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Trace Metals in the Oceans

Evolution, Biology and Global Change

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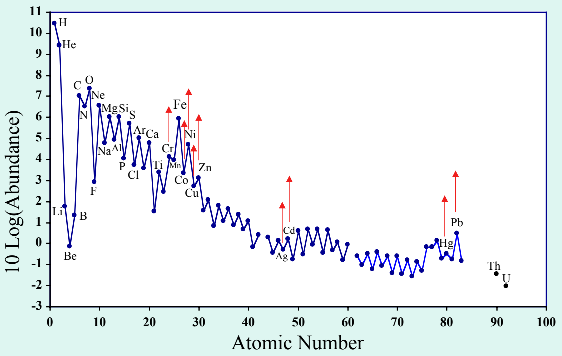
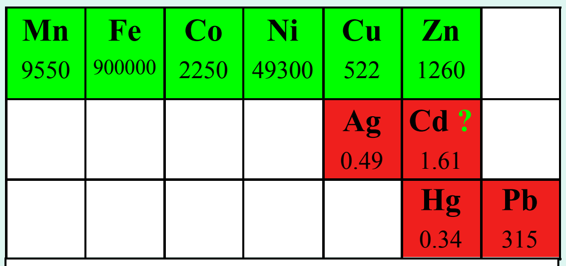
This poster highlights a synthesis chapter in the book *Marine Science Frontiers for Europe*, (eds. Wefer, Lamy & Mantoura), Springer Verlag, Heidelberg. Please take your own copy of the complete chapter. Downloading pdf-file from the Ironages website:
http://www.nioz.nl/projects/ironages

1. Evolution

Once upon a time, at the 4.6 billion years B.P onset of our solar system, nucleosynthesis had led to decreasing abundances of the elements with increasing atomic number (Fig 1.) However multiples of ^{4}He are more abundant, notably iron (Fe) is the fourth abundant in the crust of our planet Earth.



When life evolved after some 1 billion years (~3.6 By ago) it took advantage of the ample supply of dissolved iron, manganese, copper, zinc (Fe, Mn, Cu, Zn) in the then evolving biosphere. Hence these first row transition metals nowadays are essential in all living organisms (Fig. 2). On the other hand the far less abundant second row metals (Ag, Cd) and third row metals (Hg, Pb) were not utilized in biological evolution, nowadays on the contrary they are deemed to be merely toxic elements (Fig. 2).



Mn 9550	**Fe** 900000	**Co** 2250	**Ni** 49300	**Cu** 522	**Zn** 1260	
				Ag 0.49	**Cd** ? 1.61	
					Hg 0.34	**Pb** 315

numbers of atoms versus 1 million Si atoms
Evolution used abundant metals: essential
Low abundant metals no bio-functions: toxic

Figure 2. Central part of the Periodic Table of Elements

Mankind, due to mining and industrial use as well as land use change (e.g. irrigation), has greatly increased the abundance of these metals in the biosphere (red arrows in Fig. 1). This causes many known or suspected toxic effects on all biota. Toxicity is often by competition or substitution of essential first row metals.

Initially the ample pool of reduced Fe(II) in an overall reducing ocean/atmosphere, easily neutralized the photosynthetic production of oxygen (O_2) by its capture and burial in vast iron-oxide deposits. However after a long era eventually all dissolved Fe(II) was depleted, and some 2 billion years ago the O_2 in the air accumulated to the now common level of about 21 percent. Unfortunately in the oxic oceans the virtually insoluble Fe(III) did become the common Fe species. Hence effectively due to photosynthesis the marine biota had deprived itself from its primary essential metal element. On the other hand the availability of Cu, Zn, Cd did improve due to disappearance of reducing sulphides from the water column. The sulphides of these metals are very insoluble. (*In the modern analogs of the primordial ocean, anoxic porewaters of marine sediments, and anoxic basins like the Black Sea, dissolved Fe(II) and Mn(II) are present while Cu, Zn, Cd are low.)*

2. Biological Oceanography ?

Reliable oceanic distributions of trace metals have become available only since 1976. Remarkably Zn (Fig. 3) and Cd (Fig. 4) as well Cu and Ag (Fig. 5) were found to be very closely related with the major biological nutrients silicate, phosphate and nitrate.

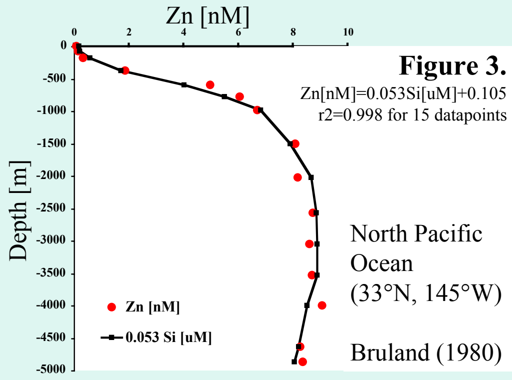


Figure 3.
Zn[nM]=0.053Si[uM]+0.105
r2=0.998 for 15 datapoints

North Pacific Ocean (33°N, 145°W)

Bruland (1980)

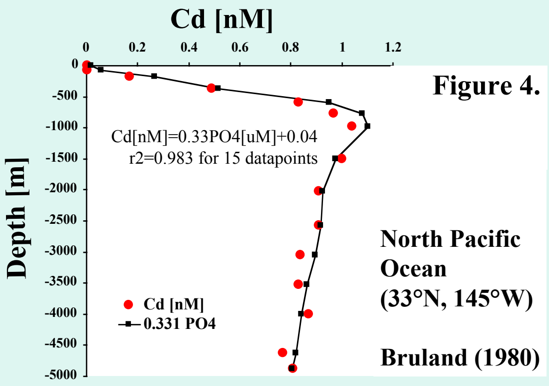


Figure 4.
Cd[nM]=0.33PO4[uM]+0.04
r2=0.983 for 15 datapoints

North Pacific Ocean (33°N, 145°W)

Bruland (1980)

This suggests strong involvement of these metals with the biological cycle. For Zn and Cu as well this makes sense, as these are known to have biological functions. The strong covariance of Zn with silicate hints at a virtually exclusive role of Zn in the diatom cycle, however until now this has not been assessed or proven.

Quite surprisingly Cd, always deemed to be merely a toxic metal, actually has a very tight relationship with phosphate. Indeed more recently a distinct Cd-based carbonic anhydrase has been identified in phytoplankton, next to the well-known Zn-based carbonic anhydrase. Thus a true biological function for Cd, rather than merely a substitution of Zn, is now proven.

The vertical distribution of Ag mimics that of Cu (Fig. 5) and both correlate well with silicate. Another clue for a biochemical function in diatoms perhaps ? One more extensive recent dataset shows Ag in the Pacific to be more tightly related with silicate than Cu with silicate. Paradoxically there is no biochemical functionality known for Ag and the cause of the relation of Ag with the biological cycle remains a mystery.

For these metals the oceanographic co-variances with major nutrients are known for some 20-30 years, but still hardly understood.

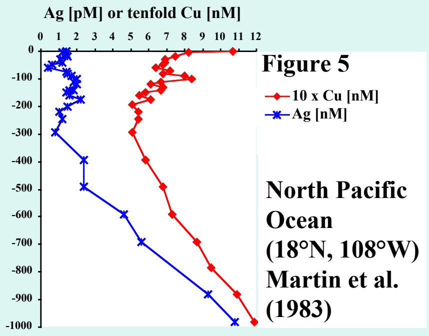


Figure 5

North Pacific Ocean (18°N, 108°W)
Martin et al. (1983)

3. Chemical Fractionations

The very similar distributions of Ag and Cu in the oceans (Fig. 5) are to be expected as they are both in the same group of the Periodic Table (Fig. 2), hence have similar chemistries. The oceanic values can be expressed as an elemental ratio Cu/Ag of about 91, i.e. there are 91 times more Cu atoms than Ag atoms in seawater. So far so good. However the Cu/Ag ratio of abundance in the crust is much higher at about 1060 (Cu/Zn = 522 / 0.49 =1060, see Fig. 2). Therefore either during the weathering of continental rocks or within the ocean themselves, an apparent fractionation with a factor of about 12 is taking place. Why and how ?? An intriguing problem yet to be resolved.

The metals Zn and Cd are also within a same group (Fig. 2) of the periodic table. Indeed we found both to be closely linked to the biological cycle (Figures 3 and 4). From this an oceanic ratio of about 5-10 in seawater can be calculated, in strong contrast with the much higher ratio of about 600-800 in continental rocks as well as marine sediments. The latter reservoirs being seen as the source and sink respectively for the oceanic water column, one realizes once again that an enormous fractionation with a factor ~100 is taking place between Zn and Cd in the oceans.

In the coastal North Sea somewhat intermediate Zn/Cd ratio's had been found. So would there be a fractionation going from rivers via estuaries and coastal seas into the open oceans ? For the estuary of the river Scheldt indeed a major fractionation effect was found in the low salinity region (Fig. 6).

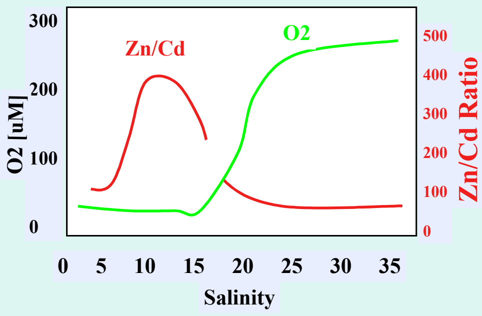


Figure 6. The maximum of dissolved Zn/Cd ratio at low salinity in the Scheldt estuary is consistent with stronger removal of highly insoluble CdS in the low oxygen, sulphidic bottom waters. (Gerringa et al., 2001)

Here due to strong organic loading the O_2 content of the waters is very low, and sulphide is present in bottom waters. Here different solubilities of ZnS and CdS are the perfect explanation. Otherwise the remaining Zn/Cd ratio in seawater tends to increase, rather than decrease as hoped for to explain the above large scale land/ocean trend. Moreover at the outer estuary (salinity 35) the ratio is back again to the about 100 value of the river input, i.e. no lasting effect whatsoever on the input into the oceans.

Right now we have no clue for the above fractionations Cu/Ag and Zn/Cd in the oceans, other than realizing that the more abundant and true biological metals Cu and Zn (Fig. 2) appear to have a much shorter oceanic residence time than the more or less abiotic Ag and Cd.

4. The Iron Age in Oceanography

Ever since the first reliable Fe enrichment experiments in the North Pacific Ocean in August 1987, there has been a scientific revolution in oceanography. When reviewing all experimental findings of the past decade, DeBaar and Boyd (2000) found a consistent and dramatic impact of added Fe on the largest size class of oceanic diatoms. This is largely confirmed in the most recent *in situ* Fe enrichment experiments (Southern Ocean experiments SOIREE, February 1999; Polarstern, November 2000; SOFEX, February 2002; North Pacific experiments SEEDS, summer 2001 and SERIES, summer 2002).

Confirmation by growth response studies of individual diatom species is difficult for two reasons. Firstly the dissolved Fe in natural seawater is distributed over a suite of physico-chemical pools (Fig. 7). Manipulation of the seawater medium, notably the commonly applied EDTA buffering of dissolved metal species, grossly disturbs this natural chemical speciation. Secondly the class of very large oceanic diatoms (10-1000 micron size classes) is very fragile, often with extended spines and naturally occurring in long chains of individual cells. Standard incubation techniques give rise to far too much shear stress for these big diatoms to survive.

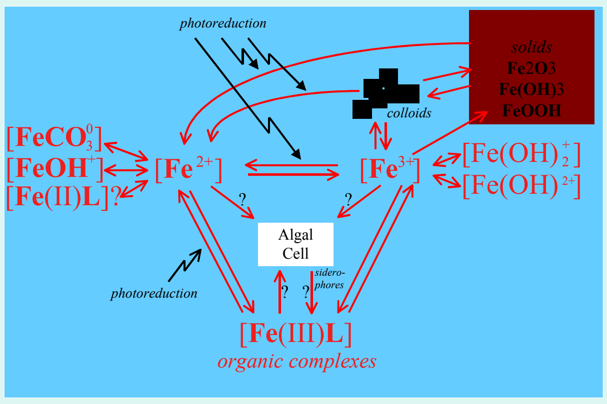


Figure 7. The many chemical species and fine colloids in the so-called dissolved (<0.2 micron-filtered) Fe pool of seawater. Reactions exists with the solid (> 0.2 micron) particles. Today we still do not know which of the many chemical species is preferably taken up by the algae. Photoreduction in surface w aters produces much more reduced Fe(II) than otherwise would be present. This Fe(II) pool may well be crucial for uptake by the algae.

Nevertheless upon improving methodology and several years of tender loving care, Klaas Timmermans and co-workers have been able to isolate and keep alive many of these very large Antarctic diatoms. Among these are Fragiliariopsis kerguelensis, Chaetoceros dichaeta, Pseudonitzschia. These are exactly the species which have been responding strongly to natural as well as artificial Fe enrichments in the open sea.

Next Klaas has taken these single species cultures back again to where they came from: the Southern Ocean. There he provided them with natural, pristine and untreated surface seawater (Figure 8). The very large chain-forming Chaetoceros dichaeta hardly survived at the natural dissolved Fe concentration of 0.16 nM. However, upon addition of some extra Fe, the growth was enhanced, and a Michaelis-Menten curve led to a K_m=1.1 x 10^{-9} M for half-saturation of growth. Thus oceanic C.dichaeta has a life strategy of waiting for the once or twice per year high Fe supply (e.g. dust input or fertilization by mad scientists) for growth and reproduction: diatom blooms.

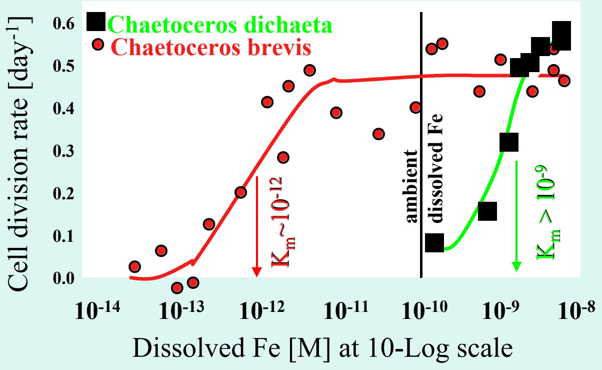


Figure 8. The rate of growth of large C.dichaeta and tiny C. brevis as function of dissolved Fe in seawater Note the logarithmic scale. (Timmermans et al., 2001).

In contrast the about 1000-fold smaller size Chaetoceros brevis was growing at maximum rate even at the low ambient dissolved Fe=0.16 nM. In order to drive this tiny species into Fe limitation, Klaas added a suite of small amounts of the siderophore desferrioxamine-B (DFOB) which has a very strong affinity for dissolved Fe. The DFOB-bound Fe being no longer available for C. brevis did cause the intended decrease in its growth. Next by careful calculations of all dissolved Fe species including the measured natural organic Fe-binding ligands (Fig. 7), it was reconstructed that only at the extremely low natural Fe level of about Km=10^{-12} M the growth of C. brevis would become Fe-limited. This is well below the lowest Fe ever found in surface waters. In other words in the real ocean C.brevis never is Fe-limited. Thus the life strategy of tiny C. brevis is for growing fast at all times. However being small it is an easy prey and its loss rate by grazing is high as well.

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