2.4: Chemical budgets of oceanic elements

To the extent that the composition of the ocean remains constant, the rate at which any one element is introduced into seawater must equal the rate of its removal. A listing of the various routes of addition and removal, together with the estimated rate of each process, constitutes the budget for a given element. If that budget is greatly out of balance and no other transport routes are apparent, then it is likely that the ocean is not in a steady state with respect to that element, at least on a short time scale. It is important to understand, however, that short-term deviations from constant composition are not necessarily inconsistent with a long-term steady state. Deviations from the latter condition are most commonly inferred from geological evidence.

The major input of elements to the oceans is river water. Groundwater seepage constitutes a very small secondary source. These were considered the only sources until the 1970's, when the existence of hydrothermal springs at sites of seafloor spreading became known. There are presently no reliable estimates of the magnitude of this source. Pollution represents an additional input, mainly dissolved in river water, but also sometimes in rain and by dry deposition.

Routes of removal are formation and burial of sediments, formation of evaporite deposits, direct input to the atmosphere by sea-salt aerosol transfer associated with bubble-breaking, and burial with sediments, either in interstitial water or adorbed onto active surfaces. Reaction with newly-formed basalt associated with undersea volcanic activity appears to be an important removal mechanism for some elements.

Table 7: Input and output rates of major elements in seawater by two routes. The units are Tg y−1. The other major routes involve interaction with the seafloor through hyrothermal vents and incorporation into sediments, but only river input and loss to the atmosphere are quantifiable with any degree of accuracy.

Species	Addition from Rivers	Loss to Atmosphere
Cl^-	308	40
Na^+	269	21
S (mostly SO_4^{2-})	143	4
Mg^{2+}	137	3
K^+	52	1
Ca^{2+}	550	0.5
HCO_3^-	1980	
H_4SiO_4	180	

Phosphorus

The major elements undergoing steady-state dynamic change in the ocean are connected with biological processes. The key limiting element in the development of oceanic biomass is phosphorus, in the form of the phosphate ion. For terrestrial plant life, nitrogen is more commonly the limiting element, where it is taken up in the form of the nitrate ion. In the ocean, however, the ratio of the nitrate ion concentration to that of phosphorus has been found to be everywhere the same; this implies that the concentration of one controls that of the other. The source of nitrate ion is atmospheric N_2, which is freely soluble in water and is thus always present in abundance. The conversion of N_2 to NO_3^- is presumed to be biologically mediated, probably by bacteria. The constancy of the NO_3^-/P concentration ratio implies that the phosphorus concentration controls the activity of the nitrogen-fixing organisms, and thus the availability of nitrogen to oceanic life.

Photosynthetic activity in the upper part of the ocean causes inorganic phosphate to be incorporated into biomass, reducing the concentration of phosphorus; in warm surface waters, phosphate may become totally depleted. A given phosphorus atom may be traded several times among the plant, animal and bacterial populations before it eventually finds itself in biodebris (a dead organism or a fecal pellet) that falls into the deep part of the sea. Only about 1% of the phosphorus atoms that descend into deeper waters actually reach the bottom, where they are incorporated into sediments and permanently removed from circulation. The other 99% are released in the form of soluble phosphate, which is eventually brought to the surface in regions of upwelling. An average phosphorus atom will undergo one cycle of this circulation in about 1000 years; only a few months of this cycle will be spent in biomass. After an average of 100 such cycles, the atom will be removed from circulation and locked into the bottom sediment, and a new one will have entered the sea with river or juvenile water.

Phosphorus is unique in that its major source of input to the oceans derives ultimately from pollution; in the long term, this represents a transfer of land-based phosphate deposits to the oceans. About half of the phosphorus input is in the form of suspended material, both organic and inorganic, the latter being in a variety of forms including phosphates adsorbed onto clays and iron oxide paticles, and calcium phosphate (apatatite) eroded from rocks. These various particulates are known to dissolve to some extent once they reach the ocean, but there is considerable uncertainty about the rates of these processes under various conditions.

The major sink for oceanic phosphorus is burial with organic matter; this accounts for about two-thirds of the phosphorus removed. Most of the remainder is due to deposition with $CaCO_3$. A minor removal route is through reaction with Fe(II) formed when seawater attacks hot basalt, and in the formation of evaporite deposits. However, there is more phosphorus in evaporite deposits in the Western U.S. than in all of the ocean, so it is apparent that the long-term phosphorus budget is still not clearly understood.

Carbon

Carbon enters the ocean from both the atmosphere (as CO_2) and river water, in which the principal species is HCO_3^-. Once in solution, the carbonate species are in equilibrium with each other and with H_3O^+, and the concentrations of all of these are influenced by the partial pressure of atmospheric CO_2. The mass budget for calcium is linked to that of carbon through solubility equilibria with the various solid forms of $CaCO_3$ (mainly calcite). During photosynthesis, C^{12} is taken up slightly more readily than the rare isotope C^{13}. Since the rate of photosynthesis is controlled by the phosphate concentration, the C^{13}/C^{12} ratio in the dissolved carbon dioxide of surface waters is slightly higher than in the ocean as a whole. Observations of carbon isotope ratios in buried sediments have been useful in tracking historical changes in phosphate concentrations.

The C:P ratio and the regulation of atmospheric CO_2

The ratio of carbon to phosphorus in sea salt is about eight times greater than the same ratio measured in organic debris. This implies that in exhausting the available phosphate, the living organisms in the upper ocean consume only 12.5% of the dissolved carbon. Even this relatively small withdrawal of carbon from the carbonate system is sufficient to noticeably reduce the partial pressure of gaseous CO_2 in equilibrium with the ocean; it has been estimated that if all life in the ocean should suddenly cease, the atmospheric CO_2 content would rise to about three times its present level. The regulation of atmospheric CO_2 pressure by the oceans also works the other way: since the amount of dissolved carbonate in the oceans is so much greater than the amount of CO_2 in the atmosphere, the oceans act to buffer the effects of additions of CO_2 to the atmosphere. Calculations indicate that about half of the CO_2 that has been produced by burning fossil fuel since the Industrial Revolution has ended up in the oceans.

Bicarbonate

This is of course the major carbonate species in the ocean. Although it is interconvertible with CO_2 and is thus coupled to the carbon and photosynthetic cycles, itself can neither be taken up nor produced by organisms, and so it can be treated somewhat independently of biological activity. In this sense the only major input of into the oceans is river water. The two removal mechanisms are formation of CO_2

$$H^+ + HCO_3^- \rightarrow H_2O + CO^2 \tag{2.4.1}$$

and the (biologically mediated) formation of $CaCO_3^-$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \tag{2.4.2}$$

Since the pH of the oceans does not change, H^+ is conserved and the removal of HCO_3^- by biogenic secretion of $CaCO_3$ can be expressed by the sum of these reactions:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{2.4.3}$$
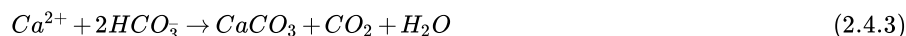
whose reverse direction represents the dissolution of the skeletal remains of dead organisms as they fall to lower depths.

Calcite

The upper parts of the ocean tend to be supersaturated in $CaCO_3$. Solid $CaCO_3$, in the form of calcite, is manufactured by a large variety of organisms such as foraminifera. A constant rain of calcite falls through the ocean as these organisms die. The solubility of increases with pressure, so only that portion of the calcite that falls to shallow regions of the ocean floor is incorporated into sediments and removed from circulation; the remainder dissolves after reaching a depth known as the lysolcline. At the present time, the amounts of carbonate and Ca^{2+} supplied by erosion and volcanism appear to be only about one-third as great as the amount of calcite produced by organisms. As the carbonate concentration in a given region of the ocean becomes depleted due to higher calcite production, the lysocline moves up, tending to replenish the carbonate, and reducing the amount that is withdrawn by burial in sediments. Organic residues that fall into the deep sea are mostly oxidized to CO_2, presumably by bacterial activity.

Other Elements

Calcium

Calcium is removed from seawater solely by biodeposition as $CaCO_3$, a process whose rate can be determined quite accurately both at the present and in the past.

Table 2.4.1 : Present-day budget for oceanic calcium (Tg Ca/yr).

inputs		outputs	
rivers	550	$CaCO_3$ into shallow water	520
volcanic basalt	191	$CaCO_3$ into deep water	440
cation exchange	37		
total	**778**		**960**

As is explained above, the upper part of the ocean is supersaturated in calcite but the lower ocean is not. For this reason, less than 20% of the $CaCO_3$ that is formed ends up as sediment and is eventually buried.

The main questions about the calcium budget tend to focus on the rates and locales at which dissolution of skeletal carbonates occurs, and on how to interpret the various kinds of existing carbonate sediments. For example, the crystalline form aragonite is less stable than calcite, and will presumably dissolve at a higher elevation. The absence of aragonite-containing pteropod shells in deeper deposits seems to confirm this, but in the absence of rate data is it difficult to know at what elevations these particular organisms originated.

The data in the above Table indicate that at the present time there is a net removal of calcium from the oceans. This is due to the rise in sea level since the decline of the more recent glacial epoch during the past 11,000 years. The additional water has covered the continental shelves, increasing the amount of shallow ocean where the growth of organisms is most intense. Over the more distant past (25 million years) the calcium budget appears to be well balanced.

Chloride

Evidence from geology and peleontology indicates that the salinity, and hence the chloride concentration of sewater has been quite constant for about 600 million years. There have been periods when climatic conditions and coastal topography have led to episodes of evaporite formation, but these have evidently been largely compensated by the eventual return of the evaporite deposits to the sea. The natural input of chloride from rivers is about 215 Tg/yr, but the present input is about half again as great (Table 7 on page 33), due to pollution. Also, there are presently no significant areas where seawater is evaporating to dryness. Thus the oceanic chloride budget is considerably out of balance. However, the replacement time of Cl^- in the oceans is so long (87 million years) that this will probably have no long-term effect.

Sodium

Although sodium is tied to chloride, it is also involved in the formation of silicate minerals, the weathering of rocks, and in cation exchange with clay sediments. Its short-term budget is quite out of balance for the same reasons as is that of chloride. On a longer time scale, removal of sodium by reaction with hot basalt associated with undersea volcanic activity may be of importance.

Sulfate

Considerably more sulfate is being added to seawater than is being removed by the major mechanisms of sediment formation (mainly $CaSO_4$ and pyrites). The natural river input is 82 Tg of S per year, while that due to pollution is 61 Tg/yr from rivers and 17 Tg/yr from rain and dry deposition.

Magnesium

This element is unusual in that its river-water input is balanced mostly by reaction with volcanic basalt; removal through biogenic formation of magnesian calcite (dolomite) accounts for only 11% of its total removal from the ocean. The present-day magnesium budget seems to have been balanced for the past 100 million years. However, most of the extensive dolomite deposits were formed prior to this time, so the longer-term magnesium budget is poorly understood.

Potassium

The potassium budget of the ocean is not well understood. The element is unusual in that only about 60% of its input is by rivers; the remainder is believed to come from newly formed undersea basalt. The big question about potassium is how it is removed; fixation by ion-exchange with illite clays seems to be a major mechanism, and its uptake by basalt (at lower temperatures than are required for its release) is also believed to occur.

Silica

About 85% of the silicon input to the oceans comes from river water in the form of silicic acid, H_4SiO_4. The remainder probably comes from basalt. It is removed by biogenic deposition as opaline silica, $SiO_2 \cdot n\ H_2O$ produced mainly by planktonic organisms (radiolaria and diatoms). Unlike the case for $CaCO_3$, the ocean is everywhere undersaturated in silica, especially near the surface where these organisms deplete it with greater efficiency than any other element.

Because opaline silica dissolves so rapidly, only a small fraction makes it to the bottom. The major deposits occur in shallower waters where coastal upwelling provides a good supply of N and P nutrients for siliceous organisms. Thus over half of the biogenic silica deposits are found in the Antarctic ocean.

In spite of the fact that dissolved silica has the shortest replacement time (21,000 years) of any major element in the ocean, its concentration appears to have been remarkably constant during geological time. This is taken as an indication of the ability of siliceous organisms to respond quickly to changes in local concentrations of dissolved silica.

Nitrogen

This element is complicated by its biologically-mediated exchange with atmospheric nitrogen, and by its existence in several oxidation states, all of which are interconvertible. Unlike the other major elements, nitrogen does not form extensive sedimentary deposits; most of the nitrogen present in dead organic material seems to be removed before it can be buried. Through this mechanism there is extensive cycling of nitrogen between the shallow and deep parts of the oceans.

The real difficulty in constructing a budget for oceanic nitrogen is the very large uncertainty in the rates of the major input (fixation) and output. Both of these processes are biologically mediated, but little is known about what organisms are responsible, where they thrive and how they are affected by local nutrient supply and other conditions.

Contributors and Attributions

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