

## 2.3: Chemistry and geochemistry of the oceans

### Composition of seawater

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts.

As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

		cations	g/kg	anions	g/kg
<b>Major ions of seawater</b> These values, expressed in parts per thousand, are for seawater of 35‰ salinity.		Na <sup>+</sup>	10.77	Cl <sup>-</sup>	19.354
		Mg <sup>2+</sup>	1.29	SO <sub>4</sub> <sup>2-</sup>	2.712
		Ca <sup>2+</sup>	0.412	Br <sup>-</sup>	0.087
		K <sup>+</sup>	0.399		
		Sr <sup>2+</sup>	0.0079		
		Al <sup>3+</sup>	0.005		

The best way of characterizing seawater is in terms of its ionic content, shown above. The remarkable thing about seawater is the constancy of its relative ionic composition. The overall salt content, known as the salinity (grams of salts contained in 1 kg of seawater), varies slightly within the range of 32-37.5‰, corresponding to a solution of about 0.7% salt content. The ratios of the concentrations of the different ions, however, are quite constant, so that a measurement of Cl<sup>-</sup> concentration is sufficient to determine the overall composition and total salinity. Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si<sup>32</sup>, presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

**pH balance.** Reflecting this constant ionic composition is the pH, which is usually maintained in the narrow range of 7.8-8.2, compared with 1.5 to 11 for fresh water. The major buffering action derives from the carbonate system, although ion exchange between Na<sup>+</sup> in the water and H<sup>+</sup> in clay sediments has recently been recognized to be a significant factor.

### Conservative and non-conservative substances

The major ionic constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow. This is another way of saying that their residence times are very large.

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/10 <sup>6</sup> years
Cl <sup>-</sup>	250	558,000	87
Na <sup>+</sup>	315	479,000	55
Mg <sup>2+</sup>	150	54,300	13
SO <sub>4</sub> <sup>2-</sup>	120	28,900	8.7
Ca <sup>2+</sup>	367	10,500	1
K <sup>+</sup>	36	10,400	10
HCO <sub>3</sub> <sup>-</sup>	870	2000	0.083

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/ $10^6$ years
H <sub>4</sub> SiO <sub>4</sub>	170	100	0.021
NO <sub>3</sub> <sup>−</sup>	10	20	0.072
H <sub>2</sub> PO <sub>4</sub> <sup>−</sup>	0.7	1	0.080

### Replacement time with respect to river addition for some components of seawater

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and  $\text{HPO}_4^{2-}$ , which may become depleted near the surface in regions of warmth and light. As was explained in the preceding subsection on coastal upwelling, offshore prevailing winds tend to drive Western coastal surface waters out to sea, causing deeper and more nutrient-rich water to be drawn to the surface. This upwelled water can support a large population of phytoplankton and thus of zooplankton and fish. The best-known example of this is the anchovy fishery off the coast of Peru, but the phenomenon occurs to some extent on the West coasts of most continents, including our own.

Other non-conservative components include  $\text{Ca}^{2+}$  and  $\text{SiO}_4^{2-}$ . These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of  $\text{SiO}_4^{2-}$  tend to vary with depth. The gases  $\text{O}_2$  and  $\text{CO}_2$ , being intimately involved with biological activity, are also non-conservative, as are  $\text{N}_2\text{O}$  and  $\text{CO}$ .

### Organic matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as "Gelbstoffe". It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

### Regulation of ocean composition

The salinity of the ocean appears to have been about the same for at least the last 200 million years. There have been changes in the relative amounts of some species, however; the ratio of Na/K has increased from about 1:1 in ancient ocean sediments to its present value of 28:1. Incorporation of calcium into sediments by the action of marine organisms has depleted the Ca/Mg ratio from 1:1 to 1:3.

#### Mass balance of P, C, and Ca for the oceans

Element	input to ocean	dissolved in seawater	in dead organisms	loss to sediments	residence time, y
phosphorus	1 (erosion)	1	1	1 (organic)	10,000
carbon	100 as $\text{CO}_2$ 500 as carbonate	1000	125	100 (organic) 600 (carbonate)	165,000
calcium	500 (erosion)	5000	25	500 (as $\text{CaCO}_3$ )	$10^6$

If the composition of the ocean has remained relatively unchanged with time, the continual addition of new mineral substances by the rivers and other sources must be exactly balanced by their removal as sediment, possibly passing through one or more biological systems in the process.

#### Where does the salt come from?

In 1715 Edmund Halley suggested that the age of the ocean (and thus presumably of the world) might be estimated from the rate of salt transport by rivers. When this measurement was actually carried out in 1899, it gave an age of only 90 million years.

*This is somewhat better than the calculation made in 1654 by James Ussher, the Anglican Archbishop of Armagh, Ireland, based on his interpretation of the Biblical book of Genesis, that the world was created at 9 A.M. on October 23, 4004 BC, but it is still far too recent, being about when the dinosaurs became extinct. What Halley actually described was the residence time, which is about right for Na but much too long for some of the minor elements of seawater.*

The commonly stated view that the salt content of the oceans derives from surface runoff that contains the products of weathering and soil leaching is not consistent with the known compositions of the major river waters (See Table). The halide ions are particularly over-represented in seawater, compared to fresh water. These were once referred to as “excess volatiles”, and were attributed to volcanic emissions. With the discovery of plate tectonics, it became apparent that the locations of seafloor spreading at which fresh basalt flows up into the ocean from the mantle are also sources of mineral-laden water. Some of this may be seawater that has cycled through a hot porous region and has been able to dissolve some of the mineral material owing to the high temperature. Much of the water, however, is “juvenile” water that was previously incorporated into the mantle material and has never before been in the liquid phase. The substances introduced by this means (and by volcanic activity) are just the elements that are “missing” from river waters. Estimates of what fraction of the total volume of the oceans is due to juvenile water (most of it added in the early stages of mantle differentiation that began a billion years ago) range from 30 to 90%.

#### Geochemical processes involving the oceans

The oceans can be regarded as a product of a giant acid-base titration in which the carbonic acid present in rain reacts with the basic materials of the lithosphere. The juvenile water introduced at locations of ocean-floor spreading is also acidic, and is partly neutralized by the basic components of the basalt with which it reacts. Surface rocks mostly contain aluminum, silicon and oxygen combined with alkali and alkaline-earth metals, mainly potassium, sodium and calcium. The  $\text{CO}_2$  and volcanic gases in rainwater react with this material to form a solution of the metal ion and  $\text{HCO}_3^-$ , in which is suspended some hydrated  $\text{SiO}_2$ . The solid material left behind is a clay such as kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . This first forms as a friable coating on the surface of the weathered rock; later it becomes a soil material, then an alluvial deposit, and finally it may reach the sea as a suspended sediment. Here it may undergo a number of poorly-understood transformations to other clay sediments such as illites. Sea floor spreading eventually transports these sediments to a subduction region under a continental block, where the high temperatures and pressures permit reactions that transform it into hard rock such as granite, thus completing the geochemical cycle.

Deep-sea hydrothermal vents are now recognized to be another significant route for both the addition and removal of ionic substances from seawater.

#### Distribution and cycling of elements in the oceans

Although the relative concentrations of most of the elements in seawater are constant throughout the oceans, there are certain elements that tend to have highly uneven distributions vertically, and to a lesser extent horizontally. Neglecting the highly localized effects of undersea springs and volcanic vents, these variations are direct results of the removal of these elements from seawater by organisms; if the sea were sterile, its chemical composition would be almost uniform.

Plant life can exist only in the upper part of the ocean where there is sufficient light available to drive photosynthesis. These plants, together with the animals that consume them, extract nutrients from the water, reducing the concentrations of certain elements in the upper part of the sea. When these organisms die, they fall toward the lower depths of the ocean as particulate material. On the way down, some of the softer particles, deriving from tissue, may be consumed by other animals and recycled. Eventually,

however, the nutrient elements that were incorporated into organisms in the upper part of the ocean will end up in the colder, dark, and essentially lifeless lower part.

Mixing between the upper and lower reservoirs of the ocean is quite slow, owing to the higher density of the colder water; the average residence time of a water molecule in the lower reservoir is about 1600 years. Since the volume of the upper reservoir is only about 1/20 of that of the lower, a water molecule stays in the upper reservoir for only about 80 years.

Except for dissolved oxygen, all elements required by living organisms are depleted in the upper part of the ocean with respect to the lower part. In the case of the major nutrients P, N and Si, the degree of depletion is sufficiently complete (around 95%) to limit the growth of organisms at the surface. These three elements are said to be biolimiting. A few other biointermediate elements show partial depletion in surface waters: Ca (1%), C (15%), Ba (75%).

The organic component of plants and animals has the average composition  $C_{80}N_{15}P$ . It is remarkable that the ratio of N:P in seawater (both surface and deep) is also 15:1; this raises the interesting question of to what extent the ocean and life have co-evolved.

In the deep part of the ocean the elemental ratio corresponds to  $C_{800}N_{15}P$ , but of course with much larger absolute amounts of these elements. Eventually some of this deeper water returns to the surface where the N and P are quickly taken up by plants. But since plants can only utilize 80 out of every 800 carbon atoms, 90 percent of the carbon will remain in dissolved form, mostly as  $HCO_3^-$ .

*To work out the balance of Ca and Si used in the hard parts of organisms, we add these elements to the average composition of the lower reservoir to get  $Ca_{3200}Si_{50}C_{800}N_{15}P$ . Particulate carbon falls into the deep ocean in the ratio of about two atoms in organic tissue to one atom in the form of calcite. This makes the overall composition of detrital material something like  $C_{120}N_{15}P$ ; i.e., 80 organic C's and 40 in  $CaCO_3$ . Accompanying these 40 calcite units will be 40 Ca atoms, but this represents a minor depletion of the 3200 Ca atoms that eventually return to the surface, so this element is only slightly depleted in the upper waters. Silicon, being far less abundant, is depleted to a much greater extent.*

## The oceanic sediments

### The particulate shower.

A continual rain of particulate material from dead organisms falls through the ocean. This shower is comprised of three major kinds of material: calcite ( $CaCO_3$ ), silica ( $SiO_2$ ), and organic matter. The first two come from the hard parts of both plants and animals (mainly microscopic animals such as foraminifera and radiolarians). The organic matter is derived mainly from the soft tissues of organisms, and from animal fecal material. Some of this solid material dissolves before it reaches the ocean floor, but not usually before it enters the deep ocean where it will remain for about 1600 years.

The remainder of this material settles onto the floor of the sea, where it forms one component of a layer of sediments that provide important information about the evolution of the sea and of the earth. Over a short time scale of months to years, these sediments are in quasi-equilibrium with the seawater. On a scale of millions of years, the sediments are merely way-stations in the geochemical cycling of material between the earth's surface and its interior.

The oceanic sediments have three main origins:

- **Detrital** material is derived largely from particles deposited in the ocean by rivers and also directly by the wind. These materials are mostly aluminosilicates (clays), along with some quartz. These substances accumulate on the deep ocean floor at a rate of about  $0.3 \text{ g cm}^{-2}$  per 1000 years.
- **Authigenic** materials are formed by precipitation within the ocean or by crystallization within the sediment itself. These constitute only a small fraction of the total sediment.
- **Biogenic** components consist mainly of the calcium carbonate and silica that make up the hard parts of organisms. Scavenging by other organisms is so efficient that only about 0.3 % of the total deep sea sediment consists of actual organic material.

Our main interest lies with the silica and calcium carbonate, since these substances form a crucial part of the biogeological cycle. Also, their distributions in the ocean are not uniform- a fact that must tell us something.

The skeletons of diatoms and radiolarians are the principal sources of silica sediments. Since the ocean is everywhere undersaturated with respect to silica, only the most resistant parts of these skeletons reach the bottom of the deep ocean and get incorporated into sediments. Silica sediments are less common in the Atlantic ocean, owing to the lower content of dissolved silica.

The parts of the ocean where these sediments are increasing most rapidly correspond to regions of upwelling, where deep water that is rich in dissolved silica rises to the surface where the silica is rapidly fixed by organisms. Where upwelling is absent, the growth of the organisms is limited, and little silica is precipitated. Since deep waters tend to flow from the Atlantic into the Pacific ocean where most of the upwelling occurs, Atlantic waters are depleted in silica, and silica sediments are not commonly found in this ocean.

For calcium carbonate, the situation is quite different. In the first place, surface waters are everywhere supersaturated with respect to both calcite and aragonite, the two common crystal forms of  $\text{CaCO}_3$ . Secondly,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  are never limiting factors in the growth of the coccoliths (plants) and forams (animals) that precipitate  $\text{CaCO}_3$ ; their production depends on the availability of phosphate and nitrogen. Because these elements are efficiently recycled before they fall into the deep ocean, their supply does not depend on upwelling, and so the production of solid is more uniformly distributed over the world's oceans.

More importantly, however, the chances that a piece of carbonate skeleton will end up as sediment will be highly dependent on both the local  $\text{CO}_3^{2-}$  concentration and the depth of the ocean floor. These factors give rise to small-scale variations in the production of carbonate sediments that can be quite wide-ranging.

### Ocean sediments and continental drift

New crust is being generated and moving away from the crests of the mid-ocean ridges at a rate of a few centimetres per year. Although the crests of these ridges are relatively high points, projecting to within about 3000 m of the surface, the continual injection of new material prevents sediments from accumulating in these areas. Farther from the crests, carbonate sediments do build up, eventually reaching a depth of about 500 m, but by this time the elevation has dropped off below the saturation horizon, so from this point on the carbonate sediments are overlaid by red clay.

If we drill a hole down through a part of the ocean floor that is presently below the saturation horizon, the top part of the drill core will consist of clay, followed by  $\text{CaCO}_3$  at greater depths. The core may also contain regions in which silica predominates. Since silica production is very high in equatorial regions, the appearance of such a layer suggests that this particular region of the oceanic crust has moved across the equator.

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