The co-evolution of phytoplankton and trace element cycles in the oceans

FRANÇOIS M. M. MOREL

Department of Geosciences, Princeton University, Princeton, NJ 08544, USA

ABSTRACT

The composition of the oceans and of its biota have influenced each other through Earth's history. Of all the biologically essential elements, nitrogen is the only one whose seawater concentration is clearly controlled biologically; this is presumably the main reason why the stoichiometry of nitrogen (defined as its mol ratio to phosphorus), but not that of the trace nutrients manganese, iron, cobalt, nickel, copper, zinc and cadmium, is the same in seawater and in the plankton. Like the major nutrients, the trace nutrients are depleted in surface seawater as a result of quasi-complete utilization by the biota. This is made possible in part by the ability of marine phytoplankton to replace one trace metal by another in various biochemical functions. This replacement also results in an equalization of the availability of most essential trace metals in surface seawater. The difference in the stoichiometric composition of the plankton and of deep seawater, which is the dominant source of new nutrients to the surface, indicates that some nutrients are likely recycled with different efficiencies in the photic zone. The difference in the composition of the ocean and its biota provides insight into the coupling of biochemistry and biogeochemistry in seawater.

Corresponding author: François M. M. Morel. Tel.: 609-258-2416; fax: 609-258-5242; e-mail: morel@princeton.edu

PROLOGUE

Terry Beveridge wrote a great deal about the role of microbes in the biogeochemical cycles of trace elements. As witnessed by many of the articles in this special issue of *Geobiology*, he also inspired many others to work on this topic. I met Terry for the first time in 1995 at a meeting in Nancy (France). We found each other by accident the day before our talks, and had a wonderful time talking (and drinking Belgian beer) late in the night. I was very much taken by Terry's charm, and inspired by our long discussion and by his elegant (and surprisingly lucid) talk the following day. While he studied how bacteria and archea transform, mobilize and immobilize trace elements in terrestrial systems, my work has dealt chiefly with the interactions of trace metals and phytoplankton in the ocean. This article bears witness that Terry's inspiration reaches far and wide, bridging taxonomic distances and the chasm between continents and oceans. In the spirit of that evening in Nancy I have tried to focus here on the 'big picture' knowing full well that critical details may eventually falsify the corresponding 'big ideas'.

INTRODUCTION

Salt is not the only or even the main thing that distinguishes the oceans from freshwater systems. The immensity of the oceans effectively isolates open ocean processes from those on the continents and their margins. So we might consider the oceans as an ideal aquatic system, one in which, for the most part, internal processes dominate over the forcing by inputs from land. For the purpose of our discussion, we consider a piece of ideal open ocean to be made up of two boxes, one on top of the other (Fig. 1): (i) the euphotic zone at the surface where phytoplankton take up all essential elements necessary for the photosynthetic generation of planktonic biomass; and (ii) the deep ocean where the essential nutrients in the sinking biomass are remineralized. As a result of the great depth of the ocean, the return of the nutrients by mixing processes from the deep to the surface is very slow, resulting in impoverishment of the euphotic zone. Clearly the chemical composition of surface seawater is controlled to a large extent by the activity of the planktonic biota. In turn, over the course of Earth's history, the chemical composition of surface
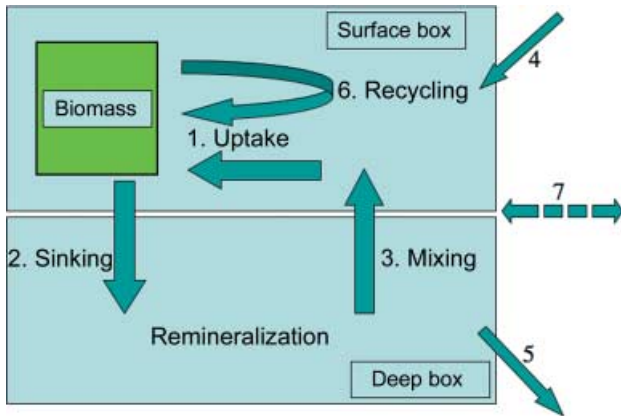
Fig. 1 Diagram of a two-box model of the open ocean showing the principal fluxes of nutrients.
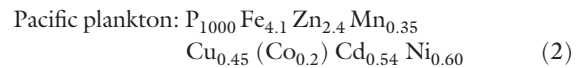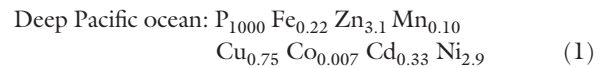
seawater must have influenced the genetic make-up of the planktonic organisms. It is my purpose here to examine how the chemistry of trace metals in the surface water of the oceans and the biochemistry of the organisms that inhabit that water have affected each other. After a small detour toward the major nutrients nitrogen (N) and phosphorus (P), I wish to identify in the trace metal physiology of the plankton and in the chemistry of seawater some telltale signs of their long history of mutual influence, of their 'co-evolution'.

In our idealized two-box model of the ocean, the cycle of any nutrient consists of six processes: (i) uptake by the biota at the surface; (ii) sinking and remineralization of the biomass; (iii) advection/diffusion of the remineralized nutrient to the surface; (iv) inputs (outputs) to the surface box from the outside (chiefly the atmosphere); (v) outputs (inputs) from the deep box to the outside (atmosphere and sediments); and (vi) recycling at the surface (Fig. 1). Although lateral fluxes are usually neglected in such vertical model, they actually matter

in many parts of the oceans for, even if the horizontal concentrations gradients are small, the currents and thus the horizontal fluxes can be large. These lateral fluxes which are implied, for example, by linear correlations between salinity and metal concentrations in surface water (Bruland & Franks, 1983; Saito & Moffett, 2002) are represented by the dashed arrow (7) in Fig. (1); they account for the distant influence of river and hydrothermal sources which constitute the major inputs of most elements to the global ocean.

STOICHIOMETRY OF SEAWATER AND PHYTOPLANKTON

The simplest way to look at the mutual influence of ocean chemistry and the plankton is simply to compare the stoichiometric composition of the two. I focus here on the essential trace elements that are present as cations in seawater – manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn) and cadmium (Cd) – leaving aside the oxoanions selenium (Se) and molybdenum (Mo). Using P to normalize all other essential elements as is customary, we find the following typical formulae from a perusal of the literature:

$$\text{Deep Pacific ocean: } P_{1000} Fe_{0.22} Zn_{3.1} Mn_{0.10}$$
$$Cu_{0.75} Co_{0.007} Cd_{0.33} Ni_{2.9} \qquad (1)$$

$$\text{Pacific plankton: } P_{1000} Fe_{4.1} Zn_{2.4} Mn_{0.35}$$
$$Cu_{0.45} (Co_{0.2}) Cd_{0.54} Ni_{0.60} \qquad (2)$$

The deep Pacific data correspond to concentrations measured at about 1000-m depth in the North Pacific (Station T7, (Martin *et al.*, 1989) + Ni data from station H77 (Bruland, 1980), which are most relevant for quantifying the input to the surface water by vertical mixing. As illustrated in the vertical profiles of P, Zn, Cd and Co in Fig. 2, the concentrations of nutrients, including most trace metals, are generally higher in
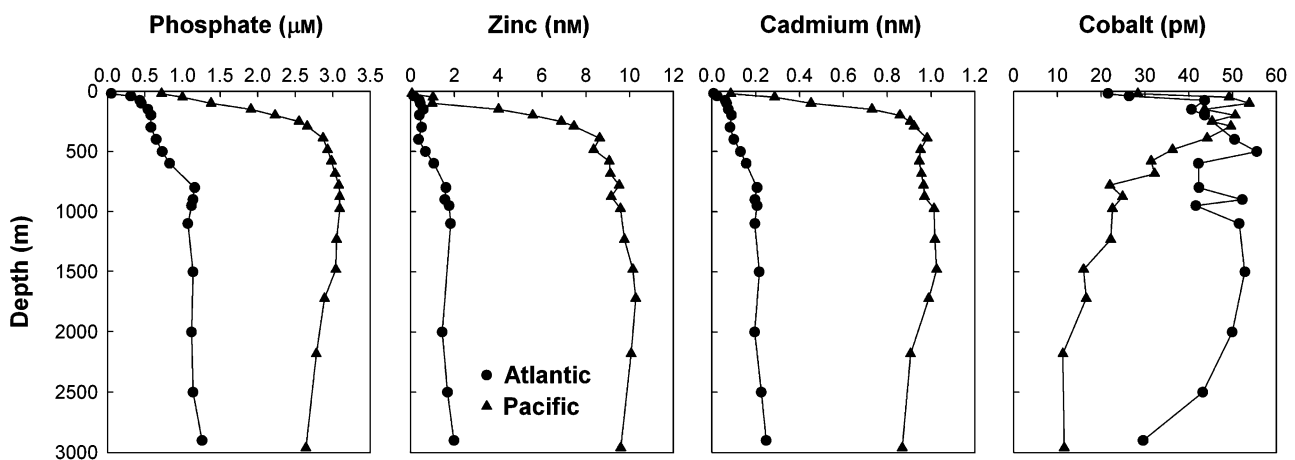

Fig. 2 Concentrations profiles of P, Zn, Cd and Co in the Pacific and Atlantic oceans. Pacific data are from station T7 (50.0°N, 145.0°W) (Martin *et al.*, 1989); Atlantic data are from a station at 47°N, 20°W (Martin *et al.*, 1993).

the deep Pacific than in the deep Atlantic, but their stoichiometric ratios to P are rather similar in both oceans. The exceptions are Fe, Mn and Co which exhibit deep scavenging and whose stoichiometric coefficients are a factor of 2 to 5 higher in the deep Atlantic.

Except for Co, the phytoplankton data are based on average concentrations in samples from the surface Pacific (Martin et al., 1976; Collier & Edmond, 1984). Samples with a high aluminum content (indicating the presence of terrigenous material) have been eliminated (Bruland et al., 1991; Ho et al., 2003). Co data for phytoplankton from the Pacific not being available, the chosen coefficient is an average value reported for Atlantic samples (Kuss & Kremling, 1999). It is to be expected that the metal content of the plankton should vary with ambient conditions. For example, metal concentrations averaged from measurements of Fe, Zn Mn and Ni in individual phytoplankters from the Southern Ocean yielded the following formula: $P_{100}Fe_{1.3} Zn_{4.4} Mn_{027} Ni_{0.56}$, but Fe-limited specimens had a three times lower Fe stoichiometry (Twining et al., 2004).

While these formulae are only approximate, it is clear that the stoichiometric coefficients of the essential trace metals (defined as their mol ratio to P) are for the most part within the same order of magnitude in the deep ocean and in the planktonic biomass, although they are clearly not the same. In contrast, as noted by Redfield 75 years ago, the N:P ratio in seawater is roughly constant at 16, and, on average, about the same in seawater and in the plankton (Redfield, 1934). Why is that so? And why is that true of the stoichiometry of N but not of the stoichiometry of trace nutrients? It hardly seems accidental that seawater and phytoplankton should have the same N stoichiometry. Either the N:P ratio of seawater has evolved to resemble that of the plankton or the N:P ratio of the plankton has evolved to resemble that of seawater, or both. In principle, the plankton can influence the chemistry of seawater by modifying any one of the inputs/outputs from/ to outside our two ocean boxes (fluxes 4 and 5; Fig. 1). For example, the biota might affect the loss of nutrients to the sediments by modulating the material flux to the bottom. But the net long-term loss of nutrients to the sediments (flux 5) is apparently controlled by diagenetic processes over which organisms have little influence, except indirectly through their effect on the degree of oxidation of deep seawater and sediments (Bruland & Lohan, 2003). It has also been argued that phytoplankton can influence the atmospheric inputs of nutrients (flux 4) via emission of dimethylsulfide (DMS) [from dimethylsulfoniopropionate (DMSP)] which generates sulfate aerosols that seed cloud formation and promote scavenging and dissolution of metal-rich dust (Zhuang et al., 1992). But this effect is very indirect and, with the notable exception of Fe, the atmospheric input of trace nutrients to the surface in most areas of the ocean is small compared to their upward flux from deep seawater.

Nitrogen is really the only nutrient whose average concentration in seawater is markedly affected, in fact controlled, by biological processes. The principal flux of biologically available N out of the open ocean is from denitrification at depth and this loss is made up by an input of new N through N_2 fixation at the surface (Gruber & Sarmiento, 1997). As argued by Redfield, this particularity of the oceanic N cycle is a major reason why the ocean and its biota have co-evolved to reach the same N:P ratio: '. . . in a world populated by organisms of these two types (i.e. N_2 fixers and denitrifiers) the relative proportion of phosphate and nitrate must tend to approach that characteristic of protoplasm in general . . .' The adaptation of the organisms to their environment is the other plausible reason given by Redfield: 'By the balancing of such communities (i.e. algae with different N/P ratios) the ratio of the elements in the plankton as a whole might come to reflect the ratio of the nutrient substances in sea water rather closely.' But this second reason appears insufficient by itself: over Earth's history, the stoichiometric coefficients of N in the ocean and the plankton have effectively become the same on average; but this is not true for the other essential nutrients whose average seawater concentrations are not directly controlled by the biota.

The net result of the equal proportions of N and P in seawater and biomass is that both are eliminated simultaneously at the surface by phytoplankton uptake. But the trace nutrients Fe, Co, Cu, Zn and Cd are also effectively eliminated from surface seawater (Mn and Ni less so, as discussed below). This seems to indicate that these trace metals, along with N and P, are in some way co-limiting phytoplankton growth when averaging over appropriate time and space scales. For this to be true, there must be a close match between the utilization of these metals by the biota and their fluxes to the surface ocean. Let us consider the two facets to this balancing of demand and supply: (i) adaptation of the phytoplankton to make use of available trace nutrients and the consequent effect on trace metal chemistry in surface water; and (ii) modulation of the nutrient fluxes to match the needs of the plankton.

METAL REPLACEMENT

Over the past 30 years of work on the trace metal physiology of marine phytoplankton, it has become apparent that these organisms are particularly apt at replacing one essential trace metal by another. In pure cultures of several model species, when the growth rate is limited by an insufficient concentration of a particular metal, addition of another metal enhances growth; Zn, Co and Cd provide a well-documented example of this phenomenon. It is also well documented from the study of some enzymes such as superoxide dismutase in which diverse metals can serve as alternative active centers.
1 Under Zn limitation, several phytoplankton species can grow faster when supplied with Co and, sometimes, Cd. Some species grow as well (or even faster) when given only Co and no added Zn to the cultures; some species require a minimum of Zn and can only replace part of it with Co or Cd (Price & Morel, 1990; Sunda & Huntsman, 1995; Xu et al., 2007). The

biochemical basis for this replacement is not fully understood but *in vivo* replacement of Zn by Co or Cd in the carbonic anhydrases of diatoms has been demonstrated in model species (Yee & Morel, 1996; Lane & Morel, 2000; Xu *et al.*, 2007).
2 The highly reactive and noxious superoxide anion, O_2^-, is produced by light-induced reactions in cells exposed to sunlight. The enzyme superoxide dismutase (SOD) is thus essential to the survival of photosynthetic organisms and is known to require a sizable fraction of cellular metals in phytoplankton. There are now four known distinct types of SOD which utilize different metal cofactors: Fe, Mn, Cu + Zn and Ni. All four have been identified in various species of phytoplankton (Wolfe-Simon *et al.*, 1983; Palenik *et al.*, 2007) and some species can use more than one. For example, under Fe limitation, some diatoms can use Mn instead of Fe in SOD (Peers & Price, 2004).

The ability to use one trace metal for another in marine phytoplankton seems an adaptation to life in a metal poor environment. It is obviously a way to make use of whatever metabolically useful metal is supplied to the euphotic zone, and, by replacing a poorly available metal by one that is more available, to match utilization to supply.

COMPOSITION OF SURFACE SEAWATER

Understanding the consequence of the inter-replacement of essential trace metals on the trace metal chemistry of surface seawater requires that we delve into the kinetics of metal uptake by phytoplankton, and that we define the notion of availability. In a first approximation, the rate of uptake (mol cell^{-1} s^{-1}) of an essential trace metal, M, by a phytoplankton cell is determined by the rate of reaction of M with uptake ligands on the cell surface (Hudson *et al.*, 1992):

$$\text{uptake rate of M} = \rho^M = k_f^M \cdot M' \cdot L^M$$

where k_f^M is the second order rate constant for the reaction (L mol^{-1} s^{-1}), M' is the unchelated concentration of M in the external medium (mol L^{-1}) and L^M is the concentration of uptake ligands for M on the cell surface (mol cell^{-1}). The rate constant k_f^M is characteristic of the metal and relatively insensitive to the nature of the ligand with which it reacts. As a result, the product $k_f^M \cdot M'$ gives a measure of the 'availability' of M to all cells. For each cell, the concentration of uptake ligands L^M determines the individual rate of uptake of M. This 'kinetic model' of trace metal uptake by phytoplankton is equivalent to the 'free ion uptake model' if the rate of the back reaction of metal dissociation from the uptake ligand is negligible as appears supported by laboratory data (see, for example, Hudson & Morel, 1993; Sunda & Huntsman, 1998).

At steady state, the uptake of M by all the phytoplankton in the euphotic zone must match its total supply which, in the absence of a significant lateral flux, is the sum of its upward vertical flux, its recycling flux and its atmospheric input (which is small for most metals except Fe; Fig. 1):

$$\text{total flux of M} = \sum \rho^M = k_f^M \cdot M' \cdot \sum L^M$$

Since the total flux of M to the euphotic zone is limited, the cells compete for M. If a cell increases its uptake rate of M by increasing its number of uptake ligands, L^M, it decreases M' and, hence, the availability of M to all phytoplankton:

$$k_f^M \cdot M' = (\text{total flux of M})/\sum L^M$$

Consider now the ideal case where two metals, say Zn and Co, can replace each other perfectly in their cellular function(s). Consider further that the cellular cost of uptake (energy, transport molecules, area of membrane) are the same for both. If one metal is more available than the other, say k_f^{Zn} Zn$' > k_f^{Co}$ Co$'$, it is advantageous for some species to switch uptake resources, from Co to Zn. So some cells increase their concentration of Zn uptake ligands L^{Zn} at the expense of Co uptake ligands L^{Co}. The result is a decrease in Zn availability and an increase in Co availability. The eventual consequence of competition among cells for Zn and Co will be an equalization of the availabilities of the two metals: k_f^{Zn} Zn$' = k_f^{Co}$ Co$'$. Ultimately, to the extent that any essential metal can replace any other through a series of substitutions in various enzymes (e.g. replacing Co by Zn in carbonic anhydrases, replacing Zn by Mn, Fe or Ni in SOD, etc.), we expect the availabilities of all essential metals in surface seawater to be the same. This is approximately what is observed for several metals of interest whose free concentrations M' vary proportionally to $1/k_f^M$ (Fig. 3). For example, according to available data, the large difference between the unchelated concentrations of Zn and Ni in surface seawater matches the difference in their kinetics of reaction with ligands. The relative inertness of Ni^{2+}, which reacts about a thousand times slower than the other transition
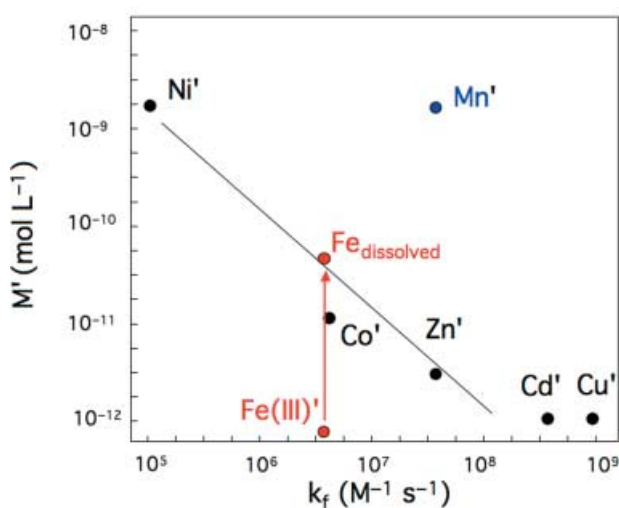

Fig. 3 Inverse proportionality between the unchelated concentrations of essential trace metals in surface seawater and the second order rate coefficient for complexation. Modified from Hudson & Morel (1993).
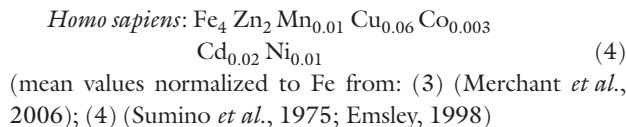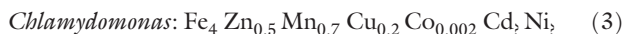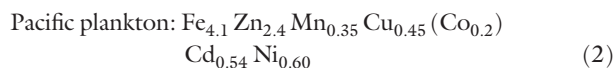
metals of interest likely explains why Ni in surface seawater is apparently not chelated (Saito *et al.*, 2004).

The two metals that do not fit well with the others on the graph of Fig. 3 are Mn, which is far above the line, and Fe, which is far below. The vertical (dissolved) concentration of Mn in the ocean exhibits not a minimum at the surface like other essential metals but a maximum caused by reductive photochemical dissolution of Mn oxides and inhibition of biological oxidation of dissolved Mn (Sunda & Huntsman, 1988). The uptake of Mn by phytoplankton is apparently not limited by reaction kinetics with transport ligands like the other metals; rather, it seems that Mn uptake is controlled by the lack of specificity of cellular uptake systems (Hudson & Morel, 1993; Sunda & Huntsman, 1996). The case of Fe, the only trace nutrient positively demonstrated to be limiting phytoplankton growth in some regions of the ocean, is more complicated. Some species of phytoplankton are now known to take up Fe(III) bound in chelators such as siderophores by using surface reductases that release Fe(II) from the chelator and make it available for cellular uptake (Soria-Dengg & Horstmann, 1995; Maldonado & Price, 2001; Shaked *et al.*, 2005). The 'available' Fe concentration is thus larger than the unchelated concentration and may in fact approximate the total dissolved concentration. It is remarkable that the total dissolved Fe concentration fits with the free concentrations of the other metals on Fig. 3.

One may note that the points for Cd and Cu at the bottom right of the graph in Fig. 2 are somewhat above the line. At very low concentrations of free metals, it is the diffusion in the boundary layer next to the cell surface that limits uptake rather than the kinetics of reaction with uptake ligands. The diffusion flux of a trace metal present at 1 pM unchelated concentration in seawater to a cell of 10 μm in diameter would be about 10^{-18} mol day^{-1}, about a quarter of the average cellular quota of Cu or Cd for cells of this size. Such a cell would thus have to minimize its use of Cu and Cd or be limited to a relatively slow growth rate by the diffusion flux of these trace metals. Depending on the size of a particular organism and the ambient free metal concentration, the uptake of Zn and Co might be similarly limited by diffusion (Sunda & Huntsman, 1995).

BIOLOGICAL RECYCLING

A comparison of the elemental composition of oceanic plankton with that of other organisms (for which few data are available) shows that the stoichiometric coefficients of the various trace metals are much more uniform in the plankton than in other organisms:

$$\text{Pacific plankton: } Fe_{4.1} \, Zn_{2.4} \, Mn_{0.35} \, Cu_{0.45} \, (Co_{0.2})$$
$$Cd_{0.54} \, Ni_{0.60} \tag{2}$$

$$\textit{Chlamydomonas: } Fe_4 \, Zn_{0.5} \, Mn_{0.7} \, Cu_{0.2} \, Co_{0.002} \, Cd_? \, Ni_? \tag{3}$$

$$\textit{Homo sapiens: } Fe_4 \, Zn_2 \, Mn_{0.01} \, Cu_{0.06} \, Co_{0.003}$$
$$Cd_{0.02} \, Ni_{0.01} \tag{4}$$

(mean values normalized to Fe from: (3) (Merchant *et al.*, 2006); (4) (Sumino *et al.*, 1975; Emsley, 1998)

For example, the freshwater alga *Chlamydomonas* and the human body contain much less Co and Cd compared to other metals than the oceanic plankton. The much lower stoichiometric coefficients of Co or Cd compared to a metal such as Zn in *Chlamydomonas* or *Homo sapiens* seem to match what we know of the biochemical use of metals: Zn is known to serve as metal center or structural element in hundreds of proteins, while Co is known to be used in only few, and Cd in only one, so far. The unusual composition of the phytoplankton must result in part from their aptitude for metal replacement. But, as discussed below, there may also be more subtle reasons why the stoichiometric coefficients of the essential trace elements in planktonic biomass are confined to such a narrow range.

Part of the explanation for the peculiar composition of phytoplankton is simply given in our second quote from Redfield: the phytoplankton has evolved to resemble seawater. While not exactly the same as that of deep seawater, the stoichiometry of the planktonic biomass is much more similar to it than to the stoichiometry of *Chamydomonas* or *Homo sapiens*. For example, the relatively high Cd:Zn ratio in plankton is only a factor of two greater than that of the deep ocean. It is easy to conceive that this situation results from the mechanism of metal replacement discussed above which makes it advantageous to utilize equally efficiently the vertical flux of all metals that can be used biochemically. Since the total concentrations of Zn and Cd at the surface are negligible compared to their deep concentrations, the corresponding upward fluxes (flux 3 on Fig. 1) are simply proportional to the deep Zn and Cd concentrations. The complete utilization of Zn and Cd as alternative micronutrients must then result in their similar ratio in phytoplankton and the deep ocean. More generally, the utilization of all biologically useful metals by appropriate substitution in various biochemical functions must lead to a rough matching of the stoichiometric composition of the phytoplankton and deep seawater – except for metals like Fe that have a significant atmospheric input.

But this explanation appears insufficient for the stoichiometric coefficients of the various trace metals (except Fe) are apparently more uniform in the plankton than in deep seawater. Most extreme, according to a comparison of formulae 1 and 2, is the case of Co, which is highly enriched in the plankton compared to the deep ocean, although this enrichment is likely exaggerated by the geographic mismatch between the deep Pacific water concentration and the Atlantic phytoplankton data (the Co/P mol ratio is about five times larger at 1000 m in the North Atlantic than in the Pacific (Martin *et al.*, 1993). The biogeochemical cycle of Co in the oceans, like that of Fe and Mn, is also complicated by deep scavenging processes. In contrast, Cd is an extremely 'well-behaved' nutrient in the oceans
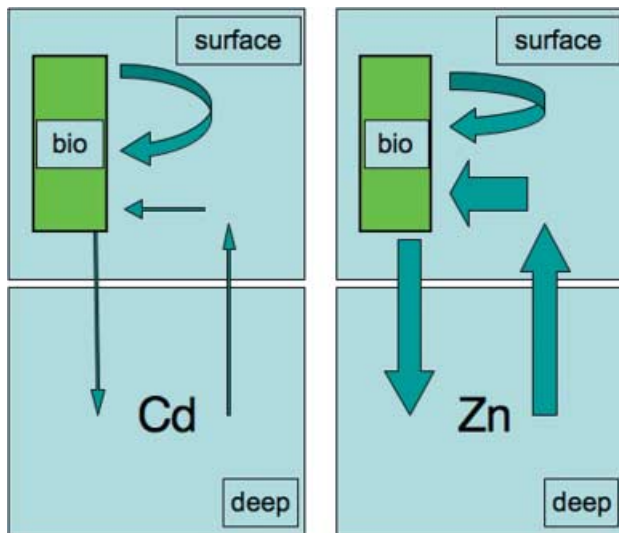
Fig. 4 Illustration of the contrast between the oceanic cycles of Zn and Cd: the proportion of Cd taken up by the plankton that comes from recycling in surface water is much larger than that of Zn. This is necessitated by a larger Cd:Zn ratio in plankton than in deep seawater.

and although its enrichment, relative to P, in phytoplankton compared to deep seawater is relatively modest, it is seen in all three available data sets (Martin *et al.*, 1976; Collier & Edmond, 1984; Kuss & Kremling, 1999). Comparing Cd with Zn, the metal it is known to replace in phytoplankton, seems most appropriate. The upward fluxes of Cd and Zn are proportional to their concentrations in deep water multiplied by the rate of vertical mixing, while their rates of incorporation into the biomass are proportional to their concentrations in the biomass multiplied by the average growth rate. Hence, the upward flux of Zn is 10 times greater than the upward Cd flux, while its incorporation into the biota is only a factor of four or so greater than that of Cd. Absent a significant atmospheric input of Cd, the high stoichiometric coefficient for Cd in the plankton can only be explained by a relatively large recycling flux at the surface. In other words, it appears that Cd may be recycled more efficiently than Zn in the surface ocean (Fig. 4). Despite the paucity of data, it seems likely that Co, which is the least abundant of the essential metals in the deep sea, is also recycled efficiently in the surface ocean. But determining the relative importance of the recycling flux of various trace metals in surface seawater requires more data than presently available, and a region-by-region analysis that takes into account atmospheric metal inputs and the variable stoichiometry of phytoplankton adapted to different conditions.

The relative recycling efficiency of the various nutrients in surface seawater must result in some way from the co-evolution of the chemistry and biology of the ocean. A difference in the efficiency of recycling among essential trace metals should be controlled in part by their different coordination in cellular compounds and the chemical nature of these compounds. The efficiency of recycling of any nutrient should thus reflect the

biochemical evolution of the planktonic biota. Over Earth's history, phytoplankton may have evolved simultaneously biochemistries that make maximum use of the available trace metal fluxes and strategies to promote more efficient recycling of some metals compared to others. For example, if a phytoplankter had evolved the ability to use Cd or Co instead of Zn and it were the only species to do so, it would behoove that organism to also evolve the ability to recycle this substitutive metal efficiently. Since a Cd or Co specialist must, on average, grow as fast as a Zn specialist to survive, the total fluxes of the metals may tend to become equal over time if they are used by the cells with the same efficiency. But if planktonic organisms have such an ability to increase the recycling efficiency of a trace nutrient, why shouldn't they simply recycle Zn more efficiently rather than replacing it by the relatively rare Cd or Co in various biochemical functions?

To fully understand the long-term mutual relationship of the trace element composition of the oceans and the planktonic biota, it appears that we shall need to figure out what limits the biochemical utilization of various elements and the ability of organisms to promote differential recycling of these elements. But it is also possible that what we now see in the chemistry and biology of the surface waters of the oceans does not reflect some type of optimum exploitation of resources, as we have assumed implicitly, but rather the long trajectory of evolution. In that case we shall also need to understand how elements like Zn, Cd or Co became more or less available to the biota during Earth's history (Saito *et al.*, 2003) and how that availability forced the evolution of organisms down biochemical paths that are essentially irreversible. Regardless of the underlying cause, the difference in the stoichiometric compositions of the planktonic biota and of deep seawater, which serves as the principal source of most 'new' nutrients to the surface, provides a clue regarding the coupling of biochemistry and biogeochemistry in the modern ocean and, perhaps, throughout Earth's history.

ACKNOWLEDGMENTS

REFERENCES

Bruland KW (1980) Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth and Planetary Science Letters* **47**, 176–198.

Bruland KW, Franks RP (1983) Mn, Ni, Cu, Zn and Cd in the western North Atlantic. In *Trace Metals in Seawater, NATO Conference Series 4* (eds Wong CS, Boyle E, Bruland KW, Burton JD and Goldberg ED). Plenum, pp. 379–414.

Bruland KW, Lohan MC (2003) Controls of Trace Metals in Seawater. In *Treatise in Geochemistry* (eds Elderfield H, Holland HD, Turekian KK). Elsevier, pp. 23–47.

Bruland KW, Donat JR, Hutchins DA (1991) Interactive influences of bioactive trace metals on biological production in oceanic waters. *Limnology and Oceanography* **36**, 1555–1577.

Collier R, Edmond J (1984) The trace element geochemistry of marine biogenic particulate matter. *Progress Oceanography* **13**, 113–199.

Emsley J (1998) *The Elements.* Clarendon Press, Oxford

Gruber N, Sarmiento JL (1997) Global patterns of marine nitrogen fixation and denitrification. *Global Biogeochemical Cycles* **11**, 235.

Ho TY, Quigg A, Finkel ZV, Milligan AJ, Wyman K, Falkowski PG, Morel FMM (2003) The elemental composition of some marine phytoplankton. *Journal of Phycology* **39**, 1145–1159.

Hudson RJM, Morel FMM (1993) Trace metal transport by marine microorganisms: implications of metal coordination kinetics. *Deep-Sea Research* **40**, 129–150.

Hudson RJM, Covault DT, Morel FMM (1992) Investigations of iron coordination and redox reactions in seawater using 59Fe radiometry and ion-pair solvent extraction of amphiphilic iron complexes. *Marine Chemistry* **38**, 209–235.

Kuss J, Kremling K (1999) Spatial variability of particle associated trace elements in near-surface waters of the North Atlantic (30 degrees N/60 degrees W to 60 degrees N/2 degrees W), derived by large-volume sampling. *Marine Chemistry* **68**, 71–86.

Lane TW, Morel FMM (2000) A biological function for cadmium in marine diatoms. *Proceedings of the National Academy of Sciences of the USA* **97**, 4627–4631.

Maldonado MT, Price NM (2001) Reduction and transport of organically bound iron by *Thalassiosira oceanica* (Bacillariophyceae). *Journal of Phycology* **37**, 298–309.

Martin JH, Bruland KW, Broenkow WW (1976) Cadmium transport in the California current. In *Marine Pollutant Transfer* (eds Windom HL, Duce RA). Lexington Books, pp. 159–184.

Martin JH, Gordon RM, Fitzwater SE, Broenkow WE (1989) Vertex: phytoplankton/iron studies in the Gulf of Alaska. *Deep-Sea Research* **36**, 649–680.

Martin JH, Fitzwater SE, Gordon RM, Hunter CN, Tanner SJ (1993) Iron, primary production and carbon–nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment. *Deep-Sea Research II* **40**, 115–134.

Merchant SS, Allen MD, Kropat J, Moseley JL, Long JC, Tottey S, Terauchi AM (2006) Between a rock and a hard place: Trace element nutrition in Chlamydomonas. *Biochimica et Biophysica Acta* **1763**, 578–594.

Palenik B, Grimwod J, Aerts A, Rouze P, Salamov A, Putman N, Dupont C, Jorgensen R, Derelle E, Rombauts S, Zhou K, Otillar R, Merchant SS, Poell S, Gaasterland T, Napoli C, Gendler K, Manuell A, Tai V, Vallon O, Piganeau G, Jancek S, Heijde M, Jabbari K, Bowler C, Lohr M, Robbens S, Werner G, Dubchak I, Pazour GJ, Ren Q, Paulsen I, Delwiche C, Schmutz J, Rokhsar D, Van de Peer Y, Moreau H, Grigoriev IV (2007) The tiny eukaryote Ostreococcus provides genomic insights into the paradox of plankton speciation. *Proceedings of the National Academy of Sciences of the USA* **104**, 7705–7710.

Peers G, Price NM (2004) A role for manganese in superoxide dismutases and growth of iron-deficient diatoms. *Limnology And Oceanography* **49**, 1774–1783.

Price NM, Morel FMM (1990) Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* **344**, 658–660.

Redfield AC (1934) *On the Proportions of Organic Derivations in Sea Water and Their Relation to the Composition of Plankton.* University Press of Liverpool, Liverpool, UK.

Saito MA, Moffett JW (2002) Temporal and spatial variability of cobalt in the Atlantic Ocean. *Geochimica et Cosmochimica Acta* **66**, 1943–1953.

Saito MA, Sigman DM, Morel FMM (2003) The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean – Proterozoic boundary? *Inorganica Chimica Acta* **356C**, 308–318.

Saito MA, Mofett JW, Ditullio GR (2004) Cobalt and nickel in the Peru upwelling region: a major flux of labile cobalt utilized as a micronutrient. *Global Biogeochemical Cycles* **18** doi: 10.1029/2003GB002216.

Shaked Y, Kustka AB, Morel FMM (2005) A general kinetic model for iron acquisition by eukaryotic phytoplankton. *Limnology and Oceanography* **50**, 872–882.

Soria-Dengg S, Horstmann U (1995) Ferrioxamines B and E as iron sources for the marine diatom *Phaeodactylum tricornutum. Marine Ecology Progress Series* **127**, 269–277.

Sumino K, Hayakawa K, Shibata K, Kitamura S (1975) Heavy metals in normal Japanese tissues. *Archives of Environmental Health* **30**, 487–495.

Sunda WG, Huntsman SA (1988) Effect of sunlight on redox cycles of manganese in the southwestern Sargasso Sea. *Deep-Sea Research* **35**, 1297–1317.

Sunda WG, Huntsman SA (1995) Cobalt and zinc interreplacement in marine phytoplankton: biological and geochemical implications. *Limnology And Oceanography* **40**, 1404–1417.

Sunda WG, Huntsman SA (1996) Antagonisms between cadmium and zinc toxicity and manganese limitation in a coastal diatom. *Limnology and Oceanography* **41**, 373–387.

Sunda WG, Huntsman SA (1998) Processes regulating cellular metal accumulation and physiological effects: phytoplankton as model systems. *Science of the Total Environment* **219**, 165–181.

Twining BS, Baines SB, Fisher NS (2004) Element stoichiometries of individual plankton cells collected during the Southern Ocean Iron Experiment (SOFeX). *Limnology and Oceanography* **49**, 2115–2128.

Wolfe-Simon F, Grzebyk D, Schofield O, Falkowski PG (1983) The role and evolution of superoxide dismutases in algae. *Nature* **301**, 234–236.

Xu Y, Tang D, Shaked Y, Morel FMM (2007) Zinc, cadmium, and cobalt interreplacement and relative use efficiencies in the coccolithophore Emiliania huxleyi. *Limnology And Oceanography* **52**, 2294–2305.

Xu Y, Feng L, Jeffrey PD, Shi YG, Morel FMM (2008) Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. *Nature* **452**, 56–61.

Yee D, Morel FMM (1996) In vivo substitution of zinc by cobalt in carbonic anhydrase of a marine diatom. *Limnology and Oceanography* **41**, 573–577.

Zhuang G, Zhen Y, Duce RA, Brown PR (1992) Link between iron and sulphur cycles suggested by detection of Fe(II) in remote marine aerosols. *Nature* **355**, 537–539.