}) 0°C	K_H (10^{-3}) 24°C
N_2	Nitrogen	78.084 %	0.80	0.51
O_2	Oxygen	20.952 %	1.69	1.03
Ar	Argon	0.934 %	1.83	1.13
CO_2	Carbon Dioxide	350 ppm	63	29
Ne	Neon	18 ppm	0.44	0.37
He	Helium	5 ppm	0.34	0.32
Kr	Krypton	1 ppm	3.8	2.1
Xe	Xenon	0.08 ppm	8.4	4.3
CH_4	Methane	2 ppm		
H_2	Hydrogen	0.5 ppm		
N_2O	Nitrous Oxide	0.3 ppm		
CO	Carbon Monoxide	0.05-0.2 ppm		
O_3	Ozone	0.02-10 ppm		
NH_3	Ammonia	4 ppb		
NO_2	Nitrogen Dioxide	1 ppb		
SO_2	Sulfur Dioxide	1 ppb		
H_2S	Hydrogen Sulfide	0.05 ppb		

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Some comments about units of gases

<u>Units</u>

in air   partial pressure of gas i (atm) = (pressure of gas i) / (total gas pressure)

one atmosphere = 760 mm Hg

partial pressure = (liters gas / liter air) = atm.; ppm = µl / l

in water   volume gas / volume or weight seawater

liters gas (STP) / kg. Seawater [STP = standard T and P => 1 atm, 0 °C]

@ STP, 1 mole gas = 22.414 liters

The pressure and volume units are the same at 760 mm Hg

Dalton's Law

Gas concentrations are expressed in terms of pressures.
Total Pressure = $\sum Pi$ = Dalton's Law of Partial Pressures

$$P_{TOTAL} = P_T = P_{N2} + P_{O2} + P_{H2O} + \dots\dots\dots$$

Dalton's Law implies ideal behavior -- i.e. all gases behave independently on one another. Gases are dilute enough that this is a good assumption.

Variations in partial pressure (Pi) result from:
1- variations in P_T (atmospheric pressure highs and lows)
2- variations in water vapor (P_{H2O})

Solubility

The exchange or chemical equilibrium of a gas between gaseous and liquid phases can be written as: A (g) $\longleftrightarrow$ A (aq)

At equilibrium: K = [A(aq)] / [A(g)] (K is the equilibrium constant)

There are two main ways to express solubility.

Henry's Law:

We can express the gas concentration in terms of partial pressure using the ideal gas law:

$$PV = nRT$$

so that the number of moles n divided by the volume is equal to [A(g)]

n/V = [A(g)] = P_A / RT where P_A is the partial pressure of A Then K = [A(aq)] / P_A /RT

or [A(aq)] = (K/RT) P_A K/RT is defined as Henry's Law Constant (K_H) This constant changes with temperature and salinity some values are listed above.

$$[A(aq)] = K_H\, P_A$$

Units for K are mol kg^{-1} atm^{-1}; for P_A are atm; and for [A(aq)] mol kg^{-1}

Henry's Law states that the solubility of a gas is proportional to its overlying partial pressure.

Example: The value of K_H for CO_2 at 24ºC is 29 x 10^{-3} moles kg^{-1} atm^{-1}. The partial pressure of CO_2 in the atmosphere is 350 ppm, or 350 x 10^{-6} atm.

The concentration of CO_2 in water in equilibrium with that partial pressure is:

$$[CO_2(aq)] = K_H \times P_A$$

$K_H \times P_A = 29 \times 10^{-3}$ moles kg^{-1} atm^{-1} x 350 x 10^{-6} atm = 10.15 x 10^{-6} moles kg^{-1} = 10.15 µM

Bunson Coefficients

Since oceanographers frequently deal with gas concentrations not only in molar units but also in ml / l, we can also define

$$[A(aq)] = \alpha\, P_A$$

where α = 22,400 x K_H (e.g., one mol of gas occupies 22,400 cm^3 at STP)

α is called the Bunsen solubility coefficient. Its units are cm^3 mol^{-1}.

Solubility of gases is a function of their molecular weight, temperature and salinity.

Rates of Gas Exchange

There are many situations for which we'd like to know the rate of gas exchange to estimate the time for gases to reach equilibrium.

The transfer of gases between the ocean and atmosphere is important for understanding:

1- The influence of the ocean on atmospheric chemistry

2- The fate of anthropogenic gases and their utility as tracers of ocean circulation

3- The relationships between heat transfer and gas transfer

There are many models of gas transfer, and most assume that the final process of exchange is governed by molecular diffusion across a thin layer at the air-water interface. The simplest physical paradigm is **The Stagnant Film Model.**

Because D/Z has velocity units, it has been called the **Piston Velocity** or mass transfer velocity. Typical values for are $D = 1 \times 10^{-5}\ cm^2\ sec^{-1}$ and for Z_{film} = 10 to 60 μm

Example: $D = 1 \times 10^{-5}\ cm^2\ sec^{-1}$, Z_{film} = 17 μm (= 17 x 10-6 m = 1.7×10^{-3} cm)

The piston velocity = $D/Z = 1 \times 10^{-5} / 1.7 \times 10^{-3} = 0.59 \times 10^{-2}\ cm\ sec^{-1} \sim 5\ m\ day^{-1}$

Each day a 5 m thick layer of water will exchange its gas with the atmosphere.

For a 100 m thick mixed layer the exchange will be completed every 20 days.