

# Seawater



Clear ocean water near a beach on Grand Bahama Island in The Bahamas.

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**seawater**, water that makes up the oceans and seas, covering more than 70 percent of Earth's surface.

Seawater is a complex mixture of 96.5 percent water, 2.5 percent salts, and smaller amounts of other substances, including dissolved inorganic and organic materials, particulates,

and a few atmospheric gases.

Seawater constitutes a rich source of various commercially important chemical elements. Much of the world's magnesium is recovered from seawater, as are large quantities of bromine. In certain parts of the world, sodium chloride (table salt) is still obtained by evaporating seawater. In addition, water from the sea, when desalted, can furnish a limitless supply of drinking water. Many large desalination plants have been built in dry areas along seacoasts in the Middle East and elsewhere to relieve shortages of fresh water.

## CHEMICAL AND PHYSICAL PROPERTIES OF SEAWATER

The six most abundant ions of seawater are chloride ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), sulfate ( $\text{SO}_4^{2-}$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), and potassium ( $\text{K}^+$ ). By weight these ions make up about 99 percent of all sea salts. The amount of these salts in a volume of seawater varies because of the addition or removal of water locally (e.g., through precipitation and evaporation). The salt content in seawater is indicated by salinity ( $S$ ), which is defined as the amount of salt in grams dissolved in one kilogram of seawater and expressed in parts per thousand. Salinities in the open ocean have been observed to range from about 34 to 37 parts per thousand (0/00 or ppt), which may also be expressed as 34 to 37 practical salinity units (psu).

Inorganic carbon, bromide, boron, strontium, and fluoride constitute the other major dissolved substances of seawater. Of the many minor dissolved chemical constituents, inorganic phosphorus and inorganic nitrogen are among the most notable, since they are important for the growth of organisms that inhabit the oceans and seas. Seawater also contains various dissolved atmospheric gases, chiefly nitrogen, oxygen, argon, and carbon dioxide. Some other components of seawater are dissolved organic substances, such as carbohydrates and amino

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acids, and organic-rich particulates. These materials originate primarily in the upper 100 metres (330 feet) of the ocean, where dissolved inorganic carbon is transformed by photosynthesis into organic matter.

Many of the characteristics of seawater correspond to those of water in general, because of their common chemical and physical properties. For example, the molecular structure of seawater, like that of fresh water, favours the formation of bonds among molecules. Some of the distinctive qualities of seawater are attributable to its salt content. The viscosity (i.e., internal resistance to flow) of seawater, for example, is higher than that of fresh water because of its higher salinity. The density of seawater also is higher for the same reason. Seawater's freezing point is lower than that of pure water, and its boiling point is higher.

## **CHEMICAL COMPOSITION**

The chemical composition of seawater is influenced by a wide variety of chemical transport mechanisms. Rivers add dissolved and particulate chemicals to the oceanic margins. Wind-borne particulates are carried to mid-ocean regions thousands of kilometres from their continental source areas. Hydrothermal solutions that have circulated through crustal materials beneath the seafloor add both dissolved and particulate materials to the deep ocean. Organisms in the upper ocean convert dissolved materials to solids, which eventually settle to greater oceanic depths. Particulates in transit to the seafloor, as well as materials both on and within the seafloor, undergo chemical exchange with surrounding solutions. Through these local and regional chemical input and removal mechanisms, each element in the oceans tends to exhibit spatial and temporal concentration variations. Physical mixing in the oceans (thermohaline and wind-driven circulation) tends to homogenize the chemical composition of seawater. The opposing influences of physical mixing and of biogeochemical input and removal mechanisms result in a substantial variety of chemical distributions in the oceans.

## **DISSOLVED INORGANIC SUBSTANCES**

The principal components of seawater are listed in the table.

## Principal constituents of seawater\*

ionic constituent	g/kg of seawater	moles/kg**	relative concentration
chloride	19.162	0.5405	1.0000
sodium	10.679	0.4645	0.8593
magnesium	1.278	0.0526	0.0974
sulfate	2.680	0.0279	0.0517
calcium	0.4096	0.01022	0.0189
potassium	0.3953	0.01011	0.0187
carbon (inorganic)	0.0276	0.0023	0.0043
bromide	0.0663	0.00083	0.00154
boron	0.0044	0.00041	0.00075
strontium	0.0079	0.00009	0.000165
fluoride	0.0013	0.00007	0.000125

\*Concentrations at salinity equal to 34.7.

\*\*Ionic concentrations are conventionally expressed in molecular units. One mole per kilogram is equivalent to  $6.023(10^{23})$  ions or molecules per kilogram of seawater. The relative concentrations in column 4 provide the number of ions of each constituent in one kilogram of seawater as compared to the number of chloride ions in one kilogram of seawater.

In contrast to the behaviour of most oceanic substances, the concentrations of the principal inorganic constituents of the oceans are remarkably constant. Calculations indicate that, for the main constituents of seawater, the time required for thorough oceanic mixing is quite short compared with the time that would be required for input or removal processes to significantly change a constituent's concentration. The concentrations of the principal constituents of the oceans vary primarily in response to a comparatively rapid exchange of water (precipitation and evaporation), with relative concentrations remaining nearly constant.

Salinity is used by oceanographers as a measure of the total salt content of seawater. Practical salinity, symbol  $S$ , is determined through measurements of the electrical conductivity and temperature of seawater, which are interpreted by an algorithm developed by the United Nations Educational Scientific and Cultural Organization (UNESCO). Practical salinity, along with temperature, can be used to calculate precisely the density of seawater samples. Because of the constant relative proportions of the principal constituents, salinity can also be used to directly calculate the concentrations of the major ions in seawater. The measure of practical salinity was originally developed to provide an approximate measure of the total mass of salt in

one kilogram of seawater. Seawater with  $S$  equal to 35 contains approximately 35 grams of salt and 965 grams of water, or 35 ppt (35 psu).

Many other constituents are of great importance to the biogeochemistry of the oceans. Such chemicals as inorganic phosphorus ( $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) and inorganic nitrogen ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ ) are essential to the growth of marine organisms. Nitrogen and phosphorus are incorporated into the tissues of marine organisms in approximately a 16:1 ratio and are eventually returned to solution in approximately the same proportion. As a consequence, in much of the oceanic waters dissolved inorganic phosphorus and nitrogen exhibit a close covariance. Dissolved inorganic phosphorus distributions in the Pacific Ocean strongly bear the imprint of phosphorus incorporation by organisms in the surface waters of the ocean and of the return of the phosphorus to solution via a rain of biological debris remineralized in the deep ocean. Inorganic phosphate concentrations in the western Pacific range from somewhat less than 0.1 micromole/kg ( $1 \times 10^{-7}$  mole/kg) at the surface to approximately 3 micromoles/kg ( $3 \times 10^{-6}$  mole/kg) at depth. Inorganic nitrogen ranges between somewhat less than 1 micromole/kg and 45 micromoles/kg along the same section of ocean and exhibits a striking covariance with phosphate.

A variety of elements essential to the growth of marine organisms, as well as some elements that have no known biological function, exhibit nutrient-like behaviour broadly similar to nitrate and phosphate. Silicate is incorporated into the hard structural parts of certain types of marine organisms (diatoms and radiolarians) that are abundant in the upper ocean. Dissolved silicate concentrations range between less than 1 micromole/kg ( $1 \times 10^{-6}$  mole/kg) in surface waters to approximately 180 micromoles/kg ( $1.8 \times 10^{-4}$  mole/kg) in the deep North Pacific. The concentration of zinc, a metal essential to a variety of biological functions, ranges between approximately 0.05 nanomole/kg ( $5 \times 10^{-11}$  mole/kg) in the surface ocean to as much as 6 nanomoles/kg ( $6 \times 10^{-9}$  mole/kg) in the deep Pacific. The distribution of zinc in the oceans is observed to generally parallel silicate distributions. Cadmium, though having no known biological function, generally exhibits distributions that are covariant with phosphate and concentrations that are even lower than those of zinc.

Many elements, including the essential trace metals iron, cobalt, and copper, show surface depletions but in general exhibit behaviour more complex than that of phosphate, nitrate, and silicate. Some of the complexities observed in elemental oceanic distributions are attributable to the adsorption of elements on the surface of sinking particles. Adsorptive processes, either exclusive of or in addition to biological uptake, serve to remove elements from the upper ocean and deliver them to greater depths. The distribution patterns of a number of trace elements are complicated by their participation in oxidation-reduction (electron-exchange) reactions. In general, electron-exchange reactions lead to profound changes in the solubility

and reactivity of trace metals in seawater. Such reactions are important to the oceanic behaviour of a variety of elements, including iron, manganese, copper, cobalt, chromium, and cerium.

The processes that deliver dissolved, particulate, and gaseous materials to the oceans ensure that they contain, at some concentration, very nearly every element that is found in Earth's crust and atmosphere. The principal components of the atmosphere, nitrogen (78.08 percent), oxygen (20.95 percent), argon (0.93 percent), and carbon dioxide (0.038 percent), occur in seawater in variable proportions, depending on their solubilities and oceanic chemical reactions. In equilibrium with the atmosphere, the concentrations of the unreactive gases, nitrogen and argon, in seawater (0 °C [32 °F], salinity 35) are 616 micromoles/kg and 17 micromoles/kg, respectively. For seawater at 35 °C (95 °F), these concentrations would decrease by approximately a factor of two. The solubility behaviours of argon and oxygen are quite similar. For seawater in equilibrium with the atmosphere, the ratio of oxygen and argon concentrations is approximately 20:45. Since oxygen is a reactive gas essential to life, oxygen concentrations in seawater that are not in direct equilibrium with the atmosphere are quite variable. Although oxygen is produced by photosynthetic organisms at shallow, sunlit ocean depths, oxygen concentrations in near-surface waters are established primarily by exchange with the atmosphere. Oxygen concentrations in the oceans generally exhibit minimum values at intermediate depths and relatively high values in deep waters. This distribution pattern results from a combination of biological oxygen utilization and physical mixing of the ocean waters. Estimates of the extent of oxygen utilization in the oceans can be obtained by comparing concentrations of oxygen with those of argon, since the latter are only influenced by physical processes. The physical processes that influence oxygen distributions include, in particular, the large-scale replenishment of oceanic bottom waters with cold, dense, oxygen-rich waters sinking toward the bottom from high latitudes. Due to the release of nutrients that accompanies the consumption of oxygen by biological debris, dissolved oxygen concentrations generally appear as a mirror image of dissolved nutrient concentrations.

While the atmosphere is a vast repository of oxygen compared with the oceans, the total carbon dioxide content of the oceans is very large compared with that of the atmosphere. Carbon dioxide reacts with water in seawater to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ions ( $\text{HCO}_3^-$ ), and carbonate ions ( $\text{CO}_3^{2-}$ ). Approximately 90 percent of the total organic carbon in seawater is present as bicarbonate ions. The formation of bicarbonate and carbonate ions from carbon dioxide is accompanied by the liberation of hydrogen ions ( $\text{H}^+$ ). Reactions between hydrogen ions and the various forms of inorganic carbon buffer the acidity of seawater. The relatively high concentrations of both total inorganic carbon and boron—as  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ —in seawater are sufficient to maintain the pH of seawater between 7.4 and 8.3. (The term pH is defined as the negative logarithm of the hydrogen ion concentration in moles per

kilogram. Thus, a pH equal to 8 is equivalent to  $1 \times 10^{-8}$  mole of  $H^+$  ions per kilogram of seawater.) This is quite important because the extent and rate of many reactions in seawater are highly pH-dependent. Carbon dioxide produced by the combination of oxygen and organic carbon generally produces an acidity maximum (pH minimum) near the depth of the oxygen minimum in seawater. In addition to exchange with the atmosphere and, through respiration, with the biosphere, dissolved inorganic carbon concentrations in seawater are influenced by the formation and dissolution of the calcareous shells ( $CaCO_3$ ) of organisms (foraminiferans, coccolithophores, and pteropods) abundant in the upper ocean.

## DISSOLVED ORGANIC SUBSTANCES

Processes involving dissolved and particulate organic carbon are of central importance in shaping the chemical character of seawater. Marine organic carbon principally originates in the uppermost 100 metres of the oceans where dissolved inorganic carbon is photosynthetically converted to organic materials. The "rain" of organic-rich particulate materials, resulting directly and indirectly from photosynthetic production, is a principal factor behind the distributions of many organic and inorganic substances in the oceans. A large fraction of the vertical flux of materials in the uppermost waters is converted to dissolved substances within the upper 400 metres (about 1,300 feet) of the oceans. Dissolved organic carbon (DOC) accounts for at least 90 percent of the total organic carbon in the oceans. Estimates of DOC appropriate to the surface of the open ocean range between roughly 100 and 500 micromoles of carbon per kilogram of seawater. DOC concentrations in the deep ocean are 5 to 10 times lower than surface values. DOC occurs in an extraordinary variety of forms, and, in general, its composition is controversial and poorly understood. Conventional techniques have indicated that, in surface waters, about 15 percent of DOC can be identified as carbohydrates and combined amino acids. At least 1-2 percent of DOC in surface waters occurs as lipids and 20-25 percent as relatively unreactive humic substances. The relative abundances of reactive organic substances, such as amino acids and carbohydrates, are considerably reduced in deep ocean waters. Dissolved and particulate organic carbon in the surface ocean participates in diel cycles (i.e., those of a 24-hour period) related to photosynthetic production and photochemical transformations. The influence of dissolved organic matter on ocean chemistry is often out of proportion to its oceanic abundance. Photochemical reactions involving DOC can influence the chemistry of vital trace nutrients such as iron, and, even at dissolved concentrations on the order of one nanomole/kg ( $1 \times 10^{-9}$  mole/kg), dissolved organic substances in the upper ocean waters are capable of greatly altering the bioavailability of essential trace nutrients, as, for example, copper and zinc.

## EFFECTS OF HUMAN ACTIVITIES

Although the oceans constitute an enormous reservoir, human activities have begun to influence their composition on both a local and a global scale. The addition of nutrients (through the discharge of untreated sewage or the seepage of soluble mineral fertilizers, for example) to coastal waters results in increased phytoplankton growth, high levels of dissolved and particulate organic materials, decreased penetration of light through seawater, and alteration of the community structure of bottom-dwelling organisms. Through industrial and automotive emissions, lead concentrations in the surface ocean have increased dramatically on a global scale compared with preindustrial levels. Certain toxic organic compounds, such as polychlorinated biphenyls (PCBs), are found in seawater and marine organisms and are attributable solely to the activities of humankind. Although most radioactivity in seawater is natural (approximately 90 percent as potassium-40 and less than 1 percent each as rubidium-87 and uranium-238), strontium-90 and certain other artificial radioisotopes have unique environmental pathways and potential for bioaccumulation (that is, concentration in higher levels of the food chain).

Among the most dramatic influences of human activities on a global scale is the remarkable increase of carbon dioxide levels in the atmosphere. Atmospheric carbon dioxide levels are expected to surpass 420 parts per million by volume by the middle of the 21st century, with potentially profound consequences for global climate and agricultural patterns. It is thought that the oceans, as a great reservoir of carbon dioxide, will ameliorate this consequence of human activities to some degree. However, ocean acidification due to the absorption of carbon dioxide is an emerging environmental problem. (For more specific information on how rising levels of carbon dioxide affect Earth's climate, see global warming.)

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## **SALINITY DISTRIBUTION**

A discussion of salinity, the salt content of the oceans, requires an understanding of two important concepts: (1) the present-day oceans are considered to be in a steady state, receiving as much salt as they lose, and (2) the oceans have been mixed over such a long time period that the composition of sea salt is the same everywhere in the open ocean. This uniformity of salt content results in oceans in which the salinity varies little over space or time.

The range of salinity observed in the open ocean is from 33 to 37 grams of salt per kilogram of seawater or psu. For the most part, the observed departure from a mean value of approximately 35 psu is caused by processes at Earth's surface that locally add or remove fresh water. Regions of high evaporation have elevated surface salinities, while regions of high precipitation have depressed surface salinities. In nearshore regions close to large freshwater sources, the salinity may be lowered by dilution. This is especially true in areas where the

region of the ocean receiving the fresh water is isolated from the open ocean by the geography of the land.

Areas of the Baltic Sea may have salinity values depressed to 10 psu or less. Increased salinity by evaporation is accentuated where isolation of the water occurs. This effect is found in the Red Sea, where the surface salinity rises to 41 psu. Coastal lagoon salinities in areas of high evaporation may be much higher. The removal of fresh water by evaporation or the addition of fresh water by precipitation does not affect the constancy of composition of the sea salt in the open sea. A river draining a particular soil type, however, may bring to the oceans only certain salts that will locally alter the salt composition. In areas of high evaporation where the salinity is driven to very high values, precipitation of particular salts may alter the composition too. At high latitudes where sea ice forms seasonally and icebergs are often released into the open ocean, the salinity of the seawater is reduced when ice melts and is elevated during ice formation. This saltier water can then sink down into the deep ocean (see density current).

At depth in the oceans, salinity may be altered as seawater percolates into fissures associated with deep-ocean ridges and crustal rifts involving volcanism. This water then returns to the ocean as superheated water carrying dissolved salts from the magmatic material within the crust. It may lose much of its dissolved load to precipitates on the seafloor and gradually blend in with the surrounding seawater, sharing its remaining dissolved substances.

Salt concentrations as high as 256 psu have been found in hot but dense pools of brine trapped in depressions at the bottom of the Red Sea. The composition of the salts in these pools is not the same as the sea salt of the open oceans.

The salinities found at the greater depths of the open oceans are quite uniform in both time and space with average values of 34.5 to 35 psu. These salinities are determined by surface processes such as those described above when the water, now at depth, was last in contact with the surface.

The intertropical convergence, with its high precipitation centred about 5° N, supports the tropical rainforests of the world and leaves its imprint on the oceans as a latitudinal depression of surface salinity. At approximately 30°–35° N and 30°–35° S, the subtropical zones called the horse latitudes are belts of high evaporation that produce major deserts and grasslands on the continents and cause the surface salinity to rise. At 50°–60° N and 50°–60° S, precipitation again increases.

## TEMPERATURE DISTRIBUTION

Mid-ocean surface temperatures vary with latitude in response to the balance between incoming solar radiation and outgoing longwave radiation. There is an excess of incoming solar radiation at latitudes less than approximately 45° and an excess of radiation loss at latitudes higher than approximately 45°. Superimposed on this radiation balance are seasonal changes



in the intensity of solar radiation and the duration of daylight hours due to the tilt of Earth's axis to the plane of the ecliptic and the rotation of the planet about this axis. The combined effect of these variables is that average ocean surface temperatures are higher at low latitudes than at high latitudes. Because the Sun, with respect to Earth, migrates annually between the Tropic of Cancer and the Tropic of Capricorn, the yearly change in heating of Earth's surface is small at low latitudes and large at mid- and higher latitudes.

Water has an extremely high heat capacity, and heat is mixed downward during summer surface-heating conditions and upward during winter surface cooling. This heat transfer reduces the actual change in ocean surface temperatures over the annual cycle. In the tropics the ocean surface is warm year-round, varying seasonally about 1 to 2 °C (1.8 to 3.6 °F). At midlatitudes the mid-ocean temperatures vary about 8 °C (14.4 °F) over the year. At the polar latitudes the surface temperature remains near the freezing point of seawater, about -1.9 °C (28.6 °F).

Land temperatures have a large annual range at high latitudes because of the low heat capacity of the land surface. Proximity to land, isolation of water from the open ocean, and processes that control stability of the surface water combine to increase the annual range of nearshore ocean surface temperature.

In winter the prevailing winds carry cold air masses off the continents in temperate and subarctic latitudes, cooling the adjacent surface seawater below that of the mid-ocean level. In summer the opposite effect occurs, as warm continental air masses move out over the adjacent sea. This creates a greater annual range in sea surface temperatures at midlatitudes on the western sides of the oceans of the Northern Hemisphere but has only a small effect in the Southern Hemisphere, as there is little land present. Instead, the oceans of the Southern Hemisphere act to control the air temperature, which in turn influences the land temperatures of the temperate zone and reduces the annual temperature range over the land.

Ocean currents carry water having the characteristics of one latitudinal zone to another zone. The northward displacement of warm water to higher latitudes by the Gulf Stream of the North Atlantic and the Kuroshio (Japan Current) of the North Pacific creates sharp changes in temperature along the current boundaries or thermal fronts, where these northward-moving flows meet colder water flowing southward from higher latitudes. Cold water currents flowing from higher to lower latitudes also displace surface isotherms from near constant latitudinal positions. At low latitudes the trade winds act to move water away from the lee coasts of the landmasses to produce areas of coastal upwelling of water from depth and reduce surface temperatures.

Temperatures in the oceans decrease with increasing depth. There are no seasonal changes at the greater depths. The temperature range extends from 30 °C (86 °F) at the sea surface to -1 °C (30.2 °F) at the seabed. Like salinity, the temperature at depth is determined by the conditions

that the water encountered when it was last at the surface. In the low latitudes the temperature change from top to bottom in the oceans is large. In high temperate and Arctic regions, the formation of dense water at the surface that sinks to depth produces nearly isothermal conditions with depth.

Areas of the oceans that experience an annual change in surface heating have a shallow wind-mixed layer of elevated temperature in the summer. Below this nearly isothermal layer 10 to 20 metres (33 to 66 feet) thick, the temperature decreases rapidly with depth, forming a shallow seasonal thermocline (i.e., layer of sharp vertical temperature change). During winter cooling and increased wind mixing at the ocean surface, convective overturning and mixing erase this shallow thermocline and deepen the isothermal layer. The seasonal thermocline re-forms when summer returns. At greater depths a weaker nonseasonal thermocline is found separating water from temperate and subpolar sources.

Below this permanent thermocline, temperatures decrease slowly. In the very deep ocean basins, the temperature may be observed to increase slightly with depth. This occurs when the deepest parts of the oceans are filled by water with a single temperature from a common source. This water experiences an adiabatic temperature rise as it sinks. Such a temperature rise does not make the water column unstable, because the increased temperature is caused by compression, which increases the density of the water. For example, surface seawater of 2 °C (35.6 °F) sinking to a depth of 10,000 metres (about 33,000 feet) increases its temperature by about 1.3 °C (2.3 °F). When measuring deep-sea temperatures, the adiabatic temperature rise, which is a function of salinity, initial temperature, and pressure change, is calculated and subtracted from the observed temperature to obtain the potential temperature. Potential temperatures are used to identify a common type of water and to trace this water back to its source.

## THERMAL PROPERTIES

The unit of heat called the gram calorie is defined as the amount of heat required to raise the temperature of one gram of water 1 °C. The kilocalorie, or food calorie, is the amount of heat required to raise one kilogram of water 1 °C. Heat capacity is the amount of heat required to raise one gram of material 1 °C under constant pressure. In the International System of Units (SI), the heat capacity of water is one kilocalorie per kilogram per degree Celsius. Water has the highest heat capacity of all common Earth materials; therefore, water on Earth acts as a thermal buffer, resisting temperature change as it gains or loses heat energy.

The heat capacity of any material can be divided by the heat capacity of water to give a ratio known as the specific heat of the material. Specific heat is numerically equal to heat capacity but has no units. In other words, it is a ratio without units. When salt is present, the heat

capacity of water decreases slightly. Seawater of 35 psu has a specific heat of 0.932 compared with 1.000 for pure water.

Pure water freezes at 0 °C and boils at 100 °C (212 °F) under normal pressure conditions. When salt is added, the freezing point is lowered and the boiling point is raised. The addition of salt also lowers the temperature of maximum density below that of pure water (4 °C [39.2 °F]). The temperature of maximum density decreases faster than the freezing point as salt is added.

At 24.70 psu salinity, the freezing point and the temperature of maximum density coincide at -1.332 °C (29.6 °F). At salinities typical of the open oceans, which are greater than 24.7 psu, the freezing point is always the temperature of maximum density.

When water changes its state, hydrogen bonds between molecules are either formed or broken. Energy is required to break the hydrogen bonds, which allows water to pass from a solid to a liquid state or from a liquid to a gaseous state. When hydrogen bonds are formed, permitting water to change from a liquid to a solid or from a gas to a liquid, energy is liberated. The heat energy input required to change water from a solid at 0 °C to a liquid at 0 °C is the latent heat of fusion and is 80 calories per gram of ice. Water's latent heat of fusion is the highest of all common materials. Because of this, heat is released when ice forms and is absorbed during melting, which tends to buffer air temperatures as land and sea ice form and melt seasonally.

When water converts from a liquid to a gas, a quantity of heat energy known as the latent heat of vaporization is required to break the hydrogen bonds. At 100 °C, 540 calories per gram of water are needed to convert one gram of liquid water to one gram of water vapour under normal pressure. Water can evaporate at temperatures below the boiling point, and ice can evaporate into a gas without first melting, in a process called sublimation. Evaporation below 100 °C and sublimation require more energy per gram than 540 calories. At 20 °C (68 °F) about 585 calories are required to vaporize one gram of water. When water vapour condenses back to liquid water, the latent heat of vaporization is liberated. The evaporation of water from Earth's surface and its condensation in the atmosphere constitute the single most important way that heat from Earth's surface is transferred to the atmosphere. This process is the source of the power that drives hurricanes and a principal mechanism for cooling the surface of the oceans. The latent heat of vaporization of water is the highest of all common substances.

## **DENSITY OF SEAWATER AND PRESSURE**

Seawater density values are listed in the table

## Density values of seawater\*

salinity	5	10	20	30	35
temperature (°C)					
0	3.97	8.01	16.07	24.10	28.13
5	4.01	7.97	15.86	23.74	27.70
10	3.67	7.56	15.32	23.08	26.97
15	3.01	6.85	14.50	22.15	25.99
20	2.07	5.86	13.42	20.98	24.78
25	0.87	4.62	12.10	19.60	23.36
30	-0.57	3.15	10.57	18.01	21.75

\*See text for density unit designation.

The density of a material is given in units of mass per unit volume and expressed in kilograms per cubic metre in the SI system of units. In oceanography the density of seawater has been expressed historically in grams per cubic centimetre. The density of seawater is a function of temperature, salinity, and pressure. Because oceanographers require density measurements to be accurate to the fifth decimal place, manipulation of the data requires writing many numbers to record each measurement. Also, the pressure effect can be neglected in many instances by using potential temperature. These two factors led oceanographers to adopt a density unit called sigma- $t$  ( $\sigma_t$ ). This value is obtained by subtracting 1.0 from the density and multiplying the remainder by 1,000. The  $\sigma_t$  has no units and is an abbreviated density of seawater controlled by salinity and temperature only. The  $\sigma_t$  of seawater increases with increasing salinity and decreasing temperature.

The relationship between pressure and density is demonstrated by observing the effect of pressure on the density of seawater at 35 psu and 0 °C. Because a one-metre (three-foot) column of seawater produces a pressure of about one decibar (0.1 atmosphere), the pressure in decibars is approximately equal to the depth in metres. (One decibar is one-tenth of a bar, which in turn is equal to  $10^5$  newtons per square metre.)

Values associated with the change in seawater density with depth are listed in the table.

## Density changes with depth (seawater 35 parts per thousand and 0 °C)

depth (m)	pressure (decibars)	density (g/cm <sup>3</sup> )
0	0	1.02813
1,000	1,000	1.03285
2,000	2,000	1.03747
4,000	4,000	1.04640
6,000	6,000	1.05495
8,000	8,000	1.06315
10,000	10,000	1.07104

Increasing density values demonstrate the compressibility of seawater under the tremendous pressures present in the deep ocean. If seawater were incompressible, each cubic centimetre of water in the water column would expand, and density values at all depths would be equal. If the average pressure occurring at a depth of 4,000 metres (about 13,100 feet, the approximate mean depth of the ocean) was somehow replaced with the average pressure that occurred at 2,000 metres (about 6,600 feet) and the area of the oceans remained constant, there would be an average sea level rise of about 36 metres (120 feet).

The temperature of maximum density and the freezing point of water decrease as salt is added to water, and the temperature of maximum density decreases more rapidly than the freezing point. At salinities less than 24.7 psu the density maximum is reached before the ice point, while at the higher salinities more typical of the open oceans the maximum density is never achieved naturally. For example, at 5 psu a density maximum is found between 0 and 10 °C (32 and 50 °F). (Its actual position is at 3 °C [37.4 °F], where the  $\sigma_t$  value is 4.04 for 5 psu.) This ability of low-salinity water and, of course, fresh water to pass through a density maximum makes them both behave differently from marine systems when water is cooled at the surface and density-driven overturn occurs.

During the fall a lake is cooled at its surface, the surface water sinks, and convective overturn proceeds as the density of the surface water increases with the decreasing temperature. By the time the surface water reaches 4 °C (39.2 °F), the temperature of maximum density for fresh water, the density-driven convective overturn has reached the bottom of the lake, and overturn ceases. Further cooling of the surface produces less dense water, and the lake becomes stably stratified with regard to temperature-controlled density. Only a relatively shallow surface layer is cooled below 4 °C. When this surface layer is cooled to the ice point, 0 °C, ice is formed as the

latent heat of fusion is extracted. In a deep lake the temperature at depth remains at 4 °C. In the spring the surface water warms up and the ice melts. A shallow convective overturn resumes until the lake is once more isothermal at 4 °C. Continued warming of the surface produces a stable water column.

In seawater in which the salinity exceeds 24.7 psu, convective overturn also occurs during the cooling cycle and penetrates to a depth determined by the salinity and temperature-controlled density of the cooled water. Since no density maximum is passed, the thermally driven convective overturn is continuous until the ice point is reached where sea ice forms with the extraction of the latent heat of fusion. Since salt is largely excluded from the ice in most cases, the salinity of the water beneath the ice increases slightly, and a convective overturn that is both salt- and temperature-driven continues as sea ice forms.

The continuing overturn requires that a large volume of water be cooled to a new ice point dictated by the salinity increase before additional ice forms. In this manner, very dense seawater that is both cold and of elevated salinity is formed. Such areas as the Weddell Sea in Antarctica produce the densest water of the oceans. This water, known as Antarctic Bottom Water, sinks to the deepest depths of the oceans. The continuing overturn slows the rate at which the sea ice forms, limiting the seasonal thickness of the ice. Other factors that control the thickness of ice are the rate at which heat is conducted through the ice layer and the insulation provided by snow on the ice. Seasonal sea ice seldom exceeds about 2 metres (about 7 feet) in thickness. During the warmer season, melting sea ice supplies a freshwater layer to the sea surface and thereby stabilizes the water column (*see sea ice*).

Surface processes that alter the temperature and salinity of seawater contribute to the process of driving the vertical circulation of the oceans. Known as thermohaline circulation, it continually replaces seawater at depth with water from the surface and slowly replaces surface water elsewhere with water rising from deeper depths.

## **OPTICAL PROPERTIES**

Water is transparent to the wavelengths of electromagnetic radiation that fall within the visible spectrum and is opaque to wavelengths above and below this band. However, once in the water, visible light is subject to both refraction and attenuation.

Light rays that enter the water at any angle other than a right angle are refracted (i.e., bent) because the light waves travel at a slower speed in water than they do in air. The amount of refraction, referred to as the refractive index, is affected by both the salinity and temperature of the water. The refractive index increases with increasing salinity and decreasing temperature. This relationship allows the refractive index of a sample of seawater at a constant temperature to be used to determine the salinity of the sample.

Some of the Sun's radiant energy is reflected at the ocean surface and does not enter the ocean. That which penetrates the water's surface is attenuated by absorption and conversion to other forms of energy, such as heat that warms or evaporates water, or is used by plants to fuel photosynthesis. Sunlight that is not absorbed can be scattered by molecules and particulates suspended in the water. Scattered light is deflected into new directional paths and may wander randomly to eventually be either absorbed or directed upward and out of the water. It is this upward-scattered light and the light reflected from particles that determine the colour of the oceans as seen from above.

Water molecules, dissolved salts, organic substances, and suspended particulates combine to cause the intensity of available solar radiation to decrease with depth. Observations of light attenuation in ocean waters indicate that not only does the intensity of solar radiation decrease with depth but also the wavelengths present in the solar spectrum are not attenuated at the same rates. Both short wavelengths (ultraviolet) and long wavelengths (infrared) are absorbed rapidly and are not available for scattering. Only blue-green wavelengths penetrate to any depth, and, because the blue-green light is most available for scattering, the oceans appear blue to the human eye. Changes in the colour of the ocean waters are caused either by the colour of the particulates in suspension and dissolved substances or by the changing quality of the solar radiation at the ocean surface as determined by the angle of the Sun and atmospheric conditions. In the clearest ocean waters only about 1 percent of the surface radiation remains at a depth of 150 metres (about 500 feet). No sunlight penetrates below 1,000 metres (about 3,300 feet).

There are many ways of measuring light attenuation in the oceans. A common method involves the use of a Secchi disk, a weighted round white disk about 30 cm (about 12 inches) in diameter. The Secchi disk is lowered into the ocean to the depth where it disappears from view; its reflectance equals the intensity of light backscattered from the water. This depth in metres divided into 1.7 yields an attenuation, or extinction, coefficient for available light as averaged over the Secchi disk depth. The light extinction coefficient,  $x$ , may then be used in a form of Beer's law,  $I_z = I_0 e^{-xz}$ , to estimate  $I_z$ , the intensity of light at depth  $z$  from  $I_0$ , the intensity of light at the ocean surface. This method gives no indication of the attenuation change with depth or the attenuation of specific wavelengths of light.

A photocell may be lowered into the ocean to measure light intensity at discrete depths and to determine light reduction from the surface value or from the previous depth value. The photocell may sense all available wavelengths or may be equipped with filters that pass only certain wavelengths of light. Since  $I_z$  and  $I_0$  are known, changing light intensity values may be used in Beer's law to determine how the attenuation coefficient changes with depth and quality of light. Measurements of this type are used to determine the level of photosynthesis as

a function of radiant energy level with depth and to measure changes in the turbidity of the water caused by particulate distribution with depth.

Values associated with the loss of light in one metre of seawater are presented in the table.

### Loss of light (percent) in one metre of seawater\*

	violet		blue-green			yellow	orange	red
<b>wavelength (micrometre)</b>	0.30	0.40	0.46	0.50	0.54	0.58	0.64	0.70
<b>oceanic water, most transparent</b>	16%	4%	2%	3%	5%	9%	29%	42%
<b>oceanic water, least transparent</b>	57%	16%	11%	10%	13%	19%	36%	55%
<b>coastal water, average</b>		63%	37%	29%	28%	30%	45%	74%

\*According to Jerlov.

Different areas of the oceans tend to have different optical properties. Near rivers, silt increases the suspended particle effect. Where nutrients and sunlight are abundant, phytoplankton (unicellular plants) increase the opacity of the water and lend it their colour. Organic substances from excretion and decomposition also have colour and absorb light.

Values associated with the change in sunlight reflectance with the Sun's elevation angle are listed in the table.

### Sunlight reflectance

<b>Sun's elevation angle (in degrees)</b>	90	50	40	30	20	10	5
<b>reflectance (percent)</b>	3	3	4	6	12	27	42

Solar radiation received at the ocean surface is constantly changing in time and space. Cloud cover, atmospheric dust, atmospheric gas composition, roughness of the ocean surface, and elevation angle of the Sun combine to change both the quality and quantity of light that enters the ocean. When the Sun's rays are perpendicular to a smooth ocean surface, reflectance is low. When the solar rays are oblique to the ocean surface, reflectance is increased. If the ocean is rough with waves, reflectance is increased when the Sun is at high elevation and decreased when it is at low elevation. Since latitude plays a role in the elevation of the Sun above the horizon, light penetration is always less at the higher latitudes. Cloud cover, density layering, fog, and dust cause refraction and atmospheric scattering of sunlight. When strongly scattered, the Sun's rays are not unidirectional, and there are no shadows. Light enters the ocean from all angles under this condition, and the elevation angle of the Sun loses its importance in controlling surface reflectance. Water is a good absorber of solar radiation,



and the solar energy available to penetrate the ocean is 100 percent minus its reflectance value.

## ACOUSTIC PROPERTIES

Water is an excellent conductor of sound, considerably better than air. The attenuation of sound by absorption and conversion to other energy forms is a function of sound frequency and the properties of water.

The attenuation coefficient,  $x$ , in Beer's law, as applied to sound, where  $I_z$  and  $I_0$  are now sound intensity values, is dependent on the viscosity of water and inversely proportional to the frequency of the sound and the density of the water. High-pitched sounds are absorbed and converted to heat faster than low-pitched sounds. Sound velocity in water is determined by the square root of elasticity divided by the water's density. Because water is only slightly compressible, it has a large value of elasticity and therefore conducts sound rapidly. Since both the elasticity and density of seawater change with temperature, salinity, and pressure, so does the velocity of sound.

In the oceans the speed of sound varies between 1,450 and 1,570 metres (about 4,760 to 5,150 feet) per second. It increases about 4.5 metres (about 15 feet) per second per each 1 °C increase in temperature and 1.3 metres (about 4 feet) per second per each 1 psu increase in salinity. Increasing pressure also increases the speed of sound at the rate of about 1.7 metres (about 6 feet) per second for an increase in pressure of 100 metres in depth, which is equal to approximately 10 bars, or 10 atmospheres.

The greatest changes in temperature and salinity with depth that affect the speed of sound are found near the surface. Changes of sound speed in the horizontal are usually slight except in areas where abrupt boundaries exist between waters of different properties. The effects of salinity and temperature on sound speed are more important than the effect of pressure in the upper layers. Deeper in the ocean, salinity and temperature change less with depth, and pressure becomes the important controlling factor.


In regions of surface dilution, salinity increases with depth near the surface, while in areas of high evaporation salinity decreases with depth. Temperature usually decreases with depth and normally exerts a greater influence on sound speed than does the salinity in the surface layer of the open oceans. In the case of surface dilution, salinity and temperature effects on the speed of sound oppose each other, while in the case of evaporation they reinforce each other, causing the speed of sound to decrease with depth. Beneath the upper oceanic layers the speed of sound increases with depth.

If a sound wave (sonic pulse) travels at a right angle to these layers, as in depth sounding, no refraction occurs; however, the speed changes continuously with depth, and an average sound speed for the entire water column must be used to determine the depth of water. Variations in

the speed of sound cause sound waves to refract when they travel obliquely through layers of water that have different properties of salinity and temperature. Sound waves traveling downward and moving obliquely to the water layers will bend upward when the speed of sound increases with depth and downward when the speed decreases with depth. This refraction of the sound is important in the sonar detection of submarines because the actual path of a sound wave must be known to determine a submarine's position relative to the transmitter of the sound. Refraction also produces shadow zones that sound waves do not penetrate because of their curvature.

At depths of approximately 1,000 metres, pressure becomes the important factor: it combines with temperature and salinity to produce a zone of minimum sound speed. This zone has been named the SOFAR (sound fixing and ranging) channel. If a sound is generated by a point source in the SOFAR zone, it becomes trapped by refraction. Dispersed horizontally rather than in three directions, the sound is able to travel for great distances. Hydrophones lowered to this depth many kilometres from the origin of the sound are able to detect the sound pulse. The difference in arrival time of the pulse at separate listening posts may be used to triangulate the position of the pulse source.

Hearing is an important sensory mechanism for marine animals because seawater is more transparent to sound than to light. Animals communicate with each other over long distances and also locate objects by sending directional sound signals that reflect from targets and are received as echoes. Information about the size of a target is gained by varying the frequency of the sound; high-frequency (or short-wavelength) sound waves reflect better from small targets than low-frequency sound waves. The intensity and quality of the returning signal also provide information about the properties of the reflecting target.

 *Alyn C. Duxbury*

## **CHEMICAL EVOLUTION OF SEAWATER**

The chemical history of seawater in the oceans has been divided into three stages. The first is an early stage in which Earth's crust was cooling and reacting with volatile or highly reactive gases of an acidic reducing nature to produce the oceans and an initial sedimentary rock mass. This stage lasted until about 3.5 billion years ago. The second stage was a period of transition to essentially modern conditions, and it is estimated to have ended 2 to 1.5 billion years ago. Since that time it is likely that there has been little change in seawater composition.

## **THE EARLY OCEANS**

Estimates of excess volatile substances released from Earth's interior is given in the table.

## Estimate of "excess volatiles" (units of $10^{20}$ grams)

<b>water</b>	16,600
<b>total carbon as carbon dioxide</b>	910
<b>sulfur</b>	22
<b>nitrogen</b>	42
<b>chlorine</b>	300
<b>hydrogen</b>	10
<b>boron, bromine, argon, fluorine, etc.</b>	4

Source: W.W. Rubey (1951).

Earth's initial accretion by the agglomeration of solid particles occurred about 4.56 billion years ago. Heating of this initially cool unsorted conglomerate by the decay of radioactive elements and the conversion of kinetic and potential energy to heat resulted in the development of a liquid iron core and the gross internal zonation of Earth. It has been concluded that formation of Earth's core took about 500 million years. It is likely that core formation resulted in the escape of an original primitive atmosphere and its replacement by one derived from loss of volatile substances from Earth's interior. Whether most of this degassing took place during core formation or soon afterward or whether there has been significant degassing of Earth's interior throughout geologic time is uncertain. Recent models of Earth formation, however, suggest early differentiation of Earth into three major zones (core, mantle, and crust) and attendant early loss of volatile substances from the interior. It is also likely that Earth, after initial cold agglomeration, reached temperatures such that the whole Earth approached the molten state. As the planet's initial crust solidified, volatile gases would be released to form an atmosphere that would contain water, later to become the hydrosphere; carbon gases, such as carbon dioxide, methane, and carbon monoxide; sulfur gases, mostly hydrogen sulfide; and halogen compounds, such as hydrochloric acid. Nitrogen also may have been present, along with minor amounts of other gases. Gases of low atomic number, such as hydrogen and helium, would escape Earth's gravitational field. Substances degassed from the planetary interior have been called excess volatiles because their masses cannot be accounted for simply by rock weathering.

At an initial crustal temperature of about 600 °C (about 1,100 °F), almost all these compounds, including water ( $H_2O$ ), would be in the atmosphere. The sequence of events that occurred as the crust cooled is difficult to construct. Below 100 °C (212 °F) all the  $H_2O$  would have condensed, and the acid gases would have reacted with the original igneous crustal minerals

to form sediments and an initial ocean. There are at least two possible pathways by which these initial steps could have been accomplished.

One pathway assumes that the 600 °C atmosphere contained, together with other compounds, water (as vapour), carbon dioxide, and hydrochloric acid in the ratio of 20:3:1 and would cool to the critical temperature of water. The water vapour therefore would have condensed into an early hot ocean. At this stage, the hydrochloric acid would be dissolved in the seawater of the period (about 1 mole per litre), but most of the carbon dioxide would still be in the atmosphere with about 0.5 mole per litre in the ocean water. This early acid ocean would react vigorously with crustal minerals, dissolving out silica and cations and creating a residue that consisted principally of aluminous clay minerals that would form the sediments of the early ocean basins. This pathway of reaction assumes that reaction rates were slow relative to cooling.

A second pathway of reaction, which assumes that cooling was slow, is also possible. In this case, at a temperature of about 400 °C (about 750 °F) most of the water vapour would be removed from the atmosphere by hydration reactions with pyroxenes and olivines. Under these conditions, water vapour would not condense until some unknown temperature was reached, and Earth might have had at an early stage in its history an atmosphere rich in carbon dioxide and no ocean: the surface would have been much like that of present-day Venus.

The pathways described are two of several possibilities for the early surface environment of the planet. In either case, after Earth's surface had cooled to 100 °C, it would have taken only a short time geologically for the acid gases to be used up in reactions involving minerals from igneous rock. The presence of bacteria and possibly algae in the fossil record of rocks older than three billion years attests to the fact that Earth's surface had cooled to temperatures lower than 100 °C by this time and that the neutralization of the original acid gases had taken place. If most of the degassing of primary volatile substances from Earth's interior occurred early, the chloride released by reaction of hydrochloric acid with rock minerals would be found in the oceans and seas or in evaporite deposits, and the oceans would have a salinity and volume comparable to those that they have today.

This conclusion is based on the assumption that there has been no drastic change in the ratios of volatiles released through geologic time. The overall generalized reaction indicative of the chemistry leading to formation of the early oceans can be written in the form: primary igneous rock minerals + acid volatiles + H<sub>2</sub>O = sedimentary rocks + oceans + atmosphere. Notice from this equation that if all the acid volatiles and H<sub>2</sub>O were released early in Earth's history and in the proportions found today, then the total original sedimentary rock mass produced would be equal to that of the present time, and ocean salinity and volume would be near what they are now. If, on the other hand, degassing were linear with time, then the sedimentary rock

mass would have accumulated at a linear rate, as would oceanic volume. However, the salinity of seawater would remain nearly the same if the ratios of volatiles degassed did not change with time. The most likely situation is that presented here—namely, that major degassing occurred early in Earth's history, after which minor amounts of volatiles were released episodically or continuously for the remainder of geologic time. The salt content of seawater in the oceans based on the constant proportions of volatiles released would depend primarily on the ratio of sodium chloride (NaCl) locked up in evaporites to that dissolved in the oceans. If all the sodium chloride in evaporites were added to seawater today, the salinity would be roughly doubled. This value gives a sense of the maximum salinity the oceans could have attained throughout geologic time.

One component missing from the early terrestrial surface was free oxygen, because it would not have been a constituent released from the cooling crust. As noted earlier, early production of oxygen was by photodissociation of water in the atmosphere as a result of absorption of ultraviolet light. The reaction is  $2\text{H}_2\text{O} + h\nu = \text{O}_2 + 2\text{H}_2$ , in which  $h\nu$  represents a photon of ultraviolet light. The hydrogen produced would escape into space, and the  $\text{O}_2$  would react with the early reduced gases by reactions such as  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}$ . Oxygen production by photodissociation gave the early reduced atmosphere a start toward present-day conditions, but it was not until the appearance of photosynthetic organisms approximately 3.3 billion years ago that it was possible for the accumulation of oxygen in the atmosphere to proceed at a rate sufficient to lead to today's oxygenated environment. The photosynthetic reaction leading to oxygen production may be written  $6\text{CO}_2 + 6\text{H}_2\text{O} + h\nu = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ , in which  $\text{C}_6\text{H}_{12}\text{O}_6$  represents sugar.

## THE TRANSITION STAGE

The nature of the rock record from the time of the first sedimentary rocks (about 3.5 billion years ago) to approximately 2 to 1.5 billion years ago suggests that the amount of oxygen in the atmosphere was significantly lower than today and that there were continuous chemical trends in the sedimentary rocks formed and, more subtly, in oceanic composition. The source rocks of sediments during this time were likely to be more basaltic than would later ones; sedimentary detritus was formed by the alteration of these rocks in an oxygen-deficient atmosphere and accumulated primarily under anaerobic marine conditions. The chief difference between reactions involving mineral-ocean equilibria at this time and at the present time was the role played by ferrous iron. The concentration of dissolved iron in the present-day oceans is low because of the insolubility of oxidized iron oxides. During the period 3.5 to 1.5 billion years ago, oxygen-deficient environments were prevalent; these favoured the formation of minerals containing ferrous iron (reduced state of iron) from the alteration of basaltic rocks. Indeed, the iron carbonate siderite and the iron silicate greenalite, in close

association with chert and the iron sulfide pyrite, are characteristic minerals that occur in middle Precambrian iron formations (those about 1.5 to 2.4 billion years old). The chert originally was deposited as amorphous silica; equilibrium between amorphous silica, siderite, and greenalite at 25 °C (77 °F) and one atmosphere total pressure requires a carbon dioxide pressure of about  $10^{-2.5}$  atmosphere, or 10 times the present-day value.

Seawater at this time can be thought of as the solution resulting from an acid leach of basaltic rocks, and because the neutralization of the volatile acid gases was not restricted primarily to land areas as it is presently, much of this alteration may have occurred by submarine processes. The atmosphere at the time was oxygen-deficient; anaerobic depositional environments with internal carbon dioxide pressures of about  $10^{-2.5}$  atmosphere were prevalent, and the atmosphere itself may have had a carbon dioxide pressure near  $10^{-2.5}$  atmosphere. If so, the pH of early ocean water was lower than that of modern seawater, the calcium concentration was higher, and the early ocean water was probably saturated with respect to amorphous silica (about 120 parts per million [ppm]).

To simulate what might have occurred, it is helpful to imagine emptying the Pacific basin, throwing in great masses of broken basaltic material, filling it with hydrochloric acid so that the acid becomes neutralized, and then carbonating the solution by bubbling carbon dioxide through it. Oxygen would not be permitted into the system. The hydrochloric acid would leach the rocks, resulting in the release and precipitation of silica and the production of a chloride ocean containing sodium, potassium, calcium, magnesium, aluminum, iron, and reduced sulfur species in the proportions present in the rocks. As complete neutralization was approached, aluminum could begin to precipitate as hydroxides and then combine with precipitated silica to form cation-deficient aluminosilicates. The aluminosilicates, as the end of the neutralization process was reached, would combine with more silica and with cations to form minerals like chlorite, and ferrous iron would combine with silica and sulfur to make greenalite and pyrite. In the final solution, chlorine would be balanced by sodium and calcium in roughly equal proportions, with subordinate potassium and magnesium; aluminum would be quantitatively removed, and silicon would be at saturation with amorphous silica. If this solution were then carbonated, calcium would be removed as calcium carbonate, and the chlorine balance would be maintained by abstraction of more sodium from the primary rock. The sediments produced in this system would contain chiefly silica, ferrous iron silicates, chloritic minerals, calcium carbonate, calcium magnesium carbonates, and minor pyrite.

If the hydrochloric acid added were in excess of the carbon dioxide, the resultant ocean would have a high content of calcium chloride, but the pH would still be near neutrality. If the carbon dioxide added were in excess of the chlorine, calcium would be precipitated as the carbonate until it reached a level approximately that of the present oceans—namely, a few hundred parts per million.

If this newly created ocean were left undisturbed for a few hundred million years, its waters would evaporate and be transported onto the continents (in the form of precipitation); streams would transport their loads into it. The sediment created in this ocean would be uplifted and incorporated into the continents. Gradually, the influence of the continental debris would be felt, and the pH might shift slightly. Iron would be oxidized out of the ferrous silicates to produce iron oxides, but the water composition would not vary a great deal.

The primary minerals of igneous rocks are all mildly basic compounds. When they react in excess with acids such as hydrochloric acid and carbon dioxide, they produce neutral or mildly alkaline solutions plus a set of altered aluminosilicate and carbonate reaction products. It is highly unlikely that seawater has changed through time from a solution approximately in equilibrium with these reaction products, which are clay minerals and carbonates.

## THE MODERN OCEANS

The oceans probably achieved their modern characteristics 2 to 1.5 billion years ago. The chemical and mineralogical compositions and the relative proportions of sedimentary rocks of this age differ little from their Paleozoic-era counterparts (those dating from about 542 to 251 million years ago). The fact that the acid sulfur gases had been neutralized to sulfate by this time is borne out by calcium sulfate deposits of late Precambrian age (roughly 542 million to 1.6 billion years old). Chemically precipitated ferric oxides in late Precambrian sedimentary rocks indicate available free oxygen, whatever its percentage. The chemistry and mineralogy of middle and late Precambrian shales is similar to that of Paleozoic shales. Thus, it appears that continuous cycling of sediments like those of the present time has occurred for 1.5 to 2 billion years and that these sediments have controlled oceanic composition.

It was once thought that the saltiness of the modern oceans simply represents the storage of salts derived from rock weathering and transported to the oceans by fluvial processes. With increasing knowledge of the age of Earth, however, it was realized that, at the present-day rate of delivery of salts to the oceans or even at much reduced rates, the total salt content and the mass of individual salts in the oceans could be attained in geologically short time intervals compared with Earth's age. The total mass of salt in the oceans can be accounted for at present-day rates of stream delivery in about 12 million years. The mass of dissolved silica in ocean water can be doubled in only 20,000 years by addition of stream-derived silica; to double sodium would take 70 million years. It then became apparent that the oceans were not simply an accumulator of salts, but, as water evaporated from the oceans, the introduced salts must be removed in the form of minerals. Thus, the concept of the oceans as a chemical system changed from that of a simple accumulator to that of a steady-state system in which rates of inflow of materials into the oceans equal rates of outflow. The steady-state concept permits influx to vary with time, but it would be matched by nearly simultaneous and equal variation of efflux. Calculations of rates of addition of elements to the oceanic system and

removal from it show that for at least 100 million years the oceanic system has been in a steady state with approximately fixed rates of major element inflow and outflow and, thus, fixed chemical composition.

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"seawater". *Encyclopædia Britannica. Encyclopædia Britannica Online.*

Encyclopædia Britannica Inc., 2017. Web. 30 Oct. 2017

<<https://www.britannica.com/science/seawater>>.



