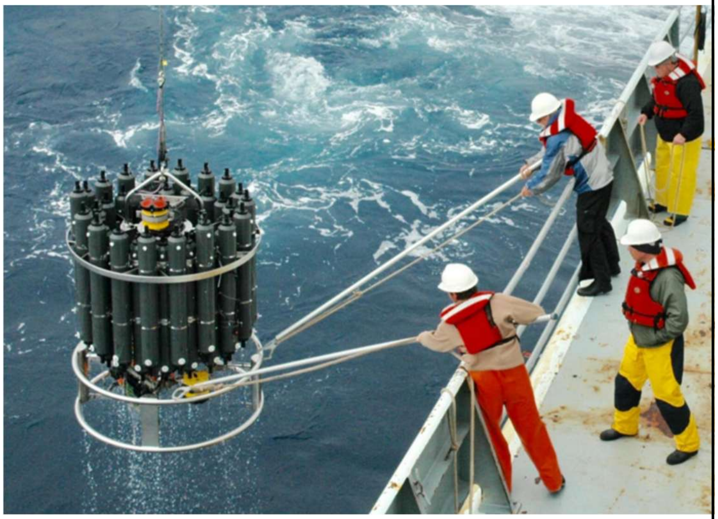
Chemical Oceanography

Minor Elements in Seawater

Ricardo Bettencourt da Silva

Segundas-feiras (8.2.12)
11:00 - 13:00 & 14:00 - 15:00

3h de dia 2025/03/24



Chemical Oceanography - Minor Elements in Seawater

Content

1. Classification of Elements
2. Residence Times
3. Distribution of Trace Elements in the Oceans
4. Biological Interactions
5. Geochemical Balance of Elements

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

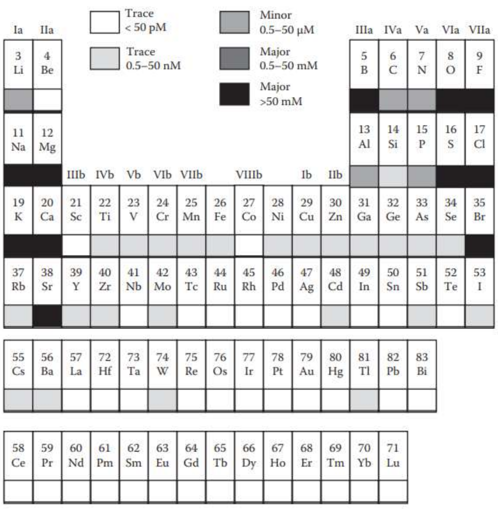
- Most elements from the periodic table are in the seawater.

- 14 elements (O, H, Cl, Na, Mg, S, Ca, K, Br, C, Sr, B, Si, and F) have concentrations greater than 1 mg/L. These elements, except Si, are generally unreactive (both chemically and biologically).

- Many of the remaining elements, called minor, are involved in inorganic and biological reactions in the marine environment. The biolimited elements N, P, and Si are discussed in another lecture.

Chemical Oceanography - Minor Elements in Seawater

Classification of Elements in ocean waters



Author: Bruland (1983)

- Table with average concentrations from seawater with salinity S_p (practical salinity) = 35

1. Major elements: 0.05 to 750 mM
2. Minor elements: 0.05 to 50 µM
3. Trace elements: 0.05 to 50 nM

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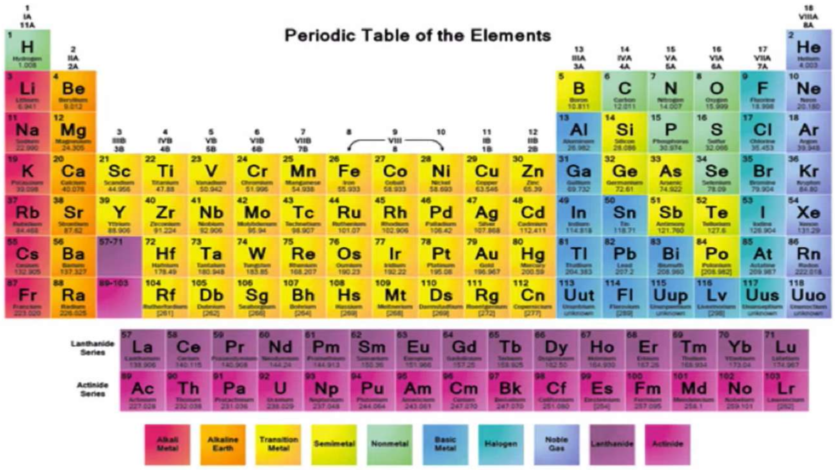
Periodic Table

Rows are periods

Columns are groups



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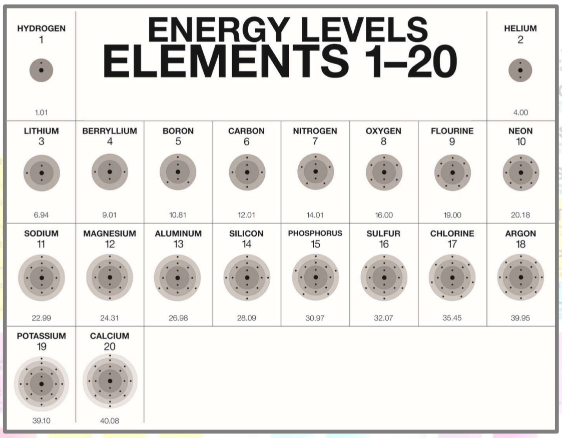
Periodic Table

Periods 1, 2, 3 and 4



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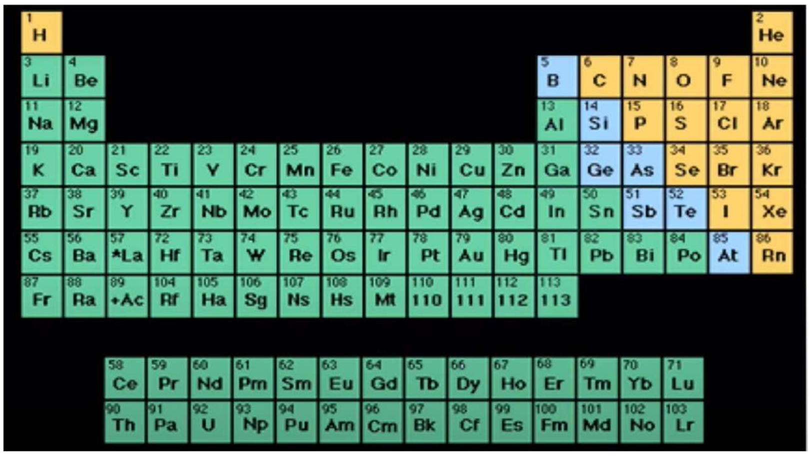
Periodic Table



Metals
Metallois
Nonmetals

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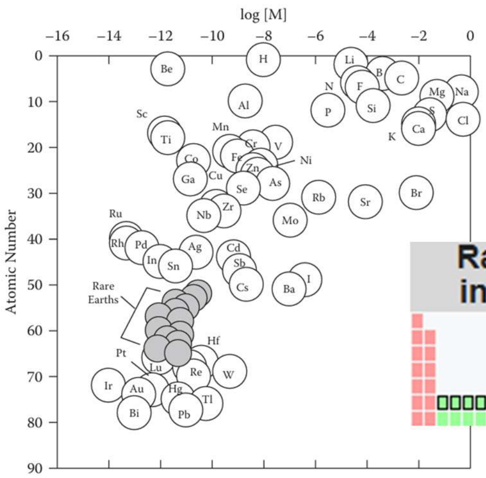
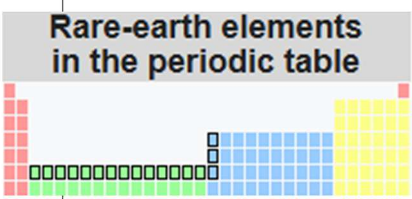
Classification of Elements in ocean waters





The range of concentrations of elements in seawater.

Chemical Oceanography - Minor Elements in Seawater

Speciation, Concentration, and Distribution Types of Elements in Ocean Waters

Author: Bruland (1983)

Speciation, Concentration, and Distribution Types of Elements in Ocean Waters

Element	Probable Species	Range and Average Concentration	Type of Distribution
Li	Li^+	25 µ*M*	Conservative
Be	$BeOH^+$, $Be(OH)_2$	4–30 p*M*, 20 p*M*	Nutrient type
B	$B(OH)_3$, $B(OH)_4$	0.416 m*M*	Conservative
C	HCO_3^-, CO_3^{2-}	2.0–2.5 m*M*, 2.3 m*M*	Nutrient type
N	NO_3^-, (N_2)	0–45 µ*M*	Nutrient type
F	F^-, MgF^+, CaF^+	68 µ*M*	Conservative
Na	Na^+	0.468 *M*	Conservative
Mg	Mg^{2+}	53.2 m*M*	Conservative
Al	$Al(OH)_4^-$, $Al(OH)_3$	5–40 n*M*, 2 n*M*	Mid-depth minima
Si	$Si(OH)_4$	0–180 µ*M*	Nutrient type
P	HPO_4^{2-}, $MgHPO_4$	0–3.2 µ*M*	Nutrient type
S	SO_4^{2-}, $NaSO_4^-$, $MgSO_4$	28.2 m*M*	Conservative
Cl	Cl^-	0.546 M	Conservative
K	K^+	10.2 m*M*	Conservative
Ca	Ca^{2+}	10.3 m*M*	Conservative
Sc	$Sc(OH)_3$	8–20 p*M*, 15 p*M*	Surface depletion
Ti	$Ti(OH)_4$	Few p*M*	?

(...)

rjsilva@ciencias.ulisboa.pt

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Speciation, Concentration, and Distribution Types of Elements in Ocean Waters

Author: Bruland (1983)

Speciation, Concentration, and Distribution Types of Elements in Ocean Waters

Element	Probable Species	Range and Average Concentration	Type of Distribution
V	HVO_4^{2-}, $H_2VO_4^-$	20–35 n*M*	Surface depletion
Cr	$Cr\,O_4^{2-}$	2–5 n*M*, 4 n*M*	Nutrient type
Mn	Mn^{2+}	0.2–3 n*M*, 0.5 n*M*	Depletion at depth
Fe	$Fe(OH)_3$	0.1–2.5 n*M*, 1 n*M*	Surface and depth depletion
Co	Co^{2+}, $CoCO_3$	0.01–0.1 n*M*, 0.02 n*M*	Surface and depth depletion
Ni	$NiCO_3$	2–12 n*M*, 8 n*M*	Nutrient type
Cu	$CuCO_3$	0.5–6 n*M*, 4 n*M*	Nutrient type, scavenging
Zn	Zn^{2+}, $ZnOH^+$	0.05–9 n*M*, 6 n*M*	Nutrient type
Ga	$Ga(OH)_4^-$	5–30 p*M*	?
As	$HAsO_4^{2-}$	15–25 n*M*, 23 n*M*	Nutrient type
Se	SeO_4^{2-}, SeO_3^{2-}	0.5–2.3 n*M*, 1.7 n*M*	Nutrient type
Br	Br^-	0.84 n*M*	Conservative
Rb	Rb+	1.4 µ*M*	Conservative
Sr	Sr^{2+}	90 µ*M*	Conservative
Y	YCO_3^+	0.15 n*M*	Nutrient type
Zr	$Zr(OH)_4$	0.3 n*M*	?

(...)

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1. Classification of Elements

- Since many of these minor elements are metals, Goldberg (1965) divided them into three classes based on their electronic structure

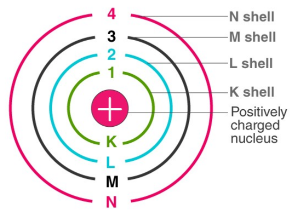
			K	L		M			N			
Period	Z	Element	s	s	p	s	p	d	s	p	d	f
1	1	H	1									
	2	He	2									
2	3	Li	2	1								
	4	Be	2	2								
	5	B	2	2	1							
	6	C	2	2	2							
	7	N	2	2	3							
	8	O	2	2	4							
	9	F	2	2	5							
	10	Ne	2	2	6							
3	11	Na	2	2	6	1						
	12	Mg	2	2	6	2						
	13	Al	2	2	6	2	1					
	14	Si	2	2	6	2	2					
	15	P	2	2	6	2	3					
	16	S	2	2	6	2	4					
	17	Cl	2	2	6	2	5					
	18	Ar	2	2	6	2	6					

(...)

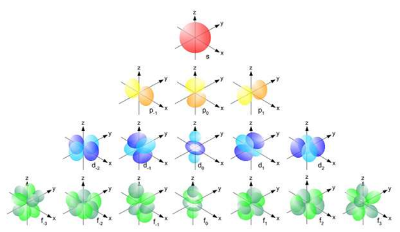
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

Bohr's Model of an atom:



Types of orbitals (s, p, d and f):



Atomic number (protons number)

			K	L		M			N			
Period	Z	Element	s	s	p	s	p	d	s	p	d	f
1	1	H	1									
	2	He	2									
2	3	Li	2	1								
	4	Be	2	2								
	5	B	2	2	1							
	6	C	2	2	2							
	7	N	2	2	3							
	8	O	2	2	4							
	9	F	2	2	5							
	10	Ne	2	2	6							
3	11	Na	2	2	6	1						
	12	Mg	2	2	6	2						
	13	Al	2	2	6	2	1					
	14	Si	2	2	6	2	2					
	15	P	2	2	6	2	3					
	16	S	2	2	6	2	4					
	17	Cl	2	2	6	2	5					
	18	Ar	2	2	6	2	6					

Chemical Oceanography - Minor Elements in Seawater

Classification of Elements

Period	Z	Element	K s	L s	L p	M s	M p	M d	N s	N p	N d	N f
1	1	H	1									
	2	He	2									
2	3	Li	2	1								
	4	Be	2	2								
	5	B	2	2	1							
	6	C	2	2	2							
	7	N	2	2	3							
	8	O	2	2	4							
	9	F	2	2	5							
	10	Ne	2	2	6							
3	11	Na	2	2	6	1						
	12	Mg	2	2	6	2						
	13	Al	2	2	6	2	1					
	14	Si	2	2	6	2	2					
	15	P	2	2	6	2	3					
	16	S	2	2	6	2	4					
	17	Cl	2	2	6	2	5					
	18	Ar	2	2	6	2	6					

Period	Z	Element	K s	L s	L p	M s	M p	M d	N s	N p	N d	N f
4	19	K	2	2	6	2	6		1			
	20	Ca	2	2	6	2	6		2			
	21	Sc	2	2	6	2	6	1	2			
	22	Ti	2	2	6	2	6	2	2			
	23	V	2	2	6	2	6	3	2			
	24	Cr	2	2	6	2	6	5	1			
	25	Mn	2	2	6	2	6	5	2			
	26	Fe	2	2	6	2	6	6	2			
	27	Co	2	2	6	2	6	7	2			
	28	Ni	2	2	6	2	6	8	2			
	29	Cu	2	2	6	2	6	10	1			
	30	Zn	2	2	6	2	6	10	2			
	31	Ga	2	2	6	2	6	10	2	1		
	32	Ge	2	2	6	2	6	10	2	2		
	33	As	2	2	6	2	6	10	2	3		
	34	Se	2	2	6	2	6	10	2	4		
	35	Br	2	2	6	2	6	10	2	5		
	36	Kr	2	2	6	2	6	10	2	6		

Chemical Oceanography - Minor Elements in Seawater

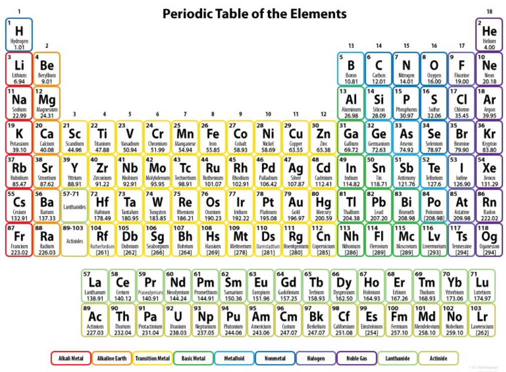
1. Classification of Elements

• Minor and trace elements have a wide range of concentration due to their reactivity.

1. Classification of Elements

1.1. d_0 Cations

d_0 Cations are metal ions that have no electrons in their d-orbital.

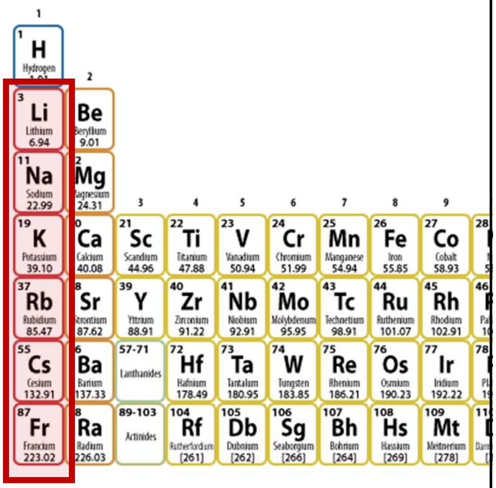


Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations

Ions of metallic elements with a rare gas configuration include the alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+ and Fr^+)(…)



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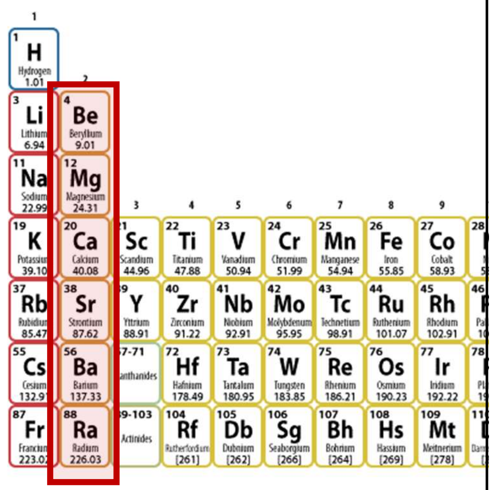
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations

The alkaline earth metals (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+})(…)



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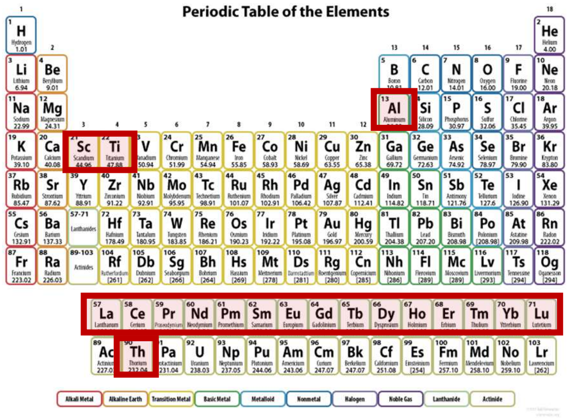
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations

Lanthanide or rare earth series (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} Lu^{3+}) plus the metals Al^{3+}, Sc^{3+}, Ti^{3+}, and Th^{3+}.



Chemical Oceanography - Minor Elements in Seawater

Classification of Elements

Examples

			K	L		M			N			
Period	Z	Element	s	s	p	s	p	d	s	p	d	f
1	1	H	1									
	2	He	2									
2	3	Li	2	1								
	4	Be	2	2								
	5	B	2	2	1							
	6	C	2	2	2							
	7	N	2	2	3							
	8	O	2	2	4							
	9	F	2	2	5							
	10	Ne	2	2	6							
3	11	Na	2	2	6	1						
	12	Mg	2	2	6	2						
Al^{3+}	13	Al	2	2	6	2	1					
	14	Si	2	2	6	2	2					
	15	P	2	2	6	2	3					
	16	S	2	2	6	2	4					
	17	Cl	2	2	6	2	5					
	18	Ar	2	2	6	2	6					

			K	L		M			N			
Period	Z	Element	s	s	p	s	p	d	s	p	d	f
4	19	K	2	2	6	2	6		1			
	20	Ca	2	2	6	2	6		2			
Sc^{3+}	21	Sc	2	2	6	2	6	1	2			
	22	Ti	2	2	6	2	6	2	2			
	23	V	2	2	6	2	6	3	2			
	24	Cr	2	2	6	2	6	5	1			
	25	Mn	2	2	6	2	6	5	2			
	26	Fe	2	2	6	2	6	6	2			
	27	Co	2	2	6	2	6	7	2			
	28	Ni	2	2	6	2	6	8	2			
	29	Cu	2	2	6	2	6	10	1			
	30	Zn	2	2	6	2	6	10	2			
	31	Ga	2	2	6	2	6	10	2	1		
	32	Ge	2	2	6	2	6	10	2	2		
	33	As	2	2	6	2	6	10	2	3		
	34	Se	2	2	6	2	6	10	2	4		
	35	Br	2	2	6	2	6	10	2	5		
	36	Kr	2	2	6	2	6	10	2	6		

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations

Form few complexes, mainly with F^- and ligands where oxygen is the donor atom (e.g., OH^-, SO_4^-, CO_3^{2-}, and PO_4^{3-}). The strength of the complexes is related to electrostatic interactions (proportional to Z^2/r, where Z is the charge and r is the radius of an ion).

Log K

Stability Constants for the Formation of Fluoride and Hydroxide Complexes

Ion	Log K_{MF}	Log K_{MOH}	Radius
Be^{2+}	4.29	10.28	0.31 Å
Mg^{2+}	1.82	2.3	0.65
Ca^{2+}	1.04	1.4	0.99
Sr^{2+}	—	0.9	1.13
Ba^{2+}	0.45	0.8	1.35

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations

Ligant

$$M^{m+} + L \rightleftharpoons ML^{(m-1)+}$$

Metal ion

$$K = \frac{[ML^{(m-1)+}]}{[M^{m+}][L]}$$

Stability Constants for the Formation of Fluoride and Hydroxide Complexes

Ion	Log K_{MF}	Log K_{MOH}	Radius
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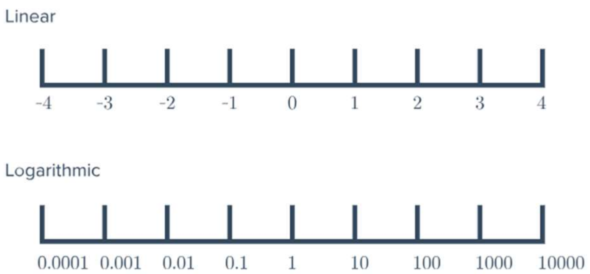
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.1. d_0 Cations



Stability Constants for the Formation of Fluoride and Hydroxide Complexes

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Ca^{2+}	1.04	1.4	0.99
Sr^{2+}	—	0.9	1.13
Ba^{2+}	0.45	0.8	1.35

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations

These are metal ions where the d-orbital is fully filled with 10 electrons. The univalent d_{10} metal ions behave in a different way from the d_0 metals. For these ions, the halide complexes increase in stability with increasing atomic weight or size of the ligand.

Constants for the formation of silver and copper(I) halide complexes as a function of the radius of the halide ion

Complex	CuX	AgX	Radius (Å)
MF	—	–0.3	1.36
MCl	2.7	3.0	1.81
MBr	3.2	4.3	1.95
MI	7.2	8.1	2.16

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations

Since the concentration of Cl^- in seawater is much larger than that of the other halides, the Cl^- complexes will normally dominate (the values of K_{MX} for the heavier halides are not large enough to compensate for the low concentration).

Constants for the formation of silver and copper(I) halide complexes as a function of the radius of the halide ion

Complex	CuX	AgX	Radius (Å)
MF	—	–0.3	1.36
MCl	2.7	3.0	1.81
MBr	3.2	4.3	1.95
MI	7.2	8.1	2.16

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations

It is possible, however, for OH^- ions to compete successfully with Cl^-. For Cl^- complexes to predominate, the value of $\log K_{MCl} - \log K_{MOH}$ must be greater than about –5.4.

Stability Constants for the Formation of Chloride and Hydroxide Complexes

Ion	Log K_{MCl}	Log K_{MOH}	Log K_{MCl} – LogK_{MOH}
Ag^+	3.1	2.3	0.8
Cd^{2+}	2.0	5.5	–3.5
Hg^{2+}	7.3	11.5	–4.2
Zn^{2+}	–0.5	4.4	–4.9
Cu^{2+}	0.4	6.3	–5.9
Pb^{2+}	1.5	7.8	–6.3

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations

It is evident that the strength of the Cl^- complexes is greater than for the OH^- complexes for Ag+, Cd^{2+}, Hg^{2+}, and Zn^{2+} but not for Cu^{2+} and Pb^{2+}.

Stability Constants for the Formation of Chloride and Hydroxide Complexes

Ion	Log K_{MCl}	Log K_{MOH}	Log K_{MCl} – LogK_{MOH}
Ag^+	3.1	2.3	0.8
Cd^{2+}	2.0	5.5	–3.5
Hg^{2+}	7.3	11.5	–4.2
Zn^{2+}	–0.5	4.4	–4.9
Cu^{2+}	0.4	6.3	–5.9
Pb^{2+}	1.5	7.8	–6.3

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations

The addition of higher concentrations of Cl^- (e.g., brines) can contribute to the formation of stronger Cl^- complexes for many metals. Mercury can form higher-order complexes with chloride.

Salmouras

$$Hg^{2+} + Cl^- \rightarrow HgCl^+$$

$$HgCl^+ + Cl^- \rightarrow HgCl_2^0$$

$$HgCl_2^0 + Cl^- \rightarrow HgCl_3^-$$

$$HgCl_{3-} + Cl^- \rightarrow HgCl_4^{2-}$$

$$HgCl_4^{2-} + Cl^- \rightarrow HgCl_5^{3-}$$

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.2. d_{10} Cations
The speciation or form of heavy metals in seawater, depends on the competition of all the ligands (Cl^-, Br^-, OH^-, HCO_3^-, CO_3^{2-}, etc.)

$$Hg^{2+} + Cl^- \rightarrow HgCl^+$$

$$HgCl^+ + Cl^- \rightarrow HgCl_2^0$$

$$HgCl_2^0 + Cl^- \rightarrow HgCl_3^-$$

$$HgCl_{3-} + Cl^- \rightarrow HgCl_4^{2-}$$

$$HgCl_4^{2-} + Cl^- \rightarrow HgCl_5^{3-}$$

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

1. Classification of Elements
1.3. Transition Metals between d_0 and d_{10}
Transition metal cations, in which the number of d electrons is greater than zero and less than 10, such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions.

Chemical Oceanography - Minor Elements in Seawater

Classification of Elements

Examples

Period	Z	Element	K s	L s	L p	M s	M p	M d	N s	N p	N d	N f
1	1	H	1									
	2	He	2									
2	3	Li	2	1								
	4	Be	2	2								
	5	B	2	2	1							
	6	C	2	2	2							
	7	N	2	2	3							
	8	O	2	2	4							
	9	F	2	2	5							
	10	Ne	2	2	6							
3	11	Na	2	2	6	1						
	12	Mg	2	2	6	2						
	13	Al	2	2	6	2	1					
	14	Si	2	2	6	2	2					
	15	P	2	2	6	2	3					
	16	S	2	2	6	2	4					
	17	Cl	2	2	6	2	5					
	18	Ar	2	2	6	2	6					

	Period	Z	Element	K s	L s	L p	M s	M p	M d	N s	N p	N d	N f
	4	19	K	2	2	6	2	6		1			
		20	Ca	2	2	6	2	6		2			
		21	Sc	2	2	6	2	6	1	2			
		22	Ti	2	2	6	2	6	2	2			
		23	V	2	2	6	2	6	3	2			
		24	Cr	2	2	6	2	6	5	1			
		25	Mn	2	2	6	2	6	5	2			
Fe^{2+}		26	Fe	2	2	6	2	6	6	2			
		27	Co	2	2	6	2	6	7	2			
Ni^{2+}		28	Ni	2	2	6	2	6	8	2			
		29	Cu	2	2	6	2	6	10	1			
		30	Zn	2	2	6	2	6	10	2			
		31	Ga	2	2	6	2	6	10	2	1		
		32	Ge	2	2	6	2	6	10	2	2		
		33	As	2	2	6	2	6	10	2	3		
		34	Se	2	2	6	2	6	10	2	4		
		35	Br	2	2	6	2	6	10	2	5		
		36	Kr	2	2	6	2	6	10	2	6		

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

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

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

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

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

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
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Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

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

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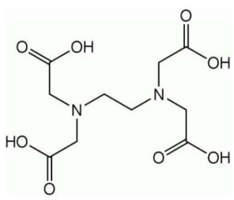
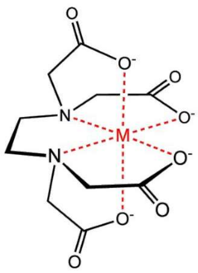


EDTA



Stability Constants for the Formation of Organic Ligands with Metals

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Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

An element can have a low concentration in seawater for two reasons:

1. It may be very reactive and thus be rapidly removed to the sediments.
2. It may occur in very low concentrations in its source from crystalline rocks or gaseous emanations from the interior of the earth.

Chemical Oceanography - Minor Elements in Seawater

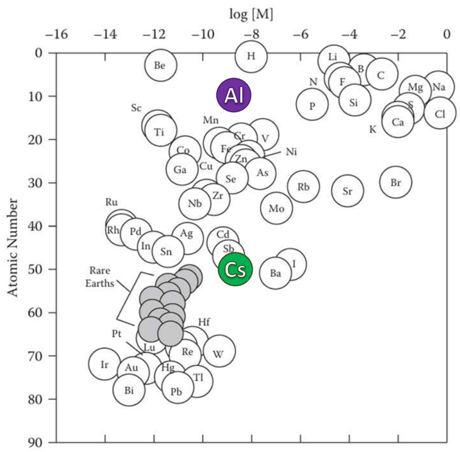
1. Classification of Elements

2. Residence Times

For example:

Al^{3+}: One of the most predominant constituents of igneous rocks ["rochas magmáticas"] has a low concentration in seawater due to its high reactivity

Cs^{+}: Has a low concentration in seawater and in crystalline rocks.



The range of concentrations of elements in seawater.

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

The comparative behaviour of elements can be gained by considering:

● the relative reactivity of the elements: Average time they spend in seawater before removal to the sediments

Or

● the degree of undersaturation of the element in seawater.

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

The ocean is a reservoir for the elements that are introduced into it during the major sediment cycle (Barth, 1952).

A steady-state system in which the amount of an element entering per unit time is equal to or compensated by the settling out of an equivalent amount.

The residence time τ can then be defined as **the average time that a substance remains in seawater before removal by some precipitation or adsorption process**.

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Considering river input Q and sediment removal R of an element A, we have Q → A → R

In a steady rate model:

» The change in A with time t (dA/ dt) = Q - R = 0.

If the removal is proportional to the concentration (first-order removal):

» R = k[A]

and

» τ = 1/k = [A]/R = [A]/Q

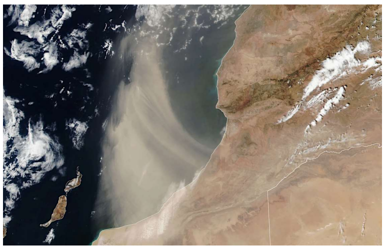
Chemical Oceanography - Minor Elements in Seawater

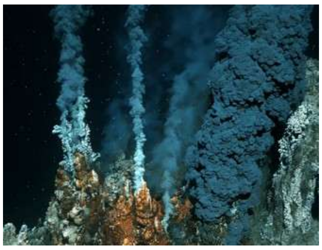
1. Classification of Elements

2. Residence Times

Elements are introduced into the ocean by three methods:

1. Fallout of substances from the atmosphere
2. Influx of river water
3. Influx from the interior of the earth





Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Barth (1952) used estimates of the river input Q of various elements, compensated for recycling processes, to estimate the residence time of elements.

The Cl^- ion, coming into the oceans from rivers is largely recycled sea salt (brines) that is transported to the land from the sea.

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Estimates of the residence times only from river inputs or sedimentation data.

These number do not consider hydrothermal vents.

The residence time = **the average time that a substance remains in seawater before removal by some precipitation or adsorption process.**

Residence Times of Elements in Seawater

	Residence Time (million of years)	
Element	**River Input**	**Sedimentation**
Na	210	260
Mg	22	45
Ca	1	8
K	10	11
Sr	10	19
Si	0.935	0.01
Li	12	19
Rb	6.1	0.27
Ba	0.05	0.084
Al	0.0031	0.0001
Mo	2.15	0.5
Cu	0.043	0.05
Ni	0.015	0.018
Ag	0.25	2.1
Pb	0.00056	0.002

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Estimates of the residence times only from river inputs or sedimentation data.

The agreement between the two methods of calculating residence times is quite reasonable considering the simplicity of the model for the oceans.

Residence Times of Elements in Seawater

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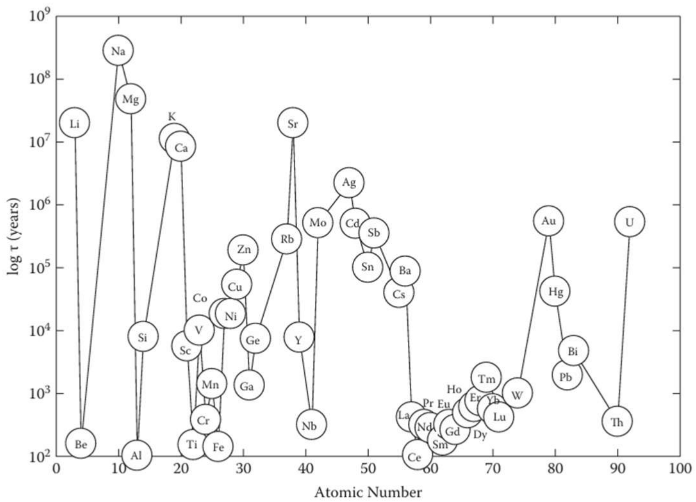
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

The residence time = **the average time that a substance remains in seawater before removal by some precipitation or adsorption process.**



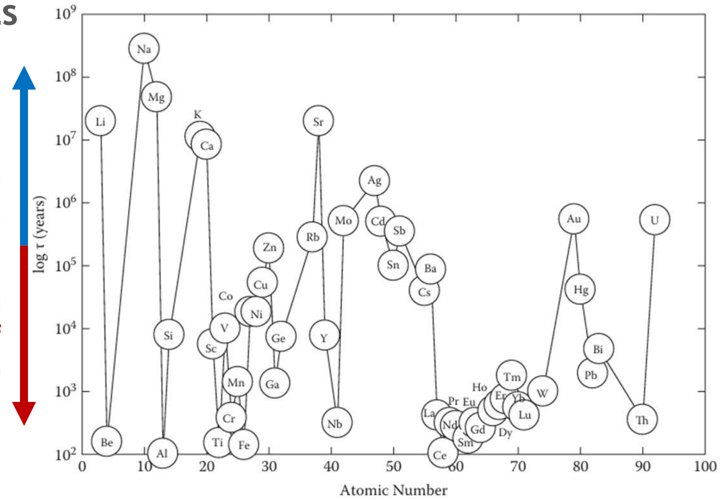
Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Low reactivity of aqueous ions

High reactivity of aqueous ions



Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

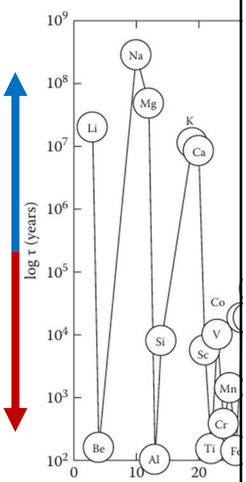
2. Residence Times

Residence times of the alkali metals ions decrease from Na^+ to Cs^+. Concentrations of the alkaline metals depends mostly on ion-exchange equilibria with clay minerals on the seafloor.

For the cations, the retention on clay surfaces increases with increasing ionic radius (i.e., decreasing hydrated radius).

Low reactivity of aqueous ions

High reactivity of aqueous ions



Chemical Oceanography - Minor Elements in Seawater

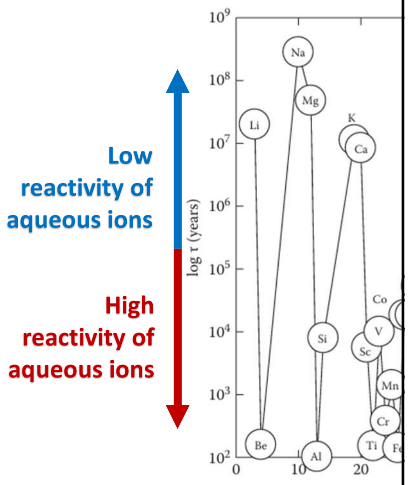
1. Classification of Elements

2. Residence Times

(...)

Decrease in residence times with increasing atomic numbers is in accord with the known behaviour of the alkali metals.

Ionic Radii
(in Picometers)



rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

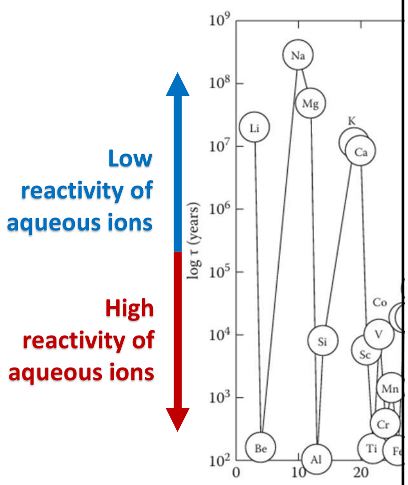
1. Classification of Elements

2. Residence Times

(...)

Certain elements (Be^{2+}, Al^{2+}, Ti^{3+}, Cr^{3+}, Fe^{2+}, Nb^{3+}, and Th^{4+}) have residence times less than 1000 yr, which is on the order of the mixing times for ocean waters.

1000 yr = This is the time it takes for the surface ocean to mix with the deep ocean.



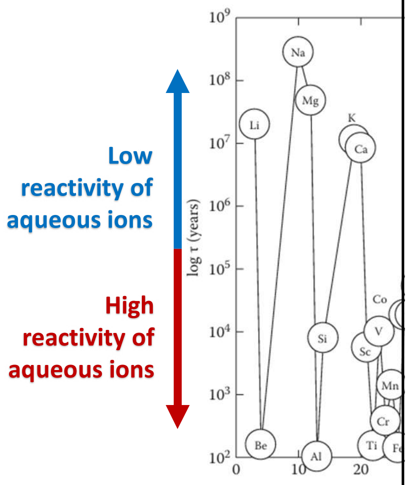
rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Certain elements (Be^{2+}, Al^{2+}, Ti^{3+}, Cr^{3+}, Fe^{2+}, Nb^{3+}, and Th^{4+}) (…)
These elements enter the oceans as particulate particles from the continents or volcanic activity in the form of clay mineral [minerais de argila], feldspars [feldspatos], and so on; thus, they rapidly settle to the sediments.

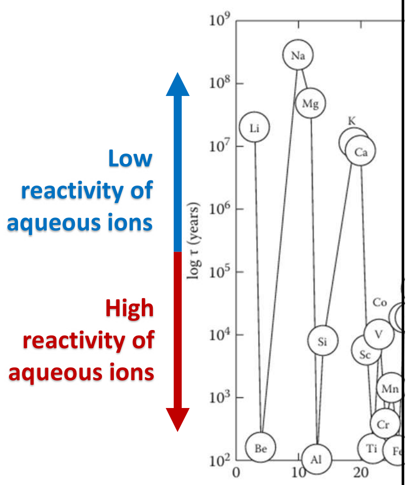


Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

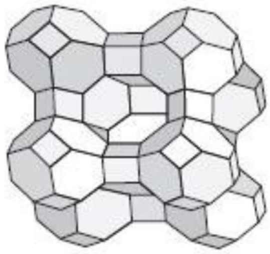
Certain elements (Be^{2+}, Al^{2+}, Ti^{3+}, Cr^{3+}, Fe^{2+}, Nb^{3+}, and Th^{4+}) (…)
(…) Some of these elements are also reactive with substances such as ferromanganese minerals [alloy of iron and manganese, with other elements] and zeolites [crystalline hydrated aluminosilicate material with a regular pore structure].
Thus, their entry as solids and their high chemical reactivity reduces residence times.



Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

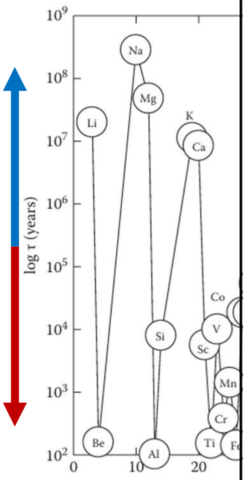
2. Residence Times



Structure of a Zeolite

Low reactivity of aqueous ions

High reactivity of aqueous ions



Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

Whitfield and Turner (1987) have developed a semiempirical correlation of the residence times for elements:

$$\log \tau = 2.6 \log[C_{SW}/C_{RW}] + a\,\Delta H_h + b$$

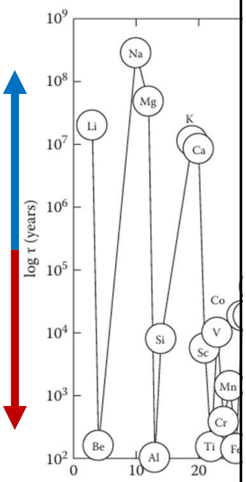
C_{SW} and C_{RW} are the concentration of the element in seawater (SW) and river water (RW), respectively

ΔH_h is the heat of hydration of the element

$a = 0.00452$ and $b = -0.6$ are adjustable parameters

Low reactivity of aqueous ions

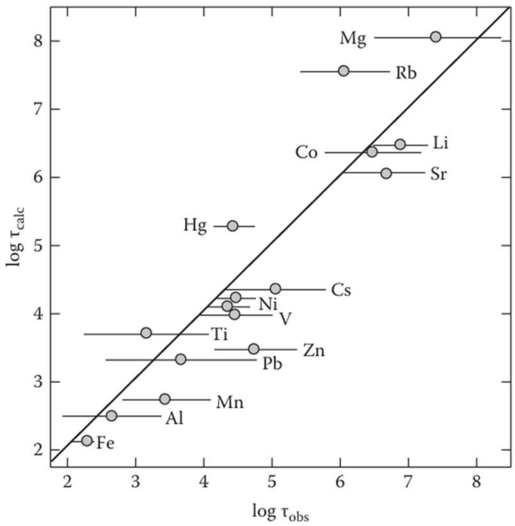
High reactivity of aqueous ions



Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times
The reliability of this equation is shown in the Figure, which compares the observed and calculated residence times.



rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times
The relative reactivity of elements in seawater can be examined considering the degree of saturation.
More soluble elements to have the longest residence times.

Comparison of Ratio of Saturated Concentration to Measured Values and Residence Times

Metal	Insoluble Compound	R[a]	Years
Pb^{2+}	$PbCO_3$	10,000–20,000	2,000
Ni^{2+}	$Ni(OH)_2$	10,000–225,000	18,000
Co^{2+}	$CoCO_3$	50,000–400,000	18,000
Cu^{2+}	$CuCO_3$	133–266	50,000
Ba^{2+}	$BaSO_4$	3.7	84,000
Zn^{2+}	$ZnCO_3$	120–250	180,000
Cd^{2+}	CdOHCl	40,000–10,000,000	500,000
Ca^{2+}	$CaCO_3$	0.25–1.2	8,000,000
Sr^{2+}	$SrCO_3$	2.75	190,000,000
Mg^{2+}	$MgCO_3$	27	450,000,000

[a] Measure of degree of undersaturation. R, saturation concentration/measured concentration.

rjsilva@ciencias.ulisboa.pt

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

The most insoluble compound for each element is given in this table along with:

$$R = \frac{\text{saturated concentration}}{\text{measured concentration}}$$

Comparison of Ratio of Saturated Concentration to Measured Values and Residence Times

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Ca^{2+}	$CaCO_3$	0.25–1.2	8,000,000
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Mg^{2+}	$MgCO_3$	27	450,000,000

Saturation ↓

[a] Measure of degree of undersaturation. R, saturation concentration/measured concentration.

Chemical Oceanography - Minor Elements in Seawater

1. Classification of Elements

2. Residence Times

One would expect that for small values of R to have the longest residence times.
However, many reactive elements have a short residence time and concentration well below the saturation limits.

- ➢ factors other than solubility control the reactivity of most elements in the oceans.

Comparison of Ratio of Saturated Concentration to Measured Values and Residence Times

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Saturation ↓

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