Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

Developments in analytical instrumentation and elimination or control of contaminations allowed assessing the distribution of minor trace elements in the oceans.

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(…)

The distributions of the elements were found to be consistent with known biological and physical behaviour.

The types of profiles found for various elements can be divided into a number of general categories:

(1) Conservative profile
(2) Nutrient type profile
(3) Surface enrichment and depletion at depth
(4) Middepth minima
(5) Middepth maxima
(…)

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Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(…)

The distributions of the elements were found to be consistent with known biological and physical behaviour.

The types of profiles found for various elements can be divided into a number of general categories:

(…)

(6) Middepth maxima or minima in the suboxic layer

(7) Maxima and minima in anoxic waters

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(…)

The type of profile: (1) Conservative profile:

A constant ratio of the concentration of the element to chlorinity or salinity due to their low reactivity.

Examples:

The major components of seawater and trace metals such as Li^+, Rb^+, and Cs^+ and anions such as molybdenum (MoO_4^{2-}) and tungsten (WO_4^{2-}) exhibit this type of behaviour.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

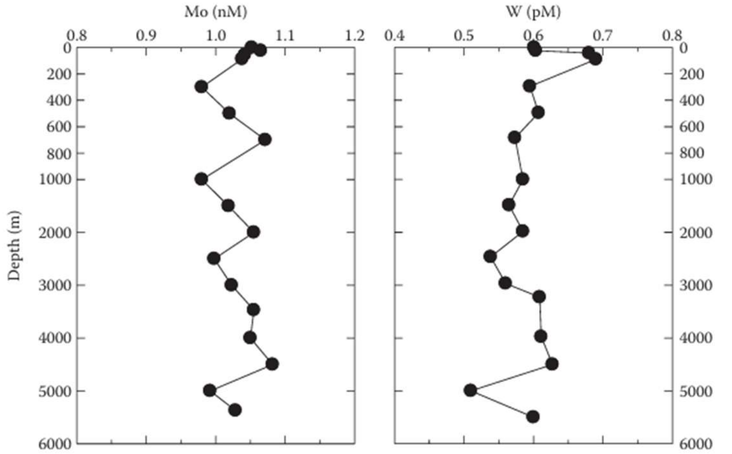
(...)

The type of profile:

(1) Conservative profile:

A constant ratio of the concentration of the element to chlorinity or salinity (...).

No relevant concentration variations.



Profiles of molybdenum (Mo) and tungsten (W) in the Pacific Ocean.

Chemical Oceanography - Minor Elements in Seawater

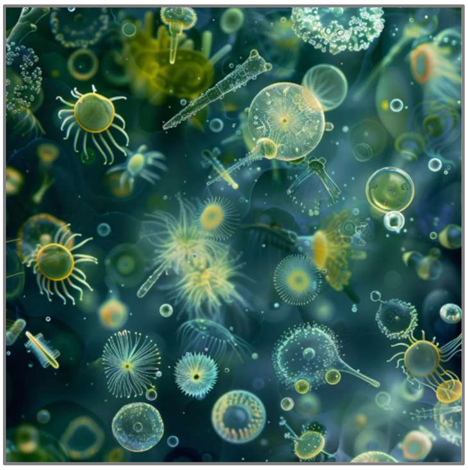
3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:

(2) Nutrient type profile:

A depletion of an element in surface waters and enrichment at depth. The element is removed from the surface waters by uptake by plankton or adsorption to biologically produced particulate matter.



Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

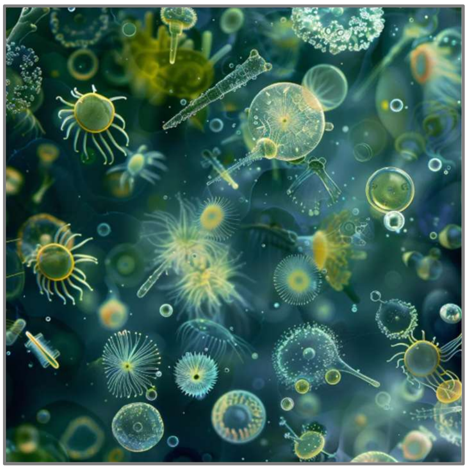
(…)

The type of profile:

(2) Nutrient type profile:

(…)

Regenerated in deep waters when the biologically produced particulate matter is oxidized by bacteria.



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Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(…)

The type of profile: (2) Nutrient type profile:

Three types of nutrient type profiles are found:

(2.1) The shallow water regeneration (max. near 1 km) (similar to the nutrients PO_4^{3-} and NO_3^-).

Example: Cd^{2+}

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Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

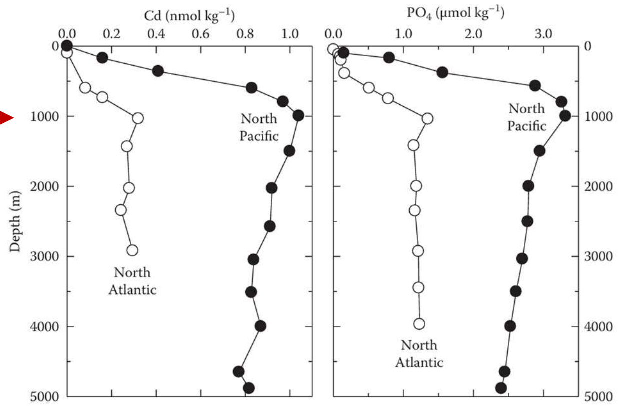
(...)

The type of profile:

(2) Nutrient type profile: **Larger conc.**

(2.1) The shallow water regeneration

This behaviour indicates that the element is associated with the soft parts of living and dead biological material.



Profiles of cadmium (Cd) and phosphate (PO_4) in the Atlantic and Pacific Oceans.

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Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

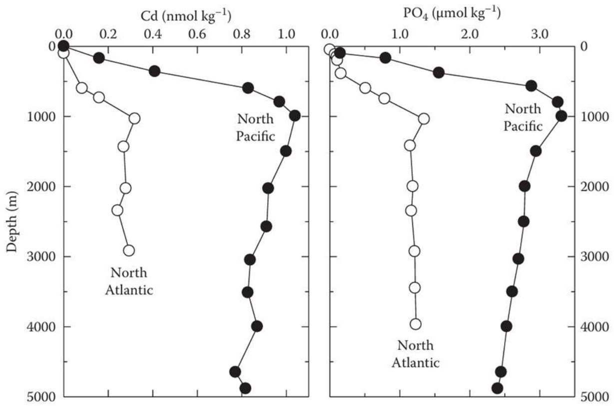
The type of profile:

(2) Nutrient type profile:

(2.1) The shallow water regeneration

Near-linear correlation with nitrate and phosphate

This relationship can be used to estimate the phosphate in ocean water from the coprecipitated Cd in shells.



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Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

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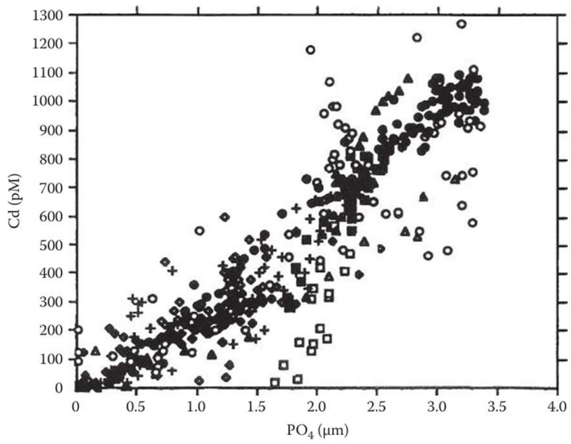


Plot of cadmium as a function of phosphate.

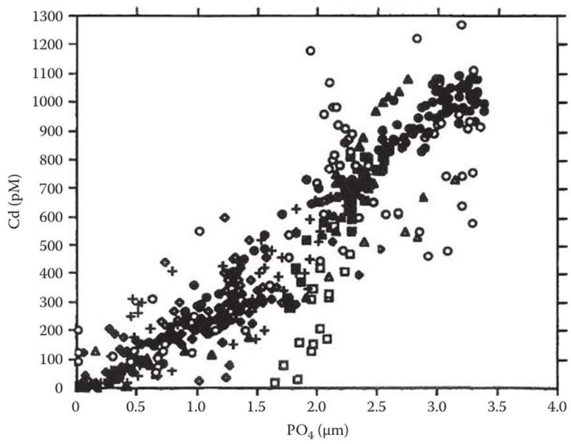
Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(2) Nutrient type profile:
(2.1) The shallow water regeneration

By dating the shells, it was possible to estimate the past phosphate in North Atlantic deep waters as a function of time.



Plot of cadmium as a function of phosphate.

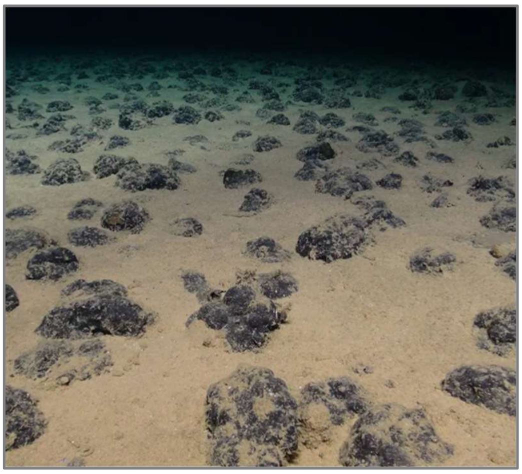
Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(2) Nutrient type profile:
(2.2) The deep regeneration cycle

Deep maximum is observed for metals of this type, similar to the distribution of silica and total alkalinity.



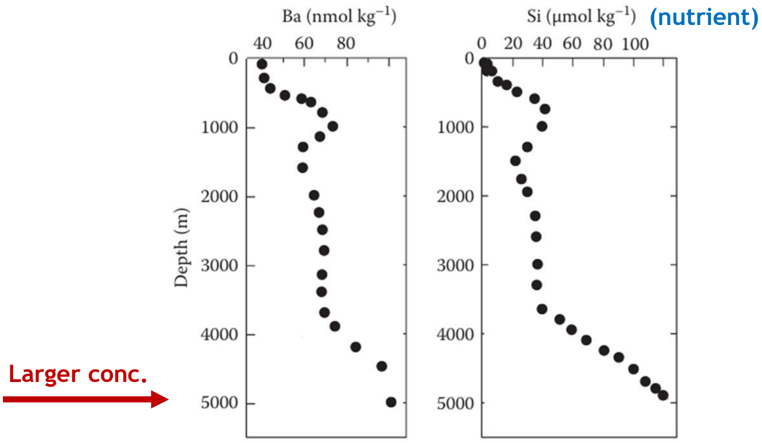
Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(2) Nutrient type profile:
(2.2) The deep regeneration cycle

Ex. Ge^{3+} and Ba^{2+}.



Comparison of barium (Ba) and silica (Si) profiles in the South Atlantic.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

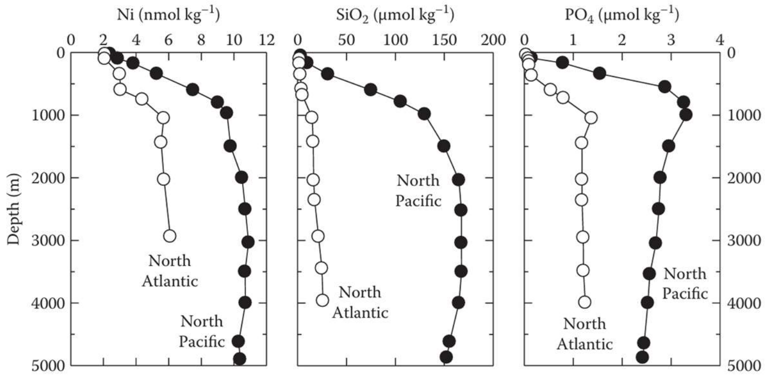
(…)

The type of profile:

(2) Nutrient type profile:

(2.3) Combination of shallow and deep generation

Ex. Ni and Se.



Comparison of the profiles of nickel (Ni) to silicate (SiO_2) and phosphate (PO_4) in the Atlantic and Pacific Oceans.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(…)

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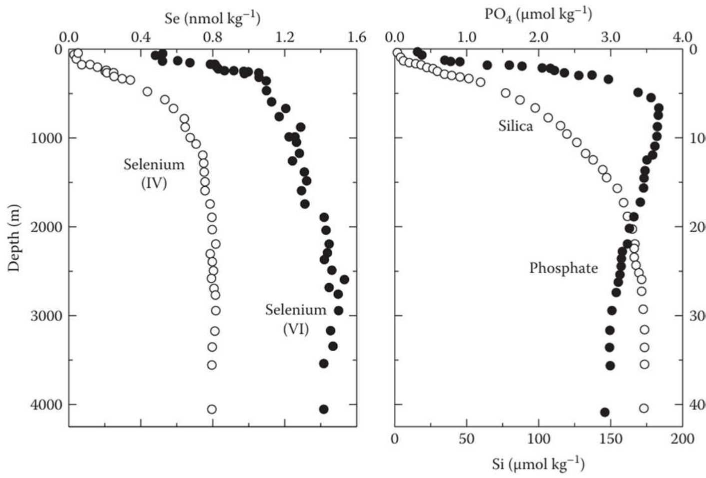


Comparison of the profiles of selenium (Se) to silica (Si) and phosphate (PO_4) in the Pacific Ocean.

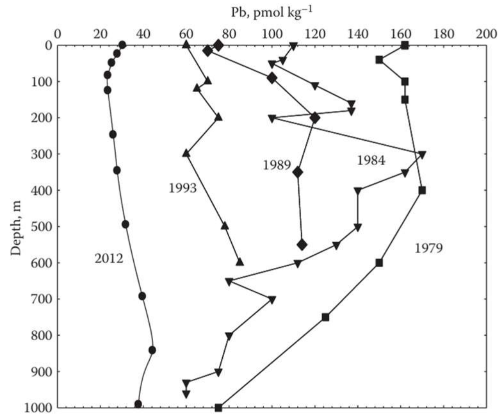
Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(3) Surface enrichment and depletion at depth

Example: Pb (element entering the oceans via the atmosphere)



Profiles of lead (Pb) in the Atlantic Ocean waters off Bermuda as a function of time.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:

Profiles of lead (Pb) in the Atlantic Ocean waters off Bermuda as a function of time.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

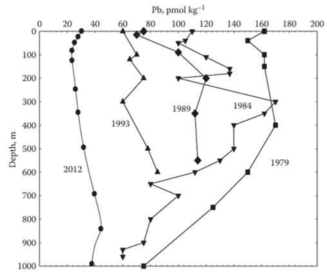
(...)

The type of profile:

(3) Surface enrichment and depletion at depth

Example: Pb (element entering the oceans via the atmosphere)

High surface input of lead result of its past use as an antiknock agent in gasoline over time removed by precipitation or adsorption to particles.



Profiles of lead (Pb) in the Atlantic Ocean waters off Bermuda as a function of time.

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3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:

(4) Middepth minima:

A middepth minimum can result from a surface input and regeneration at or near the bottom or scavenging [remoção] throughout the water column.

Examples: Cu^{2+}, Sn^{4-}, and Al^{3+}.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

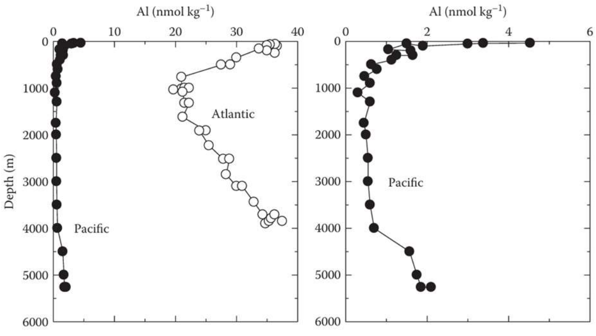
The type of profile:

(4) Middepth minima:

(...)

Examples: Cu^{2+}, Sn^{4-}, and Al^{3+}.

Input into the surface from atmospheric dust from continents (ex: Sahara Desert).



Profiles of aluminum (Al) in Atlantic and Pacific Ocean waters.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

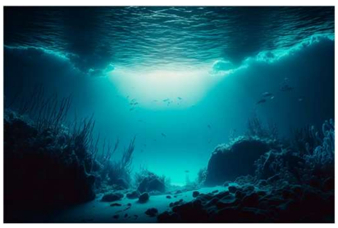
(...)

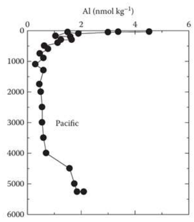
The type of profile:

(4) Middepth minima:

(...)

Examples: Al^{3+}.





Profiles of aluminum (Al) in Pacific Ocean waters.

The Al is quickly scavenged from surface water by adsorption on plant material or the uptake of plants. The particles settle into the deep oceans and are deposited in the sediment. The resuspension and flux of Al from the sediments leads to an increase in the concentration in bottom waters.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

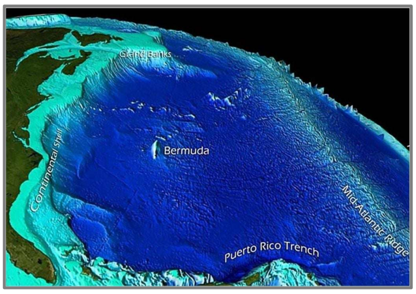
(…)

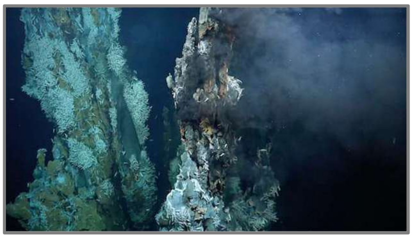
The type of profile:

(5) Middepth maxima:

Can result from a hydrothermal input from the midocean ridge system [Cordilheira meso-oceânica].

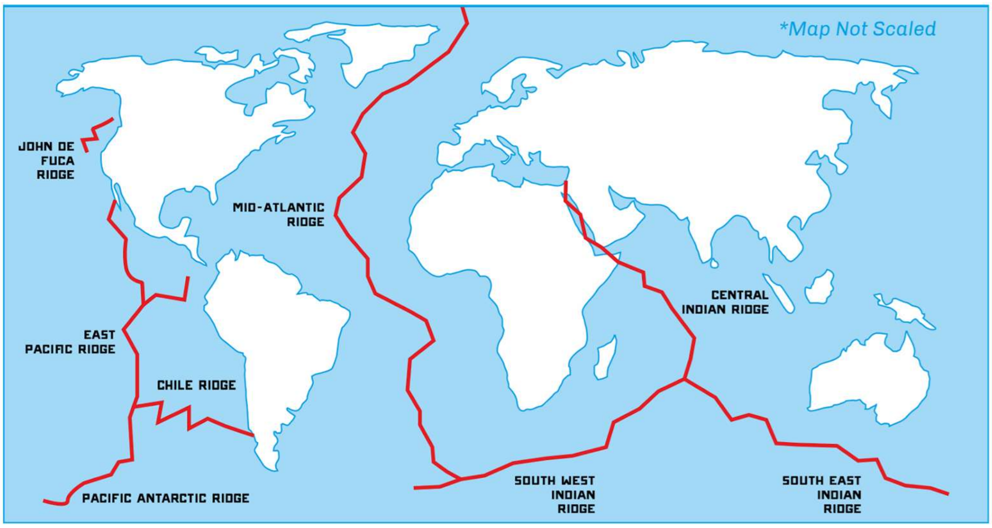
Examples: Mn^{2+} and ^3He.





Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans



Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

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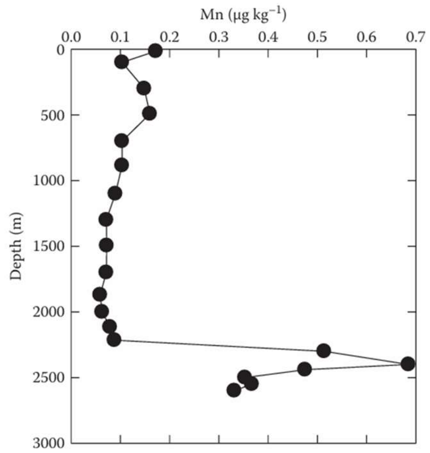

Profile of manganese (Mn) in the Pacific Ocean showing hydrothermal input from Mid-Pacific Ridge.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

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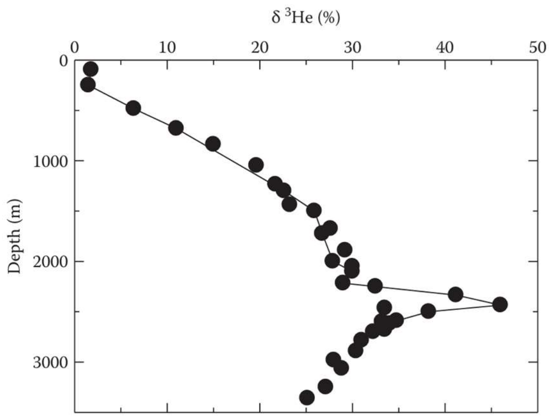
Can result from a hydrothermal input from the midocean ridge system [Cordilheira meso-oceânica].

Examples: Mn^{2+} and ^{3}He.



Profile of helium (He) in the Pacific Ocean showing hydrothermal input from Mid-Pacific Ridge.

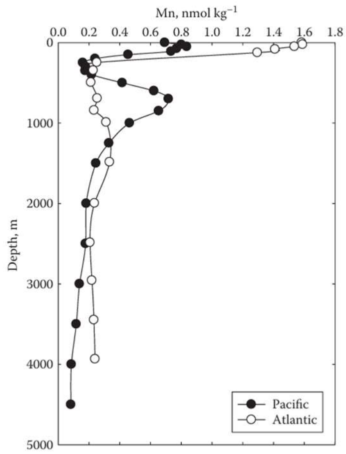
Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(6) Middepth maxima or minima
in the suboxic layer (~1 km):

A large suboxic layer exists in some regions of the Pacific and Indian Oceans.
(0.1 to 2 mg/L of O_2: can support life)
Reduction and oxidation processes in the water column or adjacent slope sediments can yield maxima of the reduced forms (Fe^{2+}, Mn^{2+}, and Co^{2+}).



Profiles of Mn in the Atlantic and Pacific Oceans.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
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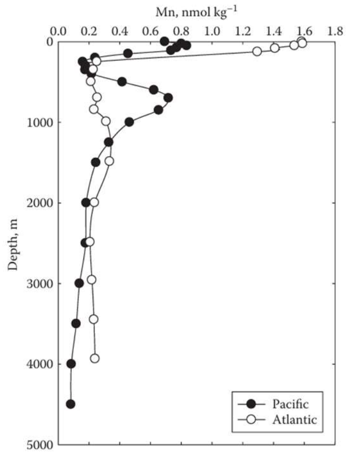

Profiles of Mn in the Atlantic and Pacific Oceans.

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

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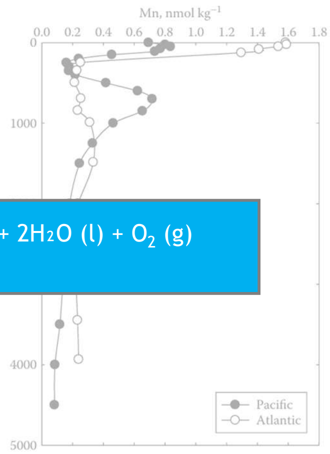


Profiles of Mn in the Atlantic and Pacific Oceans.

A large ... regions ...

$$MnO_2\ (s) + 4H^+\ (aq) + 2e^- \rightarrow Mn^{2+}\ (aq) + 2H_2O\ (l) + O_2\ (g)$$

Oxidation state: +4 ... +2

(0.1 to 2 mg/L of O_2: can support life)

Reduction and oxidation processes in the water column or adjacent slope sediments can yield maxima of the reduced forms (Fe^{2+}, Mn^{2+}, and Co^{2+}).

Chemical Oceanography - Minor Elements in Seawater

3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:

(7) Maxima and minima in anoxic waters [< 0.1 mg/L of O_2]:

(close to surface)

In areas of restricted circulation such as the Black Sea and fjords, the water can become anoxic with the production of H_2S by microbial sulfate reduction.

Chemical Oceanography - Minor Elements in Seawater

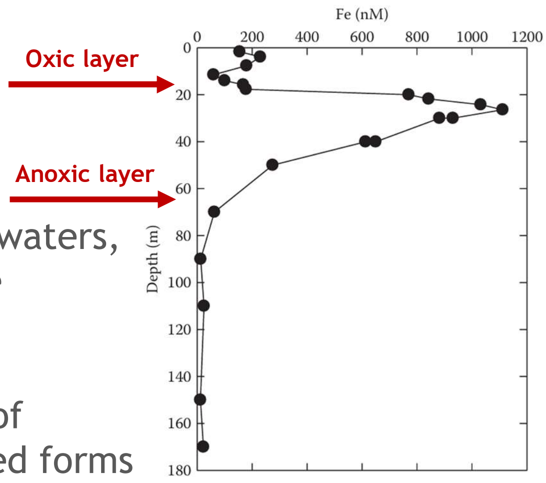
3. Distribution of Trace Elements in the Oceans

(...)

The type of profile:
(7) Maxima and minima in anoxic waters:

Near the interface between the two waters, redox processes can occur that cause maxima and minima.

Fe^{2+} and Mn^{2+} have maxima because of the increased solubility of the reduced forms near the oxic-anoxic interface.



Profile of iron(II) (Fe) in the Framvaren Fjord, Norway.

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

1. Cl^- is ?

2. Na^+, Mg^{2+}, Br^-, F^-, and SO_4^{2-} have ?

- concentration in organisms similar to seawater
- rejected by organisms.

3. Most of the other elements, with the exception of the noble gases, are strongly concentrated in living tissue.

(...)

Chemical Oceanography - Minor Elements in Seawater

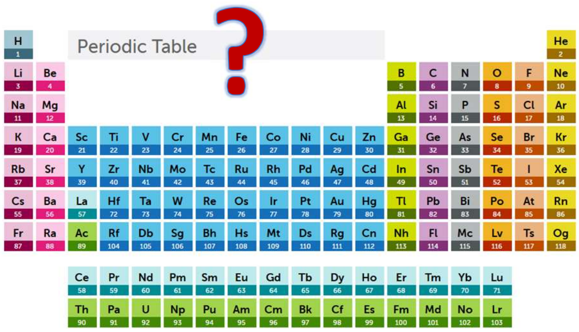
3. Biological Interactions
Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):
1. Cl^- is rejected by organisms.

2. Na^+, Mg^{2+}, Br^-, F^-, and SO_4^{2-} have concentrations in organisms similar to seawater (concentration factors of 1.0).

3. Most of the other elements, with the exception of the noble gases, are strongly concentrated in living tissue.
(…)

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions
Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):
(…)
4. The order of affinity of organisms for cations is:



- 4+ (charge) > 3+ > 2+ transition > 2+ group II > 1+ group I metals.

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions
Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):
(…)
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Chemical Oceanography - Minor Elements in Seawater

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Chemical Oceanography - Minor Elements in Seawater

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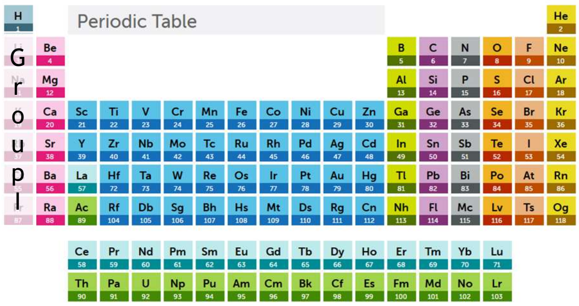

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Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(…)

For plankton, the order is

- $Fe^{3+} > Al^{3+} > Ti^{3+} > Cr^{3+} > Ga^{3+} > Zn^{2+} > Pb^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Cd^{2+}$

Does it agree with the Irving-Williams order?

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

Repeated slides

1. Classification of Elements
1.3. Transition Metals between d_0 and d_{10}

Form strong complexes with organic molecules (ligands).
Irving-Williams order: For almost every ligand, the stability of its complexes increases in the order:

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

Stability Constants for the Formation of Organic Ligands with Metals

	log K		
Ion	EDTA	Ethylenediamine	Nitrilotriacetic Acid
Mn^{2+}	14	2.7	7.4
Fe^{2+}	14	4.3	8.3
Co^{2+}	16	5.9	10.5
Ni^{2+}	18	7.9	11.4
Cu^{2+}	19	10.5	12.8
Zn^{2+}	16	6.0	10.5

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Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

Repeated slides

1. Classification of Elements
1.3. Transition Metals between d_0 and d_{10}

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

The order is related to the stability of the electronic structure of the various metals with a given ligand. Copper normally forms the strongest complexes with organic ligands. This is related to the unique ability of the eight d electrons in copper to form a hybrid configuration.

Stability Constants for the Formation of Organic Ligands with Metals

	log K		
Ion	EDTA	Ethylenediamine	Nitrilotriacetic Acid
Mn^{2+}	14	2.7	7.4
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Zn^{2+}	16	6.0	10.5

94

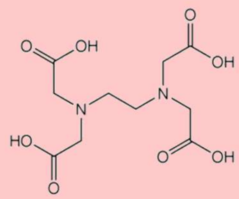
Chemical Oceanography - Minor Elements in Seawater

Repeated slides

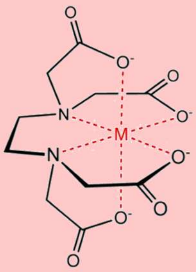
1. Classification of Elements

1. Classification of Elements
1.3. Transition Metals between d_0 and d_{10}

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$



EDTA



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95

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(…)

For plankton, the order is

- $Fe^{3+} > Al^{3+} > Ti^{3+} > Cr^{3+} > Ga^{3+} > Zn^{2+} > Pb^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Cd^{2+}$

Does it agree with the Irving-Williams order?

Irving-Williams order:
$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(...)

For plankton, the order is

- $Fe^{3+} > Al^{3+} > Ti^{3+} > Cr^{3+} > Ga^{3+} > Zn^{2+} > Pb^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Cd^{2+}$

This order does not agree with the Irving-Williams order.
The formation of complexes with surface ligands does not control the uptake by plankton.

Chemical Oceanography - Minor Elements in Seawater

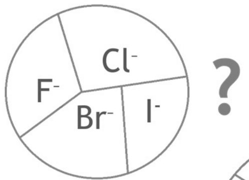
3. Biological Interactions

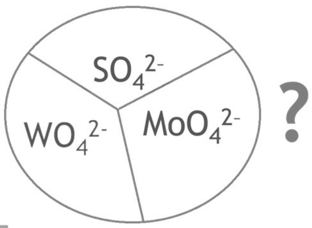
Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(...)

5. Heavy group elements of a particular class are taken up more strongly than lighter elements.

6. The affinity of organisms for anions increases with increasing ionic charge and in a given group with increasing weight of the central atom:





Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(...)

5. Heavy group elements of a particular class are taken up more strongly than lighter elements.

6. The affinity of organisms for anions increases with increasing ionic charge and in a given group with increasing weight of the central atom:

$F^- < Cl^- < Br^- < I^-$

$SO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

Interactions with marine organisms is quantified as concentration factors (concentration in the organism/ concentration in seawater):

(...)

7. The lower organisms concentrate elements more strongly than higher organisms.

8. Heavy metals are frequently concentrated in the digestive or renal organs.

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

The biosphere can affect minor elements by the following:

1. The regulation of dissolved and particulate organic material (change their reactivity).

2. The concentration of elements in living and nonliving organic material (can redistribute elements from surface to deep waters).

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

(…)

Effects that affect the movement of elements from surface waters to the sediments:

1. Active uptake by organisms (Fe^{2+}, Zn^{2+}, Mn^{2+})(ex. Use in enzyme systems)
2. Passive uptake by organisms (heavy metals) (ex. Adsorption on organic particles)

(…)

Chemical Oceanography - Minor Elements in Seawater

3. Biological Interactions

(…)

Effects that affect the movement of elements from surface waters to the sediments:

(…)

3. Adsorption on particulate matter (Pb^{2+}, Cu^{2+})
4. Remobilization from sediments by oxidation (Mn^{2+})
5. Precipitation (Fe^{3+})

ME|Chem: https://mechem.rd.ciencias.ulisboa.pt/
rjsilva@ciencias.ulisboa.pt