3

Minor Elements in Seawater

3.1 Classification of Elements

The elements found in seawater (see Figure 3.1) include most of those given in the periodic table. Of these, only 14 elements (O, H, Cl, Na, Mg, S, Ca, K, Br, C, Sr, B, Si, and F) have concentrations greater than 1 ppm. Most of these elements (with the exception of Si) are generally unreactive elements (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 will be discussed Chapter 8. The inert gases will also be discussed separately in Chapter 6.

Bruland (1983) has tabulated the range and average concentration of a number of elements in seawater (salinity [S] = 35). His results are tabulated in Table 3.1. He conveniently divides the elements into three classes based on concentration (Figure 3.1):

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

Minor and trace elements in the ocean, because of their reactivity, have a wide range of concentrations (see Table 3.1 and Figure 3.2).

Since many of these minor elements are metals, Goldberg (1965) divided them into three classes based on their electronic structure (see Table 3.2). This simple classification for metals is given below.

3.1.1 d^0 Cations

Ions of metallic elements with a rare gas configuration, these include the alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+), the alkaline earth metals (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}), and the 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^{4+}.

This group is characterized by the fact that its members 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-}). There is little or no evidence that these metal ions form complexes with the heavier halides. In a given series the stability of the complexes increases with increasing charge, and for cations of the same charge, with decreasing radius. This is shown in Table 3.3 for the formation of divalent metal complexes with F^- and OH^-. These results indicate that 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).

Later we will discuss the various inorganic complexes of the d^0 metal ions that are the major components of seawater.
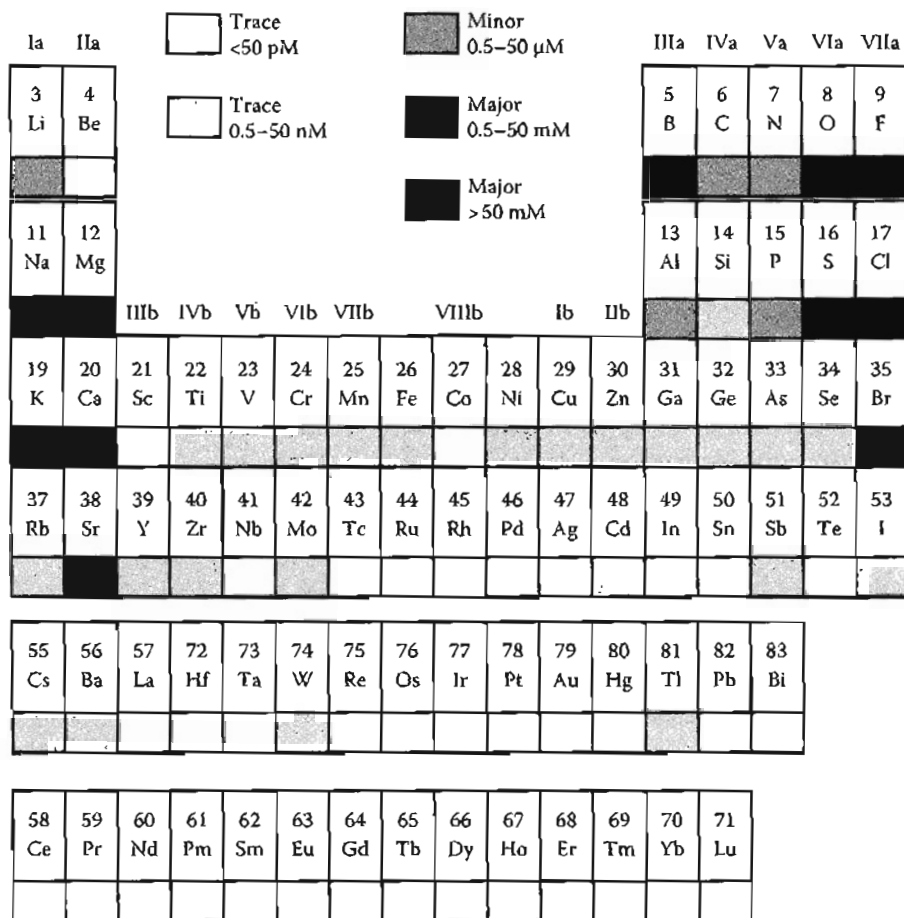
FIGURE 3.1

Classification of elements in ocean waters.

3.1.2   d¹⁰ Cations

Cations with an outer shell of 18 electrons. These include Ag^+, Zn^{2+}, Ga^{3+}, and Sc^{4+}. The univalent d^{10} metal ions behave in a different way from the d^0 metals. For these ions the halide complexes are quite strong and increase in stability with increasing atomic weight or size of the ligand. This is shown below for the stability constants for the formation of silver and copper(I) halide complexes as a function of the radius of the halide ion.

Complex	Cu⁺	Ag⁺	r(X)
MF	—	−0.3	1.36 Å
MCl	2.7	3.0	1.81
MBr	3.2	4.3	1.95
MI	7.2	8.1	2.16

This order is due to the increase in polarizability of the d^{10} electrons in the metals and the large halides ligands. The complexes thus have more covalent character. Since the concentration of Cl^- in seawater is much larger than that of the other halides, the

TABLE 3.1

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

Element	Probable Species	Range and Average Concentration	Type of Distribution
Li	Li^+	25 μM	Conservative
Be	$BeOH^+$, $Be(OH)_2$	4–30 pM, 20 pM	Nutrient type
B	$B(OH)_3$, $B(OH)_4$	0.416 mM	Conservative
C	HCO_3^-, CO_3^{2-}	2.0–2.5 mM, 2.3 mM	Nutrient type
N	NO_3^-, (N_2)	0–45 μM	Nutrient type
F	F^-, MgF^+, CaF^+	68 μM	Conservative
Na	Na^+	0.468 M	Conservative
Mg	Mg^{2+}	53.2 mM	Conservative
Al	$Al(OH)_4^-$, $Al(OH)_3$	5–40 nM, 2 nM	Mid-depth minima
Si	$Si(OH)_4$	0–180 μM	Nutrient type
P	HPO_4^{2-}, $MgHPO_4$	0–3.2 μM	Nutrient type
S	SO_4^{2-}, $NaSO_4^-$, $MgSO_4$	28.2 mM	Conservative
Cl	Cl^-	0.546 M	Conservative
K	K^+	10.2 mM	Conservative
Ca	Ca^{2+}	10.3 mM	Conservative
Sc	$Sc(OH)_3$	8–20 pM, 15 pM	Surface depletion
Ti	$Ti(OH)_4$	Few pM	?
V	HVO_4^{2-}, $H_2VO_4^-$	20–35 nM	Surface depletion
Cr	CrO_4^{2-}	2–5 nM, 4 nM	Nutrient type
Mn	Mn^{2+}	0.2–3 nM, 0.5 nM	Depletion at depth
Fe	$Fe(OH)_3$	0.1–2.5 nM, 1 nM	Surface and depth depletion
Co	Co^{2+}, $CoCO_3$	0.01–0.1 nM, 0.02 nM	Surface and depth depletion
Ni	$NiCO_3$	2–12 nM, 8 nM	Nutrient type
Cu	$CuCO_3$	0.5–6 nM, 4 nM	Nutrient type, scavenging
Zn	Zn^{2+}, $ZnOH^+$	0.05–9 nM, 6 nM	Nutrient type
Ga	$Ga(OH)_4^-$	5–30 pM	?
As	$HAsO_4^{2-}$	15–25 nM, 23 nM	Nutrient type
Se	SeO_4^{2-}, SeO_3^{2-}	0.5–2.3 nM, 1.7 nM	Nutrient type
Br	Br^-	0.84 nM	Conservative
Rb	Rb^+	1.4 μM	Conservative
Sr	Sr^{2+}	90 μM	Conservative
Y	YCO_3^+	0.15 nM	Nutrient type
Zr	$Zr(OH)_4$	0.3 nM	?
Nb	$NbCO_3^+$	50 pM	Nutrient type(?)
Mo	MoO_4^{2-}	0.11 μM	Conservative
Tc	TcO_4^-	No stable isotope	?
Ru	?	<0.05 pM	?
Rh	?	?	?
Pd	$PdCl_4$	0.2 pM	?
Ag	$AgCl_2^-$	0.5–35 pM, 25 pM	Nutrient type
Cd	$CdCl_2^-$	0.001–1.1 nM, 0.7 nM	Nutrient type
In	$In(OH)_3$	1 pM	?
Sn	$Sn(OH)_4$	1–12 pM, 4 pM	Surface input
Sb	$Sb(OH)_6^-$	1.2 nM	?
Te	TeO_3^{2-}, $HTeO_3^-$	?	?
I	IO_3^-	0.2–0.5 μM, 0.4 μM	Nutrient type
Cs	Cs^+	2.2 nM	Conservative
Ba	Ba^{2+}	32–150 nM, 100 nM	Nutrient type
La	$LaCO_3^-$	13–37 pM, 30 pM	Surface depletion
Ce	$CeCO_3^+$	16–26 pM, 20 pM	Surface depletion
Pr	$PrCO_3^+$	4 pM	Surface depletion
Nd	$NdCO_3^+$	12–25 pM, 10 pM	Surface depletion
Sm	$SmCO_3^+$	3–5 pM, 4 pM	Surface depletion
Eu	$EuCO_3^+$	0.6–1 pM, 0.9 pM	Surface depletion

TABLE 3.1 (continued)

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

Element	Probable Species	Range and Average Concentration	Type of Distribution
Gd	$GdCO_3^+$	3–7 pM, 6 pM	Surface depletion
Tb	$TbCO_3^-$	0.9 pM	Surface depletion
Dy	$DyCO_3^+$	5–6 pM, 6 pM	Surface depletion
Ho	$HoCO_3^+$	1.9 pM	Surface depletion
Er	$ErCO_3$·	4–5 pM, 5 pM	Surface depletion
Tm	$TmCO_3^-$	0.8 pM	Surface depletion
Yb	$YbCO_3^+$	3–5 pM, 5 pM	Surface depletion
Lu	$LuCO_3^+$	0.9 pM	Surface depletion
Hf	$Hf(OH)_4$	< 40 pM	?
Ta	$Ta(OH)_5$	<14 pM	?
W	WO_4^{2-}	0.5 nM	Conservative
Re	ReO_4^-	14–30 pM, 20 pM	Conservative
Os	?	?	?
Ir	?	0.01 pM	?
Pt	$PtCl_4^{2-}$	0.5 pM	?
Au	$AuCl_2^-$	0.1–0.2 pM	?
Hg	$HgCl_4^{2-}$	2–10 pM, 5 pM	?
Tl	Tl^+, TCl	60 pM	Conservative
Pb	$PbCO_3$	5–175 pM, 10 pM	Surface input, depletion at depth
Bi	$BiO^+, Bi(OH)_2^+$	<0.015–0.24 pM	Depletion at depth

Cl^- complexes will normally dominate (the values of K_{MX} for the heavier halides are not large enough to compensate for the low concentration). 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 ~–5.4. The values of log K_{MCl} and log K_{MOH} for various metal ions are shown in Table 3.4. From this table it is evident that the strength
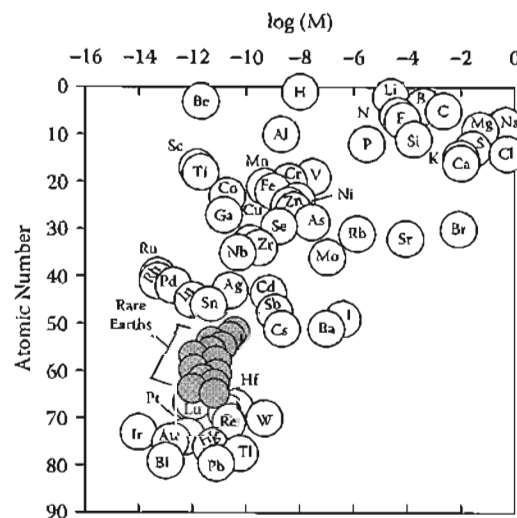

FIGURE 3.2
The range of concentrations of elements in seawater.

TABLE 3.2

Electronic Configuration of Atoms

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					
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		

TABLE 3.3

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

TABLE 3.4

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+}	3.5	7.8	−6.3

of the Cl^- complexes are greater than for the OH^- complexes for Ag^+, Cd^{2+}, Hg^{2+}, and Zn^{2+}, but not for Cu^{2+} and Pb^{2+}. The SO_4^{2-} ion cannot compete with Cl^- and OH^- ions for the formation of complexes with the d^{10} cations. The addition of more Cl^- can occur for many of these complexes. For example, mercury can form higher-order complexes with chloride

$$Hg^{2+} + Cl^- \rightarrow HgCl^+ \tag{3.1}$$

$$HgCl^+ + Cl^- \rightarrow HgCl_2^o \tag{3.2}$$

$$HgCl_2^o + Cl^- \rightarrow HgCl_3^- \tag{3.3}$$

$$HgCl_3^- + Cl^- \rightarrow HgCl_4^{2-} \tag{3.4}$$

$$HgCl_4^{2-} + Cl^- \rightarrow HgCl_5^{3-} \tag{3.5}$$
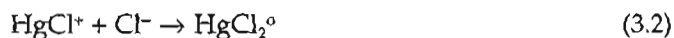
To evaluate the complete speciation or form of these heavy metals in seawater, it is necessary to consider the competition of all the ligands (Cl^-, Br^-, OH^-, HCO_3^-, CO_3^{2-}, etc.) for a given metal and the major divalent cations in seawater (Mg^{2+}, Ca^{2+}, and Sr^{2+}). The speciation of the divalent heavy metals (Cd^{2+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+}) in seawater and river waters will be discussed later.

3.1.3 Transition Metals between d^0 and d^{10}

The transition metal cations in which the number of d electrons is greater than zero and less than 10 represent this group. These include Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} ions. These metals have been extensively studied. From such work has evolved the so-called Irving Williams order, which states that for almost every ligand the stability of its complexes increases in the order

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
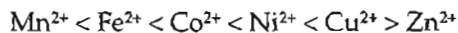
An example of this order is shown in Table 3.5 for the formation of complexes with the organic ligands EDTA (ethylenediammine N, N, N′, N′ tetraacetic acid), ethylenediamine, and nitrilotriacetic acid. The cause of this order is related to the stability of the electronic structure of the various metals 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.

TABLE 3.5

Stability Constants for the Formation of Organic
Ligands with Metals

Ion	EDTA	log K 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

3.2   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 — crystalline rocks or gaseous emanations from the interior of the earth.

For example, Al^{3+}, although a minor element in seawater, is one of the most predominant constituents of igneous rocks; its high reactivity in the marine environment reduces its concentration. The element Cs^+, on the other hand, has a low concentration in seawater and in crystalline rocks. Insight into the comparative behavior of elements can thus be gained by considering the relative reactivity of the elements on the basis of the average time they spend in seawater before removal to the sediments or the degree of undersaturation of the element in seawater. These areas are discussed in the following sections.

Barth (1952) was the first to introduce the concept of the ocean being a simple reservoir for the elements that are introduced into it during the major sediment cycle. He assumed 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 and is given by

$$\tau = \frac{\text{Total mass of element in sea}}{\text{Mass supplied per year}}$$

It is further assumed that there is complete mixing of the element in a time that is short compared to the residence time. If one uses a steady rate model for the river input (Q) and sediment removal (R) of an element, A,

$$Q \rightarrow \boxed{A} \rightarrow R$$

input   removal
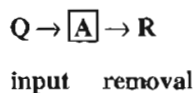
TABLE 3.6

Residence Times of Elements in Seawater

Element	Residence Time (million of years)	
	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

one has $dA/dt = Q - R = 0$. If the removal is proportioned to the concentration (first order removal), we have $R = k[A]$, and the residence time is given by

$$\tau = 1/k = [A]/R = [A]/Q \qquad (3.6)$$

Elements are introduced into the ocean by three methods:

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

Barth (1952) used estimates of the river input (Q) of various elements to estimate the residence time of elements. Since some elements come into the oceans from rivers in a solid phase (Si in clay minerals), care must be taken when estimating the river input. Care must also be taken to consider the recycling of elements from the sea to the land and back to the sea. The Cl^- ion, for example, coming into the oceans from rivers is largely recycled sea salt that is transported to the land from the sea. As will be discussed in Chapter 10, the input of elements from hydrothermal vents can change the residence times determined from inputs only from rivers. Estimates of the residence times from river inputs are given in Table 3.6 and shown plotted vs. atomic number in Figure 3.3. Also given in Table 3.6 are the resident times determined from the sedimentation rates of the elements (R).

The agreement between the two methods of calculating residence times is quite reasonable considering the simplicity of the model for the oceans. The values span six orders of magnitude: Na with 2.6×10^8 years to Al of 100 years. One further condition must be satisfied. Both A and Q should not change during a period of the order of 3 to 4 times τ. Even for Na this assumption appears to be valid since 10^9 years for the age of the oceans is in agreement with present day geological concepts.

The elements with long residence times are characterized by the lack of reactivity of their aqueous ions in the oceans. The decrease in residence times of the alkali metals in
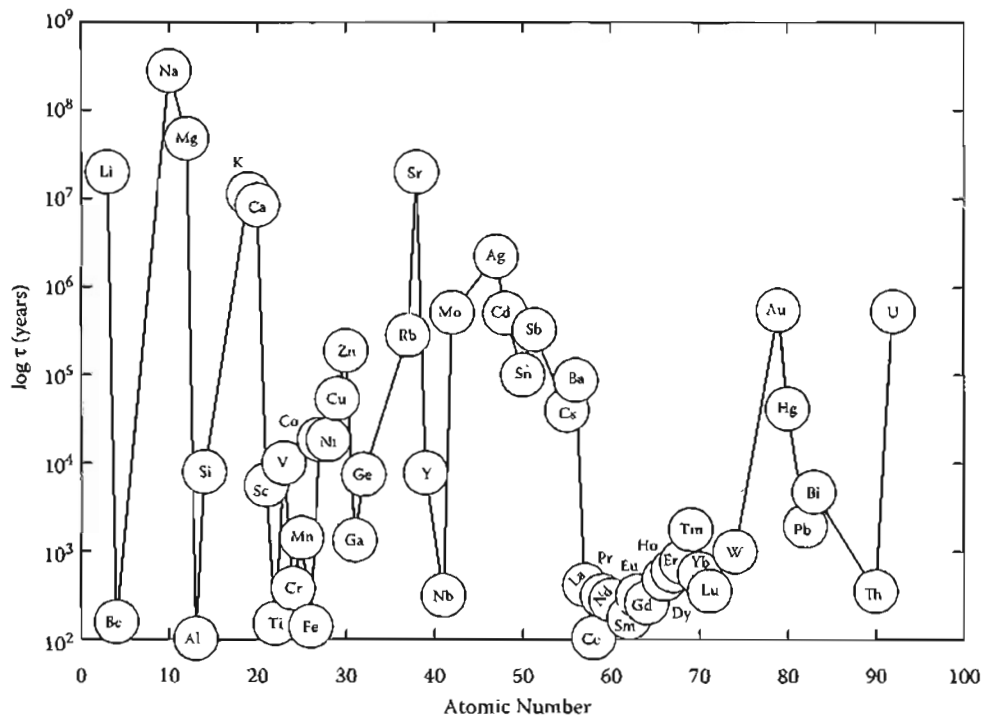
FIGURE 3.3
The residence time of elements in seawater plotted versus atomic number.

going from Na^+ to Cs^+ reflects variations in their ocean reactivities. The primary reactions regulating the concentrations of the alkaline metals may involve ion-exchange equilibria with clay minerals on the sea floor. For the cations, the retention on clay surfaces increases with increasing ionic radius (i.e., decreasing hydrated radius). Thus, the decrease in residence times with increasing atomic numbers is in accord with the known behavior of the alkali metals. Certain elements (Be^{2+}, Al^{2+}, Ti^{3+}, Cr^{3+}, Fe^{2+}, Nb^{3+}, and Th^{4+}) have residence times less than 1000 years, which is of the order of the mixing times for ocean waters. These elements enter the oceans as particulate particles from the continents or volcanic activity in the form of clay mineral, feldspars, and so on, and thus, they rapidly settle to the sediments. Some of these elements are also reactive with substances such as ferromanganese minerals and zeolites. Thus, their entry as solids and their high chemical reactivity can account for their low residence times. The absolute values of these residence times are somewhat tenuous because of the assumption that there is complete mixing of such elements in the oceans.

Nevertheless, certain deductions can be made with regard to their geochemistry. Ocean to ocean and temporal variations of these elements are to be expected. For example, the short residence times of Th^{4+} in the oceans allows for various water masses to maintain different concentrations. Certain minor elements have intermediate values of residence times: Mn (7,000 years), Zn (180,000 years), Co (18,000 years), and Cu (65,000 years). The reactivities of some of these elements are clearly connected with the formation of plant material (that is, active and nonactive uptake).
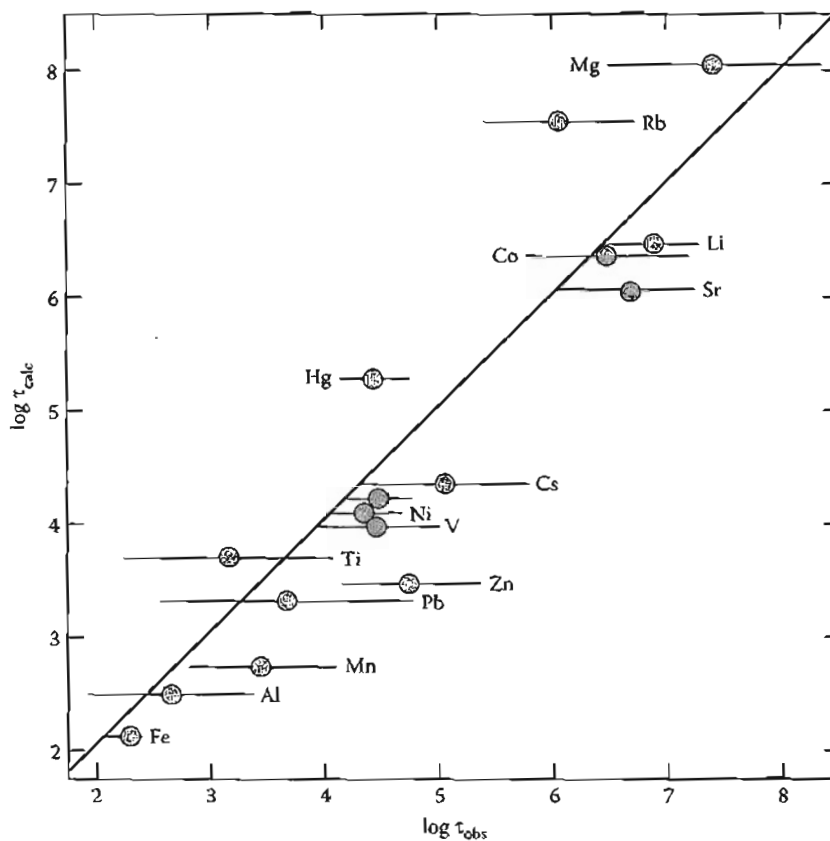
FIGURE 3.4
Calculated and observed residence times.

Whitfield et al. (1980) have developed a semi-empirical correlation of the residence times for elements

$$\log \tau = 2.6 \log [C_{SW}/C_{RW}] + a\ \Delta H_h + b \tag{3.7}$$

where C_{SW} and C_{RW} are the concentration of the element in seawater (SW) and river water (RW), ΔH_h is the heat of hydration of the element, and $a = 0.00452$ and $b = -0.6$ are adjustable parameters. The reliability of this equation is shown in Figure 3.4, which compares the observed and calculated residence times for a number of elements.

Many workers have examined the relative reactivity of elements in seawater on the basis of the degree of saturation. If the solubility of a given element controls its concentration in the ocean, one would expect the more soluble elements to have the longest residence times. Some of the metals that have been considered with this in mind (Goldberg, 1965) are given in Table 3.7. The most insoluble compound for each element is given in this table along with the ratio of the saturated concentration to the measured concentration (R). The value of R is used as a measure of the undersaturation of a given element. One would expect the elements with small values of R to have the longest residence times. Although this is generally true, many reactive elements have a short residence time and concentration well below the saturation limits. These results mean that factors other than solubility control the reactivity of most elements in the oceans.

TABLE 3.7

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.

3.3   Distribution of Trace Elements in the Oceans

In recent years there has been a rapid increase in our knowledge of the distribution of minor trace elements (mostly metals) in the oceans. This recent revolution is related to major advances in instrumentation and the elimination or control of contamination during sampling, storage, and analysis. Bruland (1983) has reviewed these developments. Preconcentration techniques such as chelation on resins and co-precipitation have been used to separate an element from the major components of seawater, and measurements of trace elements at nanomole and picomole per kilogram levels have been achieved. The distributions of the elements were found to be consistent with known biological and physical behavior. Ultra-clean room techniques pioneered by Patterson and coworkers (Schaule and Patterson, 1983) in studies of lead and the use of specially designed hydrowires (Kevlar) and sample bottles (Teflon coated) provided reliable data for trace metals such as Mn, Cu, Cd, Ni, Ba, and Fe. Surface values for Pb, Hg, Cu, Ni, and Zn were obtained using rafts and by collecting the samples by hand. The types of profiles found for various elements can be divided into a number of general categories. Some are given below:

1. **Conservative profile:** a constant ratio of the concentration of the element to chlorinity or salinity is found for some elements because of low reactivity. Along with the major components of seawater, trace metals such as Rb^+ and Cs^+ and anions such as molybdenum (MoO_4^{2-}) and tungsten (WO_4^{2-}) exhibit this type behavior (see Figure 3.5).

2. **Nutrient type profile:** a depletion of an element in surface waters and an enrichment at depth is a nutrient type profile. The element is removed from the surface waters by plankton or biologically produced particulate matter. It is regenerated in deep waters when the biologically produced particulate matter is oxidized by bacteria. Three types of nutrient type profiles are found:

    a. The shallow water regeneration that leads to a maximum near 1 km, similar to the nutrients PO_4^{3-} and NO_3^-. The metal Cd^{2+} is a good example of this type of nutrient behavior (see Figure 3.6). This behavior indicates that the element is associated with the soft parts of living and dead biological material. De Baar
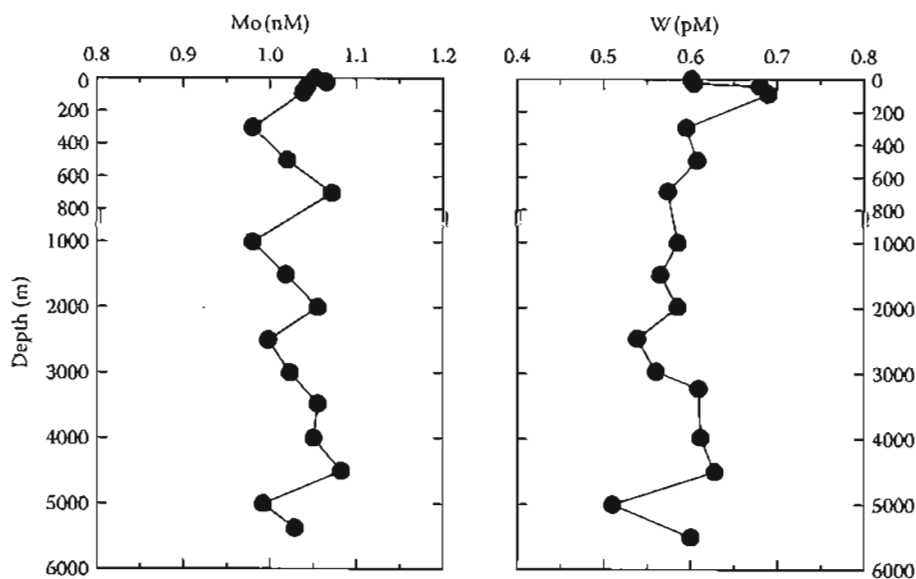
FIGURE 3.5
Profiles of molybdenum (Mo) and tungsten (W) in the Pacific Ocean.

and coworkers (De Barr et al., 1994; Löscher et al., 1997) have shown that most of the nitrate and phosphate made on ocean waters show a near linear correlation (Figure 3.7). Boyle (1992) has shown that this relationship can be used to estimate the phosphate in ocean water from the co-precipitated Cd in shells. By dating the shells he has been able to estimate the phosphate in North Atlantic deep waters as a function of time.
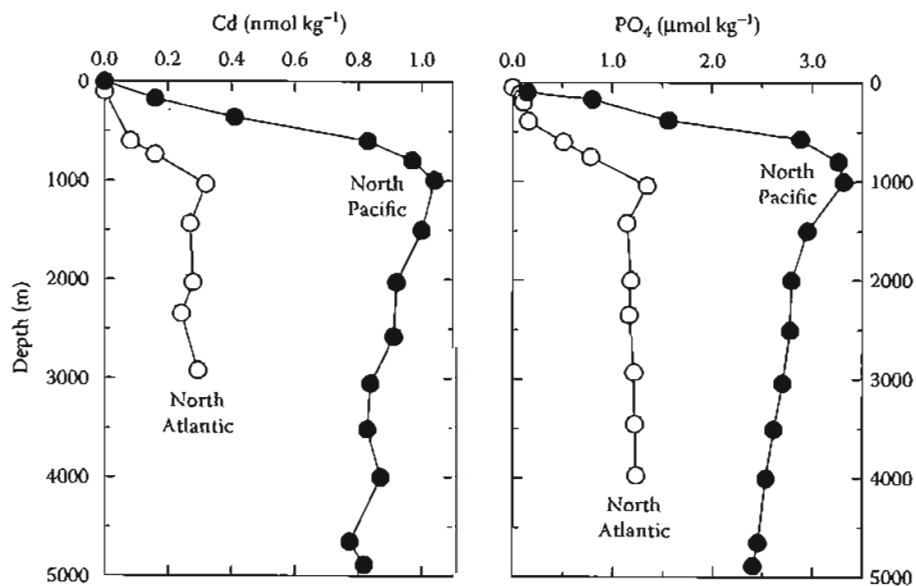

FIGURE 3.6
Profiles of cadmium (Cd) and phosphate (PO_4) in the Atlantic and Pacific Oceans.
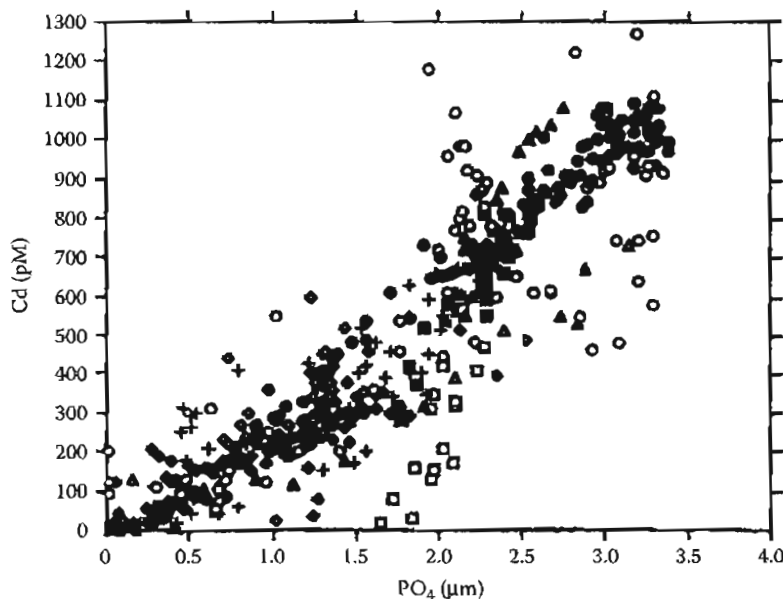
FIGURE 3.7
Plot of cadmium as a function of phosphate.

b. The deep regeneration cycle leading to a deep maximum is observed for metals of this type, similar to the distribution of Silica and total alkalinity. Examples of this type include the elements Zn, Ba, and Ge (see Figure 3.8, through Figure 3.10).

c. The combination of shallow and deep generation is inferred from the nutrient type profiles of Ni and Se (see Figure 3.11 and Figure 3.12). Recent results for Ag also show this mixed type of behavior (Figure 3.13). These metals appear to be affected by phytoplankton and diatoms or calcifiers.
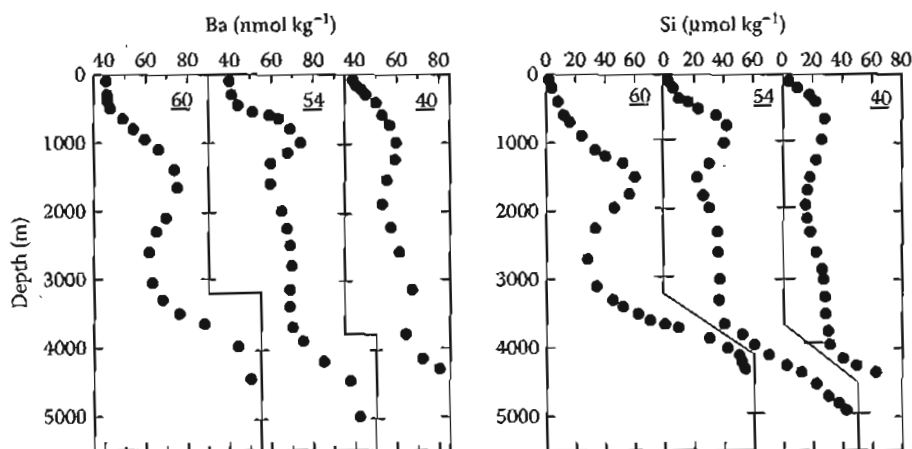
FIGURE 3.8
Comparison of barium (Ba) and silica (Si) profiles in the South Atlantic.
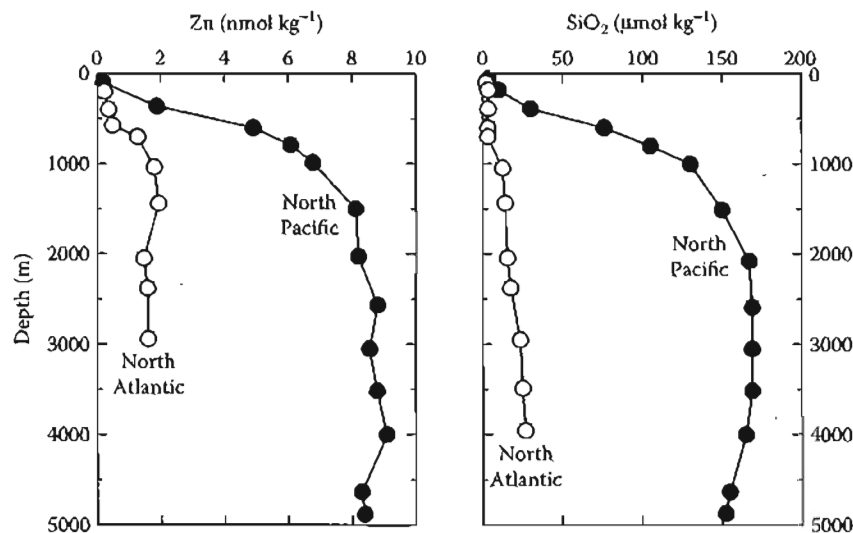
FIGURE 3.9
Profiles of zinc (Zn) and silicate (SiO_2) in the Atlantic and Pacific Oceans.

3. **Surface enrichment and depletion at depth:** Elements of this type have a surface input from the atmosphere, rivers, and land and are rapidly removed from seawater. The residence times of these elements are very short. The metal Pb is a good example of an element entering the oceans via the atmosphere (see Figure 3.14). The surface input of lead is largely the result of its past use in gasoline. As shown in Figure 3.14 the surface values of Pb off Bermuda have decreased with time (Wu and Boyle, 1992) because it is no longer used as an antiknock agent in gasoline. The mechanism for the scavenging process for lead is not well defined at present. The metal Mn^{2+} is a good example of an element that enters surface waters via rivers or release from shelf sediments off of California (see Figure 3.15). Elements that can occupy different oxidation states can also exhibit this type of profile. The reduction of metal in surface waters can be caused by biological and photochemical processes. The subsequent oxidation can lead to an oxidized form that is insoluble in seawater. The elements Cr^{3+}, As^{3+}, and I^- fall into this classification.

4. **Mid-depth minima:** A mid-depth minimum can result from a surface input and regeneration at or near the bottom or scavenging throughout the water column. The metals Cu^{2+}, Sn, and Al^{3+} show this type of profile. Profiles for the distribution of Al in the Atlantic and Pacific are shown in Figure 3.16. The input into the surface oceans comes from the fallout of atmospheric dust that originates on the continents. As is apparent from this figure, the input of dust from Africa (Sahara Desert) into the Atlantic are much higher than the values from China (Gobi Desert). The Al is quickly scavenged from surface water by adsorption or the uptake of plants or plant material. The particles settle into the deep oceans and are deposited in the sediment. The resuspension and flux of Al from the sediments lead to an increase in the concentration in bottom waters.

5. **Mid-depth maxima:** A profile of this type can result from a hydrothermal input from the mid-ocean ridge system. The elements Mn^{2+} and ^3He are good examples
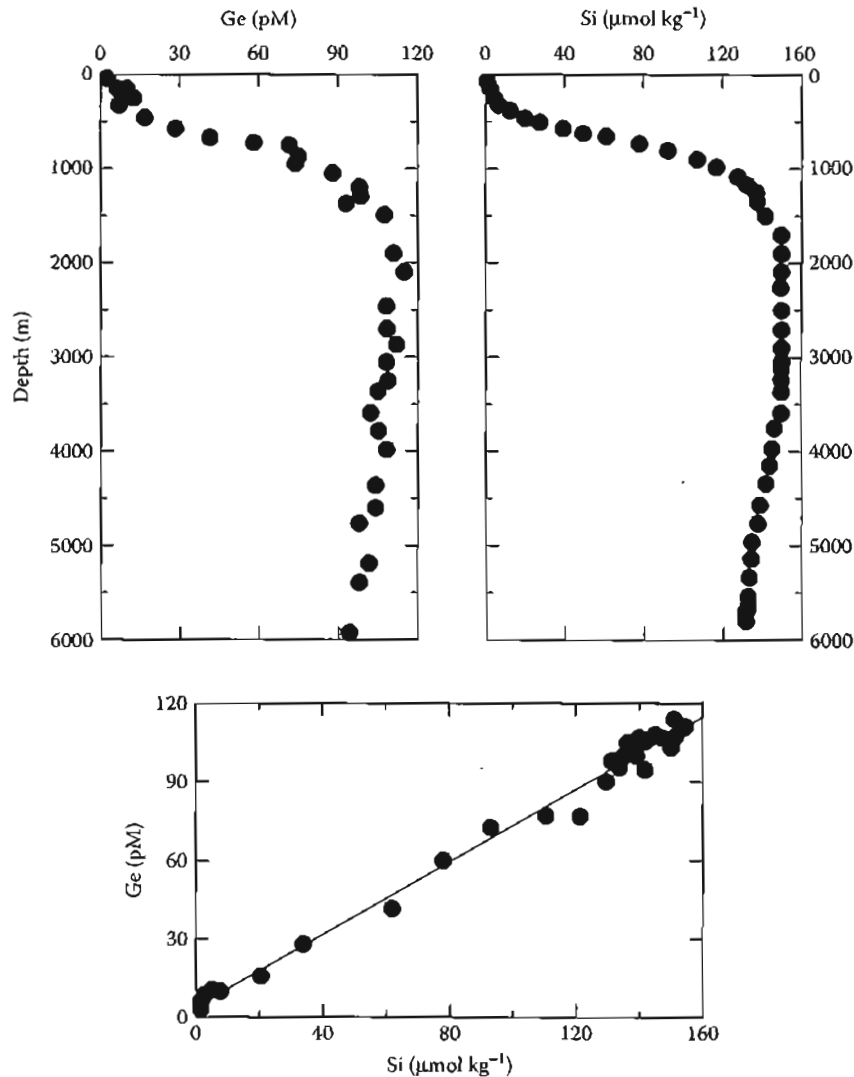
FIGURE 3.10
Comparison of the profiles of germanium (Ge) and silica (Si) in Pacific waters.

of this type profile (see Figure 3.17 and Figure 3.18). The fluxes of these elements from hydrothermal plumes have been used to trace them in deep ocean waters.

6. **Mid-depth maxima or minima in the sub-oxic layer (~1 km):** A large sub-oxic layer exists in some regions of the Pacific and Indian Oceans. Reduction and oxidation processes in the water column or adjacent slope sediments can yield maxima of the reduced form (Fe^{2+} and Mn^{2+}) and minima of the reduced form if it is insoluble or scavenged by solid phases (Cr^{3+}).

7. **Maxima and minima in anoxic waters:** In areas of restricted circulation such as the Black Sea, the Cariaco Trench, and fjords, the water can become anoxic (devoid of O_2) with the production of H_2S. Near the interface between the two waters
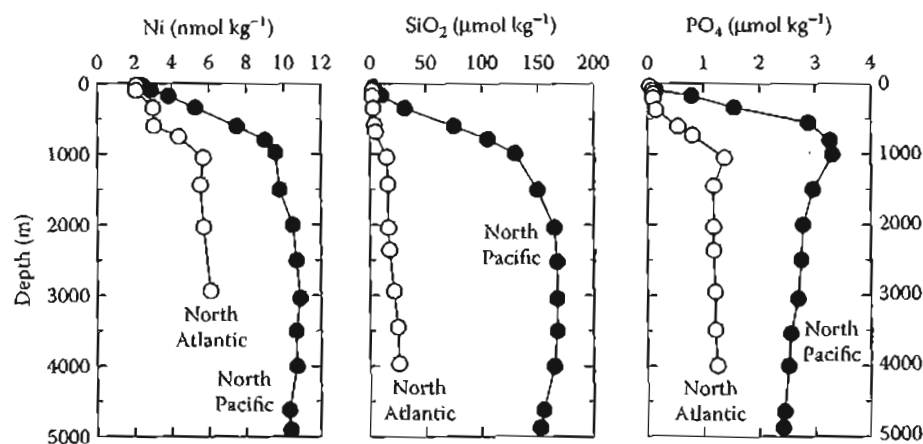
FIGURE 3.11
Comparison of the profiles of nickel (Ni) to silicate (SiO_2) and phosphate (PO_4) in the Atlantic and Pacific Oceans.

redox processes can occur that cause maxima and minima from solubility changes of the various species. Fe^{2+} and Mn^{2+}, for example, have a maxima because of the increased solubility of the reduced forms (see Figure 3.19 and Figure 3.20). These maxima are due to oxidation and reduction of iron and manganese near the oxic–anoxic interface. More will be said about anoxic waters in Chapter 10.
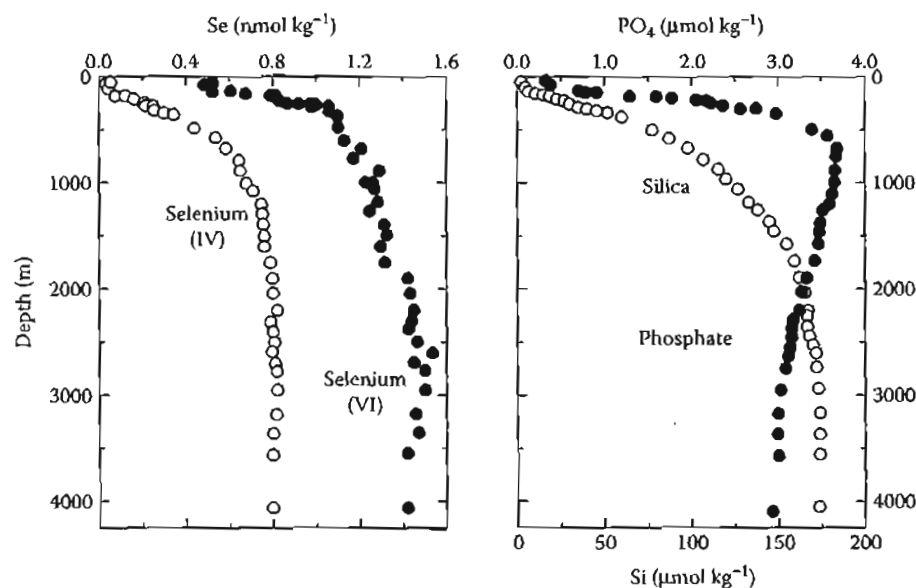
FIGURE 3.12
Comparison of the profiles of selenium (Se) to silica (Si) and phosphate (PO_4) in the Pacific Ocean.
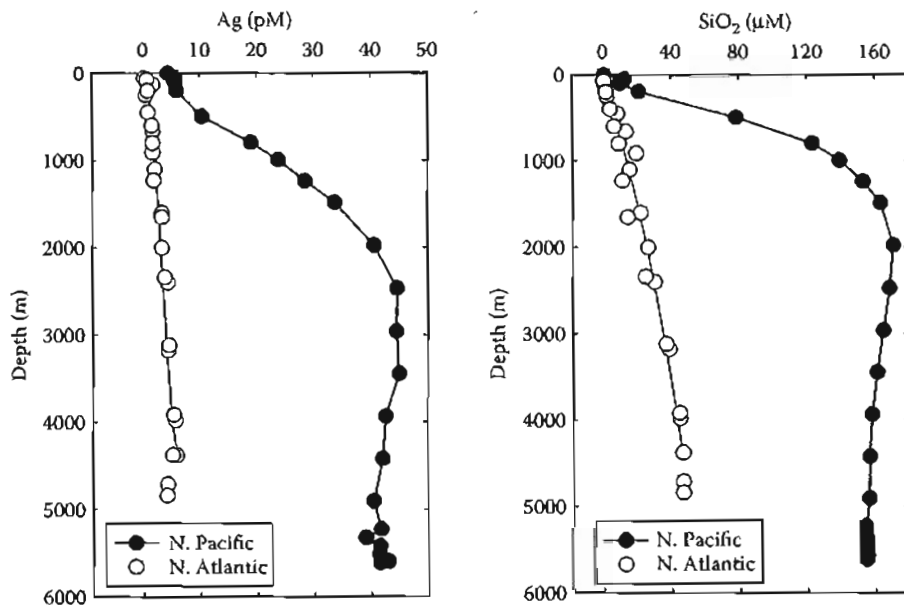
FIGURE 3.13
Comparison of the profiles of silver (Ag) to silicate (SiO_2) in the Atlantic and Pacific Oceans.

Many of the metals studied have higher concentrations in the Pacific than in the Atlantic (see Table 3.8). Exceptions are Pb^{2+} and Al^{3+}. The higher values in the deep Pacific are attributed to the older water accumulating more metals from surface waters. For Pb^{2+} and Al^{3+}, the higher surface input in the Atlantic leads to higher values in the deep Atlantic waters. Since these metals are quickly scavenged from seawater, they do not accumulate in the deep waters of the Pacific. The higher concentration of most metals on shelves (Table 3.9) indicates a land source (rivers or sediments), while the higher concentration (Table 3.10) in the Atlantic central gyre indicates an atmospheric input (from African dust).

3.4 Biological Interactions

The interactions of trace elements with marine organisms have been studied by many workers. Bowen (1966) has summarized these interactions, which are outlined below, in terms of concentration factors (concentration in the organism relative to a given volume of 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.
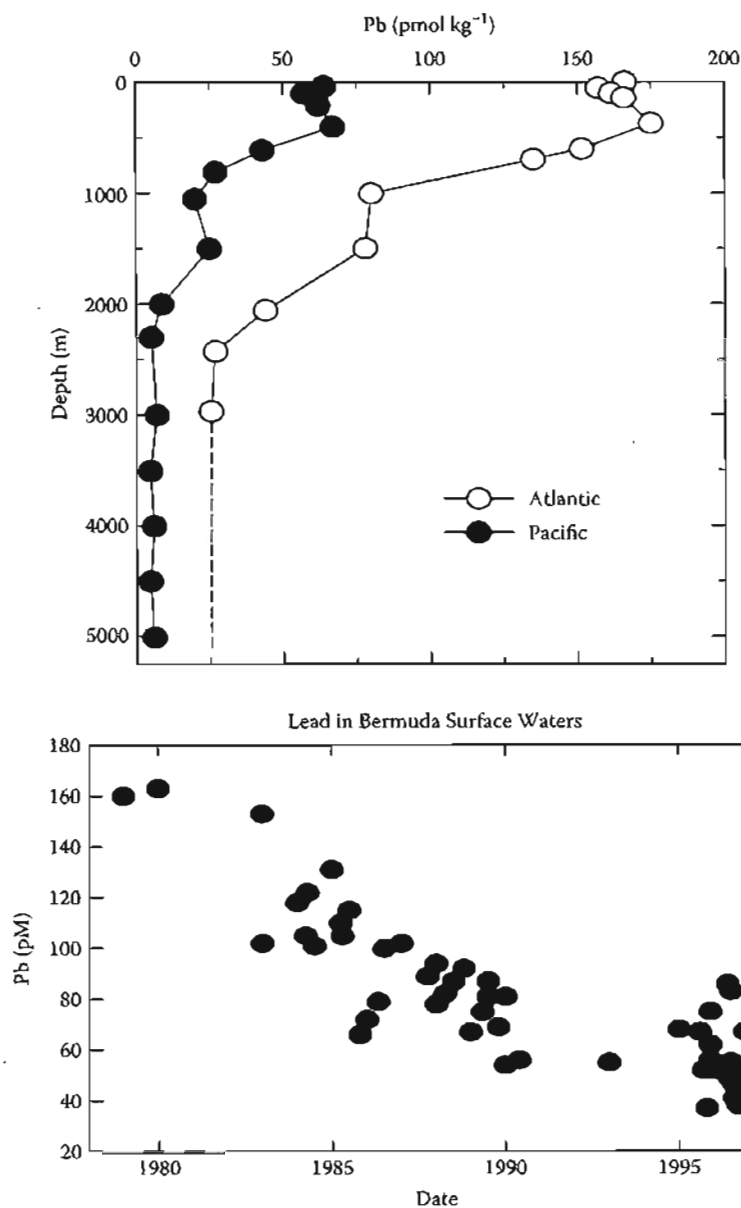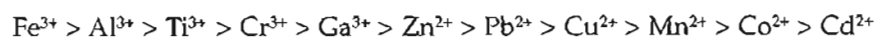
FIGURE 3.14

Lead (Pb) profiles in the Atlantic and Pacific Oceans and Pb in surface waters off Bermuda as a function of time.

4. The order of affinity of organisms for cations is

$$4+ > 3+ > 2+ \text{ transition} > 2+ \text{ Group IIA} > 1+ \text{ Group I metals.}$$

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.
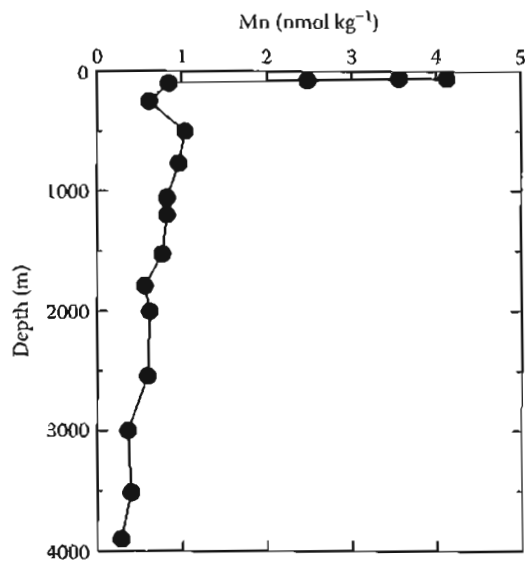
FIGURE 3.15
Profile of manganese (Mn) in the North Pacific off the coast of California.

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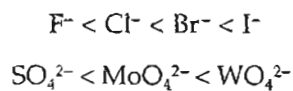
$$F^- < Cl^- < Br^- < I^-$$

$$SO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$$
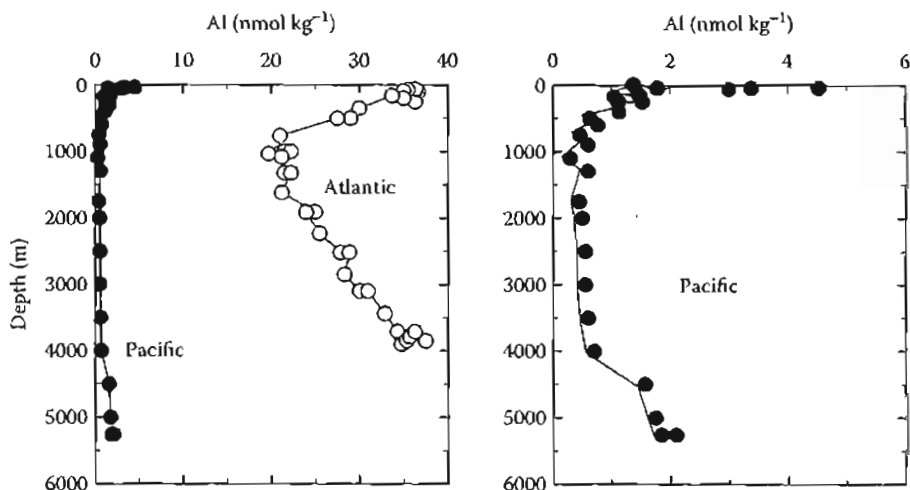
FIGURE 3.16
Profiles of aluminum (Al) in Atlantic and Pacific Ocean waters.
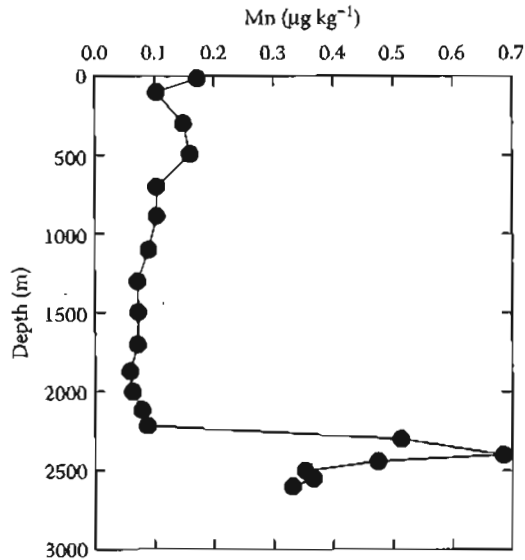
FIGURE 3.17
Profile of manganese (Mn) in the Pacific Ocean showing hydrothermal input from the Mid-Pacific Ridge.

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

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

The biosphere can effect minor elements by:

1. The regulation of dissolved and particulate organic material as a function of time and space. This material can interact with minor elements and change its reactivity.

2. The concentration of elements in living and nonliving organic material. The active and inactive uptake can redistribute elements from surface to deep waters. The concentration of organics on nonliving particles may also increase the adsorption on these particles.
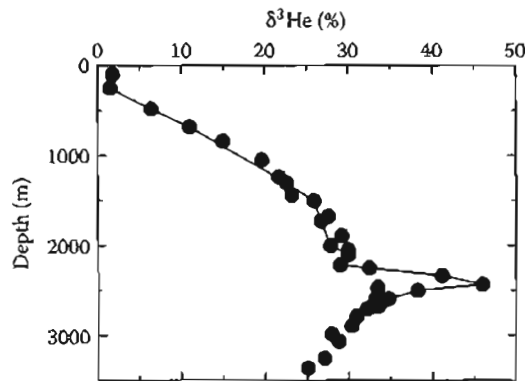

FIGURE 3.18
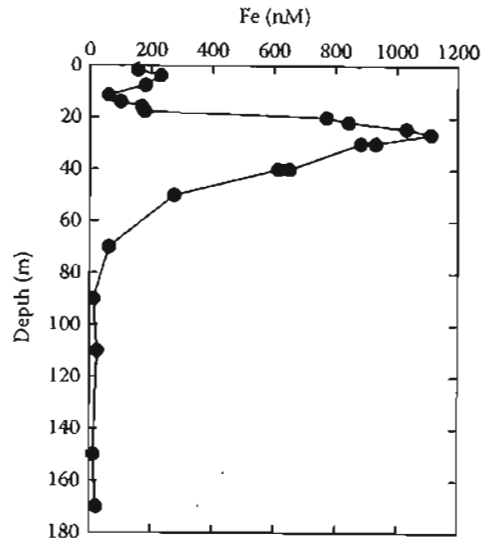Profile of helium (He) in the Pacific Ocean showing hydrothermal input from the Mid-Pacific Ridge.

FIGURE 3.19
Profile of iron(II) (Fe) in the Framvaren Fjord, Norway.

These effects can account for the movement of elements from surface waters to the sediments. This movement can be caused by:

1. Active uptake by organisms (Fe^{2+}, Zn^{2+}, Mn^{2+})
2. Passive uptake by organisms (heavy metals)
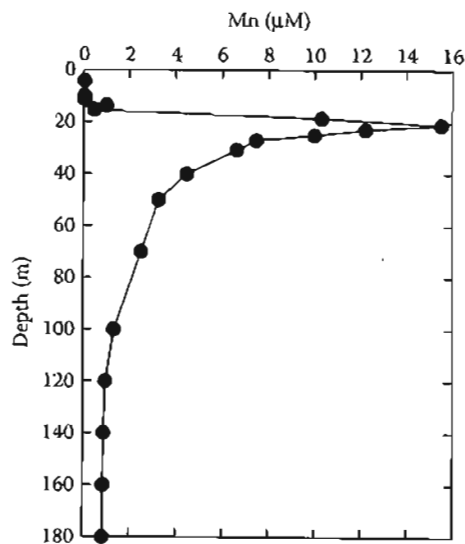3. Adsorption on particulate matter (Pb^{2+}, Cu^{2+})

FIGURE 3.20
Profile of manganese(II) (Mn) in the Framvaren Fjord, Norway.

TABLE 3.8

Metals in Atlantic and Pacific
Deep Waters (nM)

Metal	Atlantic	Pacific	P/A
Cd	0.29	0.94	3.2
Zn	1.5	8.2	5.5
Ni	5.7	10.4	1.8
Cu	1.7	2.7	1.6
Mn	0.6	—	—

TABLE 3.9

Metals on Shelf vs. Open Sea
Surface Waters

Metal	Shelf	Open
Mn	21 nM	2.4 nM
Ni	5.9 nM	2.3 nM
Cu	4.0 nM	1.2 nM
Zn	2.4 nM	0.06 nM
Cd	200 pM	2 pM

TABLE 3.10

Metals in Central Gryes

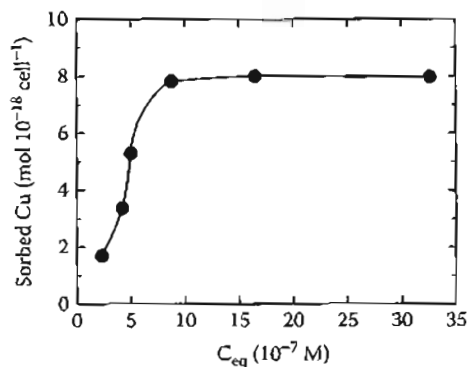| Metal	Atlantic	Pacific
Mn	2.4 nM	1.0 nM
Cu	1.2 nM	0.5 nM
Ni	2.1 nM	2.4 nM
Zn	0.06 nM	0.06 nM
Cd	2 pM	2 pM

FIGURE 3.21
Adsorption of Cu(II) to the surface of bacteria as a function of Cu.

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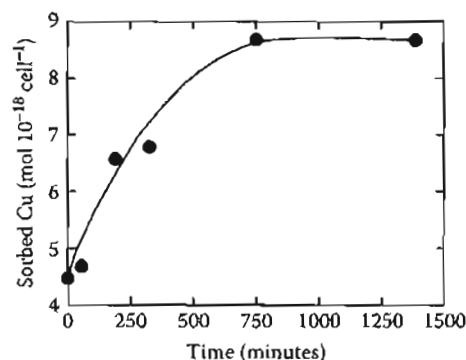tribution (

Althoug
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FIGURE 3.22
Adsorption of Cu(II) to the surface of bacteria as a function of time.

4. Remobilization from sediments by oxidation (Mn^{2+})
5. Precipitation (Fe^{3+})

The active uptake of metals may be due to their use in enzyme systems (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Mo). Passive uptake may be due to the adsorption on organic particles caused by interactions with surface groups (carboxylic, phenolic).

It is well known that a number of metals are concentrated in biological materials. This has led to the suggestion that their source in the deep ocean comes from the death of marine organisms with subsequent remineralization during oxidation. An alternate explanation may be that metals may be carried to the deep ocean by adsorption on organic matter, both living and dead. We have found, for example, that Cu^{2+} is adsorbed on bacteria that are living or dead (see Figure 3.21). The absorption is quite fast (Figure 3.22), and the Cu^{2+} can be desorbed by acidifying the solutions. The adsorption increases with increasing pH, which indicates that surface –OH and –COOH groups may be involved in the process. Fisher (1986) has shown that adsorption of a number of metals to living and dead phytoplankton was similar and proportional to the hydrolysis constants of the metals (see Figure 3.23) and to the residence times (Figure 3.24). These results suggest that the scavenging of metals in the oceans may be the result of ionic interactions with surface groups on living and dead organic matter in the oceans. Fisher also showed (see Figure 3.25) that the toxicity of metals to plankton was related to hydrolysis constants.

The above discussion is not meant to rule out nonbiological transport, since it is well known that many metals can be co-precipitated by SiO_2 and $CaCO_3$ or adsorbed on minerals in ocean waters. In an oxidizing environment, for example, many metals (Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, etc.) are concentrated on Mn nodules. In a reducing environment a number of metals are co-precipitated or adsorbed by pyrite (FeS_2). The oxidation of Fe^{2+} and Mn^{2+} results in the formation of solids that are quite active in the adsorption of metals. In summary, each metal may be influenced by biological or nonbiological processes. Future studies are needed to elucidate that these processes actually are responsible for the distribution of many of the elements present in the oceans.

Although most minor elements that enter the oceans eventually are removed to the sediments, many are recycled. The removal process is related to the interactions of elements with particles (Whitfield and Turner, 1987). The production, sinking, and decomposition of particulate matter are thus important in controlling the recycling of metals.
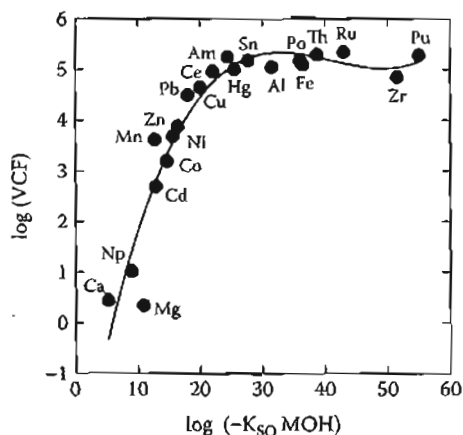
FIGURE 3.23
Values of the volume concentration factor (VCF) for metals to phytoplankton plotted vs. the solubility of metal hydroxide. (Data from Fisher, *Limnol. Oceanogr.*, 3, 443, 1986.)

Phytoplankton are the primary producers of particles in the surface oceans. These plants are grazed on by zooplankton and are packaged into fecal pellets. They have sinking rates of a few meters to thousands of meters per day. The oxidation and dissolution of these particles can recycle some of the elements. Recent work has shown that large particles are responsible for the bulk transport of materials to the deep sea. These particles have been studied by catching them in sediment traps or by using large volume pumping systems. This cycling of C, N, P, and S as well as trace metals is being studied in a large multi-institutional study called the Joint Global Ocean Flux Study (JGOFS).
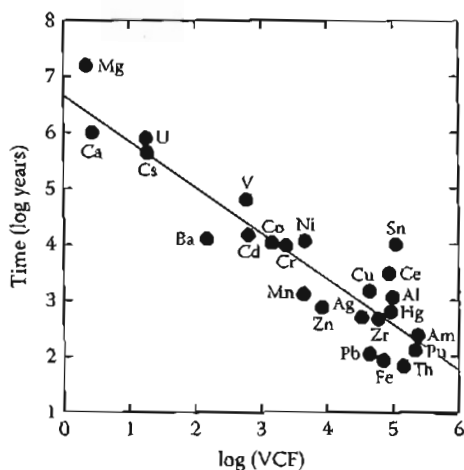

FIGURE 3.24
The residence time for metals plotted versus the volume concentration factor (VCF). (Data from Fisher, *Limnol. Oceanogr.*, 3, 443, 1986.)
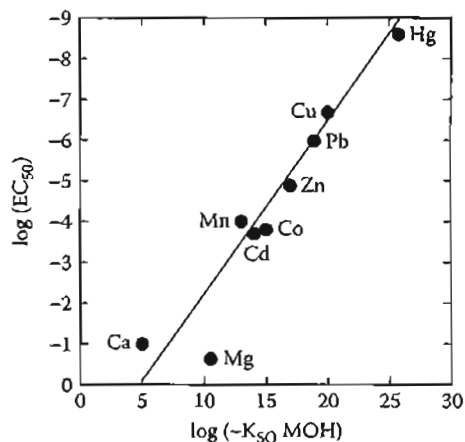
FIGURE 3.25
The effective concentration of metal that reduces phytoplankton growth rate by 50% (EC_{50}) plotted vs. the solubility of metal hydroxide. (Data from Fisher, *Limnol. Oceanogr.*, 3, 443, 1986.)

3.5 Geochemical Balance of Elements

There is a continual interaction between the oceans and the land. The water from the oceans evaporates, comes down as rain, and attacks the rocks and soil. The rivers of the world carry the weathered products (dissolved and suspended) to the oceans. Sediments are formed on continental shelves, and fine particles are carried throughout the oceans. A number of geochemists have been concerned with geochemical processes with an interest in the evolution of seawater, sedimentary cycling, and the controls of the composition of the oceans. By comparing the present composition of dissolved ions in the oceans (moles per square centimeter of the surface of the earth) with the amount delivered, attempts have been made to prepare a geochemical balance. Sillén (1967) tabulated the amounts of some of the major components of seawater delivered by rivers over the past 100 million years. These estimates are compared to the amounts in the present oceans in Table 3.11. Most of the elements show an excess amount added over this period of time. The Na^+ and Cl^- delivered to the oceans is mostly sea spray that is washed back to the oceans. The other ions, however, are the results of weathering of rocks and soils. In addition to the dissolved materials, 300 to 600 kg cm^{-3} of solid material has been delivered to the oceans in the past 100 million years. These solids are mostly clay minerals that can participate in ion-exchange reactions with the components of seawater and go through phase transformations.

Some geochemists have attempted to develop a geochemical balance between the material added to the rivers and the amount delivered to the sediments. These attempts were started in 1993 by Goldsmith. He considered the reaction

$$\text{igneous rocks} + \text{volatiles} \rightarrow \text{seawater} + \text{sediments} + \text{air} \tag{3.8}$$
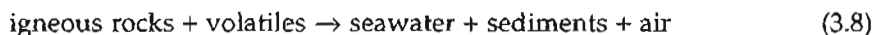
to control the composition of rocks and seawater and attempted to balance the reaction. He concluded that 600 g of rock would lead to 600 g of sediments. More recent attempts have been made by Garrels and Mackenzie (1975). The steady state model for the circulation of elements in the sedimentary cycle are shown in Figure 3.26. The fluxes are in

TABLE 3.11

Present Concentration (mol cm⁻² of surface) of Major Components of Seawater Compared with the Amount Added by Rivers over Past 100 Million Years

	Na	Mg	Ca	K	Cl	SO₄	CO₃	NO₃
Present	129	15	2.8	2.7	150	8	0.3	0.01
Added by rivers	196	122	268	42	157	84	342	11
Excess added	67	107	265	39	7	76	342	11
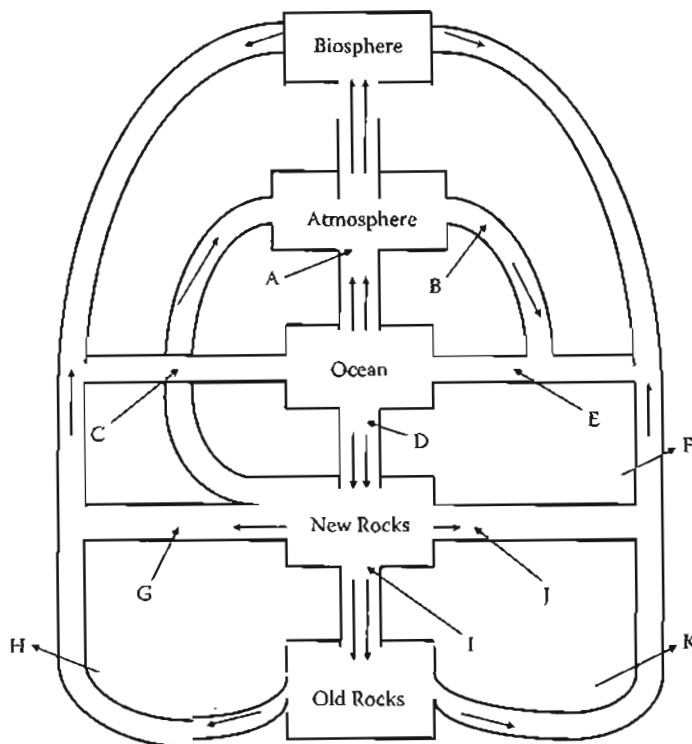
A. Ocean to Atmosphere
B. Atmosphere to Streams
C. Total Suspended Load of Streams
D. Total Sediment Flux
E. Dissolved Load of Streams
F. Total Flux Dissolved from Rocks

G. Suspended Load from New Rocks
H. Suspended Load from Old Rocks
I. Flux from New Rocks to Old Rocks
J. Dissolved Load from New Rocks
K. Dissolved Load from Old Rocks

NEW ROCKS
4800 × 10²⁰ g of
elements (150 × 10⁶ y)

BIOSPHERE
0.01 × 10²⁰ gC Living
0.04 × 10²⁰ gC Dead

OLD ROCKS
8450 × 10²⁰ g of
elements (663 × 106 y)

ATMOSPHERE
0.065 × 10²⁰ gC
as CO_2

OCEAN
500 × 10²⁰ g of
elements

FIGURE 3.26
The cycle of elements on the earth.

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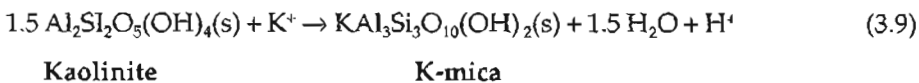
FIGURE 3.27
Sillén ion exchange

TABLE 3.12

Concentration of Various Components of the Geochemical Cycle of the Oceans

Component	Rock	Volatile	Air	SW	Sediments
H_2O	—	54.90	—	54.90	—
Cl(HCl)	—	0.94	—	0.55	0.40
Na(NaO$_5$, NaOH)	1.47	—	—	0.47	1.00
Ca(CaO, Ca(OH)$_2$)	1.09	—	—	0.01	1.08
Mg(MgO, Mg(OH)$_2$)	0.87	—	—	0.05	0.82
K(KO$_5$, KOH)	0.79	—	—	0.01	0.78
Si(SiO$_2$)	12.25	—	—	—	12.25
Al(AlO$_{1.5}$, Al(OH)$_3$)	3.55	—	—	—	3.55
C(CO$_2$)	0.03	1.05	—	0.002	1.08
C(s)	—	1.01	—	—	1.01
O$_2$	—	0.022	0.022	—	—
Fe(FeO, Fe(OH)$_2$)	0.52	—	—	—	0.53
(FeO$_{1.5}$, FeOH)	0.38	—	—	—	0.38
Ti(TiO$_2$)	0.12	—	—	—	0.12
S	0.02	0.06	—	0.03	0.05
F(HF)	0.05	—	—	—	0.05
P(PO$_{2.5}$,H$_3$PO$_4$)	0.04	—	—	—	0.04
Mn(MnO$_{1\,to\,2}$)	0.05	—	—	—	0.05
N$_2$	—	0.082	0.082	—	—

units of 10^{14} g year^{-1}. Unlike the earlier model of Goldsmith, recent work has the weathering reaction going both ways; that is, reverse weathering or igneous rocks are formed during sea floor spreading. The earlier models gave a reasonable balance between the rocks and the sediments for most elements (see Table 3.12). For the elements B, S, Cl, As, Se, Br, and I, an excess was found, presumably of a volcanic origin. With the recent discovery of the flux of materials coming from hydrothermal vents, these values will need some modification for some elements.

Sillén (1967) suggested some imaginary experiments to represent the real ocean system. He visualized the formation of the oceans as being the result of mixing water with a number of minerals. This mixing, performed perhaps by a well-known bartender, took place over a period of time to ensure equilibrium. The first model he considered is given in Figure 3.27. The ion exchange reaction

$$1.5 \, Al_2SI_2O_5(OH)_4(s) + K^+ \rightarrow KAl_3Si_3O_{10}(OH)_2(s) + 1.5 \, H_2O + H^+ \tag{3.9}$$

Kaolinite   K-mica

can control the ratio of H$^+$ in the oceans.

Gas	H$_2$O (g)		
Liquid	H$^+$, K$^+$, Cl$^-$, H$_2$O (l)		
Solid	SiO$_2$	Kaolinite	K-mica

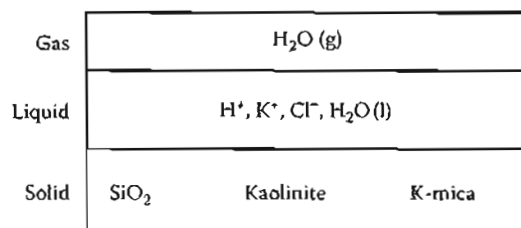FIGURE 3.27
Sillén ion exchange model.

Applying equilibrium conditions for this reaction (at constant Cl⁻ and temperature) gives

$$K = [H^+]/[K^+] \tag{3.10}$$

$$[K^+] + [H^+] = [Cl^-] + Kw/[H^+] \tag{3.11}$$

The ratio of $[H^+]/[K^+]$ is fixed; thus, the addition of HCl or KOH will return it to its original value as long as [Cl⁻] and temperature are constant. The system is thus a pH stat rather than a buffer as long as Cl⁻ and temperature are constant and no phases completely disappear. This simple result suggests that the pH and the major ionic concentrations of seawater are controlled by clay exchange reactions. When Sillén made this suggestion, most oceanographers were shocked, as they thought that the pH of the oceans was controlled by the carbonate system and the clays acted only as the walls of the container. Experimental studies yield $K = 10^{-6}$ to $10^{-6.5}$ (25°C) for the reaction, while the ratio is $10^{-6.2}$ in seawater. For the equilibrium between kaolinite and montmorillonite in a five component system with Na⁺, we have

$$1.5 \ Al_2Si_2O_5(OH)_4(s) + Na^+ \leftrightarrow NaAl_3Si_3O_{10}(OH)_2 \ (s) + 1.5 \ H_2O + H^+ \tag{3.12}$$

kaolinite   **montmorillonite**

The ratio of H^+/Na^+ also comes near the ratio in seawater. Since fresh clays are transformed in a day or two, forming new phases in a couple of years, most workers have found the silicate theory to be reasonable. Recent workers have also demonstrated that SiO_2 dissolves more rapidly in seawater than was once thought. Sillén also considered a more complicated nine-component system:

1. Seawater
2. SiO_2 (quartz)
3. $CaCO_3$ (calcite)
4. Kaolinite
5. Illite
6. Chlorite
7. Montmorillonite
8. Phillipsite
9. Atmosphere

Mg was found to be a problem, as well as SiO_2. More recent results on hydrothermal vents can explain these differences (Chapter 10). Mg is lost from the oceans and Si is added by the reactions that take place in hydrothermal vent systems.

Turner et al. (1980) have shown a correlation between the residence time of an element in the oceans and the partitioning of that element between rocks and seawater. They define the ocean-rock partition coefficient K_Y by

$$K_Y = Y_C/Y_A \tag{3.13}$$

where Y_A is the rate of transport of material from crustal rock and Y_C is the rate of transport from the oceanic reservoir. The value of Y_A has been corrected for recycled sea spray. The logarithm of the mean residence time was found to be a linear fraction of the log of the
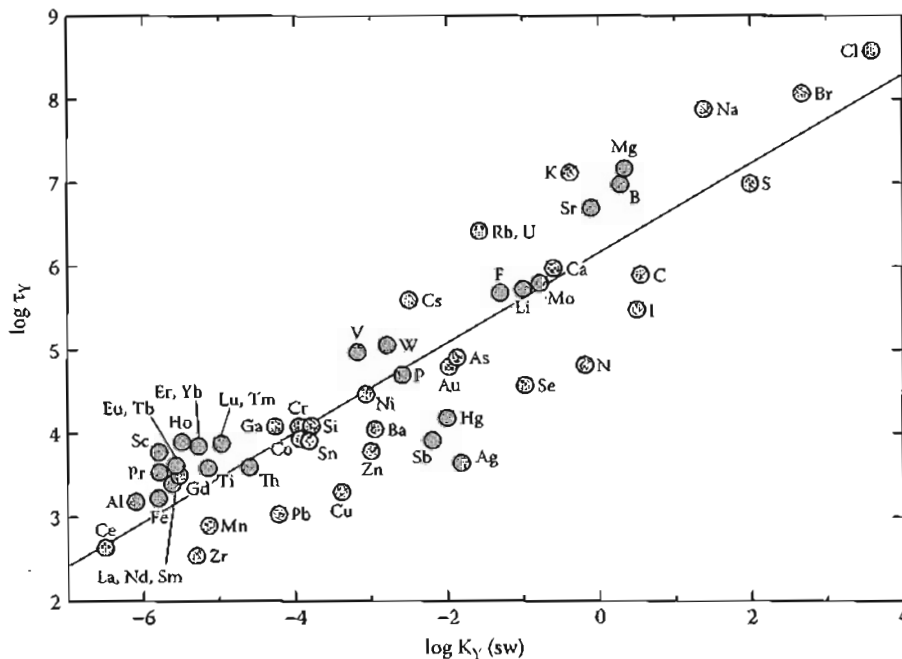
FIGURE 3.28
The log of the mean residence time (τ) vs. the log of the partition.

partition coefficient

$$\log \tau = 0.53 \log K_Y + 6.15 \tag{3.14}$$

(see Figure 3.28). The value of $\tau_R = 1000$ revs per million years is the stirring revolution of the ocean, which is assumed to be 2000 million years old and in a steady state.

Turner et al. (1980) also showed that the values of the partition coefficients (K_Y) were related to the electronegativity of the elements, Q_{YO}, by

$$\log K_Y = -1.55 \, Q_{YO} + 3.69 \tag{3.15}$$

where the electronegativities are given by (eV)

$$Q_{YO} = (X_Y - Y_O)^2 \tag{3.16}$$

where the value of Q_{YO} is a measure of the electrostatic contribution to the Y-O bond energy or a measure of the attraction of an element (Y) for the oxide-based mineral. The values for X are values of the electronegativities of various elements.

Meybeck (1987) has examined chemical weathering by considering the ions formed from various rock types. The abundance of the major rock types are given in Table 3.13. His estimates for the origins of the major components of the rock types released to the rivers is given in Table 3.14. Ca and Mg come mostly from shale and carbonate rocks, Na and Cl from rocksalt, SO_4 from shale and gypsum, HCO_3 from shale and carbonate, and K from sandstone and carbonate rocks. The sources of the dissolved river salts carried to

TABLE 3.13

Outcrop Abundance of Major Rock Types on Land (percent by area)

Plutonic rocks	11%	Granite	10.40%
		Gabbro and peridotite	0.60%
Metamorphic rocks	15%	Gneiss	10.40%
		Mica schist	1.50%
		Quartzite	0.80%
		Marble	0.40%
		Amphibolite	1.90%
Volcanic rocks	7.9%	Basalt	4.15%
		Andesite	3.00%
		Rhyolite	0.75%
Sandstones	15.8%	Quartz sandstone	12.60%
		Arkose	0.80%
		Graywacke	2.40%
Shales	33.1%		
Carbonate sedimentary rocks	15.9%	Detrital carbonate rock	5.90%
		Dolomite	3.65%
		Limestone	6.35%
Evaporites	1.3%	Gypsum	0.75%
		Halite	0.55%

TABLE 3.14

Origins of Weathering Products by Rock Types (% of total amount released)

	SiO_2	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	Σ^+
Granite	10.9	0.60	1.2	5.9	4.9		2.0	1.6	1.6
Gabbro	0.75	0.0	1.1	0	0		0.3	0.3	0.3
Gneiss and micaschists	11.7	1.10	2.8	6.6	8.2		4.6	2.0	2.4
Misc. metamorphic	1.5	4.7	3.2	0.3	1.6		1.7	4.7	3.7
Volcanic rocks	11.1	1.8	4.9	5.4	6.6		0.5	4.2	3.1
Sandstone	16.6	2.1	3.8	5.2	19.6		9.6	2.3	3.2
Shale	35.1	19.9	30.7	22.6	41.0	7.4	30.3	22.5	23.1
Carbonate rocks	11.3	60.4	39.3	3.5	13.1		8.6	59.5	46.7
Gypsum	0.5	7.2	7.2	4.9	1.6	10.0	32.7	1.7	6.8
Rock salt	0.4	2.2	5.8	45.6	3.3	82.6	9.6	1.2	9.1
TOTAL %	100	100	100	100	100	100	100	100	100
10^{12}g/year	320	504	118	132	24	120	280	1950	

Σ^+ = sum of cations (milliequivalent/liter)

TABLE 3.15

Sources of River Dissolved Load Carried to the Oceans (in % of total amount released by weathering)

							SO_4^{2-}			
Model	SiO_2	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	pyr.[a]	SO_4^b	HCO_3^-	Σ^+
Atmosphere									67	
Silicates	92.5	26	48	46	95	0	40	18		35
Carbonates	0	67	42	0	0	0	0	0	33	51
Evaporites	0	7	10	54	5	100	0	42		14
Amorphous silica	7.5									

[a] SO_4^{2-} resulting from pyrite and organic sulfur oxidation.

[b] SO_4^{2-} resulting from sulfate mineral dissolution.

Σ^+, sum of cations

the oceans by the weathering of the various rock types are given in Table 3.15. These results point out the importance of the weathering process in controlling the input of the major components to the oceans.

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