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CONSERVATIVE ELEMENTS

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Introduction

If 1 kg of sea water is evaporated and ignited according to a special procedure 35 g of solids are obtained. This is the normal (standard) salinity. Since the salinity is mainly changed by evaporation or by dilution with practically ion-free rain water the composition of the major ions in sea water is not changed by such processes. These constituents are considered to be conservative, and as a consequence their ratios are constant. Thus the concentration of a conservative constituent (element) at a salinity *S* is obtained by multiplying the values in Table 1 by *S*/35.

Determinations

The salinity can be determined with five significant figures from conductivity measurements as well as

by potentiometric titration of chloride + bromide in *m* g of sea water with *v* ml of *t* molar silver nitrate. Thereby the chlorinity is given by:

$$Cl = vt \cdot 107.87 \cdot 328.5233 / 1000m$$

where 107.87*vt*/1000 represents the mass in grams of pure silver that is necessary to precipitate the halogens in 328.5233 g of sea water. The relationship between salinity and chlorinity is:

$$S = 1.80655Cl$$

Sodium cannot be determined with four significant figures and the value in Table 1 has been calculated from the ion balance

$$\sum n[X^{n+}] = \sum n[X^{n-}]$$

Potassium can be determined gravimetrically with a precision of 0.26% by precipitation with sodium tetraphenylborate.

Calcium (+ strontium) and magnesium can be determined with four significant figures by titration procedures.

Table 1 The major constituents of average sea water with a salinity of 35

Constituent	<i>g kg⁻¹ sea water</i>	<i>mol kg⁻¹ sea water</i>
Sodium (Na ⁺)	10.76	0.4680
Potassium (K ⁺)	0.3992	0.01021
Magnesium (Mg ²⁺)	1.292	0.05315
Calcium (Ca ²⁺)	0.4128	0.01030
Strontium (Sr ²⁺)	0.00815	0.000093
Fluoride (F ⁻)	0.00141	0.000074
Chloride (Cl ⁻)	19.344	0.54563
Bromide (Br ⁻)	0.06712	0.00084
Sulfate (SO ₄ ²⁻)	2.712	0.02823
Alkalinity (A _t)	(0.143) ^a	0.00234 ^b
Boron (B)	0.00445	0.000412

^aCalculated from HCO₃⁻, the principle base.

^bMol HCl kg⁻¹ needed to titrate all bases to pH 4.5.

Strontium may be determined with three significant figures by various procedures.

Fluoride can be determined with three significant figures using a fluoride electrode. Otherwise, the recommended procedure is a spectrophotometric determination with lanthanum alizarin complexone.

Sulfate may be determined gravimetrically with a precision of 0.14% using precipitation of barium sulfate.

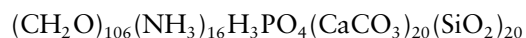
Boric acid, B(OH)₃, together with borate, B(OH)₄⁻, may be determined with three significant figures by the spectrophotometric curcumin method.

Alkalinity is determined by titration with hydrochloric acid of the main basic constituent, HCO₃⁻, together with minor basic components such as CO₃²⁻, B(OH)₄⁻, SiO(OH)₃⁻, H₂PO₄⁻, and HPO₄²⁻. It can be determined with four significant figures.

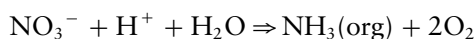
When accurate methods are used for the determinations of the main constituents slight deviations from a conservative behavior may be detected. The deviations, which are due to some fundamental processes, will be discussed below.

Plankton Production

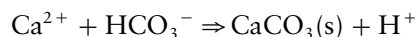
Plankton production involves the formation of hard parts (biogenic calcium carbonate and biogenic opal) in addition to soft material. The stoichiometry varies around:



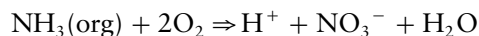
With this stoichiometry the increase in alkalinity due to the uptake of nitrate



is almost balanced by the biogenic formation of calcium carbonate



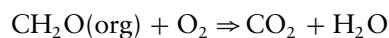
However, when the production sinks below the euphotic zone the soft parts deteriorate



lowering the increase in alkalinity due to the dissolution of calcium carbonate



The CO₂ is supplied by microbial decomposition of carbohydrates

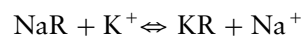


In the past, the alkalinity (A_t) was considered to be a conservative property of sea water. With high precision titration techniques variations in A_tS/35 can be measured, as well as in (Ca_t + Sr_t)S/35.

The most important carbonate-secreting organisms in the oceans are foraminifera, coccolithophorides, and pteropods. The carbonate tests vary in size, appearance, crystal form (calcite or aragonite), and magnesium content. The solubility depends on the depth (pressure), temperature, and concentration of CO₂ besides the crystal form. For example, the pteropods which secrete shells of aragonite undergo dissolution at shallower depths than the coccolithophorides which secrete calcite shells.

River Inputs

The river inputs into the oceans vary between the oceans. Ten percent of the total inflow of 10⁶ m³ s⁻¹ (1 Sverdrup, Sv) flows into the Arctic Ocean, whereby the normalized alkalinity (A_tS/35) is increased in the outflow along the east coast of Greenland. The average composition of the major ions in river water is presented in Table 2. The ratios are quite different from the ratios for the major elements in sea water that may be calculated from the concentrations in Table 1. For example, the Na/K ratio in river water is 5.2 while the ratio in sea water is 46. This is most likely due to ion exchange with the sediments:



where R represents an aluminosilicate.

Table 2 World average major ions and silica drained into the oceans

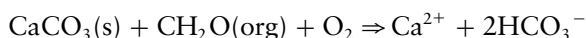
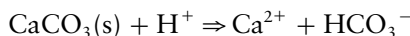
Constituent	Concentration (mmol l ⁻¹)
Sodium (Na ⁺)	0.252
Potassium (K ⁺)	0.0486
Calcium (Ca ²⁺)	0.353
Magnesium (Mg ²⁺)	0.148
Chloride (Cl ⁻)	0.192
Sulfate (SO ₄ ²⁻)	0.104
Hydrogen carbonate (HCO ₃ ⁻)	0.902
Silica (Si(OH) ₄)	0.198

Ion balance: $\sum n[X^{n+}] = \sum n[X^{n-}] = 1.302 \text{ meq l}^{-1}$

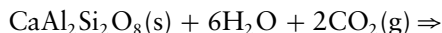
The ratio between magnesium and calcium is 0.42 in river water, but 5.2 in sea water. This may be explained by the fact that the organisms use only small amounts of magnesium, while the biogenic formation of calcium carbonate is a major process. The average ratios of SO₄²⁻/Cl⁻ and HCO₃⁻/Cl⁻ are 0.54 and 4.7 in river water; and 0.052 and 0.0043 in sea water. Only small amounts of sulfate are used by the organisms to produce essential sulfur-containing compounds, but when sea water reacts with hot basalt in rift zones sulfate is removed (see below). Hydrogen carbonate is removed upon the formation of biogenic calcium carbonate (see above).

The rivers also carry clay minerals into the ocean. The cation exchange capacity corresponds to $5.2 \cdot 10^{15} \text{ meq y}^{-1}$. This may be compared with the river input of cations of $41 \cdot 10^{15} \text{ meq y}^{-1}$ (1.302 meq l^{-1} from Table 2 in a flow of $10^6 \text{ m}^3 \text{ s}^{-1}$). In the ocean the sodium, potassium, and magnesium displace calcium in the clay minerals by ion exchange.

Man is changing the composition of river waters. Besides pollutants and an increase of particulate matter, acid rain and increased concentration of carbon dioxide in the atmosphere causes the following reactions, especially with limestone in southern Europe:



This has caused an increase in the normalized calcium concentration as well as the normalized alkalinity in the Baltic Sea. Weathering of silicate rocks is also dependent on the partial pressure of CO₂ in the atmosphere, for example:



Hot vents

About $5000 \text{ m}^3 \text{ s}^{-1}$ of sea water reacts with fresh hot basalt in the rift zones. Hydrothermal reactions produce large changes in the composition of the sea salts. The reactions lead to a loss of magnesium, sulfate, and fluoride, but to an addition of calcium and potassium. The hydrothermal activity balances some of the river inputs and contributes to maintenance of the steady state and the conservation of the constant composition of sea salts.

If the hot vent lies in a depression such as the Atlantis II Deep in the Red Sea, the results of the hydrothermal reactions are very evident (see Figure 1). Water is removed together with magnesium and sulfate, and calcium is released from the basalt. Rock salt (NaCl), anhydrite (CaSO₄), and silica (SiO₂) are formed and the brine becomes saturated with these solids. Sulfide metals are coprecipitated with iron sulfide (FeS).

Brines are also formed upon the formation of sea ice in polar regions; thereby calcium carbonate and calcium sulfate are precipitated. These processes also occur upon evaporation of sea water, e.g. for the production of sodium chloride.

Marine aerosols

Marine aerosols are formed by bursting of air bubbles at the sea's surface. Although some separations of the main constituents might occur by this process, the fallout of sea salts over the continents is in the order of 10^9 tons y^{-1} . Since the weight of the sea salts in the oceans is in the order of $13 \cdot 10^{17} \text{ tons}$ the recycling time would be 1300 million years (My). The residence times calculated from the river inputs are 210 My for sodium and 100 My for

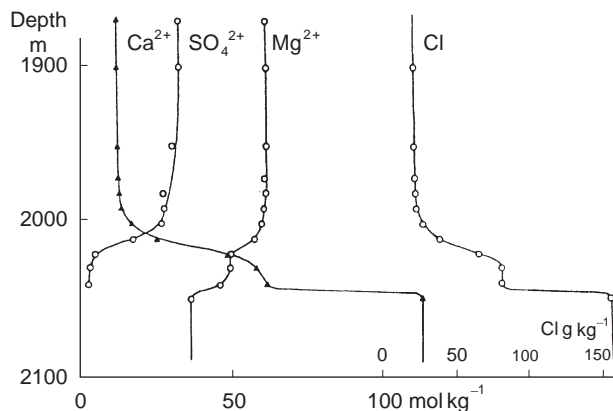


Figure 1 Depth profiles of chlorinity (Cl, g kg⁻¹), calcium, magnesium and sulfate (mol kg⁻¹) in the Red Sea Atlantis II deep on 22–23 March 1976.

chloride. This implies that weathering influences the concentrations of the major ions in the runoff from the continents.

Minor Constituents

Some minor constituents show a conservative type of distribution in the oceans. They are the alkali ions Li^+ , Rb^+ , and Cs^+ , besides MoO_4^{2-} and Tl^+ . Obviously, the organisms only use small amounts of molybdenum. However, in waters with anoxic basins (some fiords and the Black Sea), molybdate is depleted. In addition, WO_4^{2-} , ReO_4^{2-} , and U(VI) show conservative-type oceanic distributions.

Conclusions

The major constituents of sea water are present in practically constant proportions. The main ions include the alkali ions Na^+ and K^+ and the alkaline earth ions Mg^{2+} and Ca^{2+} , in addition to chloride (Cl^-) and sulfate (SO_4^{2-}). Their concentrations are also proportional to the salinity. In spite of the weathering and recycling processes and the hydrothermal reactions with hot basalt in rift zones there are only slight perturbations of the steady state. Deviations from a conservative behavior may be detected by accurate analytical methods and studies of ancient marine waters.

See also

Breaking Waves and Near-surface Turbulence. Calcium Carbonates. Carbon Cycle. Copepods. Dispersion from Hydrothermal Vents. Freshwater

Transport and Climate. Hydrothermal Vent Deposits. Hydrothermal Vent Fluids, Chemistry of. Ice–Ocean Interaction. Iron Fertilization. Nitrogen Cycle. Open Ocean Convection. Plankton. River Inputs. Stable Carbon Isotope Variations in the Ocean. Water Types and Water Masses.

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CONTINUOUS PLANKTON RECORDERS

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Introduction

The Continuous Plankton Recorder (CPR) survey is a synoptic survey of upper-layer plankton covering much of the northern North Atlantic and North Sea. It is the longest running and the most geographically extensive of any routine biological survey of the oceans. Over 4 000 000 miles of towing have resulted in the analysis of nearly 200 000 samples and the

routine identification of over 400 species/groups of plankton. Data from the survey have been used to study biogeography, biodiversity, seasonal and inter-annual variation, long-term trends, and exceptional events. The value of such an extensive time-series increases as each year's data are accumulated. Some recognition of the importance of the CPR survey was achieved in 1999 when it was adopted as an integral part of the Initial Observing System of the Global Ocean Observing System (GOOS).

History

The CPR prototype was designed by Alister Hardy for operation on the 1925-27 Discovery Expedition