REDFIELD RATIO

T. Tyrrell, University of Southampton, Southampton, UK

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Introduction

Phytoplankton are the base of almost all marine food chains. The energy locked into the biomass of phytoplankton is the fuel that ultimately powers marine life at all other trophic levels, whether zooplankton, bacteria, jellyfish, viruses, fish, or whales. Energy gets into phytoplankton via photosynthesis, whereby sunlight energy and nutrients dissolved in the water are combined to form phytoplankton biomass containing chemical energy stores in the form of carbohydrates. The rate at which new phytoplankton is produced in the ocean affects the productivity of fisheries and also affects climate, through the action of the organic carbon pump (see below) and by other means. There is therefore much interest in the factors that control the rate of phytoplankton (primary) production in the oceans, the most important of which is the supply rate of base ingredients, i.e., nutrients. Some nutrients, most notably nitrate and phosphate, are more or less exhausted throughout the majority of the surface oceans, preventing further primary production (**Figure 1**).

The focus of this article is the nutrients required by phytoplankton, and the cycling of nutrients brought about by phytoplankton cells decaying lower in the water than where they were formed. 'Redfield ratios' are described and their usefulness is explained.

Definition of a Nutrient

A nutrient is a dissolved substance in the water from which organisms can obtain an essential element for growth. For instance, phytoplankton satisfy their requirement for the chemical element phosphorus by assimilating the nutrient phosphate. Nitrate and ammonium ions are two nutrients that are alternative sources of nitrogen.

Phytoplankton require many different chemical elements in order to build the molecules essential to life. Some of these elements are very plentiful in the ocean (e.g., sodium, calcium, sulfur, carbon) and never run out as a result of uptake by phytoplankton. Others (nitrogen, phosphorus, silicon, iron) sometimes run out, preventing further growth of phytoplankton. Discussion of nutrients tends to focus on those nutrients that are occasionally or frequently limiting for phytoplankton growth, for obvious reasons.

Some nutrients (e.g., iron, zinc) are present in sea water only in trace amounts, but these trace amounts must be present in order for phytoplankton to be able to grow. These are known as micronutrients, in contrast to the more plentiful macronutrients such as nitrogen, phosphorus, and silicon. While most phytoplankton can synthesize new cells solely from inorganic nutrients, other phytoplankton require previous blooms to have added vitamin B_{12} to the water because they cannot synthesize it themselves. Vitamin B_{12} is therefore an additional essential nutrient for some phytoplankton.

Units

Nutrient concentrations are usually reported as numbers of moles (proportional to the number of molecules) in a given volume of water, or in a given mass of water. Typical units are $\mu mol\,kg^{-1}$, $\mu mol\,l^{-1}$, $mmol\,m^{-3}$ or $mol\,m^{-3}$. For trace concentrations, units of $nmol\,kg^{-1}$ ($10^{-9}\,mol\,kg^{-1}$) or even $pmol\,kg^{-1}$ ($10^{-12}\,mol\,kg^{-1}$) are used. One mole represents Avogadro's number (6.0221367×10^{23}) of atoms, molecules, or ions, which is the number of atoms in 12 g of carbon-12. Thus the mole is a dimensionless unit (a pure number) similar to a 'dozen', used to conveniently express a number of atoms or molecules. Concentrations are often expressed per unit mass because sea water is slightly compressible: a parcel of water containing a given number of water molecules will maintain its mass as it descends from the surface to depth, but it will decrease in volume to a small extent under the influence of the great pressure. Square brackets [ ] are used to denote the concentration of a given chemical species.

Terrestrial versus Marine Primary Production

Table 1 shows a comparison between biomass and amounts of primary production (photosynthesis) on land and in the oceans. Although the annual amounts of primary production are approximately the same in both realms, the biomass producing that primary production (as measured in carbon units) is much smaller in the oceans. This is because vast amounts of carbon on land are locked up in lignin

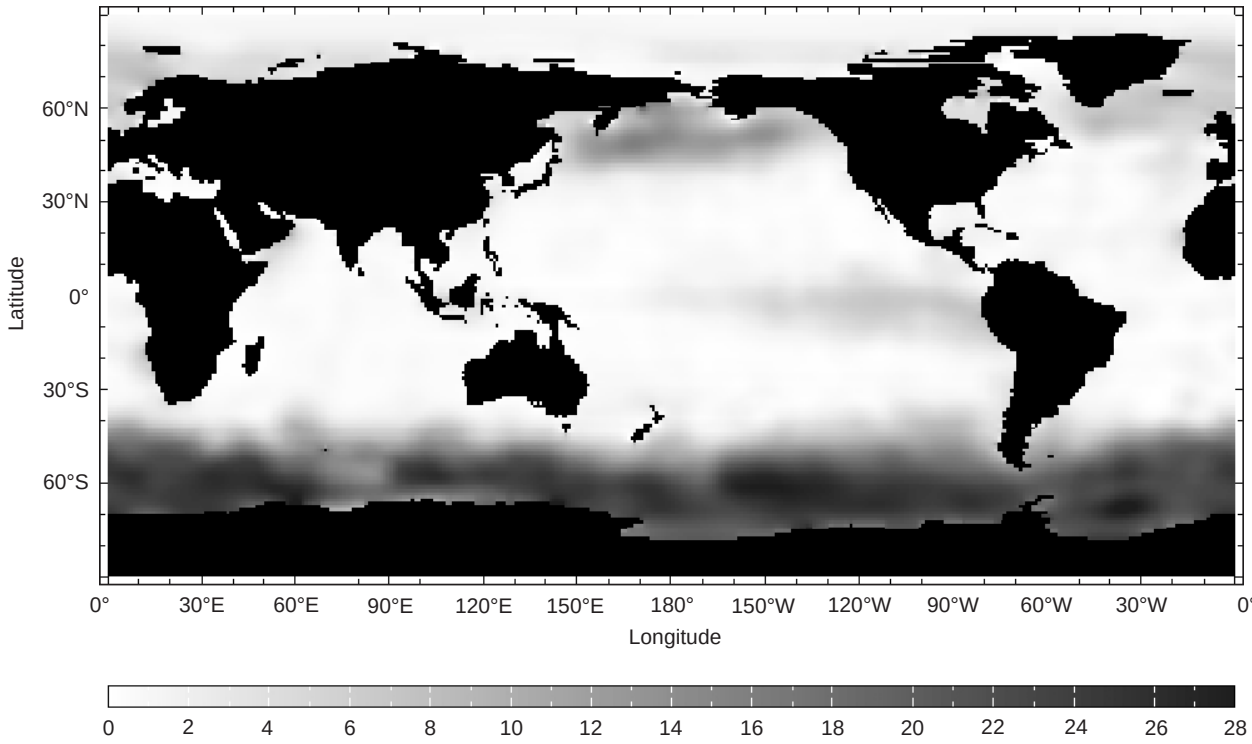

Figure 1 Annual mean surface nitrate concentration ($\mu mol\,kg^{-1}$). (Map produced from World Ocean Atlas '94 dataset using software at http://ingrid.ldeo.columbia.edu/)

(e.g. tree trunks), and these carbon-rich physical support structures do not directly participate in photosynthesis. Except for seaweeds, marine photosynthesizers do not possess stems or stalks. Another contrast between the two realms is the much smaller size of photosynthesizing organisms in the sea than on land. Excepting seaweeds once more, almost all marine photosynthesizers are microscopic and invisible to the naked eye. The much greater ratio of primary production to biomass necessarily implies a much shorter lifespan for phytoplankton than for trees, bushes, and grasses on land. Phytoplankton live on average for only a few days or a week.

This ephemeral nature of phytoplankton is of importance for nutrient cycling, because nutrients reside in phytoplankton cells for only a relatively short time. After only a few days, nutrients are released back into the environment as phytoplankton are broken apart or decomposed by, for instance, zooplankton or viruses.

Table 1 Global primary production and biomass in the ocean and on land

	Total primary production ($Gt\,C\,y^{-1}$)	*Biomass* ($Gt\,C$)
Marine	$50\,Gt\,C\,y^{-1}$	$4\,Gt\,C$
Terrestrial	$60\,Gt\,C\,y^{-1}$	$550\,Gt\,C$

Recipe for Phytoplankton

Relative Uniformity of Cellular Composition

In common with all other life, all phytoplankton cells contain certain essential biomolecules such as nucleic acids (DNA and RNA) and adenosine triphosphate (ATP), each of which must be constructed from a fixed set of chemical elements. The synthesis of lipids, proteins, carbohydrates, etc. also imposes constraints on the chemical make-up of phytoplankton cells. Although different species of phytoplankton have slightly different chemical compositions, there is still a reasonable degree of uniformity in the measured chemical composition of plankton extracted from the surface waters of different oceans. A similar set of ingredients is always used. The Redfield ratio is the ratio in which different chemical elements are present in average phytoplankton biomass. It defines the stoichiometry of photosynthesis and remineralization reactions. On average each atom of phosphorus in phytoplankton biomass is attended by 16 atoms of nitrogen and 106 atoms of carbon, and this C:N:P ratio of

106:16:1 is the most commonly used value of the Redfield ratio. This ratio is sometimes extended to other elements but is most usually restricted to C, N, P and O_2.

Considering only the more numerous and important of the chemical elements in the average recipe for phytoplankton, this leads to an idealized chemical reaction for the formation of phytoplankton (eqn [1]).

$$106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 78\,H_2O \rightleftharpoons (C_{106}H_{175}O_{42}N_{16}P) + 150\,O_2 \quad [1]$$

The term in parentheses is a simplified average formula for phytoplankton. This equation contains a two-way arrow because the reaction is reversible. The reverse reaction is the remineralization of phytoplankton, brought about by several processes. Nutrients leak back into the environment due to cell breakage during grazing, lysis of cells infected by viruses, decay and lysis of cells attacked by bacteria, excretion of digestive waste products, etc.

Laboratory experiments involving growing individual species of phytoplankton under a wide range of forced conditions obtain a wide range of Redfield ratios. However, this variability in the elemental composition of phytoplankton grown in the laboratory does not occur to the same extent in the sea. Perhaps this is because the sea contains many more than one species of phytoplankton, and each species will thrive only in the conditions that suit it best, being outcompeted by other species in conditions to which it is less well adapted.

The measurement of phytoplankton elemental compositions (and therefore Redfield ratios) in the sea is not without its problems. It is difficult automatically to separate invisible (without a microscope) phytoplankton from invisible zooplankton, bacteria, detritus, and other particles found in sea water. Some studies have ignored this problem and measured the elemental composition of all particles, regardless of origin. Others have tried to collect material that is especially rich in phytoplankton by sampling during phytoplankton blooms. The most sophisticated approach has involved two plankton nets, one inside the other. The inner net, with a large mesh size, caught the biggest particles (assumed to be zooplankton), and these were then ignored in further analyses. The second net, with a smaller mesh size, caught medium-sized particles (assumed to be phytoplankton) and allowed the smallest particles (assumed to be mainly bacteria and detritus) to escape. Even those studies that have separated particles according to size suffer from the overlap in size ranges between phytoplankton and heterotrophic bacteria (at the smaller end) and between phytoplankton and zooplankton (at the larger end). At best their samples were only 75% phytoplankton (as revealed by looking at them under a microscope).

While it needs to be kept in mind that measurements of phytoplankton elemental composition at sea have always been contaminated, it is surprising how little variation there is in the measured N:P ratio. Most measurements have produced results in the range 12–20, with an average close to 16.

Other studies have examined the relative rates of addition of different nutrients into deep water by remineralization of sinking organic matter. These studies provide an independent calculation of the Redfield ratio, and have produced an estimate of $-O_2{:}C_{org}{:}N{:}P \approx 145{:}105{:}16{:}1$ (by moles) for remineralization of pristine organic matter near to the surface. The term 'C_{org}' refers to the remineralization of carbon from organic matter only, as separate from the release of carbon from calcium carbonate cell walls (see below).

A very useful property of the Redfield ratio is that it allows an estimate to be calculated of the impact on one nutrient concentration from knowledge of the impact on another. For example, if phosphate is observed to have decreased by $0.5\,\mu mol\,kg^{-1}$ owing to phytoplankton growth, then nitrate is likely to have decreased by $(0.5 \times 16) = 8\,\mu mol\,kg^{-1}$. Likewise, if remineralization of organic matter is measured to have drawn down oxygen levels by $10\,\mu mol\,kg^{-1}$, this implies a simultaneous increment to the stock of total dissolved inorganic carbon of about $(10 \times 105/145) = 7.2\,\mu mol\,kg^{-1}$.

All the Redfield ratios given above are molar ratios, that is to say ratios of numbers of atoms, molecules or ions. Redfield ratios are also occasionally reported as mass ratios, but these are not numerically the same as those reported above because different chemical elements have different atomic masses.

Variety of Cell Walls

In contrast to the relative similarity in chemical composition of phytoplankton cell interiors, some different types of phytoplankton have adopted radically different cell walls. Most phytoplankton have cell walls built of polysaccharides, but diatoms construct coverings (tests) built out of solid silicate (opal). In order to construct these opal tests, diatoms have to take up silicon from the water in the form of dissolved silicate (SiO_4). Coccolithophore phytoplankton in turn construct their cell walls from solid calcium carbonate and have to absorb

calcium (Ca^{2+}) and bicarbonate (HCO_3^-) ions from the water in order to do so.

It is not easy to extend the Redfield ratio to include the contributions from cell walls, because diatoms and coccolithophores are more or less dominant among the phytoplankton at different times and in different places. An additional complication for silicon is the variable degree of silicification of diatom tests from different regions. Diatoms in the North Atlantic, for example, grow fairly scanty opal tests as compared to their heavily-armoured cousins from the Southern Ocean, who each accrete large amounts of silicate into their cell walls before sinking out of the surface layer.

While silicate is classified as a nutrient, it is important to be aware that it is a nutrient only for diatoms. Other phytoplankton that build non-siliceous cell walls do not require the presence of silicate.

Implications for Nutrient Distributions in the Sea

Importance of Spatial Separation of Photosynthesis and Remineralization

What is the effect on nutrient distributions in the sea of this withdrawal of nutrients into new phytoplankton biomass, and their re-injection upon decomposition of old biomass? Photosynthesis can take place only in the presence of sunlight, and so is restricted to the upper waters of the ocean. Below about 200 m depth, virtually all light has been absorbed by water molecules or by other light-absorbing substances, and photosynthesis below that depth is not viable even in the clearest tropical waters. In murky waters, photosynthesis can be restricted to the upper 10 m or even less. Therefore, the great photosynthetic demand for nutrients occurs in the upper ocean only, leading to lower concentrations there than at depth.

Remineralization, on the other hand, faces no such optical barriers and can take place in either light or dark water. Although most remineralization also takes place quite near to the surface, much of it also takes place in deep water or in seafloor sediments often at several kilometers depth. Of the nitrogen and phosphorus incorporated into new organic matter near the surface of the open ocean, $\sim$95% is liberated from the sinking particles before they reach 500 m depth, and most of the rest is remineralized into the deep ocean or into seafloor sediments and thence by diffusion into the deep ocean. The release of nutrients at depth raises concentrations there. Only 0.2% or so of the total surface production is permanently buried in seafloor sediments.

Much remineralization takes place in the same surface sunlit layer as that in which the phytoplankton grow, and it is important to realize that there is no sustained net effect on nutrient concentrations when photosynthesis and remineralization cancel each other out in the same location. As we can see from eqn [1], moving from left to right of the reaction then later moving back the other way produces no overall effect. Photosynthesis and remineralization produce large changes in nutrient concentrations only when they are separated in time or space.

In practice, it is the sinking under gravity of biological debris out of the surface mixed layer, prior to remineralization at greater depth, that depletes nutrient concentrations in the surface and increases them at depth. For this reason, oceanographers make an important distinction between total and export production. The first is the sum of all photosynthetic growth; the second is only that part that sinks out of the surface mixed layer before being decomposed. Viscous resistance is powerful for a small particle in comparison to the gravitational force pulling it downward. The sinking rate of individual phytoplankton cells is therefore very slow. For this reason, most export is in the form of fecal pellets of zooplankton, or as part of large aggregated clumps of particles known as 'marine snow.'

Impacts of Export Production on Nutrient Concentrations

The impact of export production on nutrient concentrations can be seen most clearly at times of very intense photosynthetic growth, for instance, during the spring blooms in temperate waters. Low light and low temperature, and strong winds that mix the water to several hundred meters depth, prevent phytoplankton from growing in high-latitude waters during the winter. At this time, nutrients accumulate in the surface waters. When physical conditions improve in the spring and once more allow phytoplankton growth, there is a large nutrient store for them to exploit. At this time the phytoplankton thrive on the abundant nutrients and proliferate rapidly. As many sink to depth – for instance, in fecal pellets of zooplankton – the surface waters are quickly stripped of their nutrients.

Figure 2 shows the unmistakable signature of the spring phytoplankton blooms in the NE Atlantic, apparent in the changing concentrations of nitrate, silicate, and carbon. The first two undergo severe depletion during April and May (Julian days

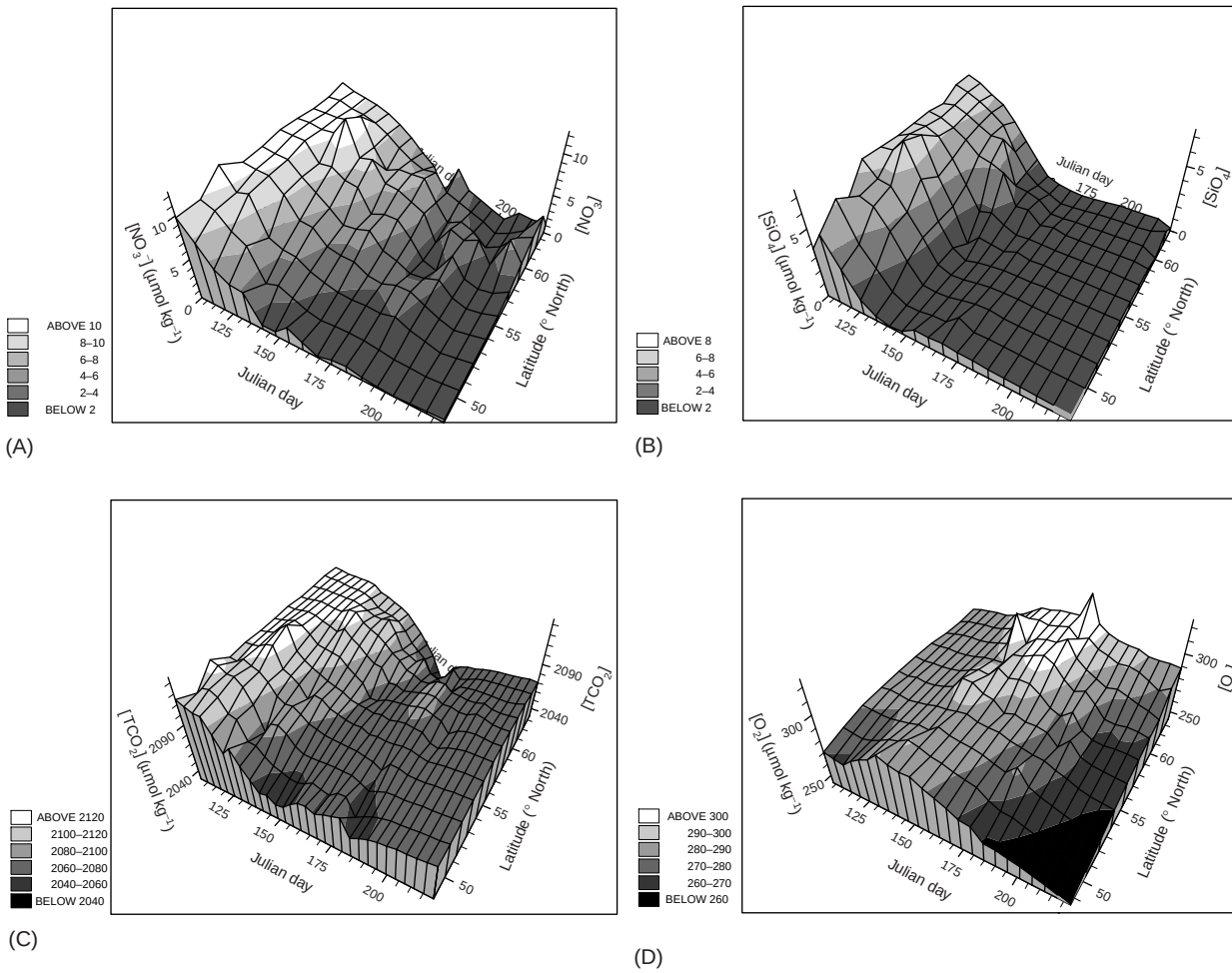

Figure 2 Variation in concentration of (A) nitrate [NO_3^-], (B) silicate [SiO_4], (C) total dissolved inorganic carbon [TCO_2], and (D) dissolved oxygen [O_2] (all μmol kg^{-1}) against date and latitude in the surface mixed layer of the NE Atlantic. All data were collected from longitudes between 10° and 30° W, from several different years.

91–151). Nitrate and silicate are almost completely removed from the water. Carbon, however, is reduced by only about 3%. Despite the patchy nature of the data and the consequent unevenness in the graphs, the overall pattern is clear. The blooms occur later farther north because conditions for initiation of phytoplankton growth are reached at a later date there. At the same time the depletion of nutrients, the logic of eqn [1] implies a concurrent injection of oxygen into the water, and this is also seen in **Figure 2D**.

These graphs illuminate the bidirectional nature of the feedback between nutrients and phytoplankton growth. Phytoplankton require nutrients to grow, but in the act of growing remove those same nutrients.

Figure 3 shows vertical profiles of several nutrients from a fairly typical location in the tropical north Pacific Ocean. Nutrients are depleted in surface waters relative to their concentrations deeper in the water. The shape of the profile for oxygen is the opposite of that for nutrients, because it is released rather than consumed during photosynthesis, and consumed rather than released during decomposition.

Straight Lines in Some Scatterplots

Another way of looking at nutrient data is to plot one nutrient concentration against another in a scatterplot, several of which are shown in **Figure 4**. These have been obtained from a global dataset, not just from one cruise. Particularly striking is the clustering of the [NO_3^-] versus [PO_4^{3-}] points about a straight line (**Figure 4A**), with a slope of 15 or so, very close to the 16:1 ratio for N:P in biomass. Why should these points lie along a straight line of that slope?

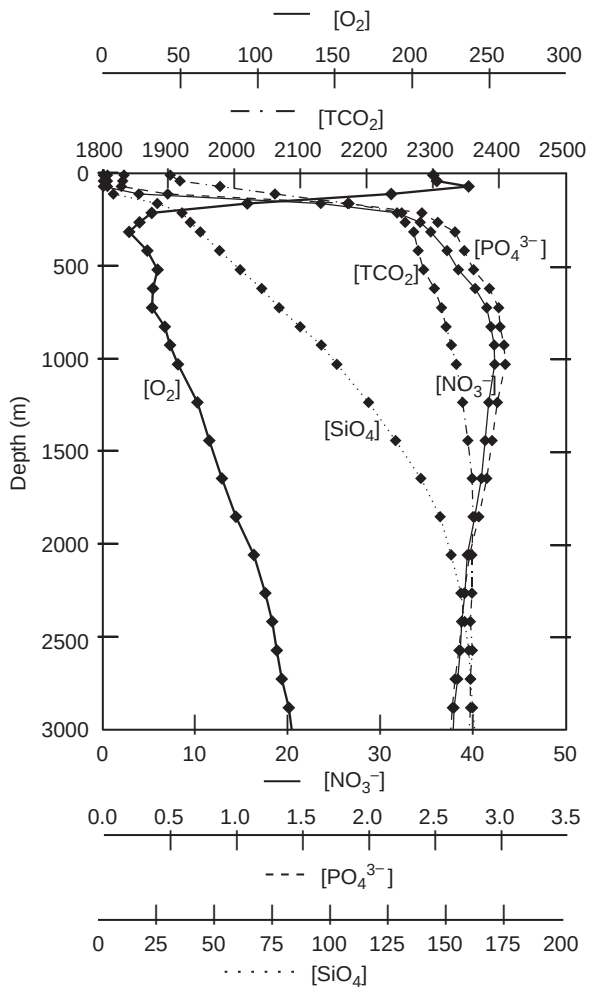

Figure 3 Vertical profiles of nitrate [NO_3^-], phosphate [PO_4^{3-}], silicate [SiO_4], total dissolved inorganic carbon [TCO_2], and dissolved oxygen [O_2] concentrations (all $\mu mol\,kg^{-1}$) from a cast in the tropical north Pacific Ocean (12°52′ N, 152°30′W) on 25 September 1991 (WOCE P16C cruise). Note the different axis scales for each property and the nonzero left-hand end of the [TCO_2] axis.

Alfred C. Redfield (after whom the Redfield ratio is named) provided the answer to this puzzle. The points form a straight line because N and P leak out of sinking particles of organic matter at the same fractional rate. As organic debris sinks down through the ocean under gravity, 16 atoms of nitrogen are released by decomposition whenever 1 atom of phosphorus is released. Nitrogen is not released more quickly or more slowly than phosphorus; they are both liberated at almost exactly the same rate, relative to the 16:1 ratio in the pristine organic matter. In the same way that the composition of a person's bloodstream reflects the metabolic wastes excreted by many individual cells (Redfield was a physiologist before becoming an oceanographer), so the nutrient composition of sea water is influenced by the way in which decomposing organisms break down biomass during its one-way voyage down toward the seafloor.

The points toward the bottom left of **Figure 4A** (nearest to the origin) therefore correspond to surface waters (containing lowest levels of nutrients), and the points toward the upper right are those measured deeper in the water (containing higher levels of nutrients).

The reason other scatterplots do not share the same straight-line quality of the [NO_3^-] versus [PO_4^{3-}] scatterplot is that the two nutrients do not reappear from organic matter at the same rate. For instance, the dissolution of the opal tests of diatoms does not proceed at the same rate as the decay of the organic matter. Instead the dissolution of these tests is fairly slow at the surface but accelerates at greater depth, relative to the rate of organic matter decay, giving rise to the curved shape of the scatterplot for [NO_3^-] versus [SiO_4] (**Figure 4B**).

Likewise, carbon from decaying organic matter is released slightly more slowly than are nitrogen and phosphorus, although not as slowly as silicon. Either bacteria preferentially target parts of a cell rich in nitrogen and phosphorus, such as proteins, or else those parts rich in carbon (such as carbohydrates) are inherently more resistant to decomposition. Regardless of the precise reason, nitrogen and phosphorus are extracted more rapidly than is carbon. Because the particles are created at the surface and are sinking as they are being remineralized, rapid remineralization means remineralization high in the water, near to the surface. Analysis of organic material caught in sediment traps hanging at different depths shows an increase in the C:N ratio of particles with depth, from values typical of pristine organic matter (6–7) at 100 m to higher values (10 or over) at 5000 m. The comparatively slow release of carbon, relative to nitrogen and phosphorus, therefore leads to carbon being released slightly lower in the water column (on average) than are nitrogen and phosphorus. The Redfield ratio or stoichiometry of remineralization is therefore not constant with depth for carbon (and also for oxygen), but instead is closer to $-O_2{:}C_{org}{:}N{:}P \approx 170{:}130{:}16{:}1$ (by moles) at 1500 m or deeper. The points in the scatterplot of [NO_3^-] against [TCO_2] (total inorganic dissolved carbon) therefore do not quite fall along a straight line, although close to it (**Figure 4C**).

The flux of carbon from surface to depth brought about by the large-scale exodus of organic biomass from the surface mixed layer is known as the organic carbon pump. The flux of carbon due to the accompanying exodus of coccoliths and

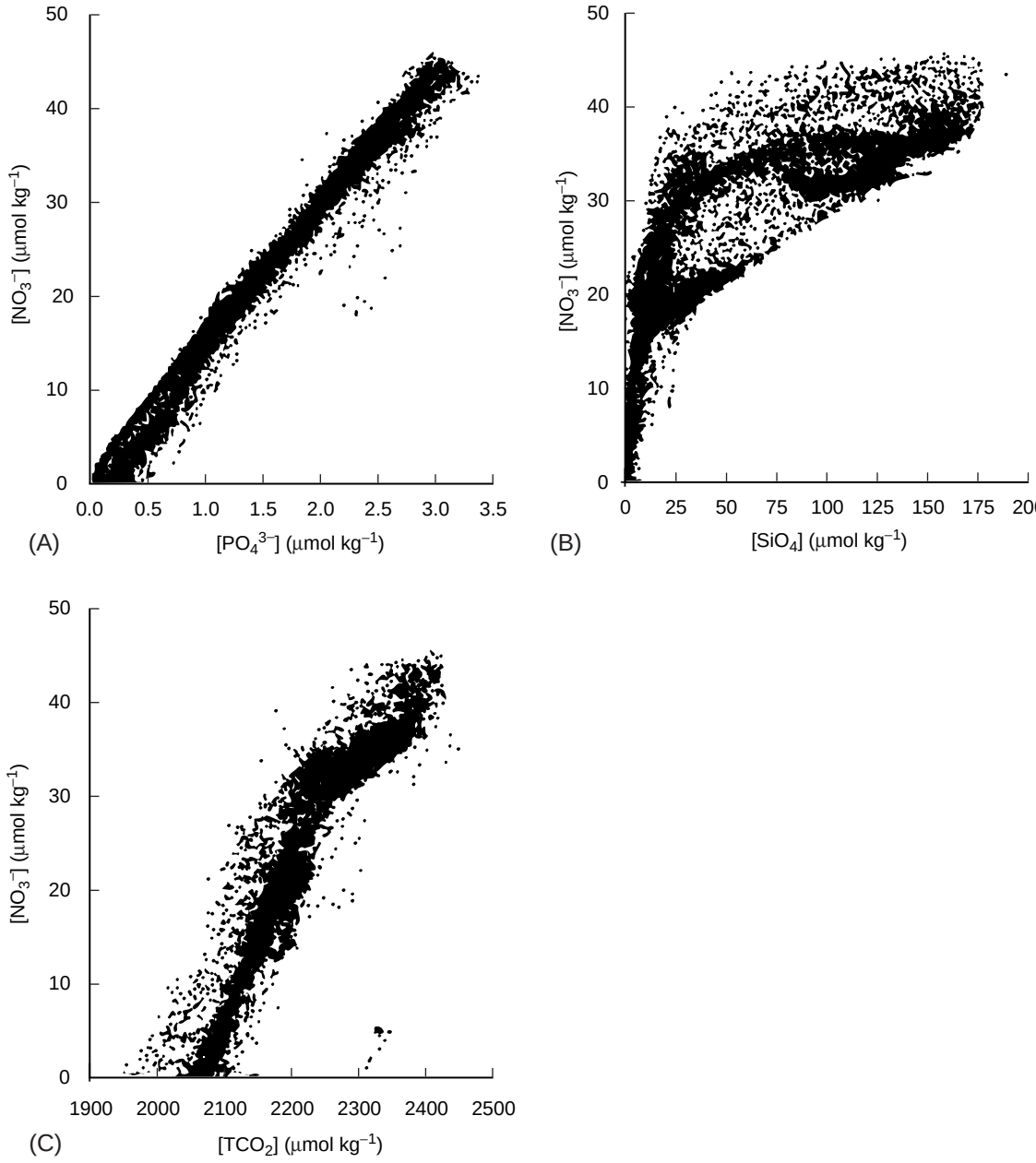

Figure 4 Scatterplots of (A) nitrate versus phosphate, (B) nitrate versus silicate, and (C) nitrate versus total dissolved inorganic carbon (all μmol kg^{-1}). Data from the GEOSECS and TTO programmes. Each point is obtained by comparing two different nutrient measurements made from the same bottle of sea water. Different bottles were collected from different locations and/or different water depths. Note the nonzero left-hand end of the $[TCO_2]$ axis in (C).

foraminiferal shells, which both also contain carbon but this time in solid calcium carbonate, is known as the inorganic carbon pump. The inorganic carbon pump also acts to prevent a straight-line correlation in **Figure 4C**, because the majority of coccoliths and foraminiferal shells dissolve only in deep waters. Below about 4500 m in the Atlantic and 3500 m in the Pacific, sea water becomes undersaturated (corrosive) with respect to calcium carbonate particles.

Intercepts of Scatter Plots

Redfield's analysis explained why points on a $[NO_3^-]$ versus $[PO_4]$ scatterplot line up along a straight line, but left one feature of **Figure 4A** unexplained. Why does that straight line intercept very close to the origin of the plot, and not some way off along either the $[NO_3^-]$ or the $[PO_4]$ axis? To put it another way, why are surface waters simultaneously

exhausted in both [NO_3^-] and [PO_4], rather than just one of the two? This is unlikely to be just an improbable coincidence, and a computer modeling study suggests that it has instead been brought about over time by the actions of nitrogen-fixing phytoplankton. The nitrogen fixers do better in competition with other phytoplankton when phosphate and other nutrients are present but nitrate is absent, but are outcompeted otherwise. Nitrogen fixers obtain their nitrogen from dinitrogen (N_2; molecular nitrogen) rather than nitrate, but their remineralization raises levels of nitrate in the same way as for other phytoplankton. Abundant growth of nitrogen-fixing phytoplankton, inevitably followed a short time later by its decay, thereby raises [NO_3^-] relative to [PO_4^{3-}]. This mechanism, which imports extra nitrate when nitrate runs out before phosphate, creates a dynamic link between the levels of [NO_3^-] and [PO_4^{3-}].

A similar explanation is required for the near-to-origin intercept of the [SiO_4] versus [NO_3^-] scatterplot (**Figure 4B**). The most likely explanation is the dominance of fast-growing diatoms (causing a flux of silicon to depth as cells sink) except when SiO_4 is scarce.

Other Processes Important in Nutrient Cycles

So far only the impacts of photosynthesis and remineralization have been considered, and these are indeed the two most important processes in most nutrient cycles. But many other processes also impact on the concentrations of nutrients and cause place-to-place variations in those concentrations.

For instance, in the phosphorus cycle (**Figure 5A**), one of the simplest of the nutrient cycles, it can be seen that rivers discharge dissolved phosphate into the ocean (raising concentrations near to river mouths) and that burial of organic matter takes phosphorus out with it. Deep water is enriched in all nutrients, phosphate included, compared to surface waters, which mostly have very low concentrations, and therefore those places in which deep waters rise to the surface (locations of upwelling) will have anomalously high nutrient concentrations compared to adjacent non-upwelled water. Horizontal currents (advection) also affect the spatial distribution of nutrient concentrations by moving relatively high- or low-nutrient waters from place to place.

There is another means of transport of nutrients by organic matter, one that is separate from transport in particles; this is the production, transport, and decay of dissolved organic matter (DOM). DOM is defined as organic matter that is so small that it passes through a 0.2 μm filter. DOM can be thought of as intermediate between particulate organic matter and inorganic nutrients. In contrast with particles (defined as greater in size than 0.2 μm), the complex organic molecules that make up DOM do not sink any great distance under gravity; water viscosity prevents them falling. But the gradual diffusion of DOM away from the

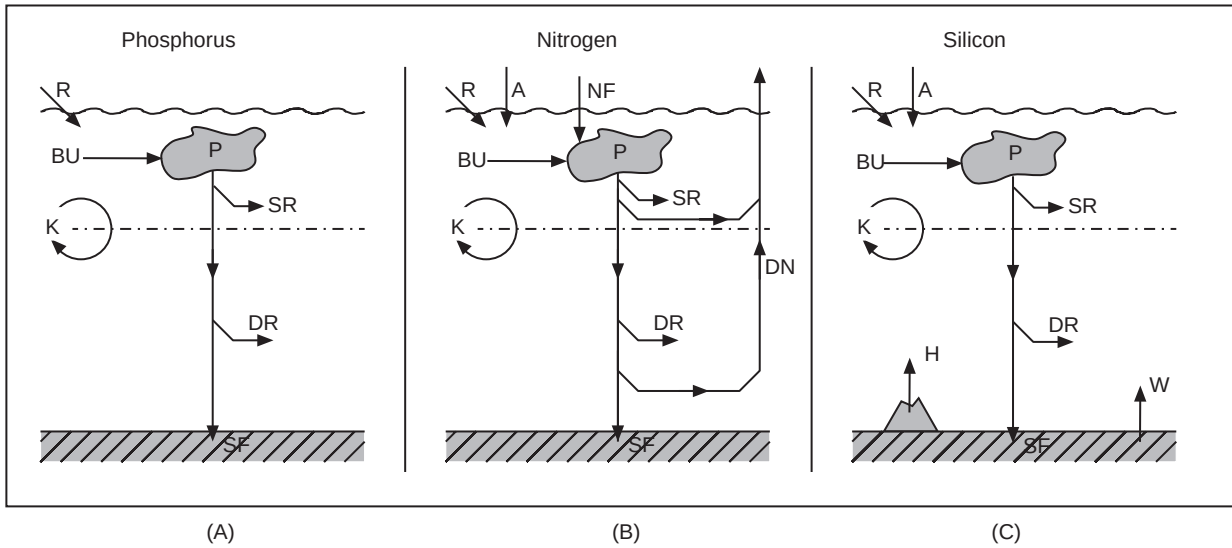

Figure 5 The biogeochemical cycles of (A) phosphate, (B) nitrate, and (C) silicate in the world ocean: R = river inputs, BU = biological uptake into plankton biomass (P), SR = remineralization into the surface box, DR = remineralization into the deep box, SF = sedimentary burial, K = flux due to mixing, DN = denitrification, NF = nitrogen fixation, H = hydrothermal inputs, W = seafloor weathering, A = atmospheric deposition. The world ocean is shown as two boxes: one surface and one deep. Only the most significant fluxes are shown.

intense biological activity in surface waters can still lead to a flux of nutrients. Although some DOM survives only for a short time, other components of DOM are resistant to bacterial breakdown and can persist for many months or years. Average concentrations of DOM are high: $40\,\mu mol\,C\,kg^{-1}$ (expressed in carbon units) or $2.5\,\mu mol\,N\,kg^{-1}$ (nitrogen units). When bacteria consume DOM and bring about the remineralization of the nutrients contained within it, then carbon, phosphorus, and nitrogen are released back into the water.

Sea water contains organically derived molecules (ligands) that absorb and bind inorganic iron. These ligands attract inorganic iron out of solution, thus depleting the inorganic concentration.

Whereas the nutrients remineralized from organic matter falling into seafloor sediments are an important input to the deep ocean, the seafloor is not otherwise a major source of most nutrients. An exception is the silicate cycle (**Figure 5C**): a significant amount of dissolved silicate enters the ocean within the super-hot water emitted from midocean ridges. Seafloor weathering also contributes an input of dissolved silicate. Water currents flowing over ocean sediments acquire nutrients diffusing out of them (of particular importance for iron), which are then transported with the water currents.

Air–sea gas exchange affects the oceanic cycles of oxygen and carbon (both exist as gases in the atmosphere). Such exchange is greatest when there is a large difference between the partial pressures in the ocean and in the atmosphere, and is also enhanced by a strong wind blowing over the water surface. Atmospheric deposition (in dust and/or in rainfall) is an important source of new silicon, nitrogen, and iron, but is of lesser importance in other cycles. Particulate scavenging (iron adheres to sinking particles) is an efficient means of removal of iron from the water column.

Residence Times

When considering the changing status of the oceans through time, for instance between glacial and interglacial periods in the past – we want to know whether the ocean could have contained substantially different concentrations of a particular nutrient at one time compared with another. Nutrient supply regulates phytoplankton production, which in turn is a major driver of climate. A measure of the speed with which the whole ocean can become depleted or enriched in a nutrient is the residence time for that nutrient. This is calculated by dividing the size of the whole ocean reservoir of a nutrient by its rate of input (or of output: in steady state they are the same). For phosphate, for instance, the residence time equals the ocean content ($\sim 2.6 \times 10^{15}\,mol\,P$) divided by the river supply ($\sim 7 \times 10^{10}\,mol\,P\,y^{-1}$), giving $\sim 40\,000$ years. For silicon the residence time is $\sim 20\,000$ years; for carbon (ignoring atmospheric inputs) $\sim 50\,000$ years; and for fixed nitrogen somewhere near 4000 years.

When Oxygen Runs Out

Equation [1] shows that photosynthesis is accompanied by the liberation, as opposed to the consumption, of dissolved oxygen. Surface waters of the ocean therefore frequently carry an excess of dissolved oxygen compared to equilibrium with the atmosphere, which is especially pronounced during times of intense photosynthesis (**Figure 2D**). When eqn [1] runs in reverse because of remineralization, dissolved oxygen is consumed as nutrients are released. This consumption of dissolved oxygen becomes critical to the ecosystem if so much is consumed that the oxygen runs out. For instance, animals living on the seafloor (shrimps, mussels, clams, fish, lobsters, etc.) will 'suffocate' owing to the lack of dissolved oxygen.

Although increased amounts of sinking biodetritus are usually beneficial to the seafloor animals, because they eat it, too great a flux of biodetritus to the seafloor causes anoxia and kills seafloor animals; this unwelcome phenomenon is known as eutrophication. Eutrophication is often stimulated by high supply rates of nutrients. Important areas that suffer from eutrophication include the Louisiana Dead Zone (in the Gulf of Mexico, caused by the nutrients delivered by the Mississippi River), the Baltic Sea (caused by high nutrient loads and also by restricted renewal of deep waters), and many other coastal areas. Dissolved oxygen is present in sufficient amounts for animal life in almost all of the open ocean, but upwelling of nutrients leads to intense production and anoxia off the coast of Peru, in the Benguela system off the western coast of southern Africa, and in the Arabian Sea. An example of the effect of anoxia, in the Benguela system, is the occasional mass strandings of crayfish and other fauna that occur as these animals migrate *en masse* right to the water's edge in an effort to escape the lethally deoxygenated water. This action is not always enough to save them, because many then become stranded on the shore by a retreating tide.

Anoxia (lack of oxygen) has chemical as well as biological implications. Oxygen is used by bacteria and animals to decompose organic matter (yielding an energy reward in the process), but if oxygen runs

Table 2 Organic matter oxidation pathways and their free energy yields

Reaction name	ΔG° *(KJ mol^{-1} of CH_2O)*
Oxic respiration	−475
Denitrification	−448
Manganese-oxide reduction	−349
Iron-oxide reduction	−114
Sulfate reduction	−77
Methane production	−58

CH_2O is carbohydrate. Adapted from Canfield DE (1993) Organic Matter Oxidation in Marine Sediments. In: Wollast R, Mackenzie FT, Chou L (eds) *Interactions of C, N, P and S Biogeochemical Cycles and Global Change* NATO ASI Series vol. 14. Berlin: Springer-Verlag.

out then other dissolved constituents can be used in its place. Specialized bacteria can break down organic matter anaerobically (in the absence of oxygen) and still gain an energy reward from it. **Table 2** shows the energy yields of the different possible reactions, and on the whole the magnitude of each energy yield determines the sequence in which the remineralization reactions take place. After oxygen runs out, nitrate is used to decompose organic matter (this process is called denitrification), but this leads to a running down of the dissolved stores of nitrate. If nitrate also runs out, reactions that use up iron and manganese come next, until these too are depleted. Then comes sulfate reduction, the remineralization of organic matter that depletes sulfate, and finally, if all the abundant sulfate is also exhausted, methane production.

As might be expected from the above description of denitrification, $[NO_3^-]$ versus $[PO_4^{3-}]$ scatterplots do not form straight lines in anoxic water, because of the depletion of nitrate. **Figure 6** shows such a plot from data collected in the Pacific Ocean off the coast of Peru, where denitrification in deeper, oxygen-depleted waters has removed nitrate and in the process shifted the scatterplot away from the more typical straight-line correlation.

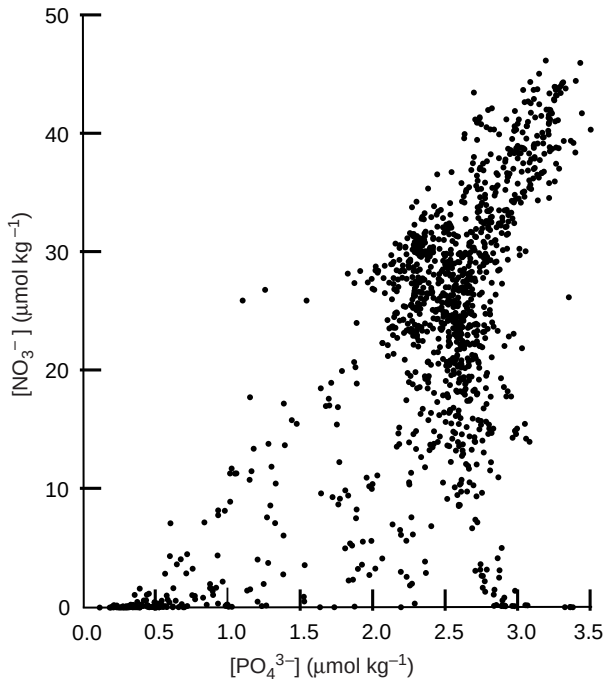

Figure 6 Scatterplot of nitrate versus phosphate (both μmol kg^{-1}) from data collected in the Pacific Ocean off the coast of Peru (several cruises). Data courtesy of L. Codispoti.

Conclusions

Oceanic nutrient cycles and spatial and temporal variations in nutrient concentrations are controlled most strongly by differences between where and when organic matter is formed and destroyed. Several other processes, in particular horizontal and vertical displacements of water masses, are also important. Redfield ratios describe the elemental recipe for phytoplankton and are useful in calculating the relative rates at which nutrients enter and leave organic matter.

See also

Bacterioplankton. Carbon Cycle. Marine Snow. Marine Silica Cycle. Microbial Loops. Phosphorus Cycle. Plankton and Climate. Plankton Viruses. Primary Production Processes. Primary Production Methods. Primary Production Distribution. Sedimentary Record, Reconstruction of Productivity from the. Trapped Particulate Flux.

Further Reading

Anderson LA and Sarmiento JL (1994) Redfield ratios of remineralisation determined by nutrient data analysis. *Global Biogeochemical Cycles* 8: 65–80.

Barnes RSK and Hughes RN (1988) *An Introduction to Marine Ecology*, 2nd edn. Oxford: Blackwell Science.

Broecker WS and Peng T-H (1982) *Tracers in the Sea*, ch. 1. New York: Lamont-Doherty Geological Observatory.

Falkowski PG (2000) Rationalizing elemental ratios in unicellular algae. *Journal of Phycology* 36: 3–6.

Fleming RH (1940) Composition of plankton and units for reporting populations and production. *Proceedings of the 6th Pacific Science Congress* 3: 535–540.

Harris E and Riley GA (1956) Oceanography of Long Island Sound, 1952–1954, VIII. Chemical composition of the plankton. *Bulletin of Bingham Oceanographic Collection* 15: 315–323.

Open University Course Team (1989) *Ocean Chemistry and Deep-Sea Sediments*, ch. 2. Oxford: Pergamon.
Redfield AC (1958) The biological control of chemical factors in the environment. *American Scientist* 46: 205–221.
Shaffer G, Bendtsen J and Ulloa O (1999) Fractionation during remineralisation of organic matter in the ocean. *Deep-Sea Research I* 46: 185–204.
Takahashi T, Broecker WS and Langer S (1985) Redfield ratio based on chemical data from isopycnal surfaces. *Journal of Geophysical Research (Oceans)* 90(C4): 6907–6924.
Tyrrell T (1999) The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature* 400: 525–531.

REFRACTORY METALS

K. J. Orians and C. L. Merrin,
The University of British Columbia,
Vancouver, British Columbia, Canada

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Introduction

The elements classified as 'refractory' here are those that are not readily dissolved in sea water. Their supply to the oceans is low relative to their abundance in the Earth's crust. In addition, they are rapidly removed from solution by interaction with the surfaces of sinking particles, a process referred to as 'scavenging.' This rapid removal means that they are in the oceans for only a short time before being removed to the seafloor. The average time they spend in the oceans, known as the oceanic residence time, ranges from a few tens to a few thousands of years. Both of these factors result in low concentrations in sea water relative to their abundance in the Earth's crust, a large range of oceanic concentrations, and distributions that typically reflect their sources.

The elements in this category exist as hydroxide species in sea water, mostly as $M(OH)_n^{X-n}$, where M is the metal, X is the oxidation state of the metal, and n is the number of hydroxide ligands in the complex. There is also the possibility that they may exist as organic complexes and/or in association with colloidal phases (particles $\leqslant \mu m$). Organic complexes have been shown to be important for iron, but not much is known about these other forms for many of these elements.

The most abundant of these elements, aluminum and iron (which comprise 8.23%, and 5.63%, respectively, of the Earth's crust, by weight) are also the most studied. The first reliable reports on dissolved aluminum in the oceans were made in the late 1970s. Since then there have been over 50 articles on the distribution of aluminum in the oceans. Reliable data on iron were not available until the late 1980s but, owing to the importance of iron in regulating primary production in some regions of the ocean, there has been a wealth of studies on this element in the past decade. Most of the other elements discussed here were not studied until the late 1980s or even the 1990s, and for many there are only a couple of articles on their oceanic distributions. There is still much we do not know about their distributions and the processes that control them in the oceans.

History

Advances in our understanding of trace metal distributions in the oceans began with the development of clean sampling methods in the late 1970s and have continued with the ongoing development of highly sensitive analytical methods. Clean sampling and handling methods are critical in the analysis of the more abundant refractory metals, aluminum and iron. Detection of the lower-abundance refractory metals, owing to their exceptionally low concentrations in sea water, has been limited by the sensitivity of available methods. Their analysis has greatly benefited from the increasing sensitivity of modern analytical instruments. The development of highly sensitive mass spectrometers that allow for aqueous sample introduction have revolutionized this field. Inductively coupled plasma mass spectrometers (ICP-MS) using quadrupole mass analyzers, made commercially available in the mid 1980s, and the magnetic and electric sector high-resolution ICP-MS instruments, available since the early 1990s, have allowed the detection of these elements without requirement for excessive sample processing and preconcentration steps.

Distributions

Rapid removal of the scavenged elements results in a low background concentration in the oceans and the potential for a large concentration range, depending on the variations in the magnitude of