

Mixing and Dilution

Many natural processes on the surface of the Earth cause mixing of two or more components having different chemical and/or isotopic compositions. This phenomenon applies especially to compositionally distinct water masses that come in contact with each other in estuaries, in streams and lakes, and below the surface of the Earth. Mixing also takes place in depositional basins where detrital mineral particles of different compositions are deposited. The concept even applies to blending of magmas and to the assimilation of country rock by cooling magmas in the continental crust.

The chemical and isotopic compositions of two-component mixtures are related to their end members in simple ways expressed by characteristic linear or hyperbolic patterns formed by their chemical and isotopic compositions. These relations are useful because they help us to recognize mixtures when they occur in nature and because the composition of the pure end members can be deduced from them under favorable circumstances.

18.1 Binary Mixtures

When two components (A and B) of different chemical composition mix in varying proportions, the chemical compositions of the resulting mixtures (M) vary systematically depending on the relative abundances of the end members. We therefore define the mixing parameter:

$$f_A = \frac{W_A}{W_A + W_B} \quad (18.1)$$

where W_A and W_B are the weights (or volumes) of the components A and B in a given mixture.

Evidently, f_A is a dimensionless number that in reality is constrained to values between zero and unity. When f_A is defined as in equation 18.1, then $f_A = 1.0$ means that the mixture is composed of component A only. When $f_A = 0$, then $W_A = 0$ and only component B is present. The mixing parameter defined above is the "weight fraction" or "volume fraction" of component A in two-component mixtures. The complementary weight fraction of B (f_B) is equal to $1 - f_A$ because:

$$\begin{aligned} 1 - f_A &= 1 - \frac{W_A}{W_A + W_B} = \frac{W_A + W_B - W_A}{W_A + W_B} \\ &= \frac{W_B}{W_A + W_B} = f_B \end{aligned} \quad (18.2)$$

The concentration of any conservative element (X) in a binary mixture of A and B depends on the concentration of that element in components A and B and on the abundances of components A and B in the mixture. Therefore, the concentration of element X in a mixture (M) of components A and B is:

$$(X)_M = (X)_A f_A + (X)_B (1 - f_A) \quad (18.3)$$

where the parentheses mean *concentration*. Equation 18.3 yields the concentrations of element X in mixtures of A and B for different values of f_A between 1.0 and 0 where X_A and X_B are known constants. By rearranging equation 18.3 we obtain:

$$(X)_M = f_A [(X)_A - (X)_B] + (X)_B \quad (18.4)$$

Equation 18.4 is a straight line in coordinates of (X) and f_A having a slope $m = (X)_A - (X)_B$ and an intercept $b = (X)_B$. Evidently, when $f_A = 1.0$, equation 18.4 yields $(X)_M = (X)_A$ (the mixture is

composed of A only), and when $f_A = 0.0$, $(X)_M = (X)_B$ (the mixture is composed of B only). If the concentration of element X is expressed in units of weight of X per unit volume of A and B, then f_A must also be defined in terms of volumes.

All conservative elements in two-component mixtures satisfy equations like 18.3. Therefore, for another element Y we have:

$$(Y)_M = (Y)_A f_A + (Y)_B (1 - f_A) \quad (18.5)$$

In any given mixture of two components the mixing parameter f_A must have the same value for all conservative elements. This statement allows us to combine equations 18.4 and 18.5 by solving both for f_A and by equating the results:

$$f_A = \frac{(X)_M - (X)_B}{(X)_A - (X)_B} = \frac{(Y)_M - (Y)_B}{(Y)_A - (Y)_B} \quad (18.6)$$

By cross multiplying and solving for $(Y)_M$ we obtain:

$$(Y)_M = (X)_M \frac{(Y)_A - (Y)_B}{(X)_A - (X)_B} + \frac{(X)_A (Y)_B - (X)_B (Y)_A}{(X)_A - (X)_B} \quad (18.7)$$

Equation 18.7 is a straight line in coordinates of (X) and (Y) having a slope:

$$m = \frac{(Y)_A - (Y)_B}{(X)_A - (X)_B} \quad (18.8)$$

and an intercept on the (Y) -axis:

$$b = \frac{(X)_A (Y)_B - (X)_B (Y)_A}{(X)_A - (X)_B} \quad (18.9)$$

Therefore, the slope and intercept of the mixing line depend only on the concentration of X and Y in components A and B. Equation 18.7 indicates that the concentrations of any two conservative elements X and Y in a series of binary mixtures lie on straight lines known as "mixing lines," which include both end members.

A linear relationship between the concentrations of two conservative elements in a suite of natural samples is evidence that they may be the

products of mixing. In such a case, the slope and intercept of the mixing equation can be determined by least-squares regression of the data array. The composition of the endmembers is constrained by the requirement that they must lie on the mixing line and that their concentrations of elements X and Y must be positive numbers. In case the concentration of either X or Y in the end members is known (e.g., $(X)_A$ and $(X)_B$), then the concentrations of the other element in the two components $(Y)_A$ and $(Y)_B$ can be calculated from the equation of the mixing line. In addition, if $(X)_A$ and $(X)_B$ (or $(Y)_A$ and $(Y)_B$) are known, then either element can be used to calculate f_A from equation 18.3 using the measured concentrations $(X)_M$ or $(Y)_M$ of any mixture in the suite.

An example of mixing occurs in the waters of the North Channel of Lake Huron between Manitoulin Island and the mainland of Canada where water from Lake Superior mingles with water in Lake Huron (Faure et al., 1967). The concentrations of Ca^{2+} and Sr^{2+} in the waters form a linear array of data points in Figure 18.1. The mixing equation fitted to these data by least-squares regression is:

$$(\text{Ca}^{2+})_M = 0.178(\text{Sr}^{2+})_M + 9.81 \quad (r^2 = 0.989) \quad (18.10)$$

where $(\text{Ca}^{2+})_M$ is the concentration in mg/L, $(\text{Sr}^{2+})_M$ is expressed in $\mu\text{g/L}$, and r^2 is the linear correlation coefficient. Next, we use equation 18.9 to calculate the concentrations of Sr^{2+} in the water of Lake Huron and Lake Superior based on $(\text{Ca}^{2+})_S = 14.4 \pm 0.2$ mg/L and $(\text{Ca}^{2+})_H = 26.9 \pm 0.3$ mg/L, where the subscripts S and H identify Superior and Huron, respectively, and the errors are one standard deviation of the mean. The results are $(\text{Sr}^{2+})_S = 25.8 \pm 1.1$ $\mu\text{g/L}$ and $(\text{Sr}^{2+})_H = 96.0 \pm 1.7$ $\mu\text{g/L}$.

This information now enables us to calculate the volume fraction of Lake Superior water in any water sample in the North Channel based on its measured concentration of either $(\text{Ca}^{2+})_M$ or $(\text{Sr}^{2+})_M$. If we select a water sample having $(\text{Ca}^{2+})_M = 22.0$ mg/L, we find from equation 18.3 that $f_S = 0.39$, which means that 39% by volume of this water originated from Lake Superior. Note

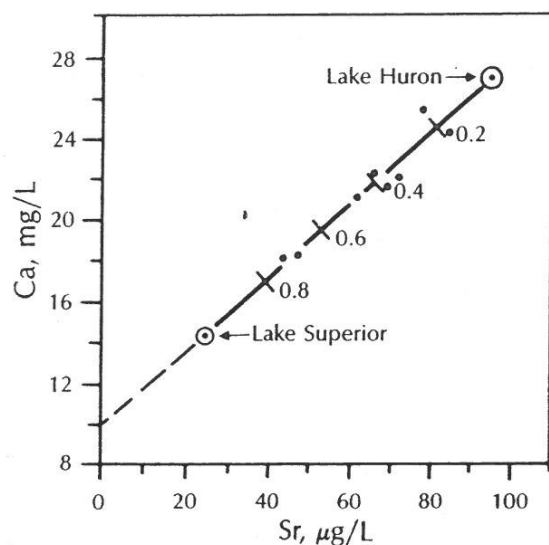


Figure 18.1 Binary mixing of water in the North Channel of Lake Huron between Manitoulin Island and the mainland of Canada. The concentrations of Ca^{2+} and Sr^{2+} define a mixing line whose equation was fitted to the data points by least-squares regression (equation 18.10). The average concentrations of Sr^{2+} in Lake Superior and Lake Huron were calculated by substituting the average measured Ca^{2+} concentrations into equation 18.10. The mixing line was subdivided in 0.2 increments of f_2 , which is the volume fraction of Lake Superior water in the North Channel in Lake Huron (data from Faure et al., 1967).

that the mixing line in Figure 18.1 has been subdivided in increments of f_2 to show how the concentrations of (Ca^{2+}) and (Sr^{2+}) vary in relation to the mixing parameter.

Real data sets representing binary mixtures commonly scatter above and below the mixing line, indicating that the assumptions of the mixing model are not strictly satisfied in nature. These assumptions are:

1. The elements under consideration are conservative; that is, their concentrations are not altered by biological activity or by adsorption on particles.
2. Only two components are contributing to the chemical composition of the mixtures.

3. The compositions of the end members are constant.

The scatter of data points about the mixing line formed by real data derived from surface water may be caused by dilution with rain or by the addition of a third component of natural or anthropogenic origin. Moreover, the chemical compositions of surface waters also vary seasonally, reflecting changes in the provenance of the water.

The chemical compositions of *sediment* formed by mixing of mineral grains derived from different sources also tend to scatter because they too may be diluted or because the chemical composition of sediment derived from different sources may vary randomly within certain limits.

18.2 Dilution

When a subsurface brine is progressively mixed with meteoric water, a special kind of linear array is produced, which is directed toward the origin. The resulting *dilution line* is a special case of equation 18.7, where the coordinates of one of the components are virtually equal to zero, excluding exceptional circumstances. If component A is the dilute end member ($(X)_A = 0$, $(Y)_A = 0$), then equation 18.7 reduces to:

$$(Y)_M = (X)_M \left(\frac{(Y)_B}{(X)_B} \right) \quad (18.11)$$

Therefore, data arrays that fit a straight line through the origin may have been generated by dilution.

Although dilution of *brines* with meteoric water is a common phenomenon in the subsurface, in estuaries, and in the open ocean, dilution is by no means restricted to the hydrosphere. For example, the concentration of K_2O and Na_2O in arkosic sandstones or in shaley limestones both vary in response to the presence of quartz and calcite, respectively, which dilute the minerals containing the alkali metals.

Figure 18.2 contains the concentrations of K_2O and Na_2O of 29 selected quartz *sandstones* taken from a compilation by Pettijohn (1963). The

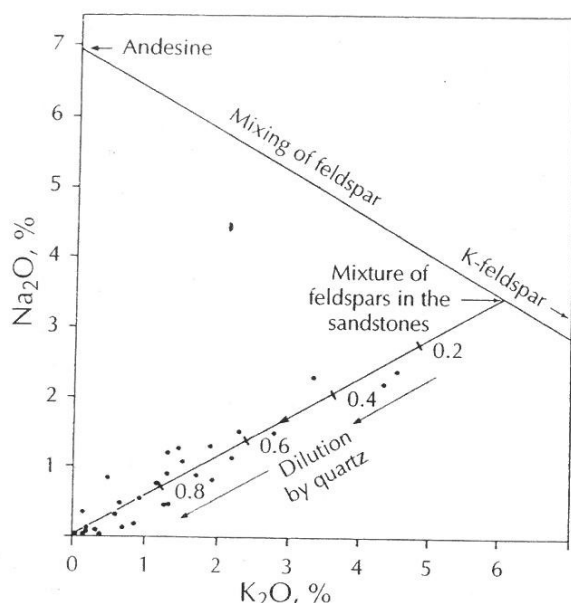


Figure 18.2 Plot of the K_2O and Na_2O concentrations of 29 selected sandstones from a compilation by Pettijohn (1963). The data points scatter about a straight line whose equation was derived by least-squares regression (equation 18.12). The alkali metals in these sandstones are assumed to reside in a mixture of K-feldspar and the plagioclase ($Ab = 60\%$ andesine) that lie on a mixing line between K-feldspar and andesine. The coordinates of the point of intersection of equation 18.12 with the feldspar mixing line represent the concentrations of K_2O and Na_2O of the feldspar in the sandstones. The addition of increasing amounts of quartz progressively dilutes the feldspar component and lowers the concentrations of K_2O and Na_2O of the resulting sandstones. The treatment of data is conjectural, but serves to illustrate the effect of dilution on the chemical composition of sandstone.

data points form a linear array directed toward the origin, which indicates that in this case the mineral constituents containing K and Na are progressively diluted with quartz. The equation of the dilution line, based on a least-squares regression, is:

$$(Na_2O) = 0.55(K_2O) + 0.05 \quad (18.12)$$

where (Na_2O) and (K_2O) are concentrations in weight percent. The linear correlation coefficient

is $r^2 = 0.9335$, which indicates a high degree of positive correlation between the two elements.

For the sake of this demonstration we assume that the minerals containing K_2O and Na_2O in these sandstones are K-feldspar and plagioclase having the composition of andesine ($Ab = 60\%$, Section 8.3), respectively. Mixtures of these feldspars lie on a straight line between two points on the K_2O and Na_2O axes in Figure 18.2 that represent K-feldspar [$(K_2O) = 16.9\%$, $(Na_2O) = 0.0\%$] and andesine [$(K_2O) = 0.0\%$, $(Na_2O) = 6.9\%$]. The quartz dilution line of the sandstones intersects the feldspar mixing line at $(K_2O) = 6.0\%$ and $(Na_2O) = 3.5\%$. As increasing amounts of quartz are added to this mixture of feldspars, the concentrations of K_2O and Na_2O decline, but the $(Na_2O)/(K_2O)$ ratio remains constant. When the sediment consists of nearly pure quartz (orthoquartzite), the concentrations of K_2O and Na_2O approach zero.

The abundance of quartz in these feldspar-bearing sandstones can be calculated by modifying equation 18.3. Let f_Q be defined as:

$$f_Q = \frac{W_Q}{W_Q + W_F} \quad (18.13)$$

Where Q and F identify quartz and the mixture of feldspars, respectively. Then, from equation 18.4:

$$(K_2O)_M = f_Q[(K_2O)_Q - (K_2O)_F] + (K_2O)_F \quad (18.14)$$

where $(K_2O)_M$ is the K-concentration of a mixture (i.e., a sandstone). Equation 18.14 was used to subdivide the dilution line in Figure 18.2 in increments of 0.2 of the mixing parameter, assuming that $(K_2O)_Q = 0.0\%$ and $(K_2O)_F = 6.0\%$. Although the treatment of data is based on assumptions that cannot be confirmed in this case, this example demonstrates that the chemical compositions of mixtures of detrital mineral grains may be treated in terms of mixing and dilution.

18.3 Evaporative Concentration

A linear array of concentrations of conservative elements may also be generated in waters undergoing *evaporative concentration* (see Section 10.1). As water is lost, the concentrations of conserva-

tive ions or molecules in the solution rise in such a way that their ratios remain constant. Therefore, the concentrations of any two conservative elements (X and Y) vary along straight lines illustrated in Figure 18.3A having slopes $m = (Y)/(X)$ and whose intercepts are $b = 0$.

The concentration of a conservative element X in a solution undergoing evaporative concentration, such that X is *not* involved in the formation of a precipitate, obeys equations of the form:

$$(X)_f = g(X)_i \quad (18.15)$$

where subscripts f and i signify *final* and *initial* concentrations of X, respectively, and g is the concentration factor. Another conservative element Y in the same solution obeys a similar equation, and the concentrations of both elements are subject to the same concentration factor. Therefore, we can combine the equations for X and Y by equating the concentration factors:

$$g = \frac{(X)_f}{(X)_i} = \frac{(Y)_f}{(Y)_i} \quad (18.16)$$

from which it follows that:

$$(Y)_f = (X)_f \left(\frac{(Y)_i}{(X)_i} \right) \quad (18.17)$$

where $((Y)/(X))_i$ is the slope of a straight line that passes through the origin and the concentrations of elements X and Y may be expressed either in terms of weights or numbers of moles of X and Y.

When one of the ions participates in the formation of an insoluble compound, the increase in its concentration is limited by the requirement that the relevant ion activity product (IAP) must remain less than the solubility product constant (K_{sp}) of the compound. In case progressive evaporative concentration of water ultimately forces an insoluble compound containing element X or Y to precipitate, the chemical *composition* of the solution is changed because the concentration of that element (X, for example) declines rapidly as progressive evaporation forces the compound out of the solution, whereas the concentration of the other element (Y) continues to rise. This process is illustrated in Figure 18.3B. As a result, waters from which a compound has precipitated become

depleted in the ions that formed the compound, and therefore such waters *deviate* from the straight line that was initially generated by evaporative concentration.

If both X and Y participate in the formation of an insoluble compound and if they enter that compound in equal *molar* amounts (i.e., XY or X_2Y_2), then the precipitation of the compound causes the *molar* concentrations of X and Y to decline along a linear trajectory whose slope is equal to unity. If the ratio of the *molar* concentrations in the water before the precipitation of the compound is $Y/X > 1.0$ as shown in Figure 18.3C, the solution becomes depleted in X and enriched in Y. In case the *molar* ratio $Y/X < 1.0$ before precipitation (Figure 18.3D), then the solution is enriched in X and depleted in Y. Therefore, the precipitation of a compound involving the ions of elements X and Y in waters undergoing evaporative concentration functions as a *geochemical divide*, which alters the *chemical composition* of waters that are subjected to this process.

18.4 Ternary Mixtures

When *three* components are mixed in varying proportions, the resulting mixtures lie within a *mixing triangle* whose corners are occupied by the three components. Mixtures of three or more components form distribution patterns in X-Y diagrams, colloquially known as "shotgun patterns," that are difficult to interpret quantitatively. However, when the compositions of the three components are known, even scattered data points representing mixtures of three components can be resolved into their end members.

Ternary mixtures in which one of the components is located at the origin can be treated as though they resulted from a combination of mixing of two components followed by dilution of the resulting mixtures by the third component. In the general case, the binary mixtures of components A and B may be distributed along a mixing line AB as shown schematically in Figure 18.4. Dilution by component C subsequently displaces them from the mixing line into a triangle of mixing that has one of its corners at the origin.

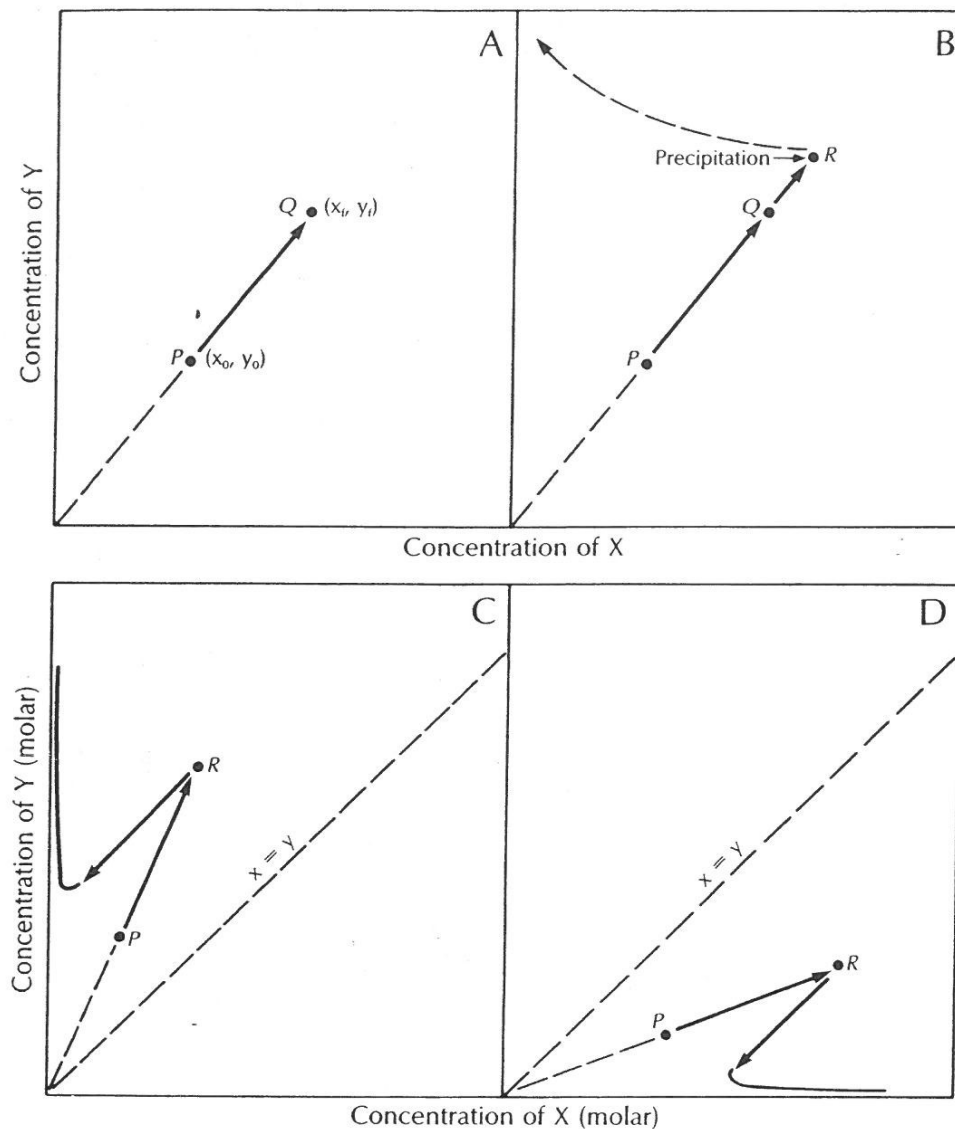


Figure 18.3 Effect of evaporative concentration of aqueous electrolyte solutions of the concentrations of two conservative elements X and Y.

A. Evaporation increases the concentrations of both elements from their initial values at point P to final values at point Q . The evaporation trajectory is a straight line represented by equation 18.17.

B. Continued evaporation increases the concentrations of X and Y to point R , when a compound begins to precipitate that removes element X from the solution but does not contain element Y. Continued evaporation depletes the solution in X but allows the concentration of Y to increase. Hence, the solution moves off the linear trajectory.

C. Evaporative concentration of a solution drives the *molar* concentrations from P to R , when a compound XY begins to precipitate. As a result, the molar concentrations of both X and Y decline along a line of slope $m = 1.0$. Since the ratio Y/X in the original solution is greater than unity, the concentration of X is reduced to near zero, whereas that of Y increases as evaporative concentration continues. The final brine is enriched in Y and is depleted in X.

D. Similar to **C** above, except that the solution is depleted in Y and enriched in X because initially at point P the ratio of *molar* concentration Y/X was less than unity. Cases **C** and **D** illustrate the concept of a geochemical divide, which was first mentioned in Section 10.1.

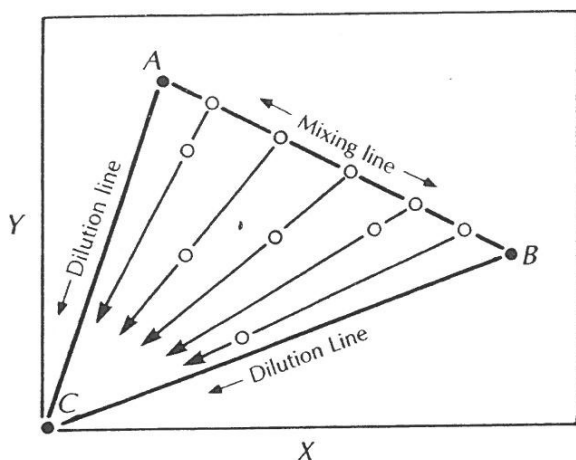


Figure 18.4 Schematic representation of mixing of two components A and B followed by variable dilution with component C. The resulting mixtures initially lie on the mixing line AB, but are subsequently drawn into a triangle of mixing by additions of component C whose concentrations of elements X and Y are both zero. The sandstone data in Figure 18.2 are a special case of ternary mixing in which the feldspar mixtures have a narrowly defined range of compositions.

The concentrations of K_2O and Na_2O of the sandstones in Figure 18.2 are a special case of mixing and dilution in which the hypothetical feldspar mixtures appear to have fairly uniform compositions. As a result, progressive dilution with quartz generates a linear array of data points directed toward the origin. However, *greywackes* from Pettijohn (1963) have more variable K_2O and Na_2O concentrations than quartz sandstones and form a cluster of data points in Figure 18.5. The alkali metals in greywackes probably reside not only in the feldspars but also in clay minerals, micas, and even in amphiboles and pyroxenes. Therefore, the quantitative interpretation based on Figure 18.5 is intended *only* as an illustration of the procedure and should *not* be taken literally.

The mixing triangle in Figure 18.5 was formed by drawing dilution lines from the origin to the most widely scattered samples and by extending these lines to the K-feldspar–andesine mixing line. The points A' and B' encompass the

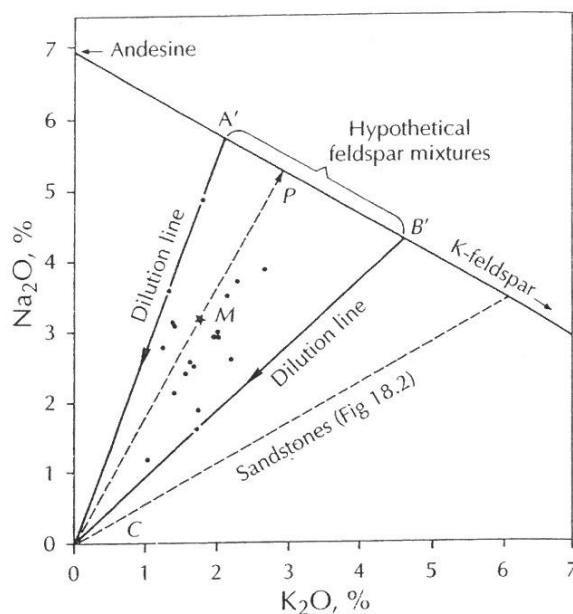


Figure 18.5 Interpretation of the K_2O and Na_2O concentrations of 20 greywackes from Pettijohn (1963) in terms of ternary mixing. We assume that the alkali metals reside in mixtures of K-feldspar and andesine between A' and B' on the feldspar mixing line. The presence of varying amounts of *alkali-free* minerals (component C) causes the feldspar mixtures to scatter within a hypothetical mixing triangle, which has one apex at the origin. The mixing triangle is defined by the mixing line A'B' and by the dilution lines A'C and B'C. Sample M (star) was chosen at random to demonstrate how it can be projected from component C at the origin to the mixing line A'B'.

entire compositional range of the hypothetical feldspar mixtures in this suite of greywackes. The starred sample (M) in Figure 18.5 was returned to the hypothetical feldspar mixing line by projecting it from the origin to point P. The coordinates of point P are $(K_2O) = 2.9\%$, $(Na_2O) = 5.25\%$, which indicates that the concentration of K-feldspar in this mixture is:

$$\frac{2.9 \times 2 \times 278.33}{94.20} = 17.1\% \quad (18.18)$$

where 94.20 is the formula weight of K_2O and 278.33 is the formula weight of K-feldspar.

Consequently, the abundance of andesine is $100 - 17.1 = 82.9\%$. The abundance of the *alkali-free* phase (f_c) in sample M is $\sim 40\%$ based on equation 18.14, given that $(K_2O)_M = 1.75\%$ and $(K_2O)_F = 2.9\%$. Therefore, the abundances of the hypothetical mineral components in sample M are:

K-feldspar:	$17.1 \times 0.6 = 10.3\%$
plagioclase:	$82.9 \times 0.6 = 49.7\%$
alkali-free minerals	$= 40\%$

Mixing and dilution may also take place in subsurface where two connate brines may mix in varying proportion and where these mixed brines are subsequently diluted with meteoric water from the surface. In such cases, one may wish to eliminate the effect of dilution from the concentrations of conservative elements in the brine mixtures. This can be accomplished by projecting data points from the origin to the mixing line, as already illustrated in Figure 18.5.

Mixing and dilution were demonstrated by Lowry et al. (1988) for brines from the Clinton sandstones of Early Silurian age in eastern Ohio. Figure 18.6 contains a plot of the concentrations of Na^+ and Sr^{2+} in these brines that scatter widely within a mixing triangle. The coordinates of the brine components A and B were derived by Lowry et al. (1988) by pairing Na and Sr with several other elements in X-Y plots. The data points in Figure 18.6 were projected from the origin to the mixing line AB. The coordinates of the projection points can be precisely calculated by simultaneous solution of the equations of the mixing line and the projection (dilution) lines using equations 18.7 and 18.11, respectively. Alternatively, the problem can be solved graphically using diagrams drawn to scale.

18.5 Isotopic Mixtures of One Element

The isotope compositions of certain elements are variable because some of their isotopes are the products of naturally occurring radioactive par-

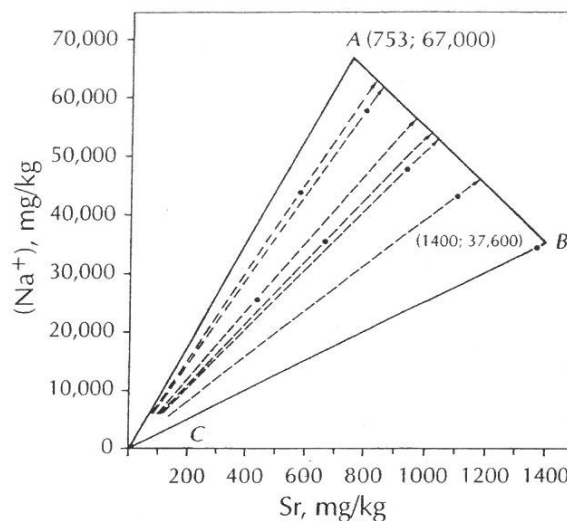


Figure 18.6 Restoration of oilfield brines from the Clinton sandstones of eastern Ohio that were contaminated with varying amounts of meteoric water from the surface. The compositions of the brine components A and B were determined by Lowry et al. (1988) from X-Y plots in which Na and Sr were paired with several other elements. The concentrations of Na^+ and Sr^{2+} in the *undiluted* brine mixtures are the coordinates of the points of intersection of the projection/dilution lines with the mixing line of brines A and B.

ents (Chapter 16) or because of isotope fractionation (Chapter 17). Therefore, we can consider cases where mixing occurs between two materials that contain the same element with different isotope compositions. For example, water masses having different $^{87}Sr/^{86}Sr$ ratios or $\delta^{18}O$ values may mix in lakes, in estuaries, or in the subsurface.

We consider first the formation of mixtures of two end members A and B having different $^{87}Sr/^{86}Sr$ ratios and Sr concentrations. Using the mixing parameter f_A defined in equation 18.1, we express the Sr concentration of any mixture M as:

$$(Sr)_M = (Sr)_A f_A + (Sr)_B (1 - f_A) \quad (18.19)$$

If the end members have different $^{87}Sr/^{86}Sr$ ratios, then the isotopic composition of any mixture must be the weighted sum of the $^{87}Sr/^{86}Sr$ ratios where the weighting factors are $(Sr)_A/(Sr)_M$ and $(Sr)_B/(Sr)_M$ (a detailed derivation was given by

Faure, 1986). Therefore, the equation for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a binary mixture is:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_M = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_A f_A \frac{(\text{Sr})_A}{(\text{Sr})_M} + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_B (1 - f_A) \frac{(\text{Sr})_B}{(\text{Sr})_M} \quad (18.20)$$

If the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of A and B are equal, equation 18.20 reduces to equation 18.19. If the Sr concentrations of components A and B are equal, then $(\text{Sr})_A/(\text{Sr})_M = (\text{Sr})_B/(\text{Sr})_M = 1.0$ and equation 18.20 reduces to:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_M = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_A f_A + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_B (1 - f_A) \quad (18.21)$$

Equations 18.19 and 18.20 can be used to predict the Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of any mixture of two components having different concentrations and isotope compositions of Sr for different values of the mixing parameter f_A . The same equations apply to all other elements that have radiogenic isotopes such as Nd, Os, Hf, and Pb.

Equation 18.21 applies also to mixtures of the same compound, such as water or carbon dioxide, containing equal concentrations of H and O, or C and O, respectively. In order to adapt equation 18.21 to mixtures of water containing O and H of different isotope compositions, we replace the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with $\delta^{18}\text{O}$ or δD values:

$$\delta^{18}\text{O}_M = \delta^{18}\text{O}_A f_A + \delta^{18}\text{O}_B (1 - f_A) \quad (18.22)$$

$$\delta\text{D}_M = \delta\text{D}_A f_A + \delta\text{D}_B (1 - f_A) \quad (18.23)$$

Note, however, that the concentrations of O and H in highly concentrated brines are *less* than those of pure water and that equation 18.20 may have to be used to predict the $\delta^{18}\text{O}$ and δD values of mixtures of such brines with other brines or with fresh water.

When two components having different concentrations and isotope compositions of Sr (or of another element) are mixed in varying proportions, the resulting mixtures differ from the end members both in terms of the Sr concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of a series of mixtures can be calcu-

lated from equations 18.19 and 18.20 for selected values of the mixing parameter f_A based on end members of known composition. However, in reality we are usually confronted by the opposite situation, that is, we measure the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of a suite of samples and then wish to test the hypothesis that they are mixtures of two components. In fact, we want to *derive* the isotopic mixing equation from an array of data points as we were able to do for binary mixtures of different chemical compositions based on equation 18.7.

The desired isotopic mixing equation can be derived from equations 18.19 and 18.20 by solving both for f_A and by equating the results. The outcome of this algebraic manipulation is:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_M = \frac{a}{(\text{Sr})_M} + b \quad (18.24)$$

where:

$$a = \frac{(\text{Sr})_A (\text{Sr})_B \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_B - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_A \right]}{(\text{Sr})_A - (\text{Sr})_B} \quad (18.25)$$

$$b = \frac{(\text{Sr})_A \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_A - (\text{Sr})_B \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_B}{(\text{Sr})_A - (\text{Sr})_B} \quad (18.26)$$

Equation 18.24 is a hyperbola in coordinates of $(\text{Sr})_M$ (x -coordinate) and $(^{87}\text{Sr}/^{86}\text{Sr})_M$ (y -coordinate) whose position and curvature are defined by the numerical values of a and b , which depend entirely on the compositions of the end members. The special virtue of equation 18.24 is that it is transformable into a straight line by defining the x -coordinate as $1/(\text{Sr})_M$. If $x = 1/(\text{Sr})_M$, then equation 18.24 becomes:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_M = ax + b \quad (18.27)$$

which is a straight line whose slope $m = a$ and whose intercept on the y -axis is equal to b . Therefore, the isotopic mixing equation for binary mixtures of components that differ in the isotope compositions of one element (such as Sr, Nd, Hf, Os, and Pb) can be derived by fitting a straight line to data points in coordinates of the appropri-

ate isotopic parameter and the reciprocals of the concentration.

This procedure was used successfully by Boger and Faure (1974, 1976) and Boger et al. (1980) to treat sediment samples from the Red Sea and by Nardone and Faure (1978) from the Black Sea. In addition, Shaffer and Faure (1976), Kovach and Faure (1977), and Faure and Taylor (1983) used it to study mixing of detrital sediment in the Ross Sea and under the Ross Ice Shelf adjacent to Antarctica.

Isotopic mixing arrays may consist of three or more components in which case the data points representing such samples scatter on the mixing diagram. If the third component in sediment samples consists of authigenic calcite, or some other acid-soluble mineral, it can be removed from the samples prior to analysis by treating them with dilute solutions of a weak acid such as acetic acid. The tests of diatoms and radiolarians, which are composed of opaline silica, can be removed by flotation in a mixture of bromoform and acetone. The presence of a component of amorphous silica in sediment samples that are binary mixtures causes a *decrease* of the Sr concentrations *without* affecting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, whereas the presence of calcite and aragonite changes *both* parameters of binary sediment mixtures.

Mixing of *water* on or below the surface of the Earth commonly affects the isotope compositions of O and H as well as those of dissolved elements such as Sr and Nd. The isotope compositions of O and H in binary mixtures of water are expressed by equations 18.22 and 18.23. These equations can be combined by eliminating f_A to yield an equation in coordinates of δD and $\delta^{18}\text{O}$ equivalent to equation 18.7. However, when a third component is present, a mixing triangle results, which can be reduced to a mixing line by projecting the data points from one of the corners of the triangle to the line connecting the other two components. Changes in the isotope composition of O and H in groundwater may *also* result from exchange reactions with minerals, by the release of water of hydration during dehydration of minerals, and by the *uptake* of water during mineral transformations that may alter the isotope composition of the residual water.

Consequently, in systems where the water/rock ratio is small, the isotope composition of water can be altered in a variety of ways that do not necessarily involve mixing.

The isotopic compositions of Sr and of other elements dissolved in groundwater are likewise changed by the preferential solution of minerals containing Sr whose isotope composition depends on the ages and Rb/Sr ratios of these minerals. However, as the water approaches chemical equilibrium with the minerals with which it is in contact, its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is stabilized and any further changes can then be attributed to mixing of water having different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations.

An example of the effect of mixing of subsurface brines on the isotope composition of Sr is presented in Figure 18.7 based on the work of Lowry et al. (1988) on brines from the Clinton sandstones of Ohio. These brines were diluted with varying amounts of meteoric water that lowered their Sr concentrations but did not appreciably alter their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Therefore, the Sr concentrations were first restored to their original values of projecting the data points in Figure 18.6 from the origin to the mixing line *AB*. The reciprocals of these restored Sr concentrations and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios form a linear array, as expected of binary mixtures. The equation of the isotopic mixing line, determined by least-squares regression, is:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = 7.786 \frac{1}{(\text{Sr})} + 0.7028 \quad (18.28)$$

This equation was plotted as a hyperbola in Figure 18.7 in coordinates of the Sr concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Because of dilution with meteoric water, the measured Sr concentrations were up to 54% *lower* than the values derived from Figure 18.6.

18.6 Isotopic Mixtures of Two Elements

Most natural materials contain not just one but several elements having different isotope compositions. For example, sediment or water derived

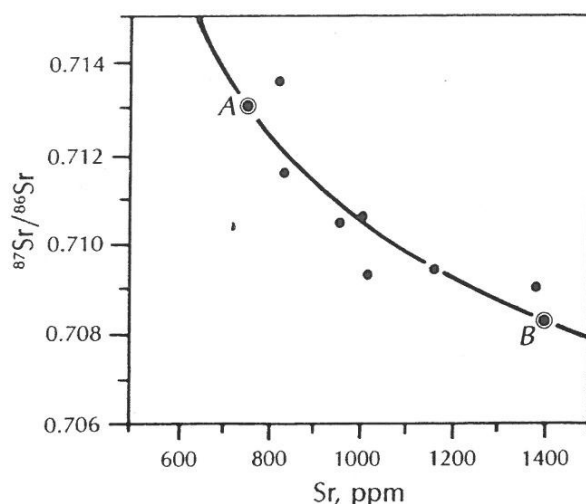


Figure 18.7 Mixing hyperbola formed by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of brines from the Clinton sandstones of Ohio. The Sr concentrations were corrected for dilution with meteoric water in Figure 18.6. The equation of the hyperbola was derived by fitting a straight line to the data points in coordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/(\text{Sr})$. The isotope compositions of the end members were determined from the mixing equation based on their Sr concentrations, which were derived by fitting mixing triangles to pairs of elements including Sr. Brine A is Na-rich, has $^{87}\text{Sr}/^{86}\text{Sr} = 0.7131 \pm 0.0006$, and $\delta^{18}\text{O} = -4.1 \pm 0.4\text{‰}$; whereas brine B is Ca-rich, has $^{87}\text{Sr}/^{86}\text{Sr} = 0.70837 \pm 0.00006$, and $\delta^{18}\text{O} = -1.0 \pm 0.3\text{‰}$ (Lowry et al. 1988).

from different sources may contain measurable concentrations of Sr and Nd or O with distinctive isotope compositions. The isotope compositions of these elements in a suite of binary mixtures vary progressively depending on the isotope compositions of the end members and on the proportions of mixing. The isotope compositions of any two elements in binary mixtures can be calculated from equation 18.20 for different values of f_A , provided the concentrations and isotope compositions of the elements in the end members are known or assumed. When the results of such systematic calculations are plotted in coordinates of the appropriate isotope ratios, isotopic mixtures of two elements are found to form hyperbolas

that are *not* transformable into straight lines because the mixing equation contains a cross product term (Faure, 1986). Therefore, such mixtures are commonly modeled by constructing mixing hyperbolas, as described above, based on end members whose isotopic and chemical compositions are assumed.

18.7 Summary

Mixing is a common phenomenon in nature that takes place in the course of geological processes. The chemical compositions of binary mixtures of water or sediment vary linearly in coordinates of the concentrations of any two conservative elements. The end members must also satisfy the mixing equation, which helps to define them and permits us to calculate their abundance in any given mixture.

Three-component mixtures scatter within a triangle of mixing that can be reduced to two components by projecting data points from one of the corners to the opposite side of the triangle. Mixing of two saline waters followed, or accompanied, by dilution with meteoric water is a special case of three-component mixing that may occur in some oilfield brines. Ternary mixing may also explain the chemical compositions of some detrital sedimentary rocks such as arkosic sandstones and greywackes.

Evaporative concentration of surface water may initially cause linear relationships among the concentrations of conservative elements. However, when the ion activities rise to critical values such that a compound can precipitate, the ions that participate in the formation of the compound deviate from the linear pattern and respond to the operation of geochemical divides. As a result, both the concentrations of the ions and the composition of the dissolved salts change.

Mixtures of two components that differ both in the concentration and in the isotope compositions of one element form data arrays in the form of hyperbolas in coordinates of an isotope ratio and concentration of the element. Such mixing hyperbolas are transformable into straight lines

by inverting the concentration. Ternary mixtures of components having different isotope compositions of *one* element can be reduced to binary mixtures by removing one of the components using appropriate treatment of the samples prior to analysis.

Binary mixtures containing *two* elements with different isotope compositions form hyperbolic arrays in coordinates of the two isotopic ratios (or a related parameter). These hyperbolas are *not* transformable into straight lines because the mixing equation contains additional terms.

Problems

1. Calculate the concentration of Mg^{2+} in a binary mixture of two components, given that $(\text{Mg}^{2+})_A = 2.4 \text{ mg/L}$ and $(\text{Mg}^{2+})_B = 6.7 \text{ mg/L}$ and $f_A = 0.75$.

(Answer: 3.47 mg/L)

2. Given two end members A and B whose concentrations of K and Mg are $(K)_A = 100 \text{ ppm}$, $(Mg)_A = 25 \text{ ppm}$; $(K)_B = 35 \text{ ppm}$, $(Mg)_B = 250 \text{ ppm}$. Calculate the slope and intercept of the mixing equation.

(Answer: Slope = -0.289, intercept = 107.2)

3. Plot the mixing equation and end members of Problem 2 on graph paper and add a data point *M* containing $(K)_M = 62.0 \text{ ppm}$ and $(Mg)_M = 89.3 \text{ ppm}$. Calculate the abundances of components A and B in that sample.

(Answer: A = 41.5%, B = 58.5%)

4. A sample P contains $(K)_P = 40 \text{ ppm}$ and $(Mg)_P = 125 \text{ ppm}$. Assume that this sample formed by mixing of components A and B defined in Problem 2 and was subsequently diluted with a third component located at the origin.

(a) Derive the equation of the dilution line.

(b) Determine the coordinates of the point of intersection of the dilution line with the mixing line AB.

(c) Determine the weight fraction of the dilute component in sample P.

5. A series of brine samples have the following concentrations of Na and Ca.

$\text{Na}^+, \text{mg/kg}$	$\text{Ca}^{2+}, \text{mg/kg}$
58,800	30,200
51,500	36,100
48,800	38,600
43,200	42,200
35,000	47,600

Derive the equation of the mixing line by least-squares regression.

6. If the end members in Problem 5 contain $(\text{Na}^+)_A = 67,000 \text{ mg/kg}$ and $(\text{Na}^+)_B = 37,600 \text{ mg/kg}$, calculate the corresponding concentrations of $(\text{Ca}^{2+})_A$ and $(\text{Ca}^{2+})_B$.

7. Additional brine samples belonging to the suite of Problem 5 have the following concentrations.

$\text{Na}^+, \text{mg/kg}$	$\text{Ca}^{2+}, \text{mg/kg}$
11,600	9,700
44,000	16,400
25,500	15,500
35,500	22,500
37,400	26,200

Plot these data points together with the mixing line from Problem 5 and the end members from Problem 6. Estimate the concentrations of Na^+ and Ca^{2+} in the brine samples prior to the dilution by a graphical procedure.

8. Calculate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr concentration of a binary mixture of A and B for $f_A = 0.40$ given that $(^{87}\text{Sr}/^{86}\text{Sr})_A = 0.725$, $(\text{Sr})_A = 100 \text{ ppm}$, $(^{87}\text{Sr}/^{86}\text{Sr})_B = 0.704$, $(\text{Sr})_B = 450 \text{ ppm}$.

9. Plot a mixing hyperbola for mixtures of A and B defined in Problem 8 by calculating the coordinates of mixtures characterized by $f_A = 0.8, 0.6, 0.4$, and 0.2.

10. Calculate the $\delta^{18}\text{O}$ value of water formed by mixing two components such that $\delta^{18}\text{O}_A = 10.0\text{‰}$, $\delta^{18}\text{O}_B = -2.0\text{‰}$, and $f_B = 0.65$.

11. Derive the equation for two-component mixtures of water in coordinates of $\delta^{18}\text{O}$ and δD .

12. Calculate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and δD values of a series of two-component mixtures defined by $(^{87}\text{Sr}/^{86}\text{Sr})_A = 0.750$, $(\text{Sr})_A = 5.0$ ppm, $\delta\text{D}_A = -150\text{‰}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_B = 0.709$, $(\text{Sr})_B = 75$ ppm, $\delta\text{D}_B = -30\text{‰}$

for $f_A = 0.2, 0.4, 0.6$, and 0.8 . Plot the results in coordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ and δD and draw a smooth curve through the points.

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V

· APPLICATIONS OF GEOCHEMISTRY TO THE SOLUTION OF GLOBAL PROBLEMS

The chapters of Part V apply the principles of geochemistry to important environmental phenomena, such as chemical weathering, variations in the quality of surface water, oxidation of sulfide-bearing mineral deposits, the transfer of chemical elements among its natural reservoirs, consequences of the contamination of the atmosphere, disposal of radioactive waste, and the effects of environmental lead on human health. The selected topics demonstrate that geochemistry is central to our efforts to understand the environment in which we live.

Consequences of Chemical Weathering

When igneous and metamorphic rocks are exposed to water and atmospheric gases at or near the surface of the Earth, the minerals they contain decompose selectively and at varying rates. The chemical reactions that cause the decomposition of minerals were discussed in Chapters 9–15 and constitute the process we call *chemical weathering*. The products of chemical weathering consist of (1) the compounds formed during incongruent solution of the primary minerals, (2) the ions and molecules that dissolve in the water, and (3) the resistant minerals in the rocks that are liberated by the decomposition of their more susceptible neighbors. In addition, the noble gases (He, Ne, Ar, Kr, Xe, and Rn) and certain other gases (H₂, hydrocarbons, N₂, etc.) are released into the atmosphere. The newly formed compounds (oxides, hydroxides, clay minerals, etc.) may accumulate at the site of weathering together with unreacted mineral grains (quartz, feldspars, micas) and undecomposed pieces of rock (pebbles, cobbles, boulders) as a residual mantle or *regolith*, also called *saprolite*. Further modification of the saprolite leads to the formation of *soils*, which sustain rooted plants and the fauna that feeds on these plants. However, ultimately, saprolite is removed by *erosion* through transport of the material downslope under the influence of gravity or by the actions of running water or wind.

Therefore, from a geological perspective, chemical weathering is the start of the mass migration of sediment from the continents into

basins of deposition in the oceans. Chemical weathering is also the start of the geochemical cycles of the elements, which are released from their rock reservoirs into solution for a trip to the oceans where they reside for varying lengths of time before they reenter the crust of the Earth in sedimentary rocks (Section 4.4).

Much of the subject matter to be discussed in the fifth part of this book is concerned with the practical consequences of chemical weathering, which not only consists of the decomposition of rocks but also affects the chemical composition of water and causes dispersion of ions from metallic and nonmetallic mineral deposits. Chemical weathering therefore contributes to the ability of the environment on the surface of the Earth to sustain life.

The natural environment is increasingly affected in unforeseen ways by the activities of the growing human population. The changes in the chemical composition of the atmosphere and hydrosphere caused by our activities may alter our habitat in ways that are difficult to predict with certainty, but may in fact be harmful to us. For this reason, geochemists are increasingly called upon to study how natural geochemical processes on the surface of the Earth are perturbed by anthropogenic activities, to predict the effect of these changes on the quality of the environment, and to sound the alarm when the resulting changes in the global environment are potentially harmful to us.

19.1 Changes in Chemical Composition of Rocks

The effects of chemical weathering on the chemical composition of rocks are readily apparent by comparing the concentrations of major-element oxides in fresh and weathered samples of a rock. However, such direct comparisons may be misleading because of the "closed table effect," which is the property of chemical analyses, expressed in weight percent, of having to add up to 100. A serious consequence of this property of chemical analyses is that a *real* change in one constituent causes *apparent* changes in all other constituents. For example, if a rock *loses* a significant amount of one major element as a result of chemical weathering, the concentrations of all other elements must *increase*, thereby erroneously suggesting additions of these elements to the rock. Similarly, if a rock actually *gains* one element, the concentrations of all others must *decrease*. As a result, differences in the concentrations of major elements expressed in percent between weathered and unweathered specimens of a homogeneous rock are *not* reliable indicators of actual gains and losses caused by chemical weathering.

The procedure for identifying real gains and losses of elements as a result of chemical weathering is based on the assumption that one of the major-element oxides has remained constant in *amount* even though its concentration may appear to have changed. The constituent chosen most often for this purpose is Al_2O_3 , consistent with the limited solubility of $\text{Al}(\text{OH})_3$ at pH values between 6 and 8 (Figure 12.6). This choice is also consistent with the convention regarding the conservation of Al during incongruent solution of aluminosilicate minerals (Section 10.6). Alternatively, Fe_2O_3 , TiO_2 , or ZrO_2 may be selected in cases where Al may have been mobile in highly acid or basic environments.

Detailed chemical and mineralogical studies of chemical weathering of igneous rocks of basaltic composition have been published by Eggleston et al. (1987), Claridge and Campbell (1984), Colman (1982), and Hendricks and Whittig (1968). Loughnan (1969), Carroll (1970), Lindsay

(1979), whereas Colman and Dethier (1986) discussed weathering of silicate minerals in general.

In order to demonstrate the effects of weathering on the chemical composition of a rock we examine the data in Table 19.1 for a basalt from the state of Paraná, Brazil, and for a sample of saprolite that formed from it.

We observe that the saprolite has significantly *lower* concentrations of SiO_2 , CaO , MgO , Na_2O , K_2O , MnO , and P_2O_5 than the basalt. However, it has *higher* concentrations of Al_2O_3 , Fe_2O_3 , TiO_2 , and LOI (loss on ignition), which includes adsorbed water, water in crystal lattices and fluid inclusions, CO_2 of carbonates, and SO_2 of sulfides. Note that the decreases and increases of the concentrations of the major-element oxides in the saprolite balance in such a way that the sum of the concentrations is equal to 100. Therefore, the real losses of some of the oxide components that may have occurred during weathering of the basalt are partly compensated by apparent increases in the concentrations of the other components. Similarly, real gains in some components of the basalt have caused apparent losses in others. When both gains and losses have occurred, the resulting chemical composition of the weathering products can only be interpreted by recalculating the analysis based on the assumption that one of the oxides has remained constant in amount.

In the case at hand, we select Al_2O_3 as the constant oxide and note that its concentration apparently increased from 12.3% to 26.3% as a result of weathering of the basalt. Note that the *concentration* of a constituent expressed in weight percent is equivalent to an *amount* in grams per 100 g of rock. Therefore, 100 g of basalt originally contained 12.3 g Al_2O_3 . If we assume that the *amount* of Al_2O_3 remained *constant*, the apparent *increase* in the *concentration* of Al_2O_3 must be caused by a *reduction* in the weight of the rock from 100 g to some smaller amount derivable from the relation

$$\frac{\text{weight of constituent}}{\text{weight of rock}} \times 100 = \text{percent concentration} \quad (19.1)$$

Table 19.1 Comparison of Chemical Analyses of Basalt from Paraná, Brazil, and Its Weathering Products

	Basalt, %	Saprolite, %	Amount remaining, g	Gain + or loss -, g	Gain + or loss -, %
SiO ₂	50.7	35.1	16.4	-34.3	-67.6
Al ₂ O ₃	12.3	26.3	12.3	0	0
CaO	7.83	0.06	0.028	-7.80	-99.6
MgO	4.18	0.26	0.12	-4.06	-97.1
Na ₂ O	2.53	0.02	0.009	-2.52	-99.6
K ₂ O	1.71	0.13	0.061	-1.65	-96.5
Fe ₂ O ₃	15.1	21.5	10.04	-5.06	-33.5
MnO	0.20	0.10	0.046	-0.15	-75.0
TiO ₂	3.19	3.96	1.85	-1.34	-42.0
P ₂ O ₅	0.46	0.11	0.051	-0.41	-89.1
LOI ^a	1.70	12.4	5.79	+4.09	+241
Sum	100.0	100.0	46.7	-53.3	

^aLoss on ignition.

SOURCE: Faure, unpublished data.

In the case under consideration, the weight of the rock must be $(12.3/26.3) \times 100 = 46.7$ g, which implies that 53.3 g of rock was removed by weathering from each 100 g of basalt.

The *amounts* of the other oxide constituents remaining in the altered basalt can now be calculated by multiplying their percent concentrations in the saprolite by the *weight-loss factor* (w) derived from the ratio of the concentrations of the constant oxide in the fresh and weathered rock. If Al₂O₃ is chosen as the constant oxide:

$$w = \frac{(\text{Al}_2\text{O}_3)_{\text{fresh}}}{(\text{Al}_2\text{O}_3)_{\text{weath.}}} = \frac{12.3}{26.3} = 0.467 \quad (19.2)$$

where the parentheses signify concentrations in weight percent of the selected oxide in the fresh and weathered rock, respectively. For example, the amount of SiO₂ remaining after weathering is $35.1 \times 0.467 = 16.4$ g. All of the concentrations of the oxide components of the saprolite in Table 19.1 were multiplied similarly by the weight-loss factor and the remaining amounts are listed in column 3. Note that these amounts sum to 46.7 g, confirming that $100 - 46.7 = 53.3$ g of material was

lost as a result of weathering per 100 g of original basalt.

The actual gains and losses of each component can now be determined by comparing the data in column 3 (amounts remaining) to the analysis of the basalt in column 1 of Table 19.1. For SiO₂ we have a real loss of $16.4 - 50.7 = -34.3$ g, whereas for Fe₂O₃ we have a real loss of $10.04 - 15.1 = -5.06$ g. Note that Fe₂O₃ was lost even though its concentration in the saprolite is higher (21.5%) than in the basalt (15.1%). The same is true for TiO₂, which was diminished by 1.34 g even though its concentration in the saprolite is higher than in the basalt. The data in column 4 indicate that weathering caused real losses of all constituents, except H₂O, CO₂, and SO₂, relative to constant Al₂O₃.

The final step in the evaluation of the data in Table 19.1 is to rank the oxide components in terms of the magnitude of the losses that have occurred. For this purpose we express the losses in terms of percent of the amount originally present in the basalt. For example, the basalt lost $(34.3/50.7) \times 100 = 67.6\%$ of its SiO₂. The greatest losses occurred for CaO and Na₂O (99.6%),

MgO (97.1%), K₂O (96.5%), and P₂O₅ (89.1%) followed by MnO (75.0%), SiO₂ (67.6%), TiO₂ (42.0%), and Fe₂O₃ (33.5%). Evidently, chemical weathering of basalt in Paraná has led to the formation of saprolite that is composed primarily of Al₂O₃, SiO₂, Fe₂O₃, and H₂O.

19.2 Normative Mineral Composition of Weathering Products

The mineral composition of the saprolite in Table 19.1 can be studied by means of x-ray diffraction or by electron-transmission microscopy. However, when weathering products are poorly crystallized or amorphous, as is often the case, identification of minerals is difficult or impossible. A similar problem arises in the study of volcanic igneous rocks, which may be cryptocrystalline or glassy. In igneous petrology this problem is overcome by calculating the abundances of selected minerals from chemical analyses of the rocks. The resulting mineral composition is called its *norm*, and the minerals that make up the norm are the *normative* minerals. The procedures used to calculate mineral norms of volcanic rocks can be adapted to estimate the abundances of selected minerals in partly amorphous weathering products.

For this purpose we recognize that saprolite contains varying amounts of certain minerals derived from the original rock as well as amorphous compounds and minerals formed during weathering. The most common primary minerals are:

quartz	biotite
K-feldspar	hornblende, pyroxene, olivine
plagioclase	rutile
muscovite	magnetite, ilmenite

Among the secondary minerals we expect to find:

kaolinite, smectite	hematite
gibbsite	goethite
amorphous silica	pyrolusite

The choice of minerals to be included in the norm must be made by the investigator and depends on

the composition of the bedrock, the climatic conditions at the site, and on any available information regarding the mineral composition of the bedrock or its weathering products. However, we recall that the mineral norm is only an *approximation* to reality and therefore the selection of minerals and their composition is arbitrary.

We have seen that the saprolite in Table 19.1 is composed primarily of Al₂O₃, SiO₂, Fe₂O₃, and H₂O, which presumably occur in the secondary minerals kaolinite and goethite. In addition, we assign K₂O to K-feldspar, Na₂O and CaO to plagioclase, MgO to the pyroxene enstatite, MnO to pyrolusite, TiO₂ to ilmenite, and P₂O₅ to apatite and berlinite. Other selections are certainly possible but seem less likely. For example, SiO₂ is not likely to occur as quartz grains in this case because basalt does not contain quartz. However, where the bedrock is composed of granite or granite-gneiss, quartz should be present in the saprolite. Similarly, K₂O could be assigned to muscovite or illite, MgO to smectite, CaO to calcite, TiO₂ to sphene or rutile, etc. In most cases such alternative selections have little effect on the conclusions derivable from the norm.

The calculation of the mineral norm of the saprolite in Table 19.1 is carried out in Table 19.2. Note that the formulas of the minerals are expressed in oxide form and that the percent concentrations of the oxide components in the analysis are recalculated to millimoles per 100 g of saprolite. Note also that LOI was *assumed* to be H₂O. The primary minerals derived from the basalt are satisfied first and the secondary weathering products (goethite, pyrolusite, kaolinite, and gibbsite) are then made from the remaining oxides. TiO₂ probably occurred in the basalt as ilmenite (FeTiO₃), which is resistant to weathering but may alter to TiO₂ and/or to a variety of sphene (CaTiSiO₅) called leucosene (Correns, 1978). However, in this case the saprolite contains insufficient CaO for leucosene to form, and TiO₂ is therefore expressed as ilmenite in the norm.

We begin the norm calculation with the primary minerals and convert all of the available K₂O, 1.38 millimoles (mmol), into K-feldspar. In accordance with the oxide formula for K-feldspar we reduce the available Al₂O₃ by 1.38 mmol and

Table 19.2 Calculation of a Mineral Norm from the Chemical Analysis of the Saprolite in Table 19.1

	<i>SiO₂</i>	<i>Al₂O₃</i>	<i>CaO</i>	<i>MgO</i>	<i>Na₂O</i>	<i>K₂O</i>	<i>Fe₂O₃</i>	<i>MnO</i>	<i>TiO₂</i>	<i>P₂O₅</i>	<i>LOI</i>	
In saprolite												
%	35.1	26.3	0.06	0.26	0.02	0.13	21.5	0.10	3.96	0.11	12.4	
mmol/100 g	584	258	1.07	6.44	0.322	1.38	134	1.41	49.5	0.775	689	
<i>Minerals</i>	<i>Millimoles/100 g</i>											<i>Normative minerals, %</i>
K ₂ O · Al ₂ O ₃ · 6SiO ₂ K-feldspar	575.7	256.6	1.07	6.44	0.322	0	134	1.41	49.5	0.775	689	0.77
Na ₂ O · Al ₂ O ₃ · 6SiO ₂ albite	573.7	256.3	1.07	6.44	0	0	134	1.41	49.5	0.775	689	0.17
3CaO · P ₂ O ₅ apatite	573.7	255.9	0	6.44	0	0	134	1.41	49.5	0.418	689	0.11
Al ₂ O ₃ · P ₂ O ₅ berlinite	573.7	255.5	0	6.44	0	0	134	1.41	49.5	0	689	0.10
CaO · Al ₂ O ₃ · 2SiO ₂ anorthite	573.7	255.5	0	6.44	0	0	134	1.41	49.5	0	689	0.00
MgO · SiO ₂ enstatite	567.3	255.5	0	0	0	0	134	1.41	49.5	0	689	0.65
FeO · TiO ₂ ilmenite	567.3	255.5	0	0	0	0	109.3	1.41	0	0	689	7.51
Fe ₂ O ₃ · H ₂ O goethite	567.3	255.5	0	0	0	0	0	1.41	0	0	579.7	19.42
MnO ₂ pyrolusite	567.3	255.5	0	0	0	0	0	0	0	0	579.7	0.12
Al ₂ O ₃ · 2SiO ₂ · 2H ₂ O kaolinite	56.3	0	0	0	0	0	0	0	0	0	68.3	66.0
Al ₂ O ₃ · 3H ₂ O gibbsite	56.3	0	0	0	0	0	0	0	0	0	68.3	0.00
SiO ₂ amorph. SiO ₂	0	0	0	0	0	0	0	0	0	0	68.3	3.38
H ₂ O water	0	0	0	0	0	0	0	0	0	0	0	1.22
											Total	99.45

SiO₂ by $6 \times 1.38 = 8.28$ mmol. The amount of K-feldspar in grams per 100 g of saprolite is:

$$\frac{1.38 \times 556.67}{1000} = 0.77 \text{ g/100 g} \quad (19.3)$$

Next, all available Na₂O is used to make albite, and the remaining molar amounts of Al₂O₃ and SiO₂ are reduced proportionately. The millimolar

amount of albite is then converted to a weight in grams, as illustrated in equation 19.3, and the amount is listed in Table 19.2. Note that the amounts of feldspar remaining in the saprolite are very small, but that the residual K-feldspar (0.77 g/100 g) is more abundant than albite (0.17 g/100 g). The amount of CaO is used to make 0.35 mmol of apatite (3CaO · P₂O₅), and the

remaining 0.418 mmol of P_2O_5 is combined with Al_2O_3 to make secondary berlinite ($Al_2O_3P_2O_5$) leaving 255.5 mmol of Al_2O_3 . Since all of the available CaO was used to make the phosphate apatite, none is left for anorthite, which presumably does not occur in the saprolite. MgO is converted into 0.65 g of enstatite ($MgOSiO_2$) without difficulty. However, in order to convert TiO_2 into ilmenite ($FeOTiO_2$), the Fe_2O_3 in the analysis must be recast as FeO. The amount of Fe in the saprolite is $134 \times 2 = 268$ mmol/100 g, which makes an equal number of moles of FeO. Therefore, 49.5 mmol of FeO is consumed in making 7.51 g of ilmenite from 49.5 mmol of TiO_2 , leaving $268 - 49.5 = 218.5$ mmol of FeO, which is equivalent to 109.3 mmol of Fe_2O_3 .

The remaining Fe_2O_3 is now converted into 19.4 g of the secondary mineral goethite ($Fe_2O_3 \cdot H_2O$) by combining Fe_2O_3 with an equal millimolar amount of H_2O . MnO in the analysis is assigned to 0.12 g of pyrolusite (MnO_2), and all of the remaining Al_2O_3 is made into 66.0 g of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). We are left with a residue of 56.3 mmol of SiO_2 and 68.3 mmol of H_2O . The former is converted into 3.38 g of amorphous silica, or opal, or chalcedony, depending on its crystallinity. The remaining H_2O is converted into 1.22 g of water, which coats the solid particles of the saprolite. Note that gibbsite does not occur in the norm because SiO_2 is more abundant than Al_2O_3 .

The calculation carried out in Table 19.2 indicates that the normative mineral composition of the saprolite in units of grams per 100 g or weight percent is:

	%		%
kaolinite	66.0	goethite	19.4
ilmenite	7.5	amorph. SiO_2	3.38
misc. traces	1.9	water	1.2

The significant conclusions to be derived from these results are that chemical weathering has converted the basalt into a mixture of kaolinite and goethite with lesser amounts of Ti-bearing minerals and amorphous silica. Only trace

amounts of the primary minerals K-feldspar, albite, pyroxene, and apatite remain. The absence of gibbsite suggests that the activity of silicic acid in the water at 25°C was greater than $10^{-4.68}$ mol/L in accordance with the kaolinite-gibbsite boundary in Figure 12.1.

19.3 Susceptibility of Minerals to Weathering

The minerals of igneous and metamorphic rocks differ widely in their susceptibility to chemical weathering. Another way of expressing this fact is to say that the dissolution reactions of minerals take place at different rates. In fact, the kinetics of many dissolution reactions have been studied, and much has been learned not only about the *rates* of these reactions but also about the *mechanisms* by which minerals dissolve in water (Colman and Dethier, 1986). Such studies were initiated by soil chemists who are interested in knowing the rates at which plant nutrients (Na^+ , K^+ , Ca^{2+} , Fe^{2+} , Mg^{2+} , and P) are released by minerals in soils under differing environmental conditions (McLelland, 1950). Later, this subject began to attract the attention of geochemists who have been increasingly interested in the processes that control the rates of congruent and incongruent dissolution. Some important contributions to this subject include papers by Wollast (1967), Helgeson (1971, 1972), Busenberg and Clemency (1976), Holdren and Berner (1979), Berner and Holdren (1979) and Tole et al. (1986).

Experimental studies with powdered mineral samples have commonly indicated a *decrease* in the rate of dissolution with time, suggesting that several different processes may occur simultaneously. For example, Garrels and Howard (1957) demonstrated that cations are released and that the pH rises within one minute after powdered feldspar is placed in water, suggesting that cations from grain surfaces are exchanged for H^+ to form a layer of "hydrogen-feldspar." This phenomenon is equivalent to *hydrolysis* (Section 10.2) if we regard feldspar as a salt of the weak hypothetical acid $HAISi_3O_8$. Subsequently, cations and silica are

lost from feldspar grains in nonstoichiometric proportions such that the feldspar grains *presumably* become coated with a layer of kaolinite or gibbsite whose presence retards further dissolution.

However, it was discovered that the surfaces of grains of powdered minerals used in dissolution experiments are coated with small adhering particles having large surface areas (Grandstaff, 1977). The presence of these particles undoubtedly increases the initial dissolution rates. In addition, grinding may damage the crystal lattice of surface layers of grains, and this phenomenon also increases initial dissolution rates of mineral powders. Moreover, when mineral grains from weathering environments were examined with a scanning electron microscope, the expected layer of alteration products was *not* found (Berner and Schott, 1982).

Apparently, mineral grains dissolve preferentially where crystallographic dislocations exist on the grain surface. As a result, etch pits are produced that expand and deepen as the process continues. The rate of dissolution of a mineral therefore depends in part on the density of etch pits per unit area of surface and hence on the abundance of dislocations within the mineral grains. The layer of weathering products that may adhere to grain surfaces is *permeable* and *nonprotective* and does *not* affect the kinetics of dissolution.

The relative susceptibility of the common rock-forming silicate and oxide minerals can also be determined directly from the observed abundances of primary minerals in saprolites formed at different stages of weathering of a particular type of rock. Such a study was carried out by Goldich (1938) on the Archean gneisses in the valley of the Minnesota River in southern Minnesota. The degree of weathering experienced by a series of saprolites that formed from the same kind of rock is indicated by their concentrations of Al_2O_3 . The reason is that Al_2O_3 is very nearly immobile during chemical weathering, whereas other oxide components are lost, so that the concentration of Al_2O_3 rises as weathering progresses. Goldich (1938) used this criterion to classify samples of saprolite that had formed from granitic gneiss in the Morton-Redwood

Falls area of Minnesota whose chemical compositions are shown graphically in Figure 19.1A.

The data of Goldich (1938) indicate that chemical weathering of granitic gneiss in southern Minnesota causes rapid apparent decreases of the concentrations of Na_2O , CaO , and MgO , whereas K_2O and SiO_2 concentrations decline more slowly as weathering progresses. However, the concentrations of H_2O , total Fe as Fe_2O_3 , TiO_2 , and Al_2O_3 actually increase. A constant-oxide calculation for the most highly weathered saprolite from Minnesota confirms that real gains in Fe_2O_3 , TiO_2 , and H_2O occurred relative to constant Al_2O_3 , whereas all other constituents were lost in varying amounts.

The changes in the chemical compositions of progressively weathered saprolites must reflect what is happening to the primary minerals as a result of chemical weathering. Goldich (1938) actually determined the mineral compositions of the granitic gneiss and of two saprolites formed from it. His data are presented in Figure 19.1B in the form of smooth curves that show the rapid loss of plagioclase and biotite and the much slower removal of K-feldspar and quartz. Whereas K-feldspar is almost completely removed from the most highly weathered saprolite, about 20% of quartz and 6% of magnetite and ilmenite remain. The principal weathering product in this case is kaolinite, which accumulates in the saprolite and makes up 66% by volume of the most highly weathered rock.

The changing abundances of the common rock-forming minerals in saprolites reflect their susceptibilities to chemical weathering. Goldich's data in Figure 19.1B clearly show that plagioclase is much more susceptible to weathering than K-feldspar and that biotite is likewise destroyed during the early stages of weathering. The abundances of quartz and K-feldspar actually increase initially because of the preferential loss of plagioclase and biotite. However, ultimately K-feldspar is completely removed, whereas the abundance of quartz decreases only by about 30% in the most highly weathered saprolite in Minnesota. The concentrations of magnetite and ilmenite in the saprolite also rise, indicating their resistance to weathering. However, both eventually do

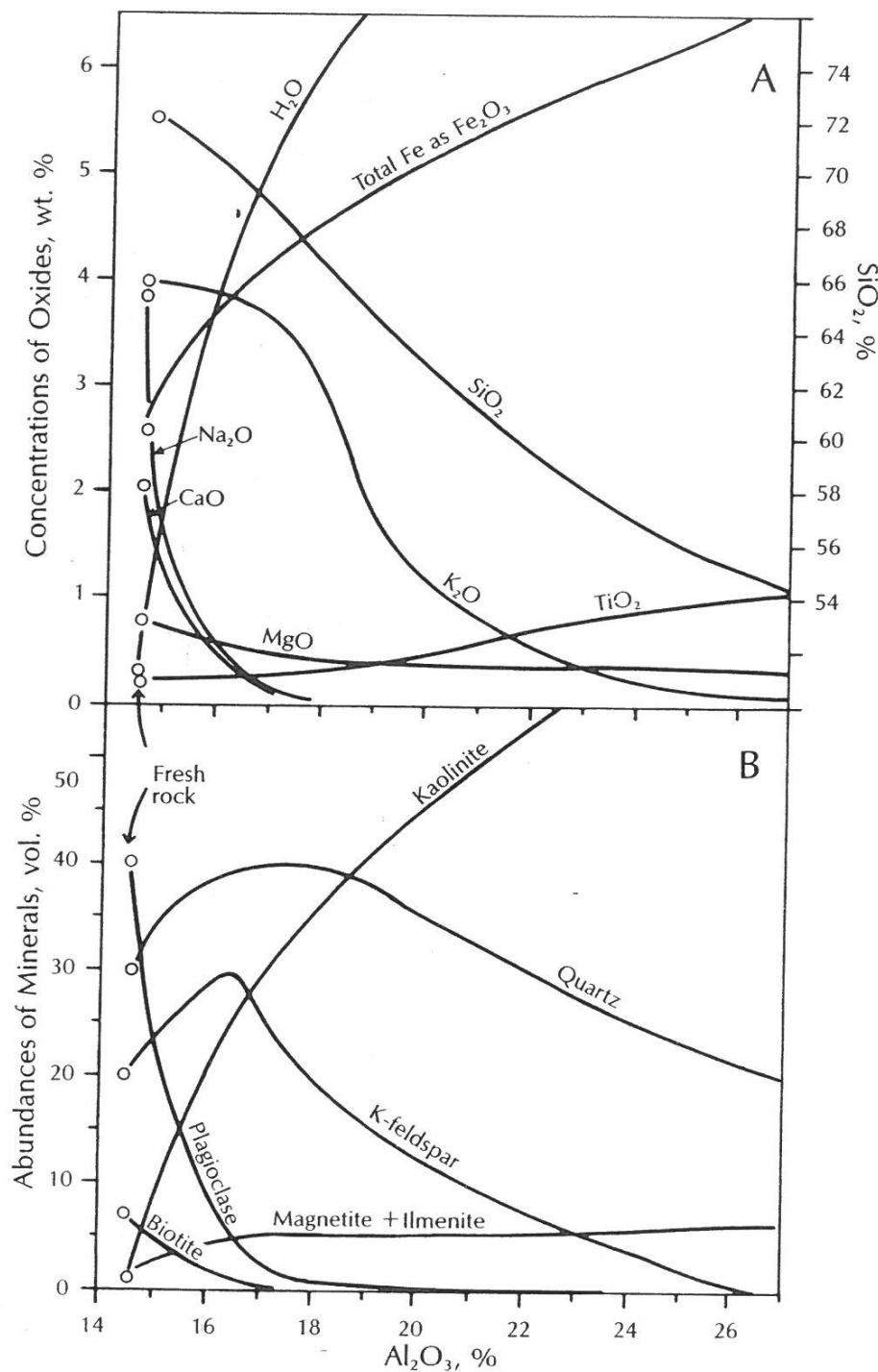


Figure 19.1 A. Variation of the chemical compositions of saprolites representing increasing intensities of chemical weathering of granitic gneisses in the Morton-Redwood Falls area of Minnesota (Goldich, 1938). Note that the concentrations of Na_2O , CaO , MgO , and SiO_2 decline continuously, whereas K_2O declines more slowly and the concentrations of total Fe as Fe_2O_3 , Al_2O_3 , and H_2O increase with increasing degree of weathering.

B. Variation of the measured abundances of minerals in the saprolites shown above. The rapid decrease in the abundance of plagioclase accounts for the loss of Na_2O and CaO shown in A. K-feldspar actually increases in abundance, as does quartz, but both ultimately decline. However, magnetite and ilmenite resist weathering and persist in the saprolite. Kaolinite is the principal weathering product and accumulates in the saprolite as the primary aluminosilicate minerals are decomposed (data from Goldich, 1938).

decompose to form secondary minerals such as goethite and leucoxene.

Goldich (1938) used information of this kind to show that the susceptibilities of the rock-forming silicate minerals to weathering can be related to their position in Bowen's reaction series depicted in Figure 19.2. Accordingly, olivine and Ca-plagioclase are most susceptible followed by pyroxene, hornblende, biotite, and Na-plagioclase. K-feldspar is more resistant than any of the minerals that precede it in the sequence of crystallization and is surpassed only by muscovite and quartz. In a general way, the susceptibility to weathering of the rock-forming silicate minerals decreases with their decreasing temperatures of crystallization from magma.

The apparent relationship between the crystallization temperature of silicate minerals, as expressed in Bowen's reaction series, and their susceptibility to weathering is a useful mnemonic device. However, we know that the progress of reactions that constitute chemical weathering is strongly dependent on environmental conditions and therefore recognize that exceptions to Goldich's generalization may occur locally.

An alternative explanation for the observed differences in the susceptibility to weathering of rock-forming silicate minerals arises from a consideration of activity diagrams. For this purpose

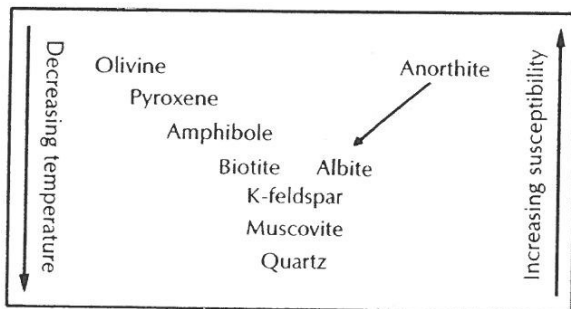


Figure 19.2 Schematic representation of Bowen's reaction series, which is used here to show that minerals that crystallize early and at high temperature from magma (olivine, Ca-plagioclase) are more susceptible to weathering than those that form later at somewhat lower temperatures (muscovite, quartz).

we return to Chapter 12, which contains activity diagrams for anorthite (Figure 12.2B) and the Mg silicates (Figure 12.5). We recall first that the anorthite diagram contains calcite, which restricts the activity of Ca^{2+} in natural solutions, depending on the partial pressure of CO_2 and the pH of the environment. The solubility limit of calcite therefore prevents the $[\text{Ca}^{2+}]/[\text{H}^+]^2$ ratio of natural solutions from rising to levels at which equilibrium with anorthite is possible. As a result, anorthite cannot be stable in contact with water at the surface of the Earth and therefore dissolves incongruently to form kaolinite or gibbsite, depending on the activity of silicic acid in the solution. The activity diagrams of K-feldspar (Figure 12.1) and albite (Figure 12.2A) do not contain solubility limits other than that of amorphous silica because the carbonates of alkali metals are soluble. Consequently, the $[\text{K}^+]/[\text{H}^+]$ and $[\text{Na}^+]/[\text{H}^+]$ ratios of natural solutions *can* rise until the solutions are in equilibrium with K-feldspar and albite, respectively. Hence, these minerals may be stable in contact with water at the surface of the Earth and therefore weather more slowly than anorthite and Ca-bearing plagioclase.

The differences in susceptibility to weathering among the Mg-bearing silicates (olivine, pyroxene, amphibole) can be rationalized similarly by means of Figure 12.5. For example, olivine in the form of forsterite (Mg_2SiO_4) dissolves congruently by releasing Mg^{2+} and H_4SiO_4 into solution. However, the $[\text{Mg}^{2+}]/[\text{H}^+]^2$ ratio of natural solutions is *restricted* by the solubility limits imposed by magnesite (MgCO_3), serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), and sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$). Therefore, natural solutions on the surface of the Earth cannot be in equilibrium with forsterite. The same is true of pyroxenes (enstatite, MgSiO_3) and amphiboles (anthophyllite, $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$), although the $[\text{Mg}^{2+}]/[\text{H}^+]^2$ ratios required to stabilize these minerals at a particular value of $[\text{H}_4\text{SiO}_4]$ are *lower* than is needed to stabilize olivine. Therefore, reactions between olivine and water are further removed from equilibrium than reactions between pyroxene and water and between amphibole and water. Consequently, olivine is more susceptible to weathering than pyroxene, which is more suscepti-

ble than amphibole, as implied also by Bowen's reaction series.

In conclusion, we consider briefly the susceptibility to weathering of other kinds of minerals such as the oxides, carbonates, and sulfides. Minerals consisting of these compounds may coexist with silicate minerals in certain kinds of rocks that may be classified as ore deposits. The effects of chemical weathering on the chemical and mineralogical compositions of such rocks are therefore of great interest to geologists in the mining industry.

The relative susceptibilities to weathering of sulfide minerals will be considered in Chapter 21 by means of Eh-pH diagrams for the sulfides of different metals. The dispersion of metals that may result from the chemical weathering of sulfide-bearing rocks causes the formation of local geochemical anomalies in the saprolite and soil derived from such deposits. These geochemical anomalies are used to locate potential ore deposits by means of systematic geochemical exploration surveys. In addition, the presence of anomalous concentrations of metals and certain nonmetals in soils associated with so-called *mineralized* rocks may pose a natural geochemical health hazard to humans living in the area or consuming food grown on such soils.

In comparison with the silicate minerals taken as a group, sulfides and carbonates (calcite, aragonite, dolomite) are *more* susceptible to weathering than silicate minerals (olivine, plagioclase, pyroxene, etc.), whereas the oxides (magnetite, ilmenite, chromite, rutile, cassiterite, etc.) are *less* susceptible. The resistance to chemical weathering of certain accessory minerals occurring in ordinary igneous and metamorphic rocks and in certain kinds of ore deposits has interesting consequences, which we consider in the next section.

19.4 Formation of Placer Deposits

All igneous, sedimentary, and metamorphic rocks may contain accessory minerals that resist both chemical and mechanical weathering. These minerals are liberated by the decomposition of the rock-forming minerals with which they are associ-

ated, and subsequently they may enter the sediment-transport system operating on the surface of the Earth. As a result of transport by mass wasting (downslope movement) and by water in motion or by wind action, the grains of accessory minerals are concentrated on the basis of size, specific gravity, and shape into deposits of sand and gravel. All deposits of sand and gravel contain some of the common accessory minerals of igneous and metamorphic rocks. In cases where these minerals have economic value and when their concentration is sufficient to make their extraction profitable, such sand and gravel deposits are called *placers* (the *a* is pronounced as in plaza).

The accessory minerals that may be concentrated in sand and gravel include the native metals or nonmetals (Au, Pt group elements, diamonds), oxides (cassiterite, magnetite, ilmenite, chromite, rutile, corundum, etc.), silicates (zircon, garnet, sphene, staurolite, tourmaline, etc.), and phosphates (apatite, monazite, etc.). Some of these are *ore minerals* from which one or several metals can be extracted at a profit (Au, Pt group metals, cassiterite, magnetite, chromite, monazite), whereas others have intrinsic value as gems, including diamond and corundum (sapphire or ruby), may be semiprecious stones (zircon, garnet), or are used as abrasives (zircon, garnet, staurolite, etc.). Placer deposits may be buried and cemented to become special kinds of sandstones or conglomerates that may be classified as ore deposits because of the presence of valuable minerals. Many such fossil placers are known, but their occurrence, origin, and mineral composition are properly the subject of Economic Geology (Park and MacDiarmid, 1970).

The resistant minerals listed above have higher densities than quartz, feldspar, calcite, etc., and therefore are grouped with the *heavy minerals*, which include also olivine, pyroxenes, amphiboles, biotite, and others whose densities are all greater than 2.90 g/cm³. Placer deposits form when grains of minerals that are resistant to weathering and have high densities settle out of water in which they were suspended.

The movement of spherical particles through water under the influence of gravity is described

by equations derived by Stokes (1851, 1901). Particles having other shapes can be treated using relations summarized by Lerman (1979). A spherical particle of radius r and density ρ suspended in water (density = 1.0 g/cm³) is acted upon by a gravitational force (F_g):

$$F_g = \frac{4}{3}\pi r^3 g(\rho - 1) \quad (19.4)$$

where g is the acceleration due to gravity. As a result, the particle acquires a velocity (v_s) that generates an opposing force known as *viscous drag* (F_d):

$$F_d = 6\pi\eta r v_s \quad (19.5)$$

Note that the magnitude of the viscous drag on the spherical particle increases with its velocity. As a result, the velocity of a sphere sinking through water increases until the magnitude of the viscous drag equals the gravitational force. When $F_g = F_d$,

$$6\pi\eta r v_s = \frac{4}{3}\pi r^3 g(\rho - 1) \quad (19.6)$$

Therefore, the velocity of a spherical particle sinking through still water can increase only to a value given by the equation:

$$v_s = \frac{2}{9} \left(\frac{r^2 g}{\eta} \right) (\rho - 1) \quad (19.7)$$

Evidently, the terminal velocity of a spherical particle increases with its density (ρ) and with the square of its radius (r). Since the viscosity of water is $\eta = 0.01$ g/cm/sec and $g = 980$ cm/sec², equation 19.7 reduces to the formula (Lerman, 1979):

$$v_s = \frac{2 \times 980}{9 \times 0.01} r^2 (\rho - 1) \\ = (2.18 \times 10^4) r^2 (\rho - 1) \text{ cm/sec} \quad (19.8)$$

where r is expressed in centimeters. This formula was used to construct the settling curves in Figure 19.3 for spherical particles of native gold ($\rho = 19.0$ g/cm³) and quartz ($\rho = 2.65$ g/cm³) in water. The diagram illustrates the point that gold particles are approximately one-third smaller in diameter than quartz grains with which they are deposited, i.e., that have the same settling velocity.

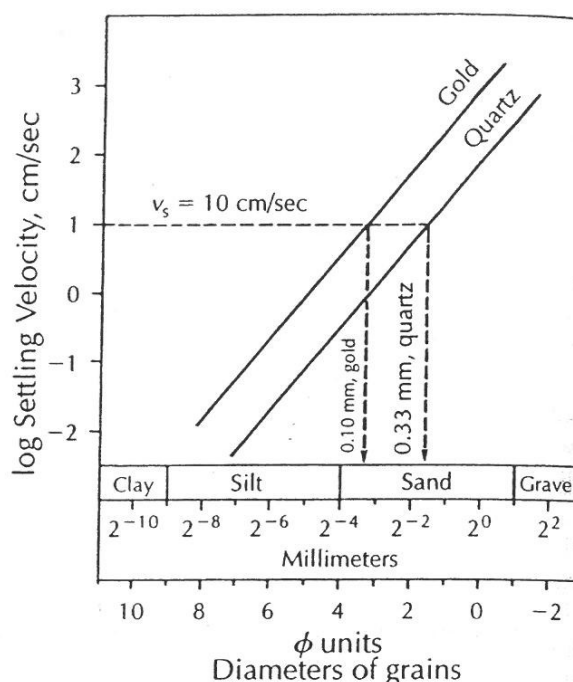


Figure 19.3 Plot of settling velocities (v_s) of gold and quartz particles in water versus their grain diameters expressed in millimeters and ϕ units in accordance with equation 19.7. The densities of gold and quartz were taken to be 19.0 and 2.65 g/cm³, respectively. In order for particles of two different densities to be deposited together from still water they must have identical settling velocities. Therefore, gold particles settling with a velocity of 10 cm/sec are about one third smaller in diameter than quartz grains.

Placer deposits of native gold have played an important role in the history of the United States, starting in 1848 when gold nuggets were discovered in present-day stream gravels at Sutter's Fort near Coloma, California. In the following year, a gold rush ensued as the so-called forty-niners moved into the area to pan for gold in the streams emerging from the Sierra Nevada Mountains near Sacramento, California. Eventually, fossil placers were discovered in the area in gravel terraces of an earlier river of Tertiary age, and the source of all of the placer gold was subsequently traced to gold-bearing hydrothermal quartz veins in the Mariposa slate of the Mother Lode mining district of California.

19.5 Provenance Determination by Isotopic Dating

The heavy minerals in detrital sedimentary rocks have been studied extensively by sedimentary petrologists in order to identify their sources or *provenance*. Certain heavy minerals originate from specific kinds of igneous or metamorphic rocks. For example, Pt group metals and chromite occur in peridotites and pyroxenites, diamonds occur in kimberlites, and cassiterite is found in certain granites, whereas garnet, staurolite, sillimanite, epidote, and glaucophane are associated most often with metamorphic rocks of various kinds. In addition, a purple variety of zircon called *hyacinth* occurs only in granitic gneisses of Archean age (>2500 Ma) because the diagnostic color is caused by radiation damage resulting from the emission of energetic alpha particles by the isotopes of U, Th, and their unstable daughters (Tyler et al., 1940; Poldervaart, 1955). However, ordinary zircon, magnetite, ilmenite, rutile, sphene, monazite, tourmaline, pyroxene, etc., occur in both igneous and metamorphic rocks, so that their presence in sand or sandstones is not necessarily diagnostic. Therefore, studies of the mineral compositions of heavy-mineral assemblages in clastic sedimentary rocks are effective only under special circumstances.

The provenance of certain minerals that resist weathering can also be determined by isotopic dating. For example, muscovite and K-feldspar both contain K and Rb and are therefore dateable by the K-Ar and Rb-Sr methods described in Section 16.3 and used in Section 13.6 to date certain clay minerals. In addition, zircon, monazite, and apatite, which contain U and Th, can be dated by the U-Pb and Th-Pb methods. The results reflect the age of the rocks from which the minerals were derived and thereby identify their provenance. For example, Faure and Taylor (1981) and Faure et al. (1983) dated detrital feldspar in samples of till from the Transantarctic Mountains by the Rb-Sr method and concluded that the feldspar had originated primarily from Cambro-Ordovician granites of the local basement complex. However, some samples appeared to be mixtures of

grains derived from sources of different ages. Moreover, efforts to date detrital feldspar from Paleozoic sandstones had only limited success because the feldspar grains disintegrated into small fragments during crushing of the rock in the laboratory (Szabo and Faure, 1987).

The difficulties encountered with provenance dating of feldspar and muscovite concentrates can be avoided by dating hand-picked suites or even single grains of zircon by the U-Pb method. Zircon crystals are more resistant to chemical weathering and have greater hardness than either feldspar or muscovite. As a result, zircon crystals tolerate weathering, transport, and deposition quite well and are preserved virtually unaltered in detrital sedimentary rocks. The problem of dating multicomponent mixtures of zircons derived from sources having different ages can be avoided by sorting them on the basis of color, shape, and magnetic susceptibility. Each variety can then be analyzed separately to identify its source from its measured U-Pb dates.

An excellent example of this technique is the study by Gaudette et al. (1981) of zircons extracted from the Potsdam sandstone of Cambrian age in upper New York State. The authors collected a rock sample weighing 35 kg from an outcrop located just east of the Adirondak Mountains, which consist of igneous and metamorphic rocks of the Grenville structural province of the Canadian Precambrian Shield. The zircons recovered from this specimen were sorted into four varieties: (1) brown, elongate, (2) brown, rounded, (3) clear, rounded, and (4) clear, elongate. The U-Pb dates of these *combined* zircon varieties range from 968 Ma to 1466 Ma and do not permit a meaningful interpretation. However, each variety yields distinctive dates on concordia diagrams, as shown in Table 19.3 and illustrated in Figure 19.4.

The upper concordia intercept date of 1170 ± 80 Ma of the brown, elongate zircons in Table 19.3 is similar to the age of charnockitic gneiss of the Adirondack Highlands. Therefore, these least-abraded zircons were probably derived from sources in the Adirondacks a short distance west of the collecting site. The brown, rounded zircons are older (1320 ± 80) than the brown,

Table 19.3 Summary of U-Pb Dates Derived from Different Varieties of Zircon Extracted from a Sample of the Potsdam Sandstone (Cambrian) from Upper New York State

Variety of zircon	Upper concordia intercept, Ma	Lower concordia intercept, Ma
Brown, elongate	1170 $\pm$ 100	325
Brown, rounded	1320 $\pm$ 80	380
Clear, rounded	2160 $\pm$ 500	985 $\pm$ 40
Clear, elongate	2700 $\pm$ 250	985 $\pm$ 15

SOURCE: Gaudette et al. (1981).

elongate ones and may have originated from the Grenville structural province of southern Quebec where rocks of this age have been recognized. The clear zircons yield upper intercept dates of 2160 $\pm$ 500 Ma (clear, rounded) and 2700 $\pm$ 250 (clear, elongate). Rocks in this age range occur in the Superior structural province about 600 km northwest of the collecting site. However, the well-defined lower intercept dates of 985 Ma indicate that both clear zircon fractions experienced severe Pb losses during the Grenville orogeny. Therefore, these zircons were initially incorporated into pre-Grenville sediment, were subsequently metamorphosed during the Grenville orogeny, and were then re-eroded and deposited in the Potsdam sandstone during the Cambrian period. The lower-intercept dates of the brown zircons (325 and 380 Ma) appear to coincide with orogenies in the Appalachian Mountains during the Paleozoic era. However, in the absence of other supporting evidence, these dates may be artifacts created by the linear extrapolations of discordia lines (Faure, 1986).

Evidently, the zircon grains in the Potsdam sandstone have participated in the major geological events on the North American continent since Archean time.

The technique of U-Pb dating has been developed to the point where single zircon grains (Schärer and Allègre, 1982a) and even fragments

of one zircon grain have been dated (Schärer and Allègre, 1982b). In addition, the ion microprobe called SHRIMP at the Australian National University was used by Froude et al. (1983) to analyze spots about 25 μ m in diameter on four zircon grains from the Mt. Narryer quartzite in the Yilgarn Block of Western Australia. The results indicate that these zircons crystallized between 4100 and 4200 Ma, which makes them the oldest known terrestrial objects and indicates that magma of granitic composition formed only about 300–400 Ma years after the accretion of the Earth about 4.5×10^9 years ago.

19.6 Formation of Soils

Perhaps the most important consequence of chemical weathering is that it permits the development of soils (Bohn et al., 1979; Sposito, 1981). Although chemical weathering is *destructive* of rocks and minerals, its products promote the existence of life on Earth and thus are certainly a very positive attribute of chemical weathering. Soils are the *interface* between the lithosphere (in the geochemical sense) and the biosphere because they permit the growth of rooted plants and other life forms, which themselves affect the chemical processes that characterize soils. We have so far presented the weathering of rock-forming minerals entirely in terms of inorganic chemical reactions. This may be a necessary oversimplification, but in reality *bacteria* and other life forms not only modify the natural environment but are active contributors to the process of chemical weathering.

Soils are characteristically layered as a result of the redistribution of material into *horizons*, which are identified by the letters O, A, E, B, C, and R. These layers form a *soil profile* described briefly in Table 19.4. The O, A, E, and B horizons constitute the actual soil or *solum*. The soil horizons are the products of soil-forming processes that are affected by environmental parameters, including temperature and meteoric precipitation (climate), vegetation, pH and O₂ content, time, and the composition of bedrock. Consequently, the principal soil hori-

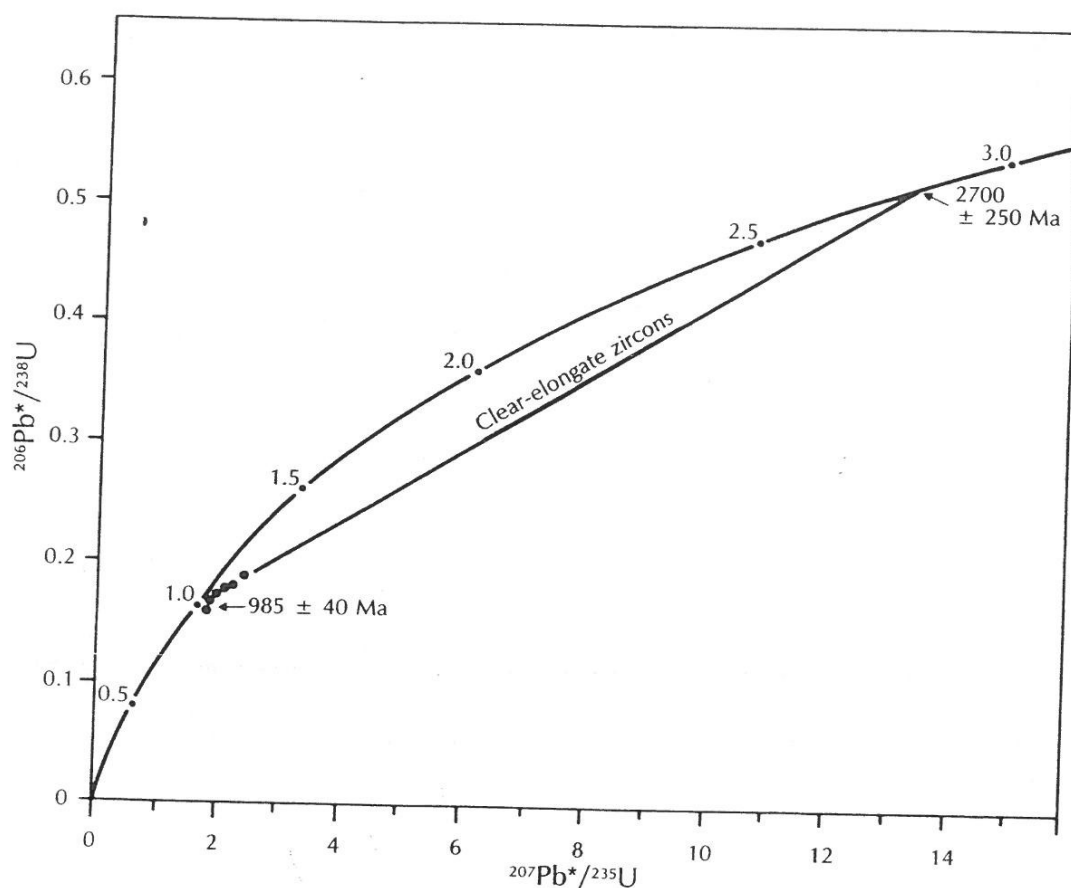


Figure 19.4 Concordia diagram for clear, elongate zircon grains from the Potsdam sandstone of Cambrian age from upper New York State. The zircons form a discordia line that intersects concordia at 2700 ± 250 and $985 \pm 40 \text{ Ma}$. The upper intercept is the crystallization age of these zircons in Archean time. The lower intercept indicates that the zircons lost a large proportion of their radiogenic Pb during the Grenville orogeny, presumably because they were liberated by weathering and were incorporated into a sedimentary rock in pre-Grenville time. Subsequently, they were liberated a second time from the resulting metamorphic rock and were redeposited in the Potsdam sandstone during the Cambrian period. (Data and interpretation from Gaudette et al., 1981.)

zons are not equally developed under the wide range of environmental conditions that exist on the surface of the Earth. For example, an O horizon forms only where the rate of production of plant debris exceeds the rate at which it is decomposed. This condition arises in tropical rainforests where plant debris accumulates rapidly and in regions where decomposition of plant debris is retarded either by low temperatures or because the soil is waterlogged and therefore becomes depleted in O_2 .

The amount of time required for a soil profile to develop from freshly deposited volcanic ash, alluvium, till, or bedrock is of the order of hundreds to thousands of years or more, depending on climatic conditions and the character of the starting material. Volcanic ash composed of small particles of silicate glass weathers relatively rapidly, whereas igneous or metamorphic rocks resist weathering and prolong the time required to develop soil. For example, lava flows extruded

Table 19.4 Description of Soil Horizons Starting at the Top

Soil horizon	Properties and origin
O	surface layer composed primarily of organic matter with only a small content of mineral material; black or dark brown in color
A	mineral particles mixed with finely divided organic matter that produces a dark grey color
E	primarily mineral grains that resist dissolution and are too large to be translocated in colloidal suspension, low content of organic matter causes light grey color
B	enriched in clay minerals, oxides, and hydroxides of Fe, Al, Mn, etc., removed from overlying A and E horizons; may also contain calcite or gypsum that can precipitate from aqueous solution within this layer
C	saprolite or sediment that is largely unaffected by soil-forming processes; may be the product of chemical weathering of the underlying bedrock (saprolite) or have been transported and deposited by water (alluvium) or ice (till) or by volcanic activity (tuff)
R	unweathered bedrock underlying the C horizon

SOURCE: Foth (1984).

through fissure eruptions on Mt. Kilauea on Hawaii can support rooted plants in only a few years, whereas outcrops of granitic gneiss north of Lake Superior in Canada show little evidence of weathering after exposure for about 14,000 years. In general, the thickness of a soil profile depends on the rate of the soil-forming processes and on the rate of erosion by running water, gravitational sliding, and wind action. In places where the rate of erosion exceeds the rate of soil formation,

the top layer of the parent material is removed before soil horizons can develop within it.

The most important factor in the development of soil profiles is the *climate*, represented by the temperature and by the amount and seasonality of meteoric precipitation. As a result, soils within a particular climatic zone tend to have similar profiles regardless of the composition of the bedrock from which they formed. However, soils *within* a climatic zone may vary locally depending primarily on their location within the topography of the landscape, which affects the movement of water, the rate of erosion, and other factors. Such topographically controlled variations in soil profiles give rise to a *catena* or a *toposequence* of soils.

The classification of soils used in Europe and the United States was formerly based on the premise that soils reflect the environmental conditions under which they formed. However, this classification was replaced in 1960 by a scheme that gives more weight to the morphology of soils than to their genesis. The new soil classification was devised by the Soil Survey Staff of the U.S. Department of Agriculture and was reissued in revised form in 1975 as USDA Handbook 436. The new classification contains ten *soil orders*, listed in Table 19.5, whose names are intended to convey important properties of the soils to which they apply. Some of these soil orders evolve sequentially as a function of time starting with the weathering of bedrock or with the deposition of volcanic ash, alluvium, or till that become the parent materials from which the soils develop. The sequential development of soil orders is indicated diagrammatically in Figure 19.5. However, the sequence of soil development may vary depending on local conditions or because of climate change.

The chemical and physical properties of soils are greatly affected by the small grain size of their constituent particles. As a result, chemical reactions in soils are strongly influenced by ion exchange phenomena discussed in Section 13.5. The cation exchange capacity (CEC) of soils depends primarily on the presence of organic matter, clay minerals, and oxides of Al and Fe in the different soil horizons. Consequently, the CEC varies with depth depending on the compo-

Table 19.5 Soil Orders and Their Properties

Order	Description
Entisols	early stage of development composed of A and C or A and R horizons but lacking a B horizon
Inceptisols	young soil with some leaching in the A horizon but only weakly developed B horizon
Alfisols	strongly leached acidic A horizon containing decomposing organic matter; B horizon well developed and clay-rich
Spodosols	composed of A and E horizons with accumulation of oxides/hydroxides of Al and Fe that form "hardpan" in the B horizon
Ultisols	highly weathered with well-developed clay-rich B horizon underlying well-leached and acidic A and E horizons
Oxisols	like Ultisols, but clay in B horizon is decomposed to oxides of Al and Fe, making this soil lateritic in character
Mollisols	thick, dark-colored A horizon that is soft when dry; clay-rich B horizon; high content of Ca^{2+} and Mg^{2+}
Aridisols	little organic material, essentially unleached mineral soil with deposits of calcite (caliche)
Vertisols	rich in swelling clay, soil profile poorly developed because of vertical mixing caused by seasonal cracking
Histosols	thick O horizon formed by accumulation of plant debris that fails to decompose

sition of the soil horizons. Moreover, the CEC of soils depends on the pH because the charges on the surfaces of both organic and inorganic particles are determined by the abundance of H^+ in the aqueous phase. The adsorbed ions are available to plants as nutrients and contribute to the *fertility* of soils. Therefore, the phenomenon of ion exchange is *vital* to the ability of soils to sustain rooted plants and the other organisms that are associated with them.

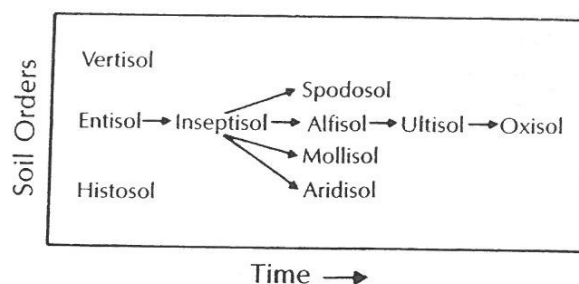


Figure 19.5 Approximate sequence of development of different soil orders. Entisols and Inceptisols are early stages of soil development leading to Spodosols, Alfisols, Mollisols, and Aridisols depending on the mineral composition of the parent material and climatic conditions. Ultisols and Oxisols occur in humid tropical regions as end stages of soil development enriched in oxides of Al and Fe. Vertisols develop only from parent material composed of swelling clay in regions with alternating wet and dry seasons. Histosols consist of partly decomposed plant material in places that are deprived of O_2 because they are waterlogged (after Foth, 1984).

The development of soil and its ability to sustain rooted plants are strongly affected by the life forms that coexist within or on it. The community of organisms that coexist in a particular environment constitutes an *ecosystem*. The organisms of an ecosystem can be classified into the *producers* (autotrophs) and *consumers* (heterotrophs). The producers are able to use C in the form of CO_2 and chemical nutrients from the environment to feed themselves, whereas the consumers sustain themselves by *decomposing* organic matter generated by the producers. The energy required to produce or decompose organic matter is derived either from sunlight or from the oxidation or reduction of chemical elements including S, Fe, and Mn. Accordingly, all organisms can be classified into the *photoautotrophs* (plants and many algae), *chemoautotrophs* (nitrifying and S-oxidizing bacteria), and *chemoheterotrophs* (animals, protozoa, fungi, and most bacteria). In a viable ecosystem the primary producers provide food for the consumers who recycle nutrients for use by the producers.

The ecosystem of soils contains rooted plants, bacteria, fungi, actinomycetes, algae, and protozoans. In addition, the animal kingdom is

represented by vertebrates (mice, voles, moles, rabbits, squirrels, gophers, foxes, badgers, bear, deer, and birds), arthropods (ants, millipedes, centipedes, mites, springtails, harvestmen, diplopoda, diptera, and crustaceans), as well as nonarthropod animals such as earthworms, nematodes, and snails. Although bacteria constitute only about 1.0% of the organic matter of a fertile soil in a temperate region, they are by far the most abundant life form with a concentration of more than 1×10^9 individuals per gram of soil (Foth, 1984).

The nutrients required by plants and the other members of the soil ecosystem can be divided into the *macronutrients* and the *micronutrients*. The former occur in plants at concentrations of more than 500 ppm, whereas the latter are usually present at concentrations of less than 50 ppm. The macronutrients required by plants include N, P, K, Ca, Mg, and S; the micronutrients are B, Fe, Mn, Cu, Zn, Mo, Co, and Cl. The nutrient elements therefore tend to be concentrated in plant material relative to their abundance in the soil water and compared to the crust of the Earth as a whole. For example, corn plants are enriched in Ca, Mg, K, N, P, and S compared to the water in the soil by factors ranging from 2.6 to 67,000 (Foth, 1984, Table 11.3).

The chemical composition of plants varies widely depending on the chemical composition of the soil on which they grow and on the additions of fertilizers and other soil conditioners used in agriculture. Native plants tend to favor soils in which certain nutrients are abundant, and their distribution may therefore reflect regional variations in the chemical composition of the soil and of the bedrock from which it formed. This principle is used in geobotanical surveys to locate geological contacts and potential ore deposits (Brooks, 1972).

The wide variation in the chemical composition of cultivated and native plants in the United States is reflected by the data in Table 19.6 based on the work of Connor and Shacklette (1975). Cultivated plants tend to have more uniform compositions than native plants, but they are also enriched in some elements (primarily P and K) that are added to soil in the form of fertilizer.

19.7 Geomicrobiology

Microscopic organisms including bacteria, algae, protozoans, and fungi are widely distributed on the Earth and occur in large numbers. The *bacteria* (Class Schizomycetes), which play an especially large role in geochemistry, are divided into ten orders of about 1500 species. They occur in virtually all environments on the Earth, including the polar regions, the oceans, the atmosphere, and the continents.

Bacteria are a highly diversified group of organisms. Most species prefer temperatures between 5 and 37°C, but some tolerate temperatures as low as 0°C, and others survive heat up to about 70°C. Most bacteria favor neutral environments, but some species thrive under acidic conditions, and others prefer basic or saline living conditions. Some bacteria become dormant when living conditions are unfavorable and can remain in this state for long periods of time. Bacteria reproduce asexually by binary fission and grow best in the dark, although photosynthetic bacteria do require ultraviolet radiation. Some bacterial colonies may grow in the absence of oxygen (anaerobes), others require oxygen (aerobes), and some can tolerate oxygen even though they do not require it (facultative anaerobes). Bacteria, which range from 1 to 5 μm in diameter, may be spherical in shape (coccus), rodlike (bacillus), or spiral (spirillum). All three types inhabit the human body. Although some cause disease (pathogens), most are benign.

The important role played by bacteria and other microorganisms in geological processes is receiving increasing attention from geochemists (Ehrlich, 1981; Krumbein, 1978a-c). In addition, the subject is represented by several scientific journals (e.g., *Geomicrobiology Journal*, *Global Biogeochemical Cycles*, *Applied Environmental Microbiology*). These publications contain a rapidly growing body of knowledge about the geochemical transformations that result from the activities of microorganisms in nature. They affect the weathering of silicate, carbonate, and sulfide minerals and participate directly in the geochemical cycles of many elements, including Fe, Mn, S, P, Se,

Table 19.6 Average Chemical Composition of Plants and Plant Ash
(in parts per million)

Element	Plants ⁽¹⁾ (dry weight)	Ash ⁽²⁾	
		Cultivated ⁽²⁾ plants	Native ⁽²⁾ plants
Li	0.1	—	4.0–15
Be	—	—	0.64–2.0
B	5	37–540	140–600
C	49.65 ^a	—	—
N	0.92 ^a	—	—
O	43.20 ^a	—	—
F	—	0.43–0.49	0.50–1.6
Na	200	25–39	200–3100
Mg	700	$(1.5–13) \times 10^4$	$(1.6–10) \times 10^4$
Al	20	200–4000	1000–39,000
Ga	—	—	1.5–2.8
Si	1500	—	—
P	700	$(1.2–22) \times 10^4$	$(0.71–3.1) \times 10^4$
S	500	—	—
K	3000	$(18–41) \times 10^4$	$(2.9–23) \times 10^4$
Ca	5000	$(0.29–20) \times 10^4$	$(13–35) \times 10^4$
Ti	2	4.7–250	69–1200
V	1	—	2.6–2.3
Mn	400	96–810	470–14,000
Cr	2.40	0.42–6.6	2.2–22
Fe	500	$(0.06–0.27) \times 10^4$	$(0.08–0.93) \times 10^4$
Co	0.40	0.50–6.2	0.65–400
Ni	3	2.7–130	0.81–130
Cu	9	21–230	50–270
Zn	70	180–1900	170–1800
Se	0.1	0.04–0.17	0.01–0.42
Rb	2	—	—
Sr	20	14–880	320–5300
Y	—	—	2.1–47
Zr	—	—	2.4–85
Mo	0.65	2.5–20	0.76–7.6
Ag	0.05	—	—
Cd	—	0.37–2.3	0.95–20
I	—	4.6–13	2.8–5.4
Ba	30	15–450	270–11,000
La	—	—	14–270
Cl	0.40	—	350
Yb	—	—	1.1–1.8
Pb	—	7.1–87	24–480
U	0.05	—	—

^a“Wood” according to Foth (1984) expressed in percent by weight.

SOURCES: (1) Brooks (1972), Table 11.2; (2) Connor and Shacklette (1975).

Te, As, Sb, and Hg. In addition, they contribute to the transformation of organic matter into peat, coal, petroleum, and natural gas.

Although geologists and geochemists have been slow to accept the importance of microorganisms in geological processes, biologists have been aware of their abilities for more than a century. For example, Ehrenberg (1838) reported that the stalked bacterium *Gallionella ferruginea* participates in the deposition of Fe hydroxides in bogs and Winogradsky in 1887 discovered that *Beggiatoa* can oxidize H_2S to elemental S. This work was later extended by V. I. Vernadsky, whose important contributions to geochemistry were mentioned in Chapter 1 of this book, and by Stutzer (1911). The importance of acid-producing microorganisms to the weathering of silicate minerals was suggested by A. Muentz in 1890 and by G. P. Merrill in 1895. It was later elaborated in a textbook by Waksman (1932). The role of bacteria in the deposition of the Precambrian iron formation of the Lake Superior district of the United States was discussed in an important paper by Harder (1919).

Microorganisms, including bacteria and algae, were the first life forms to appear on the Earth during the Archean Eon more than three billion years ago (Schopf, 1983). In fact, the oldest known fossil is a filamentous bacterium found in stromatolitic black chert of the Warrawoona Group (Pilbara Supergroup) of Western Australia (Awramik et al., 1983). The age of the rocks of the Warrawoona Group is 3.556 ± 0.032 Ga. These fossilized bacteria resemble several existing varieties, including green sulfur bacteria (*Chloroflexus aurantiacus*), methanogenic bacteria (*Methanospirillum hungatti*), and the cyanobacteria (*Oscillatoria angustissima*, *Phormidium angustissimum*). The metabolism of most of the existing bacteria that resemble their Archean ancestor requires the absence of oxygen, although some can tolerate it. However, the cyanobacteria are photosynthetic and actually release oxygen into the environment.

Bacteria are primarily heterotrophic organisms that *decompose* complex organic molecules into simpler ones. Some species also decompose inorganic compounds (carbonates, sulfides, silicates) and even corrode metals. In fact, any natu-

rally occurring substance can be degraded by some species of bacteria. The ability of bacteria to carry out biochemical transformations has been used by man to make cheese, to leaven bread dough, and to ferment carbohydrates to make alcohol. Modern sewage-treatment facilities include holding tanks in which bacteria decompose organic solids in the presence of oxygen in order to avoid the severe oxygen depletion that follows when untreated sewage is discharged into the environment.

Bacteria in soil decompose plant debris and animal waste and thereby *recycle* nutrients. Without the recycling of nutrient elements, soils could not sustain rooted plants and life on Earth as we know it would be impossible. In addition, bacteria also assist plants to obtain nitrogen, which is the most important of all the nutrients required by plants.

The atmosphere of the Earth contains about 79% N_2 , which acts like an inert gas and cannot be used by plants. Therefore, the nitrogen of the atmosphere must be processed into a form that plants can absorb through their roots. Evidently, plants have *not* evolved a N-fixing process similar to photosynthesis that enables them to absorb CO_2 from the atmosphere. Some N_2 from the atmosphere is converted to NO_3^- by lightning and enters the soil in meteoric precipitation. However, the principal suppliers of soluble N in soil are bacteria of the genus *Rhizobium* that live in the roots of leguminous plants such as soybeans, alfalfa, clover, and peas in a symbiotic arrangement. However, some N-fixing bacteria in soil are non-symbiotic (*Azotobacter* and *Clostridium*), and some nonlegumes also harbor symbiotic N-fixing bacteria. The amount of N in soil is maintained at a steady state by another group of denitrifying bacteria that convert the soluble N compounds in soil back to N_2 gas. In addition, between 2 and 4% of N in soils is converted to NH_4^+ during the decomposition of organic matter by heterotrophic bacteria. The ammonium ion can substitute for K^+ in clay minerals and mica and is thus made unavailable to plants. Consequently, the formation of NH_4^+ is called *mineralization* by soil scientists.

The diversity of bacteria and their very large numbers may be exploited in the mining industry to recover metals and fossil fuels (Murr et al., 1978).

For example, the Society of Mining Engineers organized a symposium on "Bioleaching" during their annual meeting in 1988 in Las Vegas, Nevada. The participants in this symposium discussed the feasibility of using bacteria to dissolve sulfide minerals in ore deposits, to recover Mn from MnO_2 ores, to precipitate selenates from contaminated water, and to purify water discharged by manufacturing industries. These applications include manipulation of the genetic material of native species of bacteria in order to develop strains that are selective in their metabolic processing of chemical compounds. Significant contributions to this important and rapidly growing subject are by Trudinger (1971), Meyer and Yen (1976), Lundgren and Silver (1980), Monticello and Finnerty (1985), Hutchins et al. (1986), and Eligwe (1988). These and other references to microorganisms are listed separately in the References to emphasize the importance of this subject area to geochemistry.

19.8 Food Production and Population Growth

Increases in the population of the Earth are historically related to improvements in the methods of food production and increases in the area of land being cultivated. The onset of the Industrial Revolution around 1650 marked the start of a rapid rise in the world's population from about 545 million to a projected level of 6000 million by the year 2000. This *increase* in the population has been accelerated by a *decrease* in the death rate and now threatens to exceed the existing capacity for food production. Although Figure 19.6 indicates that the problem is *global* in scope, the balance between the rate of production and the rate of consumption of food shows wide *regional* variation.

The average annual *increase* in the population of the world is about 1.7%, with a population-doubling time of 40 years. However, the growth rate ranges from 2.9% in Africa to 0.2% in Europe, with corresponding doubling times of 24 years and 423 years, respectively. Several European countries have actually achieved zero population growth (Denmark, East Germany, Italy, United

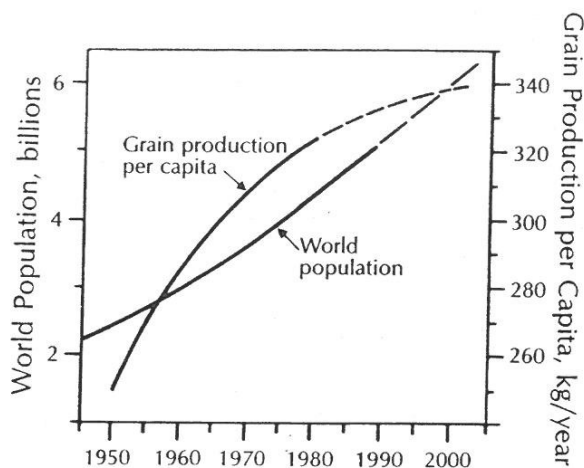


Figure 19.6 Population growth and per capita grain production worldwide. The graph indicates that the population of the world is growing and will probably exceed 6 billion by the year 2000. However, per capita grain production appears to be leveling off. The data for the world as a whole obscure regional differences in both food production and population growth. As a result, malnutrition and episodic starvation occur in some regions, whereas others have surplus food (after Foth, 1984).

Kingdom) and others even have declining populations (Austria, Hungary, West Germany).

The average per capita grain production, which has been rising worldwide, appears to be leveling off and is actually *declining* in some parts of Africa, Asia, and South America that have above-average rates of population growth. As a result, widespread malnutrition and episodes of starvation occur in these areas. The regional differences in the rates of per capita grain production are large and appear to be increasing with time, as shown in Figure 19.7.

The annual rate of grain production varies regionally for many different reasons and is not solely attributable to population growth. The contributory factors include:

1. The amount of arable land under cultivation.
2. The availability of fertilizers.
3. Effective weed and pest control.

4. Use of improved strains of cereal grains.
5. Farming practices.
6. Character of the soil.
7. Climatic conditions.
8. Economic incentives.
9. Civil wars.

In Japan, intensive farming practices result in an average yield of 5.8 metric tons of grain per hectare (ha; = 10^4 m²). However, other nations do less well (Brown et al., 1987).

	Metric tons/ha
United States	4.8
China	3.9
Indonesia	3.7
Bangladesh	2.2
Mexico	2.1
Brazil	1.8
India	1.6
Pakistan	1.6
Soviet Union	1.6
Nigeria	0.8

The high yields achieved in Japan cannot be realized elsewhere because of drought, mineral stress, shallow depth of soil development, excess water, or presence of permafrost. *Mineral stress* is caused by nutritional deficiencies in or actual toxicity of some soils depending on their chemical composition or origin.

Another way to increase food production in the world would be to increase the amount of land under cultivation. The data in Table 19.7 demonstrate that only 44% of the arable land in the world is presently under cultivation. Europe is most heavily farmed with 88% of all arable land in actual use, whereas South America and Africa still have large amounts of unused arable land. However, the productivity of the unused arable land is limited by unfavourable soil properties and climatic conditions. When these factors are taken into consideration, only a small fraction of the arable land is

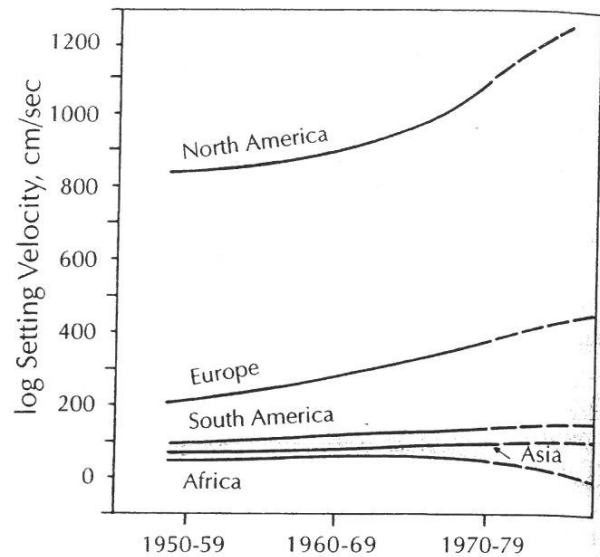


Figure 19.7 Average per capita grain production in different parts of the world. The grain production of North America and Europe is higher than those of South America, Asia, and Africa and is increasing more rapidly. The areas in the world having low rates of grain production have above-average rates of population growth. Note that "Africa" excludes South Africa and "Asia" excludes China and Japan. (Adapted from Foth, 1984, Figure 15.2.)

without limitations, ranging from 36% in Europe to 22% in North America, about 16% in Africa and South America, and 10% in north and central Asia. Consequently, it is unlikely that the present rate of grain production in the world could be doubled merely by farming all of the available arable land. Nevertheless, given the present rate of population growth, the global output of cereal grains must be doubled every 40 years to maintain the average level of nutrition. Because of the uneven distributions of population growth and grain production, some regions of the world will experience shortages, whereas others will have a surplus.

Available agricultural technology (including the use of chemical fertilizers, effective weed and pest control, improved strains of food crops, and soil-management practices) is capable of increasing grain production significantly where yields are presently low. However, the cost of fertilizers

Table 19.7 Summary of Arable Land and Its Present Use (in billions of acres)

<i>Region</i>	<i>Area</i>	<i>Potentially arable^a</i>	<i>Under cultivation^b</i>	<i>Unused arable land^c</i>
Africa	7.46	1.81 (24)	0.39 (22)	1.42 (78)
Asia	6.67	1.55 (23)	1.28 (83)	0.27 (17)
U.S.S.R.	5.52	0.88 (16)	0.56 (64)	0.32 (36)
North America	5.21	1.15 (22)	0.59 (51)	0.56 (49)
South America	4.33	1.68 (39)	0.19 (11)	1.49 (89)
Australia and New Zealand	2.03	0.38 (19)	0.08 (21)	0.30 (79)
Europe	1.18	0.43 (36)	0.38 (88)	0.05 (12)
Totals	32.49	7.88 (24)	3.47 (44)	4.41 (56)

^aNumber in parentheses is percent of total area in each region.

^bIn parentheses: percent of arable land presently under cultivation.

^cIn parentheses: percent of arable land not under cultivation.

SOURCE: Foth (1984), Table 15.2.

and pesticides is high and the introduction of more efficient farming practices may disrupt the established fabric of society. On the other hand, climate changes resulting from the greenhouse effect may be beneficial in some areas where present climatic conditions are unfavorable to agriculture.

19.9 Summary

Chemical weathering initiates the mass migration of sediment and chemical compounds in solution from the continents to the oceans and thereby starts the transport cycles of matter that together constitute the geochemical machine first mentioned in Section 4.5. In addition, chemical weathering contributes to formation of soil that sustains rooted plants whose presence on the Earth has enabled other life forms to evolve. Therefore, chemical weathering plays a vital role in making the Earth "an abode fitted for life," to use a phrase coined by Lord Kelvin in 1897.

The most obvious effect of chemical weathering is the decomposition of solid rocks into loose sediment whose chemical and mineral compositions differ greatly from those of the parent rocks. However, the apparent changes in the concentra-

tions of the major elements must be evaluated carefully in order to identify which constituents were actually lost and to determine the amounts removed from the rock.

The newly formed products of weathering are commonly amorphous or only poorly crystallized. It is therefore not easy to determine the mineral composition of weathering products just as it is difficult or impossible to identify the minerals in aphanitic or glassy volcanic rocks. This difficulty can be overcome by recasting chemical analyses of weathering products in the form of mineral norms adapted to this purpose from igneous petrology.

The changes in chemical and mineral composition caused by weathering indicate that certain rock-forming silicate minerals are more susceptible to decomposition than others. This information can be represented in the form of Bowen's reaction series, thereby implying that minerals that crystallize from magma at high temperatures are more susceptible to weathering than minerals that form at somewhat lower temperatures. However, the differences in susceptibility to weathering of minerals may also be understood in the context of the stabilities of minerals with respect to ions in aqueous solution. Certain common or accessory minerals in igneous and metamorphic rocks are

strongly resistant to weathering and enter the sediment-transport system intact.

The resistant minerals tend to become concentrated in sand and gravel deposits, which may acquire economic value if they contain nuggets of gold or Pt group elements, or particles of diamond, cassiterite, or some other valuable minerals. Such sand and gravel deposits, called placers, are a special type of ore deposit.

Some of the minerals that survive weathering and are removed from their place of origin are suitable for dating by isotopic methods. The resulting dates reflect the time elapsed since their crystallization and can therefore be helpful in identifying the rocks from which they originated. Zircons are especially good for this purpose because they strongly resist weathering and because the art of dating them by the U-Pb method has been raised to a high level.

The most important consequence of chemical weathering is the development of soil, which sustains life on the land surface of the Earth. Soils provide nutrients to rooted plants and other organisms that constitute the soil ecosystem. Microorganisms play a vital role in soils by recycling nutrients through decomposition of organic matter and by converting N_2 from the atmosphere into water-soluble forms.

We can relate these geochemical processes to our own welfare by contemplating the fact that the annual per capita grain production in some parts of the world is low and is not keeping pace with the growth of the population. The problem is aggravated by the realization that existing farming technology cannot be introduced rapidly into areas that need it the most because of social, economic, and political barriers.

Problems

1. Carry out a constant-oxide calculation to determine the gains or losses in terms of weights and percent values for a granitic gneiss from the valley of the Minnesota River (Goldich, 1938), assuming that Al_2O_3 remained constant in amount.

	Gneiss, %	Saprolite, %
SiO_2	71.45	55.25
Al_2O_3	14.60	26.23
CaO	2.08	0.16
MgO	0.77	0.33
Na_2O	3.84	0.05
K_2O	3.92	0.14
Fe_2O_3	2.51	6.55
MnO	0.04	0.03
TiO_2	0.26	1.03
P_2O_5	0.10	0.11
CO_2	0.14	0.36
H_2O^+	0.30	9.76
Sum	100.00	100.00

2. Determine whether Fe was lost or gained as a result of weathering of granitic gneiss from the

Minnesota River valley assuming that Al_2O_3 remained constant in amount.

	Gneiss, %	Saprolite, %
Al_2O_3	14.62	18.34
Fe_2O_3	0.69	1.55
FeO	1.64	0.22

3. Calculate normative K-feldspar and albite for a suite of saprolites ordered in terms of increasing intensity of weathering. Plot the results versus the concentration of Al_2O_3 and draw smooth curves through the data points. Rank the minerals in terms of their susceptibility to weathering.

	SiO_2 , %	Al_2O_3 , %	Na_2O , %	K_2O , %
1	69.89	16.54	0.43	5.34
2	68.09	17.31	0.12	3.48
3	61.75	18.54	0.10	3.54
4	70.30	18.34	0.09	2.47
5	57.53	23.57	0.06	0.35
6	55.07	26.14	0.05	0.14

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Water type	TDS, mg/L
Fresh	<1000
Brackish	1000–10,000
Saline	10,000–100,000
Brine	>100,000

The total average annual discharge of all streams is 37,400 km³/yr (Table 20.1), about 20% of which is contributed by the Amazon River of South America. The Congo (Zaire) River in Africa and the Yangtze River in China contribute 3.3% and 2.8% respectively. Some other well-known rivers, including the Mississippi in North America, the Mekong in Vietnam, the Danube in Europe, and the Nile in Africa together contribute only 3.8% of the total annual discharge. In fact, the Nile has a discharge of only 83 km³/yr (0.22% of the world's total), which makes it one of the smallest major rivers of the world in contrast to its historical and present importance in Egypt. Moreover, data compiled by Livingstone (1963) indicate a total discharge of only 0.32 km³/yr for the entire continent of Australia.

The chemical composition of surface waters was used by Gibbs (1970) to classify them based on their TDS values and their Na⁺/(Na⁺ + Ca²⁺) ratios. The resulting distribution of data points for the world's major rivers can be circumscribed by a "boomerang" shown in Figure 20.1. The rivers that define the lower end of the boomerang are dominated by meteoric precipitation, those in the upper end are affected primarily by evaporation and precipitation of calcite, whereas the rivers in the center of the boomerang are influenced by rock weathering.

The Na⁺/(Na⁺ + Ca²⁺) ratio of water in both ends of the boomerang tends toward a value of 1.0. At the lower end, the concentration of Na⁺ in *rainwater* is commonly greater than that of Ca²⁺, especially in coastal areas, so that the Na⁺/(Na⁺ + Ca²⁺) ratio approaches unity. At the other end of the boomerang, evaporative concentration causes precipitation of calcite, which depletes the water in Ca²⁺, but enriches it in Na⁺ and causes the Na⁺/(Na⁺ + Ca²⁺) ratio to increase toward

unity. Therefore, rivers in arid regions, saline lakes, and the oceans have high Na⁺/(Na⁺ + Ca²⁺) ratios. Some representative examples of each type of water are shown in Figure 20.1.

The chemical composition of river water does not necessarily reflect unambiguously the geochemical processes that affected it. For example, the elevated TDS and Na⁺/(Na⁺ + Ca²⁺) ratios of the Pecos and Rio Grande rivers in New Mexico and Texas (Figure 20.1) are caused primarily by the inflow of NaCl brines derived from halite deposits rather than by evaporative concentration and precipitation of calcite (Feth, 1971; Stallard and Edmond, 1983). In addition, Ca²⁺ is more abundant than Na⁺ in rain that falls in the interiors of continents, and the Na⁺/(Na⁺ + Ca²⁺) ratio of rainwater in continental areas is therefore less than one. For example, the Na⁺/(Na⁺ + Ca²⁺) ratio of rain in the interior of the United States is only 0.22 (Berner and Berner, 1987). Therefore, dilution by rain in continental interiors does *not* increase the Na⁺/(Na⁺ + Ca²⁺) ratio of stream water.

The difficulties of genetic classifications of natural waters are avoided by a graphical method proposed by Piper (1944) and used frequently in hydrogeology (Fetter, 1988). The so-called Piper diagram consists of two equilateral triangles and a diamond-shaped field onto which points are projected from the cation and anion triangles. The two triangles are used to represent the chemical compositions of waters expressed in percent of the milliequivalents per liter of the cations Ca²⁺, Mg²⁺, and Na⁺ + K⁺ and of the anions Cl⁻, SO₄²⁻, and HCO₃⁻ + CO₃²⁻. The triangles also serve to classify water based on the dominant cations and anions as shown in Figure 20.2.

The Piper diagram is a graphical representation of the chemical composition of water in terms of the *eight* major cations and anions, whereas the Gibbs diagram involves only *two* cations directly. Moreover, the Piper diagram serves to classify waters without genetic implications, whereas the Gibbs diagram presupposes the geochemical processes that affect waters in different parts of the boomerang.

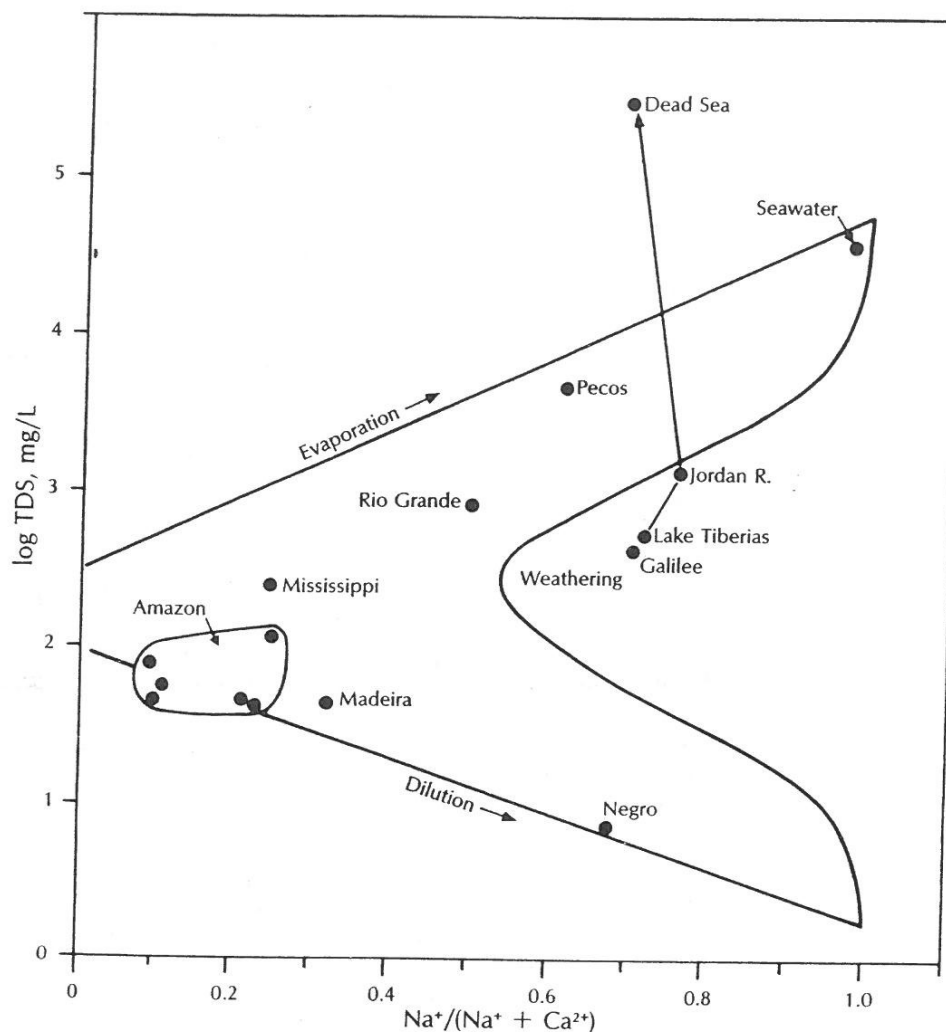


Figure 20.1 Classification of surface waters according to Gibbs (1970). Water in the central part of the “boomerang” is dominated by weathering of silicate minerals. Progressive evaporation and precipitation of calcite increase TDS and enrich the water in Na^+ while depleting it in Ca^{2+} . Hence such waters reside in the *upper* part of the boomerang. Waters in the *lower* part are dominated by rainwater of coastal areas where $\text{Na}^+ > \text{Ca}^+$. Waters from the Jordan River–Dead Sea area of Israel (Livingstone, 1963) illustrate the effect of progressive evaporation but plot outside the boomerang. The Amazon River and its tributaries (Livingstone, 1963; Stallard, 1985) exemplify water with large rainwater components. The chemical composition of the Mississippi River (Meybeck, 1979) is controlled by chemical weathering of rocks, whereas the Rio Grande (Livingstone, 1963) reflects the effects of evaporative concentration or the influx of NaCl brines. Note the location of seawater on the diagram (Berner and Berner, 1987).

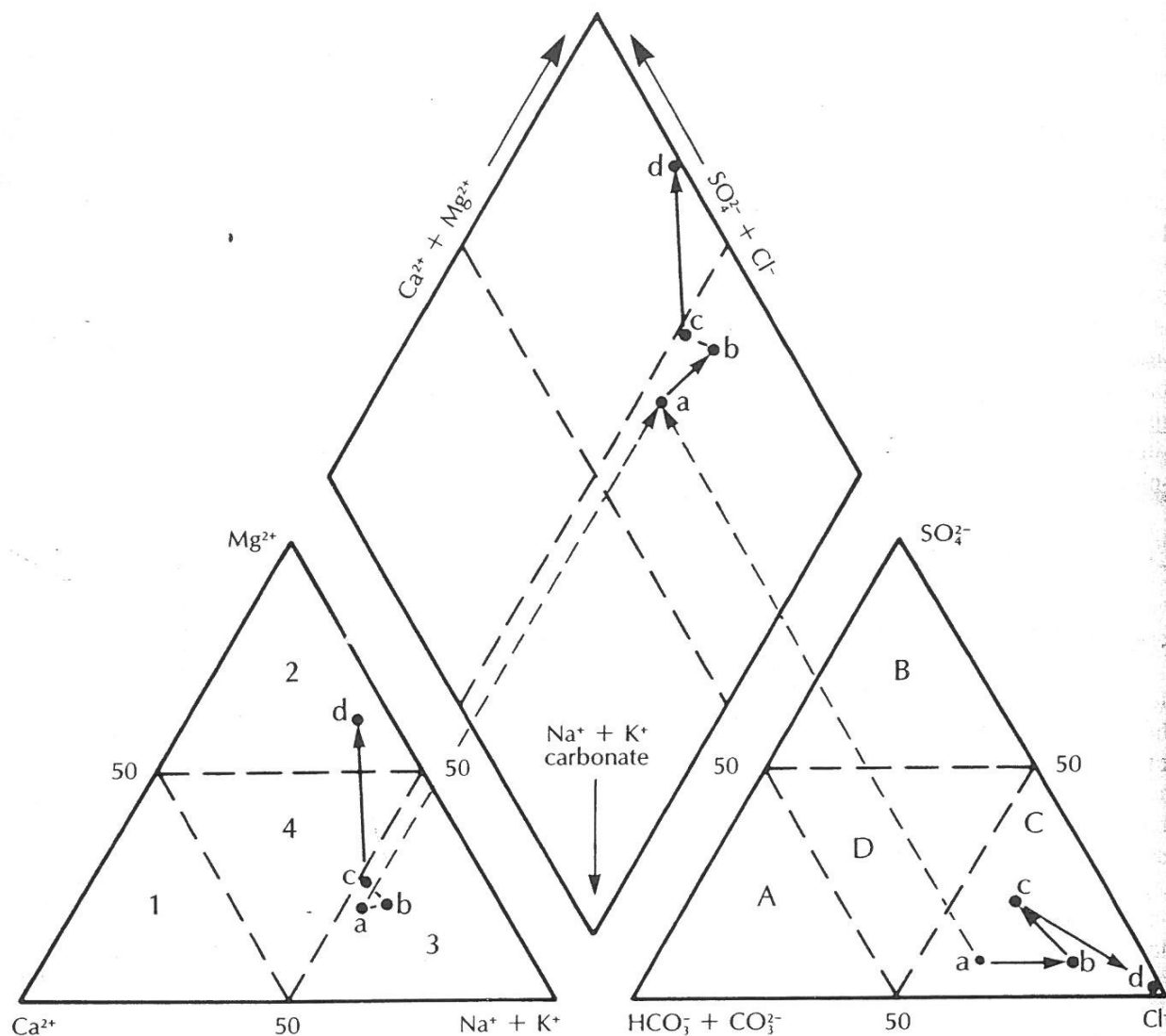


Figure 20.2 Piper diagram used to classify water on the basis of its chemical composition.

- | | |
|------------------|---------------------|
| 1. Ca-rich | A. bicarbonate-rich |
| 2. Mg-rich | B. sulfate-rich |
| 3. alkali-rich | C. chloride-rich |
| 4. mixed cations | D. mixed anions |

Data points are from the compositional triangle onto the diamond as shown by the dashed arrows. The waters are from the Dead Sea area: (a) Sea of Galilee; (b) Lake Tiberias; (c) Jordan River at Jericho; (d) Dead Sea, surface water (Livingstone, 1963, Table 51). The composition of the water in this drainage system changes from alkali chloride water (TDS ~ 500 mg/L) to a Mg-chloride brine (TDS $\sim 270,000$ mg/L). The compositions of water samples are plotted as percent milliequivalent per liter.

20.3 Chemical Composition of Meteoric Precipitation

The chemical composition of rain and snow is affected by processes that are characteristic of the atmosphere:

1. Dissolution of solid particles that serve as centers of nucleation for raindrops or snowflakes.
2. Dissolution of the gases of the atmosphere.
3. Discharge of anthropogenic contaminants into the atmosphere.

The solid particles (0.1–20 μm in diameter) include mineral grains derived from soil, volcanic ash, various kinds of combustion products, and salts derived from the surface of the ocean. *Hygroscopic* compounds such as NaCl , H_2SO_4 , and HNO_3 , which absorb water from the air and are very soluble in it, are especially effective in promoting condensation. The gases that dissolve in rainwater include CO_2 , SO_2 , and oxides of nitrogen, all of which not only occur naturally but also are released into the atmosphere as a result of combustion of fossil fuel. In the unpolluted atmosphere these gases react with water and molecular oxygen to form acids that cause rainwater to be naturally acidic.

For example, CO_2 gas reacts with water to form carbonic acid, which dissociates to form bicarbonate and hydrogen ions:



$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 10^{-7.83} \quad (20.2)$$

where the brackets represent the *activities* of ions and *fugacities* of gases (Section 9.2). If $[\text{CO}_2] = 3 \times 10^{-4} \text{ atm}$, the pH of rainwater is 5.68. However, where large amounts of SO_2 are released into the atmosphere by combustion of sulfur-bearing coal or by roasting of sulfide ore, the pH of rainwater may be significantly less than 5.68. Such *acid rain* promotes the dissolution of solid particles in the atmosphere, which affects the chemical composition of rain or snow. In addition, the acidification of surface water and soil is

harmful to plants and animals and therefore causes deterioration of the environment.

The chemical composition of rainwater varies between wide limits. The data in Table 20.2 and Figure 20.3 indicate that Na^+ and Cl^- are the dominant ions in coastal areas and in rain over the oceans and oceanic islands. However, the concentrations of these ions *decrease* rapidly with increasing distance from the coast, whereas the concentrations of Ca^{2+} and SO_4^{2-} may rise somewhat, as illustrated in Figure 20.3 for the Amazon basin of South America. Nevertheless, the average total dissolved solids of rainwater in the Amazon basin is only 1.3 mg/L compared to 11.8 mg/L in the coastal areas worldwide and 21.2 mg/L in rain over the oceans. Rain in the coastal areas of the United States has $\text{TDS} = 11.8 \text{ mg/L}$, whereas in the interior rain has $\text{TDS} = 7.0 \text{ mg/L}$ on the average.

The chloride ion in rainwater originates primarily from seawater in the form of NaCl crystals. Therefore, concentration ratios of the elements relative to Cl^- can be used to determine the presence of “excess” amounts of these elements in rain that are attributed to the dissolution of dust particles in the air and/or to anthropogenic pollution. Junge and Werby (1958) studied the distribution of Cl^- , Na^+ , K^+ , Ca^{2+} , and SO_4^{2-} in rainwater in the United States and calculated excess amounts of these elements relative to seawater based on equations of the form:

$$\left(\frac{\text{Na}}{\text{Cl}}\right)_r = \frac{\text{Na}_s + \text{Na}_x}{\text{Cl}_s} \quad (20.3)$$

where the subscripts refer to the rain (r), seawater (s), and excess (x).

A compilation of concentration ratios of ions in rainwater relative to Cl^- in Table 20.3 indicates that rain over the oceans and in coastal areas of the world resembles seawater in its chemical composition. For example, the Na^+/Cl^- and K^+/Cl^- ratios of rain over the oceans and in coastal areas differ from seawater values of these ratios by a factor of 1.3 or less. However, rain in these areas is somewhat *enriched* in Ca^{2+} and SO_4^{2-} compared to seawater, presumably because of the dissolution of mineral particles

Table 20.2 Chemical Composition of Meteoric Precipitation (in mg/L)

Region	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	pH
United States									
Coastal	3.68	0.24	—	0.58	4.83	2.45	—	—	—
Inland	0.40	0.20	0.10	1.4	0.41	3.0	1.20	0.30	—
Europe									
Coastal	11.4	0.60	1.51	1.09	20.1	6.35	1.80	0.45	4.87
Inland	0.64	0.20	0.22	0.78	1.27	3.02	1.42	0.28	4.74
U.S.S.R.	1.4	0.6	0.6	1.3	1.6	4.9	0.6	0.7	5.6
Australia									
southeast	2.46	0.37	0.50	1.2	4.43	trace	—	—	—
Japan	1.1	0.26	0.36	0.97	1.2	4.5	—	—	—
Oceans and islands of the world	5.79	0.31	0.47	0.89	11.0	2.44	0.21	0.075	5.0
World Average, coastal (<100 km)	3.45	0.17	0.45	0.29	6.0	1.45	—	—	—
Amazon River									
670 km inland	0.50	0.020	0.036	0.028	0.87	0.64	0.19	0.002	4.71
1700 km inland	0.23	0.039	0.024	0.056	0.30	0.55	0.25	0.007	5.32
1930 km inland	0.21	0.035	0.034	0.060	0.41	0.70	0.18	0.00	4.97
2050 km inland	0.12	0.094	0.012	0.056	0.24	0.56	—	—	5.04
2230 km inland	0.23	0.012	0.012	0.008	0.39	0.28	0.056	—	5.31
Peru 3000 km from Atlantic Ocean	0.039	0.039	0.020	0.184	0.12	0.18	—	—	5.67

Adapted from a compilation by Berner and Berner (1987).

derived from soil on islands and coastal areas. The abundance of Mg²⁺ in rain over the oceans and in coastal areas world-wide varies irregularly.

The data in Table 20.3 pertaining to rain along the coast and in the *interior* of the United States indicate significant *enrichments* in all five ions relative to seawater. This is especially true of inland rain, which is enriched in SO₄²⁻ by a factor of 52 with respect to seawater, followed by Ca²⁺ (34), K⁺ (23), Mg²⁺ (3.6), and Na⁺ (1.8). Rain in the coastal areas is also enriched in these ions, but the enrichment factors range only from 5.7 (Ca²⁺) to 1.4 (Na⁺). The regional variation of excess concentrations of these elements in rain over the United States was also documented by Munger and Eisenreich (1983).

20.4 Normative Minerals from Water Compositions

We now return to the discussion of river water and restate the obvious fact that its chemical composition is largely the result of the minerals that have dissolved in it. Consequently, it should be possible to use the chemical composition of water to identify these minerals and to calculate their relative abundances. Such a calculation was demonstrated by Garrels (1967) based in part on preceding work of Feth et al. (1964).

Before we proceed with the quantitative evaluation of the chemical composition of water, we recall some of the conclusions presented in earlier

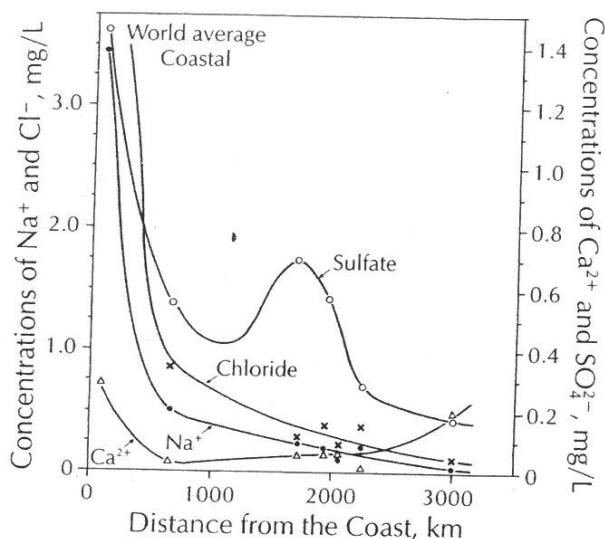


Figure 20.3 Variation of the major cations and anions in rainwater of the Amazon basin with distance from the Atlantic Ocean. The data for the Amazon basin in Table 20.2 are from Stallard and Edmond (1981) as compiled by Berner and Berner (1987).

chapters. For example, in Section 10.6 and in Chapter 12 we showed that the incongruent dissolution of aluminosilicate minerals commonly results in the formation of kaolinite, although other clay minerals or gibbsite may form in some

kinds of environments. In Chapter 14 we discussed the oxidation of Fe and showed the Fe^{2+} oxidizes to Fe^{3+} in the presence of molecular oxygen and subsequently precipitates as $\text{Fe}(\text{OH})_3$, which is ultimately converted to Fe_2O_3 (hematite). When we constructed equations to represent weathering reactions, we assumed that the necessary H^+ was provided by the environment, but we did not consider what reactions actually contribute the H^+ ions in most natural environments.

In order to interpret the chemical composition of water quantitatively we now refine our understanding of chemical weathering reactions:

1. Any H^+ required by the reaction is derived by dissociation of carbonic acid, which is in equilibrium with CO_2 whose partial pressure may exceed that of the atmosphere by a factor of 10 or more. Where pyrite/marcasite are present, H^+ may also originate by oxidation of these minerals and by the hydrolysis of Fe^{3+} to form $\text{Fe}(\text{OH})_3$.
2. Na^+ and Ca^{2+} ions in water originate by the incongruent dissolution of plagioclase to form kaolinite. Some Na^+ may be contributed by discharge of subsurface brines that previously interacted with evaporite rocks. Ca^{2+} may also be derived by dissolution of calcite, gypsum/anhydrite, or dolomite.

Table 20.3 Concentration Ratios of the Major Ions in Rainwater Relative to the Chloride Ion

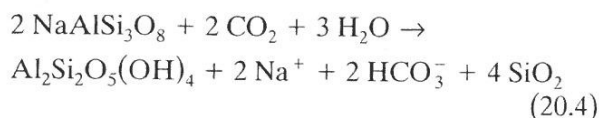
Ion	Seawater ⁽¹⁾	Rainwater ^{(2)a}			
		Oceans	Coastal Worldwide	Coastal U.S.	Inland U.S.
Na^+	0.56	0.53 (0.95)	0.58 (1.04)	0.76 (1.4)	0.98 (1.8)
K^+	0.021	0.028 (1.3)	0.028 (1.3)	0.050 (2.4)	0.49 (23)
Ca^{2+}	0.021	0.081 (3.9)	0.048 (2.3)	0.12 (5.7)	0.71 (34)
Mg^{2+}	0.067	0.043 (0.64)	0.075 (1.1)	—	0.24 (3.6)
SO_4^{2-}	0.14	0.22 (1.6)	0.24 (1.7)	0.51 (3.6)	7.3 (52)

^aNumbers in parentheses are enrichment factors relative to seawater.

SOURCES: (1) Berner and Berner (1987), Table 3.6; (2) Table 20.2, this book.

3. Mg^{2+} and K^+ are released by weathering of biotite. Additional Mg^{2+} comes from the solution of ferromagnesian minerals (olivine, pyroxenes, and amphiboles) or dolomite, and some K^+ is released by K-feldspar.
4. Silicic acid enters the water during weathering of silicate minerals, whereas quartz contributes almost none.
5. Sulfate ion is produced primarily by oxidation of sulfide minerals and by dissolution of gypsum/anhydrite or other sulfate minerals, or it originates from meteoric precipitation.
6. Chloride is likewise contributed by meteoric precipitation, by discharge to subsurface brines, and by fluid inclusions in minerals.
7. Bicarbonate forms from CO_2 gas and by dissolution of calcite and other carbonate minerals.
8. The concentration of Fe^{2+} in water is kept low by the formation of $\text{Fe}(\text{OH})_3$ except under strongly acid and reducing conditions.

The proportions of ions released by the incongruent dissolution of different aluminosilicate minerals can be determined from the appropriate equations, assuming that kaolinite is the stable phase. For *albite* we obtain:

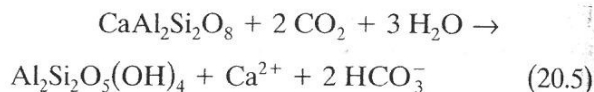


We balance this equation by assuming that Al is conserved and that H^+ is provided by the dissociation of carbonic acid, which produces both H^+ and HCO_3^- . The number of moles of HCO_3^- is determined from the requirement for *electrical neutrality*. In this case, the release of 2 moles of Na^+ requires that 2 moles of HCO_3^- appear as products of the reaction. Note that the HCO_3^- ions are derived entirely from CO_2 in this case, so that the ^{14}C content and the isotopic compo-

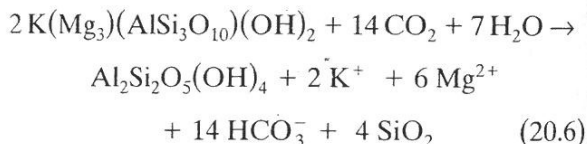
sitions of C and O of the bicarbonate ions depend on the source of the CO_2 (Section 16.4, 17.4, and 17.7).

The possible sources of CO_2 include the atmosphere, oxidation of biogenic carbon compounds in soil, oxidation of methane released by bacteria or by hydrocarbons in subsurface reservoirs, or decarbonation reactions of carbonate rocks being heated at depth. Note also that we represent silicic acid by " SiO_2 " because it is commonly expressed this way in chemical analyses of water. Therefore, the incongruent dissolution of one mole of albite releases one mole of Na^+ , one mole of HCO_3^- , and 2 moles of SiO_2 into the water.

Similarly, the weathering of *anorthite* is represented by the equation:



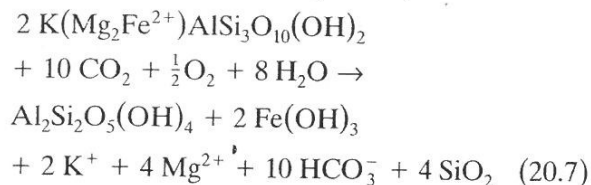
which indicates that dissolution of 1 mole of anorthite releases 1 mole of Ca^{2+} and 2 moles of HCO_3^- (but no SiO_2) into solution. *Biotite* is a bit more complicated because of its variable composition (Section 13.2b). We assume that any Fe^{2+} in the octahedral layer is oxidized to Fe^{3+} and subsequently precipitates as $\text{Fe}(\text{OH})_3$. Therefore, the Fe released into solution by biotite does not appear in the chemical analysis of the water. In the case of the Mg-mica *phlogopite*, the reaction is:



Evidently, 1 mole of phlogopite releases 1 mole of K^+ , 3 moles of Mg^{2+} , 7 moles of HCO_3^- , and 2 moles of SiO_2 into solution.

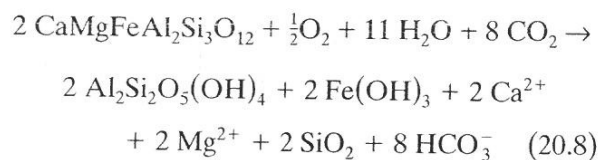
In *biotite*, some of the K^+ may be replaced by Na^+ , and the octahedral layer may contain Al^{3+} , Ti^{4+} , Fe^{3+} , Fe^{2+} , Mn^{2+} as well as Mg^{2+} . Moreover, more than one Si^{4+} in the tetrahedral layers may be replaced by Al^{3+} (Garrels, 1967). However, for

the sake of simplicity, we simulate the incongruent dissolution of *biotite* by the equation:



In this example, 1 mole of *biotite* reacts to form 1 mole of K^+ , 2 moles of Mg^{2+} , 5 moles of HCO_3^- , and 2 moles of SiO_2 . Note that $\frac{1}{2}$ mole of molecular oxygen is required to act as the acceptor of the electrons (oxidizing agent) released by Fe^{2+} .

Magnesium is also released by the incongruent dissolution of other ferromagnesian minerals such as the pyroxenes and amphiboles. The weathering of *proxene* is represented by the equation:



Each mole of this pyroxene releases 1 mole of Ca^{2+} , 1 mole of Mg^{2+} , 1 mole of SiO_2 , and 4 moles of HCO_3^- . The reactions of other minerals can be written in the same way, and the number of moles of ions released per mole of mineral are listed in Table 20.4.

We are now ready to examine the chemical composition of a sample of spring water from the Sierra Nevada Mountains in California (Garrels and Mackenzie, 1967), which has reacted with granitic igneous rocks composed primarily of feldspars, *biotite*, and quartz. The analysis of this water in Table 20.5 indicates that Ca^{2+} and HCO_3^- are the dominant ions, that the concentration of $\text{Na}^+ > \text{K}^+$ and $\text{Ca}^{2+} > \text{Mg}^{2+}$, TDS = 45.83 mg/L, and $\text{SiO}_2 = 16.4$ mg/L, which is unusually high compared to river water in Table 20.1.

We begin by converting the concentrations from milligrams per liter to micromoles per liter, followed by rounding to whole numbers. Next, we subtract the micromolar quantities of ions in melt-water derived from local snow (Garrels and Mackenzie, 1967). The concentrations of SO_4^{2-} and

Cl^- in the groundwater are thereby accounted for as well as 29% of K^+ , 24% of Mg^{2+} , 18% of Na^+ , and 13% of Ca^{2+} . Before we can distribute the remaining amounts of the ions among the minerals from which they originated, we check the solution for electrical neutrality. We find a small excess of negative charge (Table 20.5), which we correct by reducing HCO_3^- by 2 $\mu\text{mol/L}$, leaving 308 $\mu\text{mol/L}$.

Now we convert the 108 μmol of Na^+ in one liter of water into 108 μmol of albite. Therefore, we reduce SiO_2 in Table 20.5 by 216 μmol and HCO_3^- by 108 μmol , in accordance with the data in Table 20.4. The resulting amount of albite dissolved in one liter of water is:

$$\frac{108 \times 262.15}{1000} = 28.3 \text{ mg} \quad (20.9)$$

Next, we assign all of the Mg^{2+} to *biotite* and combine it with 11 μmol of K^+ , 22 μmol of SiO_2 , and 55 μmol of HCO_3^- consistent with the formula of *biotite* we adopted in equation 20.7. The Fe^{2+} of this *biotite* was oxidized to Fe^{3+} and formed solid $\text{Fe}(\text{OH})_3$ (equation 20.7). The amount of *biotite*, calculated as illustrated by equation 20.9 is 4.9 mg per liter of solution. The remainder of the K^+ is converted into K-feldspar, with proportional reductions of SiO_2 and HCO_3^- , yielding 2.5 mg of K-feldspar per liter of solution. Finally, we convert Ca^{2+} into 68 μmol of anorthite, which consumes all of the available HCO_3^- and is equivalent to 18.9 mg of anorthite dissolved in one liter of water.

We are left with a residue of 14 μmol of SiO_2 , which we attribute to the dissolution of 0.8 mg of amorphous SiO_2 and speculate that it may have been present in the soil or saprolite overlying the granitic bedrock.

The total amount of mineral matter of the granitic bedrock that dissolved per liter of water is 54.6 mg (excluding the amorphous silica). Therefore, the abundances of the minerals we have considered are albite, 51.8%; anorthite, 34.6%; K-feldspar, 4.6%; and *biotite*, 9.0%. The composition of the plagioclase that dissolved expressed by the abundance of albite (Ab), is:

$$\text{Ab} = \frac{108 \times 10^2}{108 + 68} = 61 \text{ mol \%} \quad (20.10)$$

Table 20.4 Number of Moles of Ions Released into Solution per Mole of Mineral^a in the Presence of CO₂ Gas

<i>Mineral</i>	<i>Na⁺</i>	<i>K⁺</i>	<i>Mg²⁺</i>	<i>Ca²⁺</i>	<i>SiO₂</i>	<i>HCO₃⁻</i>	<i>SO₄²⁻</i>
Albite, NaAlSi ₃ O ₈ ,	1	0	0	0	2	1	0
Anorthite, CaAl ₂ Si ₂ O ₈	0	0	0	1	0	2	0
Orthoclase, KAlSi ₃ O ₈	0	1	0	0	2	1	0
Biotite, K(Mg ₂ Fe)AlSi ₃ O ₁₀ (OH) ₂	0	1	2	0	2	5	0
Pyroxene, CaMgFeAl ₂ Si ₃ O ₁₂	0	0	1	1	1	4	0
Enstatite, MgSiO ₃	0	0	1	0	1	2	0
Diopside, CaMg(SiO ₃) ₂	0	0	1	1	2	4	0
Calcite, CaCO ₃	0	0	0	1	0	2	0
Dolomite, CaMg(CO ₃) ₂	0	0	1	1	0	4	0
Gypsum, CaSO ₄ · 2H ₂ O	0	0	0	1	0	0	1
Pyrite, FeS ₂	0	0	0	0	0	0	2
<i>Formula Weights</i>							
albite	262.2				pyroxene (eq. 20.8)		450.3
biotite (eq. 21.7)	448.7				calcite		100.1
K-feldspar	278.3				dolomite		184.4
anorthite	278.1				anhydrite		136.1
diopside	216.5				pyrite		120.0

^aNote that aluminosilicates are assumed to dissolve incongruently to kaolinite and that Fe-bearing minerals form Fe(OH)₃.

Recalling the fictitious geochemist A. O. Alba from Section 8.3 we identify the plagioclase that dissolved in the water as *andesine* (Ab₅₀ to Ab₇₀). However, the plagioclase in the rocks probably was more Na-rich than andesine because anorthite is *more* susceptible to dissolution than albite (Section 19.3). In addition, the rock may well have contained quartz, magnetite, zircon, and other accessory minerals that resist chemical weathering.

The reconstruction of the minerals dissolved in a sample of water provides a clue to the kinds of rocks with which the water has interacted. In the water from the Sierra Nevada, the composition of the solute is consistent with the expected weathering products of granitic igneous or metamorphic rocks when allowance is made for differences in the relative susceptibilities of rock-forming silicate minerals.

Table 20.5 Reconstruction of the Minerals That Contributed Ions to a Sample of Groundwater from the Sierra Nevada Mountains, California

	Na^+	K^+	Mg^{2+}	Ca^{2+}	SiO_2	HCO_3^-	SO_4^{2-}	Cl^-	mg	Wt. %
Analysis										
mg/L	3.03	1.09	0.70	3.11	16.4	20.0	1.0	0.5		
$\mu\text{mol/L}$	132	28	29	78	273	328	10	14		
Snow, $\mu\text{mol/L}$	24	8	7	10	3	18	10	14		
Net $\mu\text{mol/L}$	108	20	22	68	270	310	0	0		
Electric neutrality, $\mu\text{eq/L}$			308+			310-				
Adjusted $\mu\text{mol/L}$	108	20	22	68	270	308	0	0		
Albite, $\mu\text{mol/L}$	0	20	22	68	54	200	0	0	28.3	51.8
Biotite, $\mu\text{mol/L}$	0	9	0	68	32	145	0	0	4.9	9.0
K-feldspar, $\mu\text{mol/L}$	0	0	0	68	14	136	0	0	2.5	4.6
Anorthite, $\mu\text{mol/L}$	0	0	0	0	14	0	0	0	18.9	34.6
Amorph. silica, $\mu\text{mol/L}$	0	0	0	0	0	0	0	0	0.8	—
									54.6 ^a	100

^aExcluding the amorphous silica.

SOURCE: Garrels and Mackenzie (1967).

Bedrock containing significant amounts of sulfide minerals causes water that interacts with it to become enriched in sulfate and in certain *chalcophile* and *siderophile* elements identified in Table 8.2, such as Cu, Co, Ni, Zn, Mo, Ag, As, Sb, Se, and Te, which form soluble salts with the most abundant anions in groundwater. The presence of unusual concentrations of these elements in water samples is used in *geochemical prospecting* surveys (discussed in Chapter 22) to locate deposits of "mineralized" rocks below the surface of the Earth.

In order to demonstrate the relationship between the mineral composition of the rocks in a watershed and the resulting chemical composition of water, we consider a water sample of as yet unidentified origin in Table 20.6. The water conforms to the normal pattern in the sense that Ca^{2+} and HCO_3^- are dominant, $\text{Na}^+ > \text{K}^+$, and $\text{Ca}^{2+} > \text{Mg}^{2+}$; however, TDS = 430 mg/L compared to only 46 mg/L in the spring water from the Sierra Nevada, and the concentration of SiO_2 is low at 6.0 mg/L. In addition, the analysis includes NO_3^- and PO_4^{3-} and the pH = 7.7.

We correct the analysis for meteoric precipitation using the composition of average inland rain

in the United States in Table 20.2. The concentration of HCO_3^- in average inland rain was estimated from equation 20.2 for $[\text{CO}_2] = 3 \times 10^{-4}$ atm to be 2 $\mu\text{mol/L}$. A check of the electrical balance among the remaining ions reveals an excess of 15 μeq of negative charge, which we correct by arbitrarily decreasing HCO_3^- by that amount, thereby decreasing its concentration by only 0.3%.

The small amount of SiO_2 in this water is assigned to 50 μmol of albite, and the chloride is combined with Na^+ to make 1060 μmol of NaCl. The large amount of Mg^{2+} in the water suggests the presence of dolomite, but its amount is limited by HCO_3^- to 1118.5 μmol , which leaves a residue of 871.5 μmol of Ca^{2+} and 152.5 μmol of Mg^{2+} . We combine the remaining Ca^{2+} with SO_4^{2-} to make 871.5 μmol of anhydrite (CaSO_4) and use up the K^+ as 41 μmol K_2SO_4 , which is a common ingredient in mixed fertilizers. Similarly, the 58 μmol of PO_4^{3-} are attributed to fertilizer in the form of $\text{NH}_4\text{H}_2\text{PO}_4$, where the NH_4^+ is assumed to have oxidized to NO_3^- after application. The small amounts of Na^+ , Mg^{2+} , SO_4^{2-} , and NO_3^- are now arbitrarily assigned to 29 μmol NaNO_3 and 152.5 μmol of MgSO_4 , although other choices are certainly possible. These

Table 20.6 Reconstruction of Minerals Dissolved in the Water of an Unidentified Stream

	Na^+	K^+	Mg^{2+}	Ca^{2+}	SiO_2	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	PO_4^{3-}
Analysis										
mg/L	31	3.4	31	81	6.0	274	101	38	6.6	5.5
$\mu\text{mol/L}$	1348	87	1275	2021	100	4491	1097	1072	106	58
Rain, $\mu\text{mol/L}$	17	5	4	35	0	2	31	12	19	0
Net $\mu\text{mol/L}$	1331	82	1271	1986	100	4489	1066	1060	87	58
Electrical neutrality, $\mu\text{eq/L}$			7927+				7942-			
Adjusted $\mu\text{mol/L}$	1331	82	1271	1990	100	4474	1066	1060	87	58
Albite, $\mu\text{mol/L}$	1281	82	1271	1990	0	4474	1066	1060	87	58
NaCl, $\mu\text{mol/L}$	221	82	1271	1990	0	4474	1066	0	87	58
Dolomite, $\mu\text{mol/L}$	221	82	152.5	871.5	0	0	1066	0	87	58
Anhydrite, $\mu\text{mol/L}$	221	82	152.5	0	0	0	194.5	0	87	58
K_2SO_4 , $\mu\text{mol/L}$	221	0	152.5	0	0	0	153.5	0	87	58
$NH_4H_2PO_4$, $\mu\text{mol/L}$	221	0	152.5	0	0	0	153.5	0	29	0
$NaNO_3$, $\mu\text{mol/L}$	192	0	152.5	0	0	0	153.5	0	0	0
$MgSO_4$, $\mu\text{mol/L}$	192 ^a	0	0	0	0	0	1	0	0	0

^aThe apparent excess of positively charged ions was caused in part by our choice to treat NO_3^- as NH_4^+ .

alternatives do not affect the clear evidence that the water in Table 20.6 originated by dissolution of very different minerals than that in Table 20.5.

This point is emphasized in Table 20.7 in which the micromolar amounts of the minerals are expressed in terms of weight percent. The results indicate that dolomite, anhydrite, and halite contributed 89% of the solute and an additional 3% was derived from silicate minerals represented by albite. The remaining 8% can be attributed to various kinds of fertilizers, implying that the watershed of this stream is being farmed. The dominant minerals reflected in the chemical composition of the water are characteristic of carbonate-evaporite rocks of marine origin. Soluble minerals like halite and anhydrite may be present in subsurface, and their ions may enter the stream as effluent of saline groundwater. The SiO_2 may have been contributed by weathering of detrital silicate minerals in the carbonate rocks or in shale, by weathering of volcanic ash or igneous rocks, or by dissolution of silicate minerals in transported regolith such as till.

In fact, the water sample we have been discussing was collected from the Great Miami River at West Carrollton is southwestern Ohio. The river drains marine carbonate-evaporite rocks of early to middle Paleozoic age that are overlain by Wisconsinan and Illinoian till and

Table 20.7 Abundances of Minerals That Dissolved to Form the Water Presented in Table 20.6.

Mineral	$\mu\text{mol/L}$	mg/L	Weight %
albite	50	13.1	3.0
halite	1060	61.9	14.2
dolomite	1118.5	206.2	47.5
anhydrite	871.5	118.6	27.3
K_2SO_4	41	7.1	1.6
$NH_4H_2PO_4$	58	6.7	1.5
$NaNO_3$	29	2.5	0.6
$MgSO_4$	152.5	18.4	4.2
Totals		434.5	99.9

outwash deposits derived from the Precambrian Shield of Canada north of Ohio. Evidently, the chemical composition of the water in the Great Miami River *does* reflect the geology of its watershed.

Reconstructions of minerals are most appropriate for surface water whose chemical composition has *not* been altered by ion exchange and/or precipitation of insoluble compounds. However, mixed waters that have interacted with different kinds of rocks also provide meaningful information about the geology of the watershed from which they originated.

20.5 Evaporative Concentration

Since the chemical composition of water in streams depends on the minerals that have dissolved in it, we now consider whether these minerals can *precipitate* if the water is subjected to evaporative concentration. We already know that chemical weathering of most minerals is an *irreversible* process, and therefore we do *not* expect that evaporative concentration of water can reverse weathering. We recall that silicate minerals containing Al and Fe dissolve *incongruently*. Therefore, the ions that go into solution represent only a fraction of the original minerals. Although we can use these ions and molecules to *calculate* the amounts of the minerals that dissolved, the process is not reversible unless the ions are able to react with the appropriate secondary minerals that formed during incongruent dissolution. The weathering of sulfide minerals is commonly accompanied by the oxidation of S^{2-} to SO_4^{2-} and by the precipitation of some of the metals, so that these minerals also weather irreversibly. Even the carbonate mineral *dolomite* does not precipitate from aqueous solutions, except under unusual conditions defined in terms of the salinity and Mg/Ca ratio of the solution (Folk and Land, 1975). Other examples of the irreversibility of mineral dissolution reactions occur in the geochemistry of SiO_2 (Section 9.6) and $CaSO_4$ (Section 10.1).

Nevertheless, evaporative concentration is an important process that can change not only the

concentrations of the dissolved ions and molecules in natural water but also the *composition* of the solute (see Section 18.3). As a result, evaporative concentration of surface water may result in the formation of brines of widely differing chemical compositions and can lead to the deposition of minerals that may form nonmarine *evaporite rocks*. These rocks may be composed of calcite, dolomite, anhydrite, and a wide variety of other evaporative minerals of potential economic value. Some lacustrine carbonate rocks in the Green River Formation of Wyoming and its correlatives in Colorado and Utah contain *kerogen* in sufficient concentrations to warrant calling them *oil shale* (Eugster, 1985).

The carbonate ions of groundwater discharged by springs are not in equilibrium with CO_2 of the atmosphere. Therefore, the activities of the carbonate ions and the pH of spring water change rapidly as equilibrium is established after the water is discharged by the spring. Subsequently, the activities of all ions may increase as a result of the progressive evaporation of water, and ultimately compounds may precipitate when their ion activity products (IAP) exceed the solubility product constants (K_{sp}). Garrels and Mackenzie (1967) carried out the necessary calculations to model the evaporative concentration of spring water from the Sierra Nevada Mountains of California and concluded that the compounds most likely to form are calcite, gypsum, sepiolite, and amorphous silica. As a result, the water is depleted in Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and SiO_2 (H_4SiO_4). In addition, it is enriched in Na^+ , K^+ , and Cl^- , and its pH rises to 10 or higher.

The changes in the chemical composition of spring water from the Sierra Nevada Mountains as a result of evaporative concentration are displayed graphically in Figure 20.4 according to Garrels and Mackenzie (1967). *Calcite* precipitates first and, as water continues to evaporate, the concentration of Ca^{2+} declines, whereas that of HCO_3^- increases because the original water contained more HCO_3^- than Ca^{2+} . *Sepiolite* precipitates next after the concentrations of Mg^{2+} and SiO_2 have tripled. Dolomite does not form under these conditions because of unfavorable

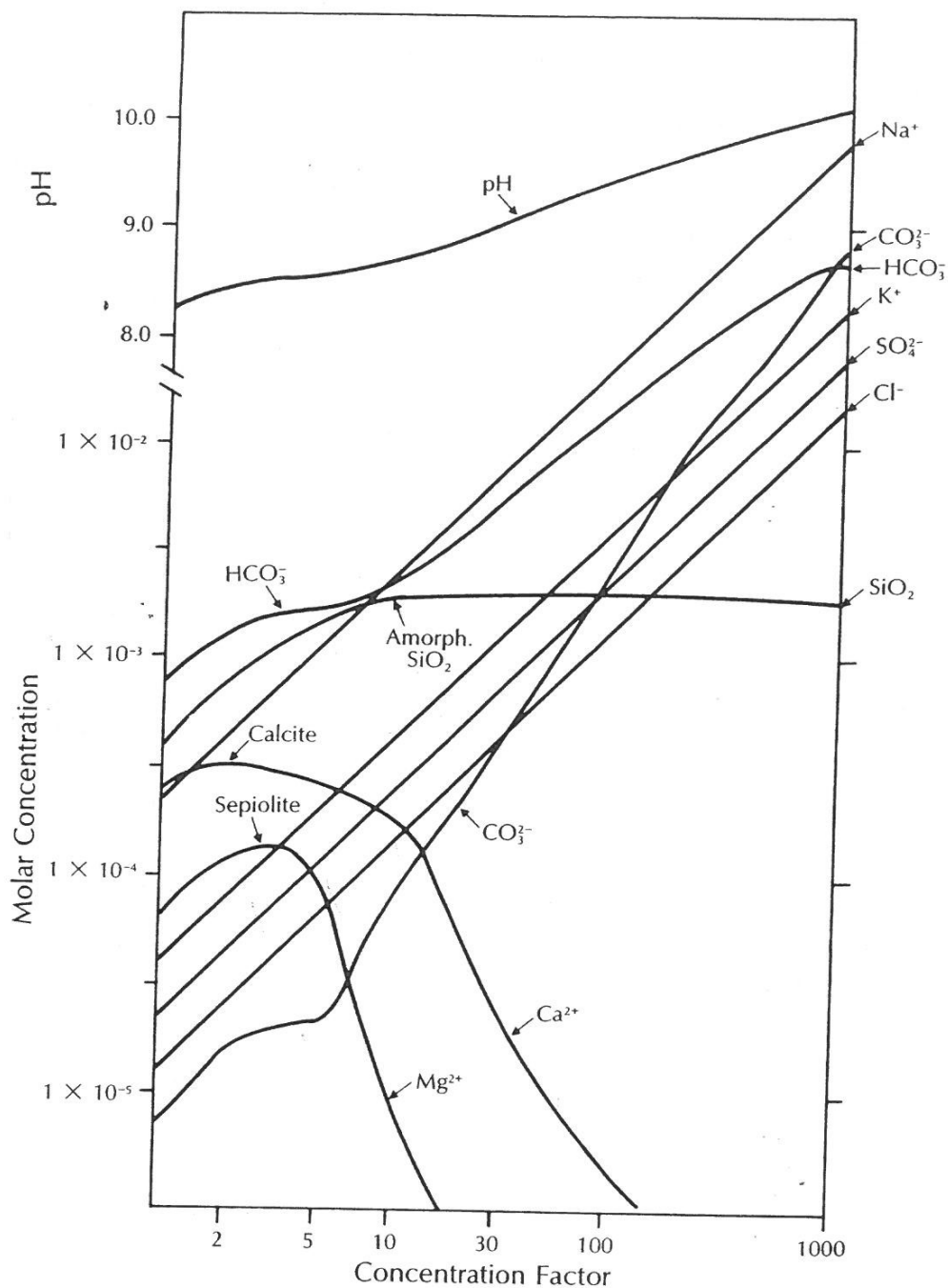
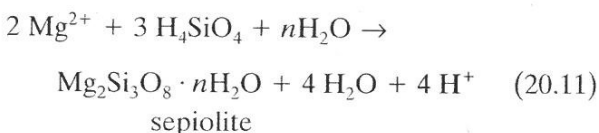


Figure 20.4 Evolution of spring water from the Sierra Nevada Mountains, California, as a result of evaporative concentration and the precipitation of calcite, sepiolite, and amorphous silica. Note that calcite precipitation caused by continuing loss of water depletes the water in Ca^{2+} but enriches it in carbonate ions because the mole ratio $\text{Ca}^{2+}/(\text{CO}_3^{2-} + \text{HCO}_3^-)$ of the spring water is less than one. Similarly, the water is depleted in Mg^{2+} but enriched in SiO_2 by sepiolite precipitation because the $\text{Mg}^{2+}/\text{SiO}_2$ ratio is less than one. The concentration of SiO_2 in the brine is ultimately held constant by the precipitation of solid amorphous SiO_2 . The result of a 1000-fold increase in the concentration of dissolved species caused by loss of water is a $\text{Na} + \text{K} + \text{carbonate} + \text{sulfate} + \text{chloride}$ brine (adapted from Garrels and Mackenzie, 1967).

kinetics, even though the solution becomes supersaturated with respect to dolomite. Progressive evaporation and continuing precipitation of sepiolite force Mg^{2+} out of the solution but cause the concentration of SiO_2 to rise. The solution ultimately becomes supersaturated with respect to amorphous SiO_2 (concentration factor = 10). Subsequently, the concentration of SiO_2 in the solution remains constant in equilibrium with solid amorphous SiO_2 (Section 9.6).

In this case the concentrations of Na^+ , K^+ , Cl^- , and SO_4^{2-} increase continuously with progressive evaporation because the chlorides, sulfates, and carbonates of the alkali metals are very soluble in water. Gypsum cannot form in this case because the water was depleted in Ca^{2+} by the precipitation of calcite. The pH of the water in the spring rises initially from 6.8 to 8.2 as the water equilibrates with CO_2 of the atmosphere ($P_{\text{CO}_2} = 10^{-3.5}$ atm) at 25°C and stabilizes temporarily at about 8.5 while sepiolite precipitates because that reaction releases H^+ :



After sepiolite precipitation ceases, the pH rises and reaches a value of about 10.1 at a concentration factor of 1000. The increase in the pH causes the concentration of CO_3^{2-} to rise even more rapidly than the progress of the evaporation because of the dissociation of bicarbonate ion.

The calculation of Garrels and Mackenzie (1967) are based on familiar concepts of aqueous geochemistry and lead to plausible conclusions regarding the evolution of the water they treated. Compounds of Na^+ and K^+ precipitate only after the brines have become so highly concentrated that the Debye-Hückel theory no longer applies and the more complete treatment of ion interactions by Pitzer (1973) must be used. Alternatively, the crystallization of minerals from highly concentrated brines may be predicted by means of the appropriate ternary phase diagrams used by Hardie and Eugster (1970).

The results of these initial attempts to model the evolution of saline lakes demonstrate that

brines of widely diverging chemical compositions can form by progressive evaporation of water and precipitation of compounds. The evolutionary paths depend on the operation of several *geochemical divides* (Section 10.1) associated with the precipitation of calcite, gypsum, and sepiolite. The subject was summarized by Eugster and Hardie (1978), Eugster and Jones (1979), Al-Droubi et al. (1980), and Drever (1982). The principles and resulting computational schemes have been used to explain the chemical compositions of many saline lakes, including Great Salt Lake in Utah (Spencer et al., 1985a,b), Lake Magadi in Kenya (Jones et al., 1977), Lake Chad in west central Africa (Al-Droubi et al., 1976; Eugster and Maglione, 1979), and many others included in the study of Hardie and Eugster (1970).

The concept of a *geochemical divide* was first discussed in Section 10.1 in connection with the precipitation of gypsum. We now return to this topic to consider more specifically how such a geochemical divide works based on an illustration by Drever (1982). We assume that the concentrations of Ca^{2+} and SO_4^{2-} in a *saturated* solution of gypsum are such that:

$$(\text{Ca}^{2+}) = 2(\text{SO}_4^{2-}) \quad (20.12)$$

and that the applicable activity coefficients are both equal to unity. Since the solubility product constant of gypsum is $10^{-4.6}$ (Table 10.1), the application of the Law of Mass Action yields:

$$2(\text{SO}_4^{2-})(\text{SO}_4^{2-}) = 10^{-4.6} \quad (20.13)$$

from which it follows that:

$$(\text{SO}_4^{2-}) = 3.54 \times 10^{-3} \text{ mol/L}$$

$$(\text{Ca}^{2+}) = 7.09 \times 10^{-3} \text{ mol/L}$$

When one liter of this solution is evaporated until the volume of the remaining water is $1/n$, where n is the concentration factor, x moles of gypsum are forced to precipitate and the concentrations of the ions in equilibrium with gypsum are modified accordingly:

$$(\text{SO}_4^{2-}) = n[(3.54 \times 10^{-3}) - x] \quad (20.14)$$

$$(\text{Ca}^{2+}) = n[(7.09 \times 10^{-3}) - x] \quad (20.15)$$

If the ions remain in equilibrium with gypsum,

$$n[(3.54 \times 10^{-3}) - x]n[(7.09 \times 10^{-3}) - x] = 10^{-4.6} \quad (20.16)$$

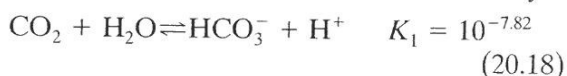
which yields the quadratic equation:

$$n^2[x^2 - (10.63 \times 10^{-3})x + (25.1 \times 10^{-6})] = 10^{-4.6} \quad (20.17)$$

This equation was solved for x for preselected values of n ranging from 1 to 100. The resulting values of x were then used to calculate the concentrations of Ca^{2+} and SO_4^{2-} from equations 20.14 and 20.15.

The results in Figure 20.5 show that the molar concentration of Ca^{2+} increases, whereas that of SO_4^{2-} decreases, with increasing values of n . In other words, as gypsum continues to precipitate in the course of evaporative concentration, the brine is enriched in Ca^{2+} and depleted in SO_4^{2-} . The decisive criterion is the cation/anion ratio of the solution at the initial point of saturation. The ion that dominates initially is ultimately concentrated in the brine, whereas the less abundant ion is depleted. Hence we can justifiably describe this phenomenon as a *geochemical divide*.

The computations required to predict the chemical evolution of spring water to form brines begin with the equilibrium of the carbonate species in water with CO_2 gas of the atmosphere. For this purpose we assume that $T = 25^\circ\text{C}$, $P = 1$ atm, $[\text{CO}_2] = 10^{-3.5}$ atm, and $[\text{H}_2\text{O}] = 1.0$, following Hardie and Eugster (1970). Therefore, the bicarbonate ion is related to carbon dioxide by:



Since $[\text{CO}_2] = 10^{-3.5}$ atm,

$$[\text{HCO}_3^-] = \frac{10^{-11.32}}{[\text{H}^+]} \quad (20.19)$$

and

$$(\text{HCO}_3^-) = \frac{10^{-11.32}}{\gamma_{\pm 1}[\text{H}^+]} \quad (20.20)$$

Similarly,



and therefore:

$$[\text{CO}_3^{2-}] = \frac{10^{-10.3}[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{10^{-21.62}}{[\text{H}^+]} \quad (20.22)$$

$$(\text{CO}_3^{2-}) = \frac{10^{-21.62}}{\gamma_{\pm 2}[\text{H}^+]^2} \quad (20.23)$$

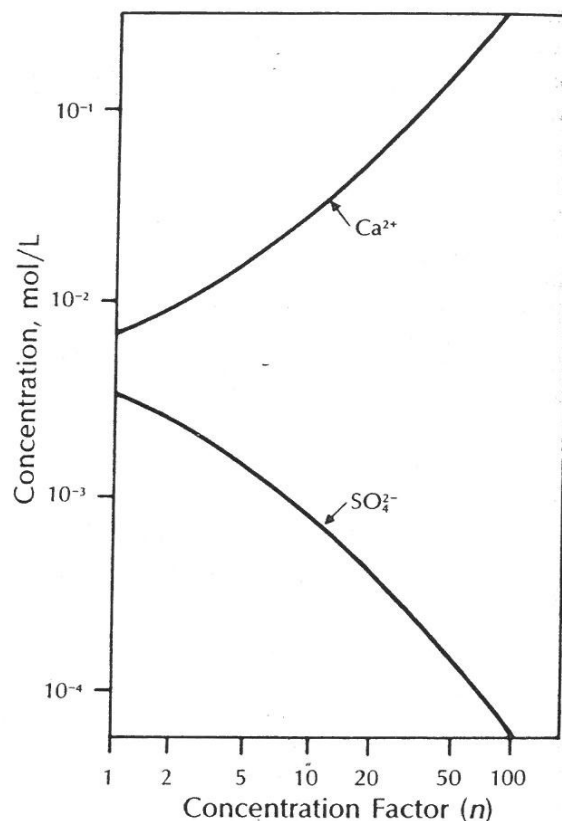


Figure 20.5 Operation of a geochemical divide caused by the precipitation of gypsum from a saturated solution as a result of progressive loss of water by evaporation. The concentration of Ca^{2+} increases and that of SO_4^{2-} decreases because the concentration of Ca^{2+} in the saturated solution before any gypsum precipitated ($n = 1$) was *twice* that of the SO_4^{2-} concentration. The concentrations of the ions were calculated by solving equation 20.17 for selected values of n and substituting the resulting values of x into equations 20.14 and 20.15.

In addition, the dissociation of water leads to the relation:

$$(\text{OH}^-) = \frac{10^{-14}}{\gamma_{\pm 1}[\text{H}^+]} \quad (20.24)$$

Since the water must maintain electrical neutrality as the carbonate ions equilibrate with CO_2 of the atmosphere, we have the requirement that the major ions must always satisfy the equation:

$$\begin{aligned} 2(\text{CO}_3^{2-}) + (\text{HCO}_3^-) + (\text{OH}^-) \\ = 2(\text{Ca}^{2+}) + 2(\text{Mg}^{2+}) + (\text{Na}^+) + (\text{K}^+) \\ - 2(\text{SO}_4^{2-}) - (\text{Cl}^-) \end{aligned} \quad (20.25)$$

Note that all of the pH-dependent ions are assembled on the *left* side and that the molar concentrations of SO_4^{2-} , Cl^- , and any other anions not related to the carbonate equilibria are moved to the *right* side of the electrical-neutrality equation. The concentrations of all of the ions on the right side of equation 20.25 are known from the chemical analysis of the water. By substituting equations 20.20, 20.23, and 20.24 into equation 20.25, we obtain:

$$\frac{2 \times 10^{-21.62}}{\gamma_{\pm 2}[\text{H}^+]^2} + \frac{10^{-11.32}}{\gamma_{\pm 1}[\text{H}^+]} + \frac{10^{-14}}{\gamma_{\pm 1}[\text{H}^+]} = A \quad (20.26)$$

where

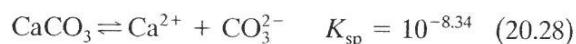
$$\begin{aligned} A = 2(\text{Ca}^{2+}) + 2(\text{Mg}^{2+}) + (\text{Na}^+) + (\text{K}^+) \\ - 2(\text{SO}_4^{2-}) - (\text{Cl}^-) \end{aligned} \quad (20.27)$$

In order to solve equation 20.26 for $[\text{H}^+]$ we must first determine the activity coefficients for CO_3^{2-} , HCO_3^- , and OH^- from the Debye-Hückel theory (Section 10.3) based on the ionic strength (I) of the solution. However, we cannot calculate the ionic strength accurately because the concentrations of the ions related by the carbonate equilibria change as a result of the equilibration of the water with CO_2 of the atmosphere. We are therefore confronted by a dilemma: in order to calculate the concentrations of the carbonate ions and the pH of the water we must *know* their concentrations. The impasse is circumvented by making a series of successive approximations. We first calcu-

late I from the analysis of the water and hence determine the activity coefficients, which then allow us to solve equation 20.26 for $[\text{H}^+]$. We then use that value to calculate (HCO_3^-) , (CO_3^{2-}) , and (OH^-) from equations 20.20, 20.23, and 20.24, respectively. These values are then used to recalculate I and a new set of activity coefficients until the $[\text{H}^+]$ and the resulting concentrations of HCO_3^- , CO_3^{2-} , and OH^- , determined by successive iterations, become constant. Only after this computation has been carried out are we able to proceed with the calculations of the effects of evaporative concentration.

We begin this process by doubling the concentrations of all ions. Next, we repeat the calculations required to maintain the carbonate ions and pH in equilibrium with CO_2 of the atmosphere. Then we calculate the IAPs of compounds that may precipitate and compare them to the respective K_{sp} values.

When *calcite* begins to precipitate from the water, the ions must maintain equilibrium with it:



and therefore:

$$[\text{Ca}^{2+}] = \frac{10^{-8.34}}{[\text{CO}_3^{2-}]} \quad (20.29)$$

Substituting equation 20.22 yields:

$$[\text{Ca}^{2+}] = \frac{10^{-8.34}[\text{H}^+]^2}{10^{-21.62}} = 10^{13.28}[\text{H}^+]^2 \quad (20.30)$$

and

$$(\text{Ca}^{2+}) = \frac{10^{13.28}[\text{H}^+]^2}{\gamma_{\pm 2}} \quad (20.31)$$

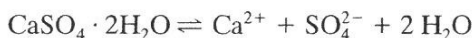
Evidently, Ca^{2+} is now a pH-dependent species and must be transferred to the left side of the electrical neutrality equation (20.25):

$$\begin{aligned} 2(\text{CO}_3^{2-}) + (\text{HCO}_3^-) + (\text{OH}^-) - 2(\text{Ca}^{2+}) \\ = 2(\text{Mg}^{2+}) + (\text{K}^+) + (\text{Na}^+) - 2(\text{SO}_4^{2-}) - (\text{Cl}^-) \end{aligned} \quad (20.32)$$

Once again we must determine activity coefficients from the Debye-Hückel theory by recalculating

lating the ionic strength of the solution until the H^+ ion activity indicated by equation 20.32 reaches a constant value.

The entire calculation must be repeated each time the concentrations are doubled until a second salt begins to precipitate. If that salt is *gypsum*, we must include it in the equation for electrical neutrality:



$$K_{sp} = 10^{-4.6} \quad (20.33)$$

$$[SO_4^{2-}] = \frac{10^{-4.6}}{[Ca^{2+}]} \quad (20.34)$$

Since Ca^{2+} is also in equilibrium with calcite, it must satisfy equation 20.30:

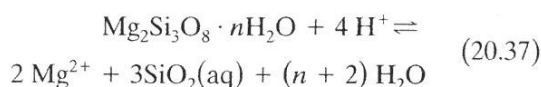
$$[SO_4^{2-}] = \frac{10^{-4.6}}{10^{13.28}[H^+]^2} = \frac{10^{-17.88}}{[H^+]^2} \quad (20.35)$$

Therefore, equation 20.35 expresses the activity of SO_4^{2-} in equilibrium with both *calcite* and *gypsum* in a solution that is also in equilibrium with CO_2 of the atmosphere. The equation for electrical neutrality is now written:

$$2(CO_3^{2-}) + (HCO_3^-) + (OH^-) - 2(Ca^{2+}) + 2(SO_4^{2-}) = 2(Mg^{2+}) + (Na^+) + (K^+) - (Cl^-) \quad (20.36)$$

which is then solved by iteration for the $[H^+]$ of the solution.

If *sepiolite* begins to precipitate after the onset of calcite formation, it is included in the calculation. According to Hardie and Eugster (1970),



where $K_{sp} = 10^{18.8}$. Therefore:

$$[Mg^{2+}] = \left(\frac{10^{18.8}[H^+]^4}{[SiO_2]^3} \right)^{1/2} = \frac{10^{9.4}[H^+]^2}{[SiO_2]^{3/2}} \quad (20.38)$$

and

$$(Mg^{2+}) = \frac{10^{9.4}[H^+]^2}{\gamma_{\pm 2}[SiO_2]^{3/2}} \quad (20.39)$$

If calcite and sepiolite precipitate together, the equation for electrical neutrality becomes:

$$2(CO_3^{2-}) + (HCO_3^-) + (OH^-) - 2(Ca^{2+}) - 2(Mg^{2+}) = (Na^+) + (K^+) - 2(SO_4^{2-}) - (Cl^-) \quad (20.40)$$

If calcite, sepiolite, and gypsum precipitate together, (SO_4^{2-}) expressed by equation 20.35 must be included among the pH-dependent species of the left side of equation 20.40.

This procedure requires knowledge of activity coefficients of the ions in brines formed by evaporative concentration. In addition, it is clear that the computations are *unmanageable* without the aid of a *computer*. In fact, Hardie and Eugster (1970) wrote a computer program to carry out the calculations outlined above and applied it to more than 60 water samples.

The chemical evolution predicted by Hardie and Eugster (1970) for average North American river water (Livingstone, 1963) is illustrated in Figure 20.6 by means of two equilateral triangles similar to those devised by Piper (1944). The diagram shows that *calcite* precipitates first, causing the water to become depleted in Ca^{2+} and $CO_3^{2-} + HCO_3^-$. As a result, the composition of the water initially moves away from the Ca^{2+} and carbonate corners or the cation and anion triangles, respectively. Since the molar $Ca^{2+}/(HCO_3^- + CO_3^{2-})$ ratio of this water is greater than one, calcite precipitation virtually eliminates carbonate ions from the solution *before* all of the Ca^{2+} has been removed. The cation path then turns away from the Mg^{2+} corner because *sepiolite* precipitates next. As evaporation continues, the concentration of Ca^{2+} rises until *gypsum* begins to precipitate. Continued precipitation of gypsum and sepiolite eventually depletes the water in Ca^{2+} and Mg^{2+} , leaving Na^+ and K^+ as the principal cations. When gypsum precipitation started, the mole ratio of Ca^{2+}/SO_4^{2-} was *less* than one. Therefore, an excess of SO_4^{2-} remains after Ca^{2+} has been virtually eliminated

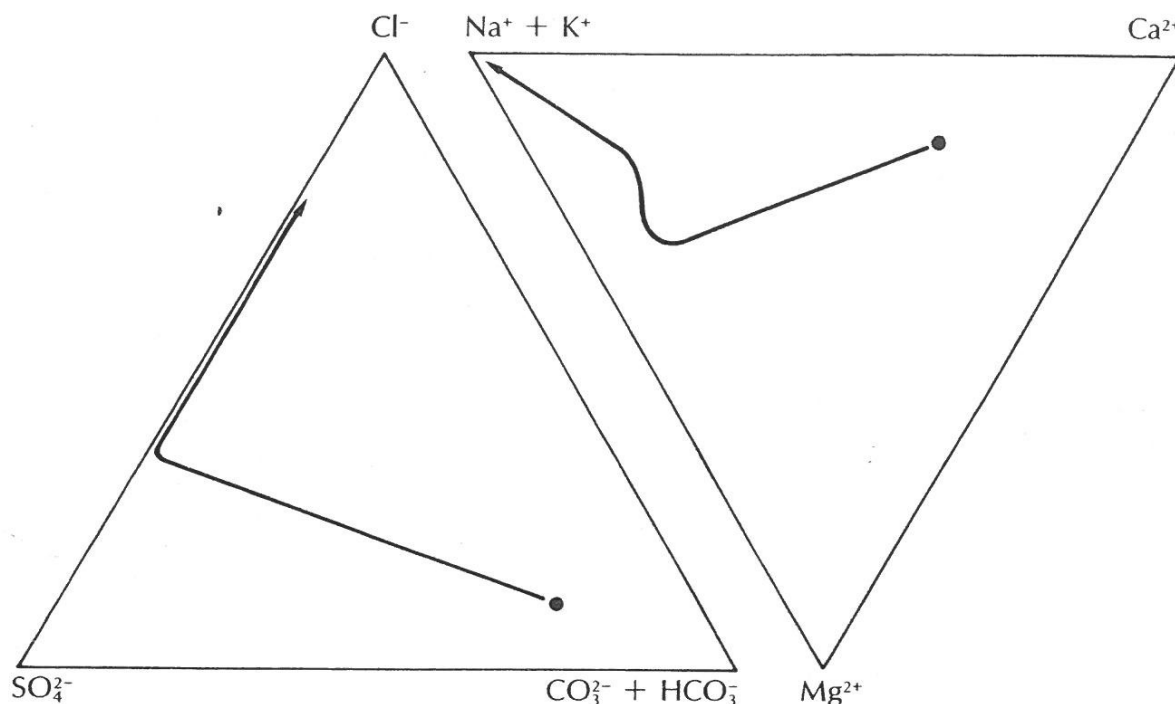


Figure 20.6 Chemical evolution of average North American river water (Livingstone, 1963) as a result of evaporative concentration according to Hardie and Eugster (1970). Calcite precipitates first, depleting the water in Ca^{2+} and carbonate ions. Since the molar $\text{Ca}^{2+}/(\text{CO}_3^{2-} + \text{HCO}_3^-)$ ratio of the water was initially greater than one, some Ca^{2+} remains when the carbonate ions are exhausted. Sepiolite precipitates next, causing the composition of the water to move away from the Mg^{2+} corner but not altering the anion composition. The abundance of Ca^{2+} rises because of the continuing loss of water until gypsum begins to precipitate. Continuing precipitation of sepiolite and gypsum depletes the water in Ca^{2+} and Mg^{2+} and enriches it in Na^+ and K^+ . At the end (ionic strength = 5.0) some SO_4^{2-} remains because the molar $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio at the onset of gypsum precipitation was greater than one. The final result is $\text{Na} + \text{K} + \text{Cl} + \text{SO}_4$ brine depleted in Ca^{2+} , Mg^{2+} , and carbonate ions (adapted from Hardie and Eugster, 1970).

from the solution. The end result is a $\text{Na} + \text{K} + \text{Cl} + \text{SO}_4$ brine depleted in Ca^{2+} , Mg^{2+} , and carbonate ions.

The chemical evolution of surface water as a result of evaporative concentration was represented by Hardie and Eugster (1970) by a flow-sheet, as shown in Figure 20.7A. *Calcite* precipitates first, either *depleting* the brine in Ca^{2+} and enriching it in carbonate ions (path I) or *enriching* the brine in Ca^{2+} and depleting it in carbonate (path II), depending on the initial molar $\text{Ca}^{2+}/(\text{CO}_3^{2-} + \text{HCO}_3^-)$ ratio. If the water takes path I, it may become supersaturated with respect to *sepiolite* as evaporation continues. In that case, all Mg^{2+} may be removed

(path IA), or all silica may be removed (path IIA), as more and more water evaporates. Water that follows paths I and IA becomes depleted in alkaline earths and forms an alkali metal-carbonate-sulfate-chloride brine exemplified by Lake Magadi in Kenya. Note that water that becomes enriched in Ca^{2+} (path II) may also precipitate sepiolite, but this is not shown explicitly in the diagram. If the water takes either path II or I plus IIA, continued evaporative concentration may enrich it in alkaline earths to the point of *gypsum* precipitation. As a result, the water may evolve into a sulfate-rich and Ca-poor brine (path III) or into a Ca + Mg-rich but sulfate-poor brine (path IV). Path III leads to

brines that are enriched in alkali metals, sulfate, and chloride like Great Salt Lake in Utah, whereas path IV produces alkali metal-alkaline earth-chloride brines exemplified by Bristol Dry Lake in California.

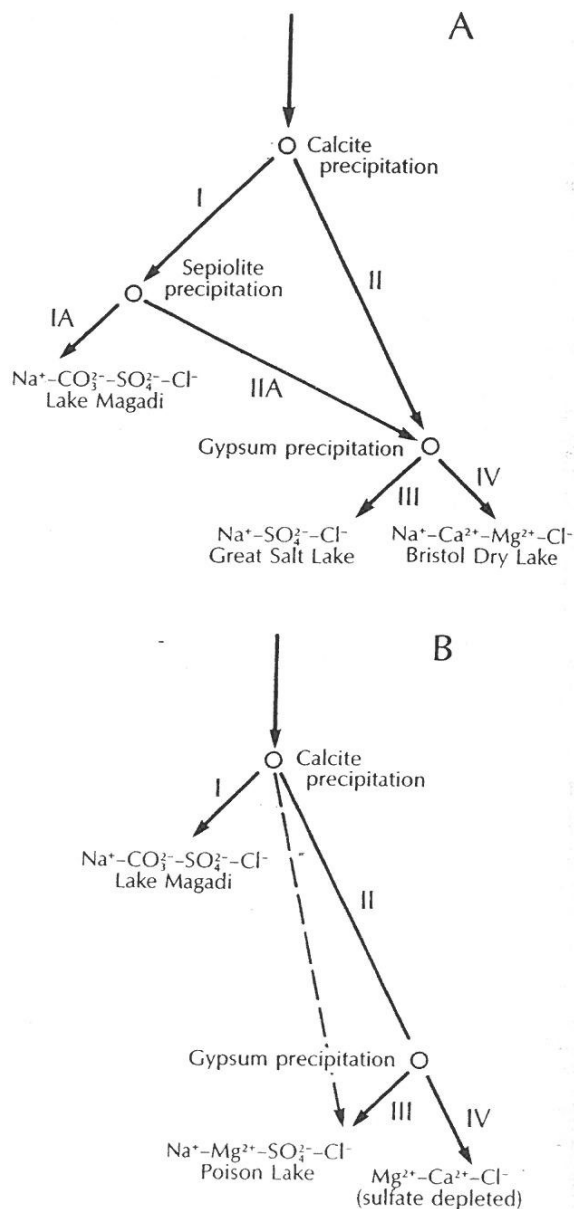
The evolutionary pathways in Figure 20.7A do not explain the origin of certain Mg-rich brines found in Little Manitou Lake in Saskatchewan and Poison Lake in Washington. For Mg-rich brines to be produced, the formation of *sepiolite* must be inhibited either by a process that removes silicic acid from the water or by a failure of sepiolite to nucleate. If Mg^{2+} is *not* removed, then two kinds of Mg-rich brines may form, as suggested in Figure 20.7B. Path II leads to gypsum precipitation and produces either a Mg sulfate (Ca-poor) brine (path III, Poison Lake) or a Mg + Ca + Cl (sulfate-poor) brine (path IV).

The point of this discussion is that a wide variety of brines may form by evaporative concentra-

tion of surface water. The mechanism depends on the operation of geochemical divides associated with the precipitation of compounds that deplete the water in either the cation or the anion, depending on their molar ratio. As a result of this process, small differences in the *initial* chemical composition of surface water in neighboring drainage basins may

Figure 20.7 A. Chemical evolution of surface water as a result of precipitation of calcite, sepiolite, and gypsum during evaporative concentration. Calcite precipitates first, and the water becomes depleted in Ca^{2+} (path I) or enriched in Ca^{2+} (path II) as evaporation of water continues. Sepiolite may precipitate next, causing the water to become depleted in Mg^{2+} (path IA) or enriched in Mg^{2+} (path IIA). The diagram implies, but does not show explicitly, that water enriched in Ca^{2+} (path II) may also precipitate sepiolite. Ultimately such waters (paths II and IIA) become supersaturated with respect to gypsum and are then either enriched in sulfate and depleted in Ca^{2+} (path III) or depleted in sulfate and enriched in Ca^{2+} (path IV).

B. Flowsheet devised to explain the formation of Mg-rich brines. If sepiolite does not form because it does not nucleate or because the concentration of H_4SiO_4 is too low, then Mg-rich brines can form by precipitation of calcite and gypsum (path II). After gypsum has precipitated, path III leads to Mg sulfate brines, whereas path IV produces Mg + Ca + Cl brines. A Mg sulfate brine may also form directly after removal of Ca^{2+} by calcite precipitation as indicated by the dashed arrow (adapted from Hardie and Eugster, 1970).



be amplified to produce brines of quite different chemical compositions.

The treatment of this process by Hardie and Eugster (1970) was limited by the failure of the Debye-Hückel theory to account for ion interactions in concentrated electrolyte solutions. Recent advances in the quantitative treatment of ion interactions by Pitzer (1973, 1979, and 1987) have made it possible to predict the solubilities of compounds in electrolyte solutions having ionic strengths of up to 20. Such calculations are exem-

plified by the work of Harvie et al. (1982, 1984), Weare (1987), and Møller (1988), which permit the study of brine evolution under a wide range of chemical and geological conditions.

The computations required to make these kinds of calculations are quite time-consuming and therefore require the use of computers. In fact, the study of the geochemistry of natural waters is so complex that computer-based models are required to carry out the necessary computations. Several such programs are listed in Table 20.8.

Table 20.8 Computer Programs for Modeling the Chemical Compositions of Water

<i>Name</i>	<i>Purpose</i>	<i>Reference</i>
WATEQ	chemical equilibria of natural waters	Truesdell and Jones (1974)
WATEQF	chemical equilibria of natural waters (Fortran IV)	Plummer et al. (1976)
EVAPOR	chemical composition of water and amount of salt precipitated by progressive concentration	Al-Droubi et al. (1976)
EQUIL	ionic speciation and degree of saturation with respect to selected minerals and salts	Al-Droubi et al. (1976)
DISSOL	incongruent dissolution of minerals in water and formation of secondary minerals	Al-Droubi et al. (1976)
MINEQL	chemical equilibria in aqueous solution	Westall et al. (1976)
ISOTOP	modeling of ^{13}C and ^{14}C in groundwater	Reardon and Fritz (1978)
GEOCHEM	ionic speciation of soil water	Sposito and Mattigod (1980)
PHREEQ	chemical equilibria in aqueous solution	Parkhurst et al. (1980)
WATEQ2	major and trace-element speciation in aqueous solution	Ball et al. (1980)
EQCALC	thermodynamic properties of reactions at elevated P and T	Flowers (1985)
SALTNORM	calculation of normative salts from chemical composition of natural water	Bodine and Jones (1986)

The mineral deposits that form by the evaporation of water in saline lakes and in isolated marine basins are important sources of certain industrial raw material including compounds of Li, B, Na, Mg, S, Cl, K, and Ca. In addition, such deposits may contain kerogen, zeolites, and certain clay minerals that have desirable chemical or physical properties. The occurrence, composition, and origin of evaporite rocks have been described by Stewart (1963), Braitsch (1971), Kirkland and Evans (1973), and Sonnenfeld (1984).

20.6 Water Quality

The chemical composition of water determines its suitability for human consumption, for use in the operation of household appliances, as drinking water for domestic animals, for irrigation of agricultural land, and for its many uses in the manufacturing industry. Each of these uses requires the water to meet certain standards that define its *quality*. The chemical composition is one of the principal criteria of the quality of water. Also considered are biological oxygen demand, chemical oxygen demand, specific conductance, hardness, alkalinity, presence of harmful trace metals and organic compounds, turbidity, temperature, and other properties as required for specific uses (Hem, 1985).

Biological oxygen demand (BOD) is the weight of oxygen consumed per unit volume of sample by the oxidation of organic matter in the water when oxygenated water is added.

Total organic carbon (TOC) includes all forms of organic matter such as live microorganisms, suspended particles, and dissolved molecules. It is determined by measuring the amount of CO_2 produced by burning of the dry residue of the water sample.

Chemical oxygen demand (COD) is a measure of the amount of oxidizable organic matter in a water sample that reacts with a strong oxidizing agent. The amount of oxidizing agent consumed by the reaction, expressed in equivalents of oxygen, is the COD of the sample.

Total dissolved solids (TDS) is determined either by weighing the residue after evaporating a known weight of the water or by summing the concentrations of ions and molecules based on a complete chemical analysis.

Specific conductance reflects the concentration of ions in a water sample and is therefore related to TDS. However, the relationship is only empirical and does not hold for complex solutions like seawater.

Alkalinity is defined as the ability of a water sample to react with H^+ ions and is based primarily on the presence of carbonate and bicarbonate ions. The determination is made by titration and depends on the pH of the solution because of its effect on the distribution of carbonate species (Section 10.4).

Hardness is expressed in terms of the concentrations of Ca^{2+} and Mg^{2+} because these ions react with soap to form insoluble compounds and precipitate as carbonates and sulfates when the water is heated. The hardness is the sum of the milliequivalent weights of Ca^{2+} and Mg^{2+} per liter, which is then converted to milligrams of CaCO_3 per liter:

$$\text{hardness} = \left(\frac{2(\text{Ca}^{2+})}{\text{at. wt. Ca}} + \frac{2(\text{Mg}^{2+})}{\text{at. wt. Mg}} \right) \times \frac{\text{mol. wt. CaCO}_3}{2} \quad (20.41)$$

where (Ca^{2+}) and (Mg^{2+}) are the concentrations in mg/L. The hardness has no geochemical significance but helps to evaluate the quality of water for domestic use.

Acidity is the capacity of water to react with hydroxyl ions and reflects the presence of H^+ , Fe^{2+} , and HSO_4^- ions. It may be expressed as the equivalent concentration of H^+ or H_2SO_4 .

The quality of water for human consumption not only is affected by the concentrations of the *major* ions but depends also on the presence of *trace* amounts of other metals, non-metals, and organic compounds, many of which become toxic above certain levels. These trace

elements and compounds may dissolve in the water as a result of chemical weathering of rocks and minerals (Salomons and Förstner, 1984). They may also be released into the hydrologic cycle by human activities, in which case they are called *contaminants*. When the concentration of a contaminant is large enough to make the water unfit for use, the contaminant is classified as a *pollutant*.

The contamination of surface water in lakes and streams takes many forms, most of which degrade its quality. For example, Beeton (1965) documented a 36% increase of TDS in Lake Ontario and Lake Erie from 1900 to 1960. The increase was caused by discharges of various kinds of wastewaters, dumping of solid waste into the lakes, and deposition of particles from the air. In addition deforestation, farming, and construction projects increase the rate of erosion, which in turn increases the amount of sediment in suspension and accelerates chemical weathering.

The introduction of nutrients such as P, N, and K by agricultural and urban runoff stimulates growth of plants, especially algae, and other unicellular organisms. The subsequent decay of organic matter in the water consumes dissolved oxygen and the lack of sufficient oxygen may ultimately kill fish and other organisms in the water. The process leading to this condition is called *eutrophication*. Lakes and streams affected by this process are degraded because of the unpleasant odor that emanates from the water, because of the accumulation of dead fish and algal slime on the beaches, and because these conditions detract from the recreational use of the water bodies.

The consequences of the contamination of the environment were brought to our attention by Rachel L. Carson through her popular books (Carson, 1951, 1962). Although her warnings initially went unheeded, others eventually took up the cause of *environmental science* and helped us to become aware that our activities are changing the world in ways we had not anticipated (Turk et al., 1972). The growing public concern about the possible deterioration of the environment is

expressed in many forms including the annual publication of the *State of the World* by the World Watch Institute of Washington, D.C. (Brown et al., 1988). The Environmental Protection Agency (EPA) of the United States government now sets and enforces standards for the purity of *drinking water* that cover not only metals and nonmetals and their ions but also organic compounds used as pesticides, industrial solvents, fuels, dyes, etc. (U.S. Environmental Protection Agency, 1975, 1976).

The authority of the EPA to set standards for the quality of drinking water is based on the Safe Drinking Water Act (U.S. Public Law 93-523). The *maximum contaminant levels* (mcl) established by the EPA are based on the known toxicity to humans of elements and compounds at a daily rate of consumption of 2 L/day per person and include appropriate safety factors. In addition, the EPA has specified analytical procedures for the determination of each contaminant. The Congress has further directed each state to set standards for the quality of water in lakes, streams, and bodies of seawater (Public Law 92-500, Section 302). These standards are intended to protect recreational users of such water bodies, the animals that live in or on them, and the persons who hunt and fish these waters. The consumers of fish, shellfish, and waterfowl may be "at risk" because of the phenomenon of *bioaccumulation* of toxic elements and compounds in the food chain. The water-quality standards for surface water are supposed to take this phenomenon into consideration, based on what is called the "latest scientific knowledge."

Virtually all elements become toxic or detrimental to human health at some level of intake, especially in cases of prolonged exposure. Therefore, the permissible concentrations of the most toxic elements in drinking water listed in Table 20.9 have been set at conservative levels. Among the most toxic elements and compounds in drinking water are arsenic, cadmium, chromium, lead, manganese, mercury, silver, selenium; the chlorinated hydrocarbons endrin, lindane, and toxaphene; the chlorophenoxys 2,4-D and

Table 20.9 Primary and Secondary Water-Quality Standards and Sources of Contamination for Selected Elements and Compounds in Drinking Water

<i>Element or compound</i>	<i>Acceptable concentration, mg/L</i>	<i>Sources of contamination</i>
<i>Cations and anions</i>		
Arsenic	0.05	herbicide used on land and water
Barium	1.0	barite (BaSO_4) and witherite (BaCO_3)
Cadmium	0.01	mine tailings and industrial effluents
Chromium	0.05	industrial effluents
Copper	1.0	aquatic herbicide
Iron	0.3	minerals of Fe
Lead	0.05	industrial effluents and uses
Manganese	0.05	minerals of Mn
Mercury	0.002	minerals of Hg, antifungal agent, combustion of coal and petroleum, mining and smelting of Hg
Silver	0.05	bactericide
Zinc	5	natural occurrence
Fluoride	2.0	industrial effluent
Chloride	250	natural occurrence
pH	6.5–8.5	NaCl brines
Nitrate (as N)	10	acid rain, mine drainage, industrial effluent
Selenium	0.01	farm runoff
Sulfide	0.002	natural occurrence, fertilizer, combustion of coal and paper
Sulfate	250	oxidation of organic matter
TDS	500	oxidation of sulfides, oilfield brines, brine lakes
		evaporative concentration, discharge of brines

Table 20.9 (continued)

Element or compound	Acceptable concentration, mg/L	Sources of contamination
<i>Chlorinated hydrocarbons</i>		pesticides
Endrin	0.0002	
Lindane	0.004	
Methoxychlor	0.1	
Toxaphene	0.005	
<i>Chlorophenoxys</i>		herbicides
2,4-D	0.1	
2,4,5-TP (Silvex)	0.01	
<i>Radioactivity</i>		
Ra	5 pCi/L	
Gross alpha	15 pCi/L	
Gross beta	4 millirem/yr	

SOURCE: U.S. Environmental Protection Agency (1986).

2,4,5-TP (Silvex) and the radioactivity in terms of Ra and emitters of α and β radiation. The dispersion of Pb is discussed in Chapter 25.

These elements and compounds are present in water partly or entirely because they are released into the environment by the activities of the human population and are therefore classified as *anthropogenic contaminants*. However, virtually all elements and many compounds also occur naturally as a consequence of chemical weathering of rocks or as a result of chemical reactions in nature. These *natural contaminants* may constitute a natural hazard to humans and other life forms living in areas where they are present.

20.7 Summary

In order to assess the rate of movement of elements and compounds from the continents into the oceans, we need to know the average chemical compositions of the world's major rivers and their total annual discharge. This information is not easy to obtain because streams are complex sys-

tems whose chemical compositions vary as a function of both time and space. Moreover, the chemical load of streams takes many forms that need to be considered in selecting appropriate methods of sampling and analysis. The information available for many of the major rivers is not as good as we would like it to be.

The chemical composition of surface water varies because of geological factors and because of the discharge of domestic, agricultural, and industrial wastewaters. Several different schemes have been devised to classify surface waters based on their chemical composition. However, genetic classifications are troubled by the problem that the chemical composition of surface water cannot be attributed to a unique source.

The chemical composition of rainwater on the continents depends on the abundance of salts derived from seawater, which decreases with distance from the coast; the dissolution of mineral particles in the atmosphere; and the presence of anthropogenic contaminants. In general, rain in the interior of the United States is strongly enriched in K^+ , Ca^{2+} , and SO_4^{2-} relative to Cl^- in seawater and slightly enriched in Na^+ and Mg^{2+} .

The chemical composition of surface water can be used to calculate the abundances of the rock-forming minerals that dissolved in it. The results are instructive because they provide information about the geology of the watershed and about the agricultural and industrial activity on it.

When water at the surface of the Earth evaporates, the concentrations of ions increase until salts begin to precipitate. The removal of ions by precipitation causes major changes in the chemical composition of the evolving brines. In most cases, calcium carbonate is the first compound to precipitate, followed by sepiolite and sometimes by gypsum, depending on the chemical composition of the brine and the extent of evaporative concentration.

The precipitation of a compound as a result of progressive evaporative concentration constitutes a geochemical divide. If the initial molar ratio of the cation and anion of a particular salt in the water was *greater* than the ratio in that compound, then the water ultimately becomes enriched in the cation and is depleted in the anion, and vice versa. The occurrence of geochemical divides during evaporative concentration explains why brines of widely differing chemical compositions can form from seemingly

similar surface waters. The minerals precipitated in saline lakes may accumulate to form valuable nonmarine evaporite deposits containing salts of Li, B, Na, K, Ca, Mg, and other elements.

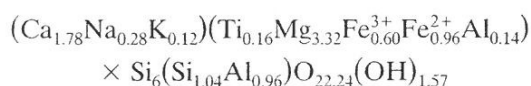
The computations necessary to predict the chemical evolution of brines during evaporative concentration are virtually unmanageable without the aid of computers. The same is true of calculations to determine the ionic speciation of natural waters, the composition of salts they contain, and the ion activity coefficients for electrolyte solutions whose ionic strength exceeds the range at which the Debye-Hückel theory applies.

The quality of water is expressed in terms of certain defined parameters and by the concentrations of toxic elements or compounds whose presence may constitute a health hazard to humans, domestic animals, and wildlife. The toxic elements and compounds may have natural and/or anthropogenic sources. The natural sources of many trace elements are rocks that contain minerals of these elements, some of which have economic value. Therefore, in the next chapter we discuss the presence of these metals in water, soil, vegetation, and atmospheric or soil gases and how they may be used to discover mineral deposits.

Problems

1. Calculate the total amount of Ca^{2+} transported annually to the oceans from North America based on the data in Table 20.1. Express the result in grams per year.

2. Write an equation for the chemical weathering of hornblende to kaolinite and ions, including HCO_3^- . The formula for hornblende is:



Assume that Ti forms solid $\text{Ti}(\text{OH})_4$ and that Fe forms $\text{Fe}(\text{OH})_3$ (Garrels, 1967).

3. Calculate the abundances of minerals that reacted with water from the Tsurukabato area of Japan to give it the following chemical composition (Takamatsu et al., 1981): $\text{Na}^+ = 7.2 \text{ mg/L}$, $\text{K}^+ = 0.77 \text{ mg/L}$, $\text{Ca}^{2+} = 13.2 \text{ mg/L}$, $\text{Mg}^{2+} = 0.79 \text{ mg/L}$, $\text{SiO}_2 = 15.5 \text{ mg/L}$, $\text{Cl}^- = 6.5 \text{ mg/L}$, $\text{SO}_4^{2-} = 10.4 \text{ mg/L}$, $\text{HCO}_3^- = 33.6 \text{ mg/L}$. Use an appropriate analysis of rainwater from Table 20.2. What kinds of rocks interacted with this water?

4. Calculate the variations of the concentrations of Ca^{2+} and SO_4^{2-} as a result of progressive precipitation of gypsum during evaporative concentration of a solu-

tion saturated with respect to gypsum in which initially $(\text{Ca}^{2+}) = 3(\text{SO}_4^{2-})$. Plot the results for a range of concentration factors from 1 to 100.

5. What should be the pH of the water in Problem 3 after it has equilibrated with $[\text{CO}_2] = 3 \times 10^{-4} \text{ atm}$?

6. At what value of the enrichment factor n does the water in Problem 3 first reach saturation with respect to calcite as a result of evaporative concentration?

7. Calculate the "hardness" of the water in Problem 3.

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Chemical Weathering of Mineral Deposits

Mineral deposits of all kinds are distinguished from ordinary rocks by the fact that they contain certain valuable minerals in uncommon concentrations. When these kinds of rocks are exposed to chemical weathering, the elements they contain can be dispersed by geological and geochemical processes. The presence of some of these elements in surface water or soil can constitute a health hazard. On the other hand, their dispersal patterns in soil or surface water can also be used to locate the rocks from which they originated. Many geochemists are engaged in the search for mineral deposits by means of geochemical surveys because the metals or compounds that can be recovered from them are of vital importance to society (Chapter 1).

In this chapter, we want to apply all of the relevant information available to us to consider the dispersal of a few selected metals and to outline how such knowledge is used to search for mineral deposits. The principles of geochemical exploration will then lead us to consider questions regarding the present and future availability of mineral resources.

21.1 Metallic Mineral Deposits

The term *mineral deposit* is applied to rocks that contain minerals that either have useful intrinsic physical or chemical properties or from which metals can be extracted by appropriate metallurgical procedures. Such rocks may be igneous, sedimentary, or metamorphic in origin. In addition, some mineral deposits form by filling of fractures

or cavities within the host rock, by replacement of the original minerals, or by the accumulation of chemical weathering products (Park and MacDiarmid, 1970; Cox and Singer, 1986; Barnes, 1988; Dennen, 1989).

The dispersal of elements from mineral deposits depends primarily on the solubility of their minerals under the conditions that can occur at the surface of the Earth and at shallow depth. Since we have already considered the solubility of the common rock-forming silicate and oxide minerals in Chapters 12 and 19, we concentrate our attention in this chapter on the *sulfides*. Consequently, we will discuss the geochemical properties of the *chalcophile* elements identified in Figure 8.3 (including Cu, Zn, Ag, Hg, Pb, As, and Sb) as well as some *siderophile* elements (Fe, Co, Ni, and Mo), which also form sulfide minerals. The elements we have just listed are important industrial metals that are recovered by mining their *ore deposits* and by smelting their ore minerals.

In this connection, an *ore deposit* is defined as a volume of rock containing one or more ore minerals in *sufficient* concentration that one or several metals can be recovered from it *at a profit*. Evidently, the distinction between a *metallic mineral deposit* and an *ore deposit* is based partly on *economic considerations*, such as the price of the metals to be recovered, the cost of the mining operation, and the initial investment of funds needed to bring the mine into production. Each of these factors depends on a multitude of other geological, geographical, economic, legal, and

even political circumstances that determine whether a mineral deposit can be mined profitably (Harris, 1984).

The geologic aspects that must be considered in the evaluation of a mineral deposit include:

1. The amount of ore in the deposit.
2. The concentrations of recoverable metals.
3. The depth of the orebody below the surface.
4. The shape of the orebody.
5. The hardness of the surrounding rocks.
6. The availability of water at the site.
7. The presence of elements whose release may be harmful to the environment.
8. The disposal of waste rock and necessary treatment of water.

These geological factors affect the choice of the mining method to be used and hence the investment of capital required to bring a mine into production. The mining method that is chosen also plays a role in determining the cost of operating the mine and hence the profit margin.

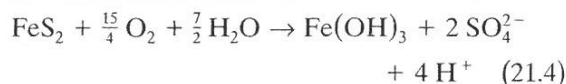
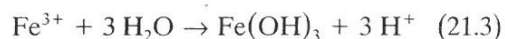
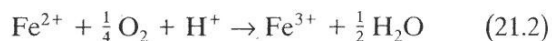
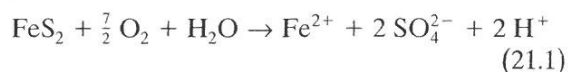
The chemical weathering of sulfide minerals is accompanied by the oxidation of the sulfide ions to sulfate or to native sulfur. In addition, some metals (Fe, Cu, Hg, As, etc.) also change oxidation state. Hence, we are concerned here with oxidation-reduction reactions presented in Chapter 14. In Section 14.1 we considered the oxidation of pyrite or marcasite to solid ferric hydroxide and sulfate ions, whereas in Section 14.5 we constructed stability diagrams for the oxides, carbonate, and sulfides of Fe in coordinates of Eh and pH (Figures 14.5–14.11).

21.2 Oxidation of Iron Sulfides and the Role of Bacteria

We now resume the discussion of the oxidation of pyrite because it is commonly associated with sulfides of other metals in mineral deposits hosted in igneous, sedimentary, and metamorphic rocks. In

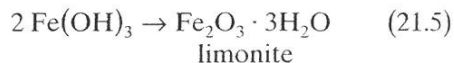
addition, pyrite occurs in many hydrothermal vein deposits formed over a wide range of temperatures, it occurs in coal and associated carbonaceous shale, and it is a common accessory mineral in carbonate rocks (limestone and dolomite), which may be quarried as building stone, for road construction, or for metallurgical applications.

The oxidation of pyrite to solid ferric hydroxide can be subdivided into a series of steps (Stumm and Morgan, 1981):



Equation 21.4, which is equivalent to equation 14.13, illustrates several important points regarding the oxidation of pyrite:

1. Ferric hydroxide is an insoluble base, which means that pyrite is ultimately converted to *limonite* by the transformation of ferric hydroxide:

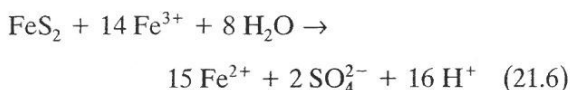


The limonite may accumulate to form a special type of saprolite known as *gossan*.

2. The oxidation of Fe^{2+} to Fe^{3+} is a slow process having a half-time of ~ 1000 days at $\text{pH} = 3$ (Stumm and Morgan, 1981). Therefore, Fe^{2+} may be *transported* by the movement of water before precipitation of ferric hydroxide takes place. This means that gossans may be *displaced* from the mineralized rocks in which the pyrite resides. However, in spite of the slowness of the oxidation of Fe^{2+} , iron is generally *not* a mobile element except in acidic environments with low O_2 fugacities ($\text{Eh} < +0.6 \text{ V}$, Figure 14.6).

3. The oxidation of pyrite releases H^+ into the environment and causes acidification of surface waters.
4. The sulfate ion goes into solution and serves as a *messenger* that the water in which it occurs has interacted with sulfide minerals.

The oxidation of pyrite can also take place in the *absence* of O_2 by the action of Fe^{3+} , which serves as the electron acceptor (oxidizing agent):



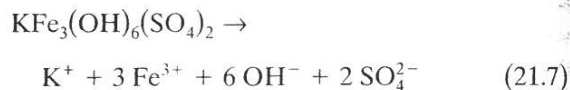
This reaction is fast and releases additional H^+ into the environment (Stumm and Morgan, 1981). The Fe^{3+} required for this reaction is provided by the oxidation of Fe^{2+} and by the dissolution of solid $Fe(OH)_3$.

The decomposition of pyrite is also accelerated by the activity of the bacterium *Thiobacillus ferrooxidans* and others that oxidize Fe^{2+} to Fe^{3+} and thereby promote reaction 21.6 (Ehrlich, 1981, ch. 12; also Section 19.7). *Thiobacillus* is a rod-shaped microorganism that feeds on Fe^{2+} and CO_2 in acid environments. It is the best known of a group of bacteria that interact with Fe in a variety of ways: (1) enzymatic oxidation of Fe^{2+} to Fe^{3+} ; (2) nonenzymatic oxidation of Fe^{2+} to Fe^{3+} by localized changes in Eh, or pH, or both; (3) adsorption of $Fe(OH)_3$ on cell walls; (4) synthesis of organic chelators for Fe^{3+} that prevent its precipitation and increase its mobility; and (5) enzymatic and nonenzymatic reduction of Fe^{3+} by *Bacillus polymyxa* and others discussed by Ehrlich (1981).

Bacteria contribute to the deposition of ochre and other varieties of Fe oxides and hydroxides that form in pipes and channels draining waterlogged soils as well as in swamps and marshes. Such places appear to be the habitat of *Gallionella ferruginea* (Section 19.7), which thrives in neutral environments (pH = 6–7) containing Fe^{2+} and CO_2 . This bacterium has also been identified in a bay of the Greek island Palaea Kameni, where Fe oxide is presently accumulat-

ing (Puchelt et al., 1973). Another example of bacterial Fe oxidation is the deposition of Fe oxides in the Pine Barrens on the coastal plain of southern New Jersey, which Crerar et al. (1979) attributed to the oxidation of Fe^{2+} by *Thiobacillus ferrooxidans* and other species. One of these is *Metallogenium*, which occurs abundantly in acid mine waters at pH > 3.5. In more acidic waters *Thiobacillus ferrooxidans* and others become dominant, including *Sulfolobus ferrooxidans*, which can attack sulfide minerals like *chalcopyrite* ($CuFe_2$) and *molybdenite* (MoS_2) by oxidizing the sulfide ions (Brierley and Murr, 1973).

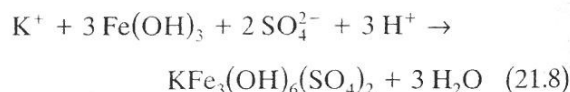
When pyrite and other sulfide minerals are in contact with sulfate-rich solutions as a result of evaporation of water or for other reasons, minerals of the *alunite* group may precipitate. Iron-bearing species of that group are called *jarosite* and have the general formula $M^+Fe_3^{3+}(OH)_6(SO_4)_2$ where the place of the metal ion M^+ may be taken by K^+ , Na^+ , NH_4^+ , or Ag^+ . Jarosite can also accommodate Pb^{2+} (plumbojarosite) in the form $PbFe_6(OH)_{12}(SO_4)_4$. The solubility product constant of potassium jarosite can be calculated from the dissolution reaction:



$$\Delta G_R^\circ = +140.596 \text{ kcal (Appendix B)}$$

$$K_{sp} = 10^{-103.07}$$

The mineral ranges in color from bright yellow to brown and occurs near hot springs and fumaroles around volcanic craters and as an alteration product of sulfide minerals where it may form from $Fe(OH)_3$:



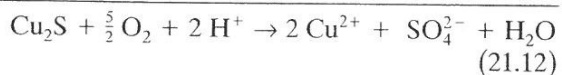
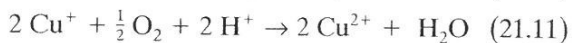
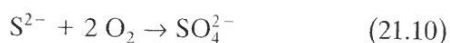
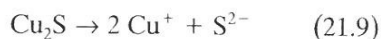
Therefore, jarosite may occur in *gossans* together with the insoluble weathering products of other metals that may be associated with Fe in a particular mineral deposit.

21.3 Eh-pH Diagram for Copper Minerals

The oxidation of sulfide minerals at or near the surface of the Earth depends on the Eh and the pH of the environment (Chapter 14). The pH is controlled largely by the presence of pyrite or other iron-bearing sulfides because the formation of insoluble $\text{Fe}(\text{OH})_3$ causes the release of H^+ . The Eh is effectively controlled by the availability of molecular O_2 , which is the principal, but not the only, oxidizing agent at the surface of the Earth. The oxidation of sulfide minerals ultimately depends on the availability of water at the site of weathering and hence on climatic and hydrologic conditions.

Copper is commonly associated with Fe in mineral deposits where it occurs either as the pure sulfides *chalcocite* (Cu_2S) or *covellite* (CuS) and as mixed sulfides: *chalcopyrite* (CuFeS_2), *bornite* (Cu_5FeS_4), *cubanite* ($\text{Cu}_2\text{Fe}_4\text{S}_6$), and other rare minerals. In addition, Cu sulfides may coexist with sulfides of other metals, including Ni, Co, Zn, Pb, Mo, Ag, As, and Sb and may also be combined with them in sulfide minerals: *stromeyerite* ($(\text{Ag}, \text{Cu})_2\text{S}$), *carrollite* ($\text{CuS} \cdot \text{Co}_2\text{S}_3$), *enargite* ($3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$), *bournonite* ($2\text{PbS} \cdot \text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$), and many others.

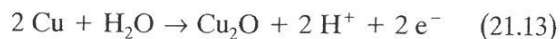
The dissolution of *chalcocite* can be expressed by the equations:



The products of these reactions are Cu^{2+} and SO_4^{2-} , both of which go into solution and are therefore mobile in the presence of water. The oxidation of Cu^+ to Cu^{2+} by molecular oxygen consumes H^+ and is favored in acid environments, which can result from the oxidation of coexisting pyrite.

The oxidation of *chalcocite* and *covellite* can be depicted in coordinates of Eh and pH by the

procedures presented in Chapter 14. We consider first a very simple system composed of only Cu, O_2 , and H_2O in which Cu appears as the *native metal*, as *cuprite* (Cu_2O), and as *tenorite* (CuO). We begin with the most reduced form of copper, which is the native metal, and write an electrode half-reaction for the oxidation of metallic Cu to tenorite (Cu_2O), which contains Cu^+ :



From Appendix B,

$$\Delta G_R^\circ = -35.1 - (-56.687) = +21.587 \text{ kcal}$$

and therefore,

$$E^\circ = \frac{21.587}{2 \times 23.06} = +0.468 \text{ V} \quad (21.14)$$

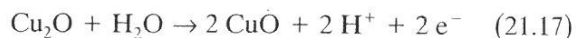
Hence:

$$\text{Eh} = 0.468 + \frac{0.0591}{2} \log [\text{H}^+]^2 \quad (21.15)$$

and

$$\text{Eh} = 0.468 - 0.0591 \text{pH} \quad (21.16)$$

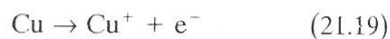
This line is the locus of points whose coordinates are the Eh and pH generated by the electrode in equation 21.13. When the Eh and pH are *imposed* on the electrode by the environment, equation 21.13 can be used to predict which phase is stable. If the point representing an environment in the Eh-pH plane lies to the *left* of the line represented by equation 21.16, an excess of H^+ for the particular Eh is present in the environment and therefore metallic Cu is stable. Therefore, equation 21.16 is a boundary between metallic Cu and cuprite on the Eh-pH diagram in Figure 21.1A. The Eh-pH equation for the cuprite-tenorite boundary is derived similarly:



$$\Delta G_R^\circ = +30.387 \text{ kcal} \quad E^\circ = +0.659 \text{ V}$$

$$\text{Eh} = 0.659 - 0.0591 \text{pH} \quad (21.18)$$

Next, we consider the solubility of native Cu to form Cu^+ :



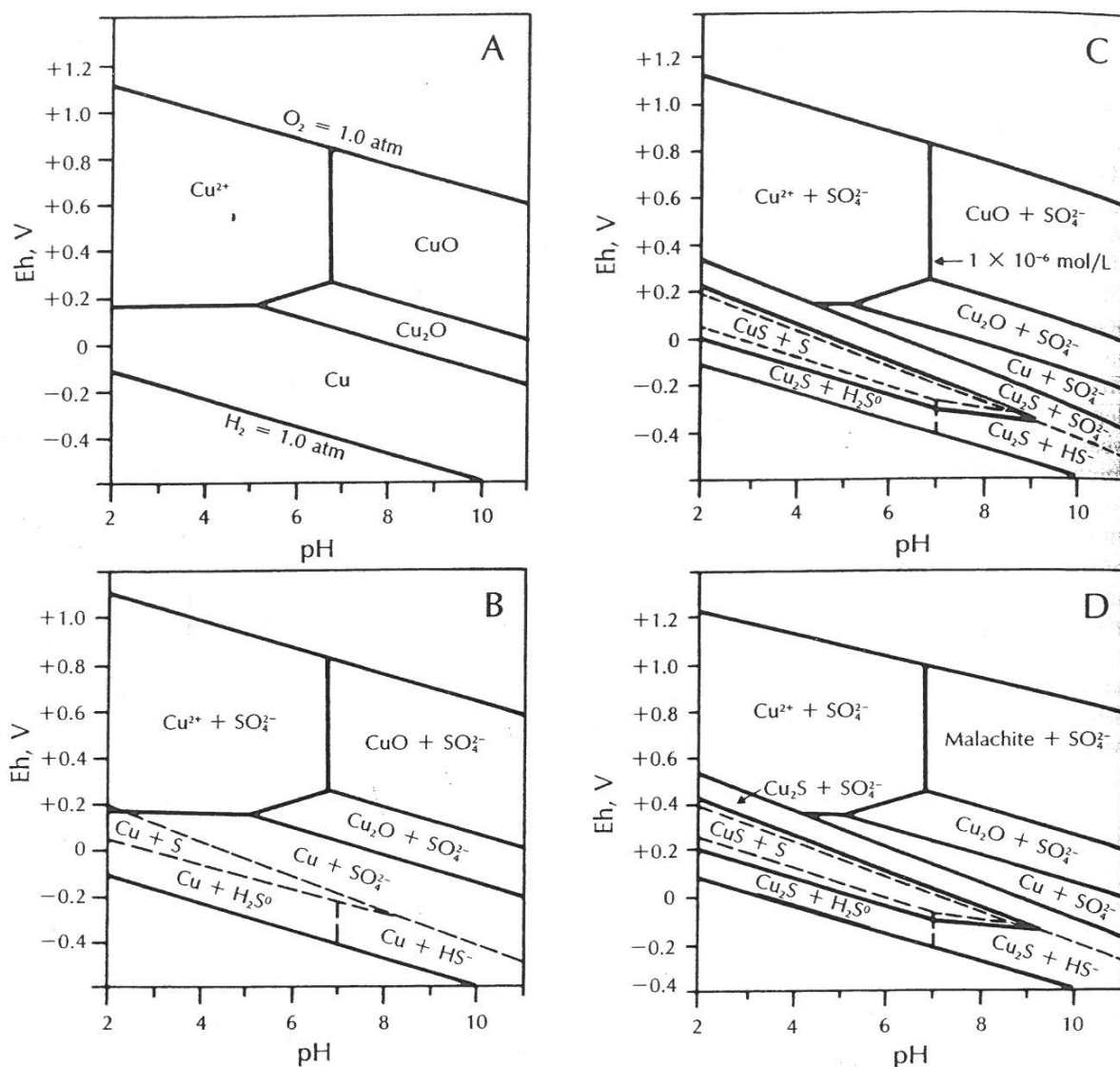


Figure 21.1 A. Eh-pH diagram for metallic Cu and its oxides cuprite (Cu_2O) and tenorite (CuO). The solids dissolve in acid solutions to form Cu^{2+} , which is more abundant than Cu^+ . The solubility boundaries are at $[\text{Cu}^{2+}] = 1 \times 10^{-6} \text{ mol/L}$. The diagram is based on equations 21.16 ($\text{Cu}-\text{Cu}_2\text{O}$), 21.18 ($\text{Cu}_2\text{O}-\text{CuO}$), and 21.24 ($\text{Cu}-\text{Cu}^{2+}$). The solubilities of Cu_2O and CuO are the subject of Problems 1 and 2. The standard free energies are compiled in Appendix B.

B. Eh-pH diagram for Cu superimposed on the Eh-pH diagram for S. The dashed lines indicate the distribution of S species taken from Figure 14.10. The sulfides of Cu that can form in this system are shown in C.

C. The stability fields of chalcocite (Cu_2S) and covellite (CuS) in a system containing $\Sigma\text{S} = 1 \times 10^{-1} \text{ mol/L}$. The boundaries are defined by equations 21.27, 21.29, 21.31, and 21.33 for chalcocite and by equations 21.35, 21.37, and 21.39 for covellite. The sulfates of Cu are soluble and occur naturally only under arid climatic conditions.

D. When the fugacity of $\text{CO}_2 > 1 \times 10^{-3.00} \text{ atm}$, tenorite becomes unstable with respect to malachite (equation 21.40), which takes its place on the Eh-pH diagram. Malachite dissolves to form Cu^{2+} in accordance with equation 21.42.

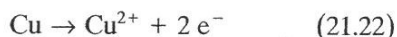
$$\Delta G_R^\circ = +11.95 \text{ kcal} \quad E^\circ = 0.518 \text{ V}$$

$$Eh = 0.518 + \frac{0.0591}{1} \log [\text{Cu}^+] \quad (21.20)$$

If $[\text{Cu}^+] = 10^{-6} \text{ mol/L}$ is taken as the limiting solubility of metallic Cu and its compounds in geologic settings (Section 14.4),

$$Eh = 0.518 + 0.0591(-6) = 0.163 \quad (21.21)$$

The oxidation of metallic Cu to Cu^{2+} is represented by the electrode half-reaction:



$$\Delta G_R^\circ = +15.66 \text{ kcal} \quad E^\circ = +0.340 \text{ V}$$

and hence,

$$Eh = 0.340 + \frac{0.0591}{2} \log [\text{Cu}^{2+}] \quad (21.23)$$

If $[\text{Cu}^{2+}] = 10^{-6} \text{ mol/L}$,

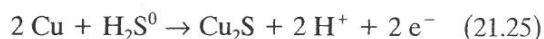
$$Eh = 0.340 + \frac{0.0591}{2} (-6) = +0.163 \quad (21.24)$$

Evidently, metallic Cu dissolves to form almost equal concentrations of Cu^+ and Cu^{2+} at $Eh = 0.163 \text{ V}$. In fact, $[\text{Cu}^{2+}]/[\text{Cu}^+] = 1.0$ at $Eh = 0.161 \text{ V}$. Therefore, at $Eh = 0.163 \text{ V}$ the concentration of Cu^{2+} is greater than that of Cu^+ . Consequently, we conclude that metallic Cu as well as cuprite and tenorite dissolve to form Cu^{2+} rather than Cu^+ as shown in Figure 21.1A (see also Problems 1–3). The same diagram was derived by Garrels and Christ (1965) and by Brookins (1988).

The stability limits of the sulfides chalcocite (Cu_2S) and covellite (CuS) can be added to Figure 21.1A by adding S to the system such that $\Sigma\text{S} = 10^{-1} \text{ mol/L}$, which is sufficient for native S to precipitate (Section 14.5d). In order to determine the speciation of S in the Eh–pH plane, the lines governing the distribution of different forms of S (Table 14.5) have been superimposed in Figure 21.1B on the Cu– O_2 – H_2O system. It becomes apparent that native copper is associated with native S, H_2S^0 , HS^- , and SO_4^{2-} in different parts of its Eh–pH stability field, whereas cuprite, tenorite and Cu^{2+} lie in the SO_4^{2-} field. Therefore, the Eh–pH boundaries for the Cu sulfides must be based on reactions involving native Cu

because it is the only form of Cu considered in Figure 21.1A that shares its stability field with reduced forms of S.

In the Cu + H_2S^0 field a reaction should occur to form chalcocite (Cu_2S). The applicable electrode reaction is:



$$\Delta G_R^\circ = -13.94 \text{ kcal} \quad E^\circ = -0.302 \text{ V}$$

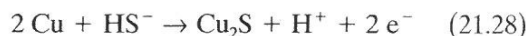
$$Eh = -0.302 - 0.0591 \text{ pH} - \frac{0.0591}{2} \log [\text{H}_2\text{S}^0] \quad (21.26)$$

When $[\text{H}_2\text{S}^0] = 10^{-1} \text{ mol/L}$, we obtain:

$$Eh = -0.272 - 0.0591 \text{ pH} \quad (21.27)$$

Because this equation plots *below* the lower stability limit of water ($\text{H}_2 = 1 \text{ atm}$), Cu and H_2S^0 cannot coexist with water and Cu_2S is the stable phase in the field labeled Cu + H_2S^0 .

The reaction between metallic Cu and HS^- in aqueous solution yields the electrode:



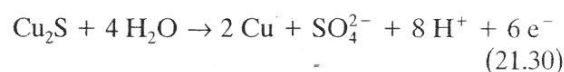
$$\Delta G_R^\circ = -23.53 \text{ kcal} \quad E^\circ = -0.510 \text{ V}$$

$$Eh = -0.480 - 0.0296 \text{ pH}$$

$$([\text{HS}^-] = 1 \times 10^{-1} \text{ mol/L}) \quad (21.29)$$

This line also lies below the lower stability limit of water; thus chalcocite is stable in the Cu + HS^- field as well.

The boundary between chalcocite and native Cu may lie in the Cu + SO_4^{2-} field, in which case the electrode half-reaction is:

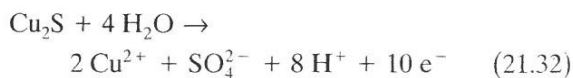


$$\Delta G_R^\circ = +69.648 \text{ kcal} \quad E^\circ = +0.503 \text{ V}$$

$$Eh = 0.493 - 0.0788 \text{ pH}$$

$$([\text{SO}_4^{2-}] = 1 \times 10^{-1} \text{ mol/L}) \quad (21.31)$$

The solubility limit of Cu_2S with respect to $[\text{Cu}^{2+}] = 10^{-6} \text{ mol/L}$ is given by:



$$\Delta G_R^\circ = +100.968 \text{ kcal} \quad E^\circ = +0.438 \text{ V}$$

$$\text{Eh} = 0.361 - 0.0473\text{pH}$$

$$([\text{SO}_4^{2-}] = 1 \times 10^{-1} \text{ mol/L}),$$

$$([\text{Cu}^{2+}] = 1 \times 10^{-6} \text{ mol/L}) \quad (21.33)$$

The stability field, of chalcocite delineated by these equations is outlined in Figure 21.1C.

Finally, we consider electrode half-reactions based on the conversion of chalcocite (Cu_2S) to covellite (CuS) and H_2S^0 , HS^- , and SO_4^{2-} . In the H_2S field we obtain:

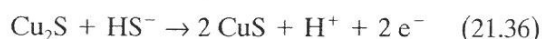


$$\Delta G_R^\circ = +1.66 \text{ kcal} \quad E^\circ = +0.0360 \text{ V}$$

$$\text{Eh} = 0.00645 - 0.0591\text{pH}$$

$$([\text{H}_2\text{S}^0] = 1 \times 10^{-1} \text{ mol/L}) \quad (21.35)$$

At $\text{pH} > 7.0$ where HS^- is the dominant S species:

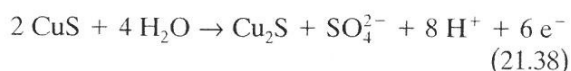


$$\Delta G_R^\circ = -7.93 \text{ kcal} \quad E^\circ = -0.172 \text{ V}$$

$$\text{Eh} = -0.142 - 0.0296\text{pH}$$

$$([\text{HS}^-] = 1 \times 10^{-1} \text{ mol/L}) \quad (21.37)$$

When SO_4^{2-} is the dominant ion, the boundary between chalcocite and covellite is defined by the equation:



$$\Delta G_R^\circ = +54.048 \text{ kcal} \quad E^\circ = +0.391 \text{ V}$$

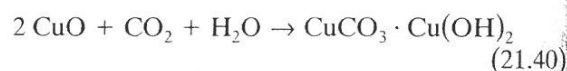
$$\text{Eh} = 0.381 - 0.0788\text{pH}$$

$$([\text{SO}_4^{2-}] = 1 \times 10^{-1} \text{ mol/L}) \quad (21.39)$$

Equations 21.35, 21.37, and 21.39 outline the stability field of covellite in Figure 21.1C, which includes the Eh-pH region in which native S is dominant in systems having a total S content of $1 \times 10^{-1} \text{ mol/L}$.

The sulfates of Cu are quite soluble and occur naturally only under arid climatic conditions. Therefore, the oxides of Cu are stable in the presence of water under oxidizing conditions in systems containing insufficient carbonate ions to precipitate the Cu carbonates *malachite* ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and *azurite* ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$). The largest deposit of Cu sulfates occurs in the ore body of the *Chuquicamata Mine* in the Atacama Desert of Chile, which formed by oxidation of enargite, bornite, chalcopryrite, and other sulfide minerals. The Cu-sulfate minerals in the oxidized ore include antlerite ($\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2$), brochantite ($\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$), kröhnkite ($\text{Na}_2\text{Cu(SO}_4)_2 \cdot 2\text{H}_2\text{O}$), chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite ($\text{Cu}_2\text{Cl(OH)}_3$), and several others described by Jarrell (1944). An Eh-pH diagram for some Cu minerals including brochantite was constructed by Hem (1977).

We complete the development of the Eh-pH diagram for Cu by adding CC_2 to the system. The carbonates *malachite* and *azurite* should now be stable depending on the fugacity of CO_2 , as shown in Figure 12.10. Since *malachite* contains divalent Cu and requires a lower fugacity of CO_2 than *azurite*, it should displace tenorite (CuO) from its stability field in Figure 21.1A by the reaction:

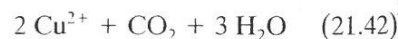


$$\Delta G_R^\circ = -4.099 \text{ kcal} \quad K = 10^{3.00}$$

Therefore, tenorite can coexist in equilibrium with malachite only when:

$$[\text{CO}_2] = 10^{-3.00} \text{ atm} \quad (21.41)$$

Partial pressures of CO_2 of this magnitude do occur in soil gases, indicating that malachite is stable with respect to tenorite in such environments. The solubility of malachite with respect to Cu^{2+} is given by:



$$\Delta G_R^\circ = -16.555 \text{ kcal} \quad K = 10^{12.137}$$

Therefore, the activity of $\text{Cu}^{2+} = 10^{-6}$ mol/L at pH = 6.78, if $[\text{CO}_2] = 1 \times 10^{-3.00}$ atm.

The Eh-pH diagrams in Figure 21.1 indicate that the sulfides of Cu, as well as the native element, are *unstable* under oxidizing conditions at the surface of the Earth and form insoluble oxides or carbonates at pH > 6.8. In addition, the oxides and carbonates become increasingly *soluble* with increasing acidity of the environment, and Cu becomes mobile in environments where pH < 6.8. Since the oxidation of pyrite, which is commonly associated with Cu sulfide minerals, acidifies the environment, the *presence of pyrite enhances the mobility of Cu^{2+} ions at the site of weathering*. Therefore, Cu^{2+} ions may be removed from the site of weathering by the movement of acidic groundwaters, but may precipitate elsewhere to form oxides or carbonates as the pH of the solution increases. The pH of acid groundwater rises because of *hydrolysis* reactions with silicate and carbonate minerals that consume H^+ to form silicic and carbonic acid, respectively.

21.4 Supergene Enrichment of Fe-Cu Sulfide Deposits

Some of the largest ore deposits of Cu and Ag were significantly enriched as a result of chemical weathering by a process called *supergene enrichment* (Garrels, 1954). Such deposits typically include mineralized breccia pipes, granitic stocks, or irregular veinlets forming stockworks. Igneous rocks of granitic composition in the form of small plutons or stocks, which contain disseminated Cu sulfide minerals, are known as *porphyry* copper deposits. Such deposits are the source of most of the Cu (and Mo) mined in the southwestern United States. In addition, Ag was recovered from supergene enrichment deposits in a belt extending from the western United States through Mexico to southern Chile (Park and MacDiarmid, 1970).

The supergene enrichment of disseminated Cu deposits depends on the common association of Cu sulfides with *pyrite* and other Fe-bearing

sulfides such as *chalcopyrite* or *bornite*. The oxidation of pyrite and other Fe-bearing sulfides creates a localized acid environment (equations 21.1–21.4). Consequently, Cu^{2+} remains in solution and is carried downward to the water table. The Cu^{2+} ions may precipitate as oxides or carbonates if the pH increases sufficiently as a result of hydrolysis of carbonate or silicate ions in the country rock. However, under ideal conditions, the Cu^{2+} is transported to the water table where it is reduced to Cu^+ and comes in contact with Fe sulfides of the unweathered rock called the *protore*. When pyrite is exposed to a solution having a large $\text{Cu}^+/\text{Fe}^{2+}$ ratio, equilibrium is reestablished by the *precipitation* of Cu sulfide and *dissolution* of Fe sulfide. In other words, pyrite is replaced by, or converted into, *chalcocite*. As a result, the rock below the water table is significantly enriched in Cu derived from the Cu sulfide minerals *above* the water table.

This process has resulted in the enrichment of Cu and Ag deposits but rarely those of Pb and Zn because the latter elements form insoluble carbonate and sulfate minerals that precipitate in the zone of oxidation. Therefore, supergene enrichment of an Fe-Cu-Pb-Zn sulfide deposit may cause *differentiation* of the deposit into an Fe-rich gossan, Pb-Zn carbonates or sulfates in the zone of oxidation, and Cu sulfides below the present or former water table. In addition, the Cu carbonates malachite and azurite may occur with *cerussite* (PbCO_3) and *smithsonite* (ZnCO_3) and attract the attention of *prospectors* by their brilliant color.

The effectiveness of supergene enrichment depends on the occurrence of favorable geologic, hydrologic, and climatic conditions:

1. The presence of pyrite or other Fe sulfides in the protore.
2. Sufficient porosity and permeability of the protore to allow movement of solutions.
3. A slow rate of erosion to provide the time required for the process to run to completion.
4. A deep water table that determines the volume of protore exposed to oxidation.

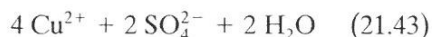
5. A low rate of annual precipitation, which provides the water required for the reactions and for transport of ions, but keeps the water table low and prevents flushing of ions released by weathering.
6. Low topographic relief, which affects the rate of erosion and controls the hydraulic gradient of the groundwater.

The ideal conditions include a semiarid climate, a deep or decreasing water table, low topographic relief, and low hydraulic gradients in rocks having good porosity and permeability. Such conditions exist in the southwestern United States and have caused significant supergene enrichment of porphyry copper deposits at Miami, Arizona (Peterson, 1962); Ely, Nevada (Bauer et al., 1966); and Bingham Canyon, Utah (Stringham, 1953). Figure 21.2 is a schematic and idealized cross section of a porphyry-Cu deposit that was modified by oxidation of sulfides and supergene enrichment.

21.5 Replacement of Pyrite by Chalcocite

The reactions of pyrite and Cu-Fe sulfides in the oxidized zone *above* the water table are embodied in the Eh-pH diagrams for Fe (Figure 14.11) and Cu (Figure 21.1C). Therefore, we consider next reactions that occur when water containing Cu^{2+} in solution percolates from the acid and oxidizing environment close to the surface to the water table where conditions are less acid and frequently reducing. The migration of the solution is marked on the combined Fe-Cu Eh-pH diagram in Figure 21.3.

At point *P* in Figure 21.3, pyrite and chalcocite are unstable. Pyrite is transformed into hematite and $\text{SO}_4^{2-} + \text{H}^+$ ions (equation 21.4), whereas chalcocite is oxidized to $\text{Cu}^{2+} + \text{SO}_4^{2-}$ in solution:



Note that the dissolution and oxidation of chalcocite are favored in acid environments created

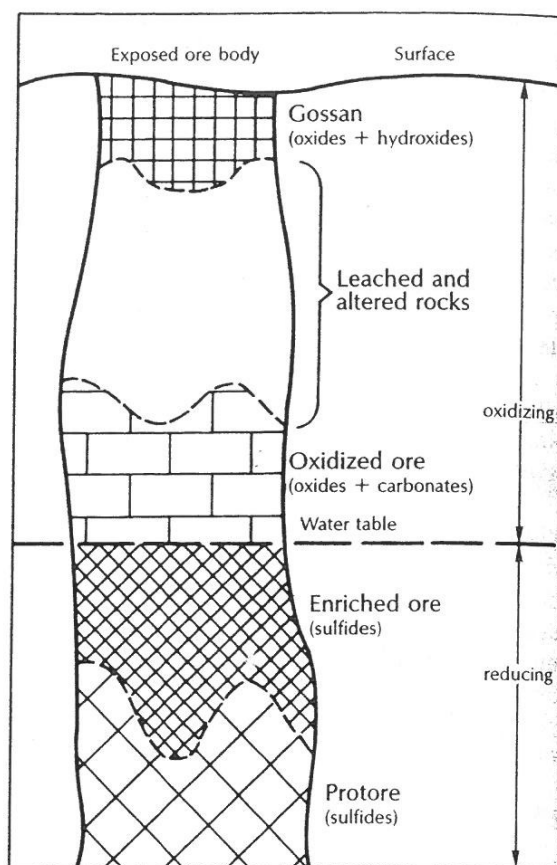


Figure 21.2 Schematic and hypothetical representation of oxidation and supergene enrichment of a low-grade mineral deposit containing disseminated sulfides of Fe, Cu, and other metals. As a result of oxidation of Cu sulfide in an acid environment caused by the oxidation of pyrite to solid $\text{Fe}(\text{OH})_3$, Cu^{2+} ions are transported from the zone of oxidation to the water table. Secondary oxides and carbonates may be precipitated on the way. The Cu^{2+} ions that reach the water table "displace" Fe^{2+} from pyrite, chalcopyrite or bornite, thereby converting them to chalcocite (Cu_2S). As a result, the low-grade protore is significantly enriched in Cu and may be converted into Cu ore that is minable at a profit (adapted from Batemen, 1950, p. 245).

by the oxidation of pyrite. Therefore, the reactions at point *P* form a solution containing Cu^{2+} , SO_4^{2-} , H^+ , and a small amount of Fe^{2+} that is in equilibrium with hematite (or ferric hydroxide).

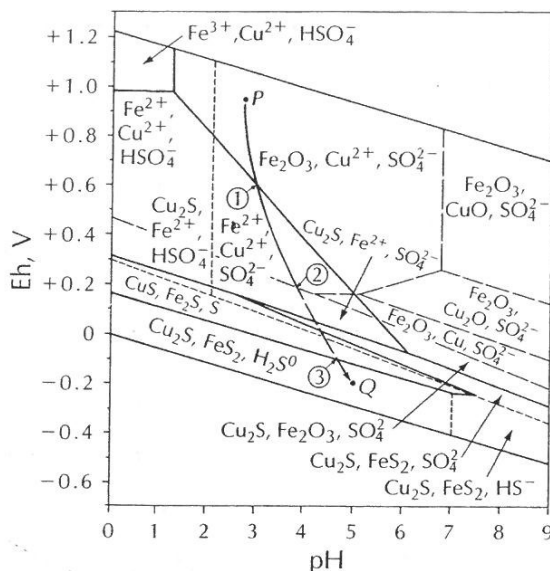


Figure 21.3 Combined Eh-pH diagram for Fe and Cu with $\Sigma S = 1 \times 10^{-1}$ mol/L, based on Figures 14.11 and 21.1D, and simplified in the area where native S precipitates. Point *P* represents a near-surface environment in which both pyrite and chalcocite are unstable. Iron is precipitated as Fe_2O_3 , whereas Cu^{2+} and SO_4^{2-} are transported in solution to the water table. As a result, the ions enter an environment represented by point *Q* where both chalcocite and pyrite are stable. Equilibrium is established by reactions that cause pyrite to dissolve and chalcocite to precipitate, thereby enriching the rock in Cu. The water table is assumed to be a major discontinuity in the Eh and pH conditions such that the environmental conditions change rapidly between points 2 and 3 on the migration path.

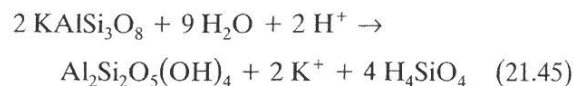
The activity of Fe^{2+} in equilibrium with hematite depends on the Eh and pH of the environment at point *P* in accordance with equation 14.89:

$$\text{Eh} = 0.65 - 0.177\text{pH} - 0.05916 \log [\text{Fe}^{2+}] \quad (21.44)$$

Since at *P* we have pH = 2.75 and Eh = +0.95 V, we obtain $[\text{Fe}^{2+}] = 10^{-13.30}$ mol/L.

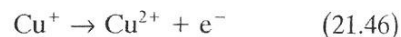
The solution percolates downward, thereby entering environments that are progressively

depleted in O_2 . The pH begins to rise slowly with depth because H^+ ions in the solution are consumed by hydrolysis of aluminosilicate minerals that are converted to kaolinite or other clay minerals. For example, the reaction of microcline to form kaolinite consumes H^+ ions by the reaction:



At point 1 along the path in Figure 21.3, the activity of Fe^{2+} in equilibrium with hematite has increased from $10^{-13.30}$ mol/L at point *P* to 1×10^{-6} mol/L. Consequently, the solution is able to dissolve a small amount of hematite as it moves from point *P* to point 1 and to transport Fe^{2+} ions downward. The activities of Cu^{2+} and SO_4^{2-} are not directly affected by the dissolution of hematite, which continues as the solution percolates into environments having decreasing Eh and increasing pH values.

At point 2 along the path, Cu^{2+} is converted into Cu^+ by the electrode reaction:



$$\Delta G_R^\circ = +3.71 \text{ kcal} \quad E^\circ = +0.161 \text{ V}$$

$$\text{Eh} = 0.161 + \frac{0.0591}{1} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \quad (21.47)$$

Therefore, $[\text{Cu}^{2+}] = [\text{Cu}^+]$ when the Eh = +0.161 V. At point 2 on the solubility boundary of chalcocite, Cu^{2+} is still the dominant Cu ion, but its activity is now limited by equation 21.33. If $[\text{SO}_4^{2-}] = 1 \times 10^{-1}$ mol/L, then $[\text{Cu}^{2+}] = 1 \times 10^{-6}$ mol/L. The activity of Fe^{2+} at point 2 (Eh = +0.190 V, pH = 3.8) in equilibrium with hematite has increased by about 10 orders of magnitude to $[\text{Fe}^{2+}] = 10^{-3.59}$ mol/L since the solution left the original site of weathering at point *P*. Therefore, the amount of hematite dissolved between point *P* and point 2 in Figure 21.3 is approximately:

$$\frac{(10^{-3.59} - 10^{-13.30}) \times 159.69}{2} \approx 2 \times 10^{-2} \text{ g/L} \quad (21.48)$$

provided that equilibrium was maintained. This explains why the Fe-rich *gossan* in Figure 21.2 is underlain by a *leached zone*, which is depleted in Fe and in which aluminosilicate minerals are altered to kaolinite and other clay minerals.

We assume that point 2 is close to the water table and that the Eh–pH conditions now change so rapidly with depth that chemical equilibria between ions and solids are *not* maintained. Consequently, the solution approaches the environment represented by point *Q* in Figure 21.3 after it enters the zone of saturation below the water table.

At point 3 along the route, SO_4^{2-} is converted to H_2S^0 , which is now the dominant S species. In addition, pyrite and chalcocite in the protore are stable in this environment, but may be out of equilibrium with Fe^{2+} and Cu^+ in the solution. Point *Q* represents the Eh–pH conditions of the environment in the zone of saturation where pyrite and chalcocite of the protore react to achieve equilibrium with Fe^{2+} , Cu^+ , and H_2S^0 .

The activity of Fe^{2+} in equilibrium with pyrite at Eh = –0.2 V and pH = 5.0 (point *Q*, Figure 21.3) in a system in which $\text{H}_2\text{S}^0 = 1 \times 10^{-1}$ mol/L is derivable from equation 14.134:

$$\text{Eh} = -0.148 + \frac{0.0591}{2} \log \frac{[\text{H}^+]^4}{[\text{Fe}^{2+}][\text{H}_2\text{S}^0]^2} \quad (21.49)$$

If $[\text{H}_2\text{S}^0] = 1 \times 10^{-1}$ mol/L,

$$\text{Eh} = -0.0889 - 0.1182\text{pH} - 0.02955 \log [\text{Fe}^{2+}] \quad (21.50)$$

Therefore, at point *Q* in equilibrium with pyrite:

$$[\text{Fe}^{2+}] = 10^{-16.24} \text{ mol/L} \quad (21.51)$$

The solubility of chalcocite with respect to Cu^+ is given by:



$$\Delta G_R^\circ = +37.84 \text{ kcal} \quad K = 10^{-27.742}$$

Therefore, at equilibrium:

$$\frac{[\text{Cu}^+]^2[\text{H}_2\text{S}^0]}{[\text{H}^+]^2} = 10^{-27.742} \quad (21.53)$$

and at pH = 5.0 and $[\text{H}_2\text{S}^0] = 1 \times 10^{-1}$ mol/L:

$$\begin{aligned} [\text{Cu}^+] &= \left(\frac{10^{-27.742} \times 10^{-10.0}}{10^{-1.0}} \right)^{1/2} \\ &= 10^{-18.37} \text{ mol/L} \end{aligned} \quad (21.54)$$

Evidently, the $[\text{Cu}^+]/[\text{Fe}^{2+}]$ ratio of a solution in equilibrium with both chalcocite and pyrite at point *Q* in Figure 21.3 is:

$$\frac{[\text{Cu}^+]}{[\text{Fe}^{2+}]} = \frac{10^{-18.37}}{10^{-16.24}} = 10^{-2.13} = 7.41 \times 10^{-3} \quad (21.55)$$

In other words, pyrite is about 270 times as soluble as chalcocite, if we include the fact that each mole of chalcocite produces two moles of Cu^+ .

Equation 21.55 explains why pyrite can be replaced by chalcocite during supergene enrichment. If the $[\text{Cu}^+]/[\text{Fe}^{2+}]$ ratio of a solution at point *Q* in Figure 21.3 is *greater* than 7.41×10^{-3} , chalcocite must precipitate and pyrite must dissolve in order to establish equilibrium between the solids and their ions. Hence, pyrite is *replaced* by chalcocite and the Cu ions, derived by oxidation of chalcocite at point *P*, are thus precipitated at point *Q*. The Cu concentration of the protore is thereby *increased* significantly.

The process we have outlined does not include the formation of carbonate or oxide minerals of Cu because the path *PQ* does not enter their stability fields in Figure 21.3. In reality, the physical and chemical conditions to which a solution, formed by oxidation of sulfides of Fe and Cu, is exposed as it percolates downward may vary widely. As a result, tenorite, cuprite, native Cu, malachite, azurite, and the Cu silicate chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$) may precipitate under appropriate conditions, thereby preventing some of the Cu ions from reaching the water table. In addition, the solution may precipitate hematite (or limonite), jarosite, or pyrite, as well as covellite and native S, depending on environmental conditions. Evidently, the outcome of this process depends on the geologic, hydrologic, and climatic factors (listed in Section 21.3), which may be highly site-specific.

21.6 Oxidation of Ore Minerals of Other Metals

We conclude from the foregoing discussion that the supergene enrichment of low-grade Cu deposits occurs because chalcocite is less soluble than pyrite under the reducing conditions that prevail in the zone of saturation below the water table. We can calculate the solubilities of the sulfides of other metals that may coexist with pyrite and thereby predict whether supergene enrichment is possible for them. The results in Table 21.1 are ordered in terms of decreasing activities of metal ions in equilibrium with their sulfides at the conditions represented by point *Q* in Figure 21.3, namely, $Eh = -0.2$ V, $pH = 5.0$, $\Sigma S = [H_2S] = 1 \times 10^{-1}$ mol/L, $T = 25^\circ C$, and $P = 1.0$ atm. The solubilities of the sulfides included in Table 21.1 range over 44 orders of magnitude from 7.46×10^{-47} mol/L for cinnabar (HgS) to 3.97×10^{-3} mol/L for alabandite (MnS). The sulfides of Hg, Ag, Cu, and Cd are *less* soluble than pyrite and therefore could replace it under favorable conditions. The sulfides of Pb, Zn, Ni, Co, and Mn are *more* soluble than pyrite in the specified environment and therefore could replace it *only* when the $[metal\ ion]/[Fe^{2+}]$ activity ratio in the solution exceeds the equilibrium value. The listing of metals in Table 21.1 resembles the

Schürmann series, which was derived experimentally more than 100 years ago on the basis of the affinity of metals for sulfur (Schürmann, 1888).

The geochemical properties of Ag, Hg, Mo, and U are illustrated by means of their Eh-pH diagrams in Figure 21.4. Silver sulfide deposits containing argentite (Ag_2S), are oxidized under near-surface conditions, and the resulting Ag^+ ions may be reduced to native Ag or may replace metals whose sulfides are *more* soluble than argentite. Therefore, supergene enrichment has significantly increased the value of the many Ag deposits in the Cordilleran ranges of North, Central, and South America (Park and MacDiarmid, 1970).

In contrast to the sulfides of Cu and Ag, ore deposits of Hg containing HgS (cinnabar) are not significantly enriched as a result of oxidation. For example, at the Mt. Jackson mine in Sonoma County, California, secondary cinnabar apparently did not form by replacement of pyrite and is not economically important (Tunnel, 1970). The aqueous geochemistry of Hg is affected by the stability of complex ions such as $HgCl_4^{2-}$ and HgS_2^{2-} , that significantly increase the amount of this element that can occur in solution (Krauskopf, 1951). Consequently, cinnabar deposits form by precipitation from aqueous solutions at low temperature

Table 21.1 Listing of the Activities of Metal Ions in Equilibrium with Their Sulfides ($Eh = -0.20$ V, $pH = 5.0$, $\Sigma S = [H_2S^0] = 1 \times 10^{-1}$ mol/L, $T = 25^\circ C$, and $P = 1.0$ atm.)

<i>Metal</i>	<i>Mineral</i>	<i>Activity of the ion, mol/L</i>
Hg	cinnabar (HgS)	$[Hg_2^{2+}] = 7.46 \times 10^{-47}$
Ag	argentite (Ag_2S)	$[Ag^+] = 9.53 \times 10^{-20}$
Cu	chalcocite (Cu_2S)	$[Cu^+] = 4.27 \times 10^{-19}$
Cd	greenockite (CdS)	$[Cd^{2+}] = 1.14 \times 10^{-18}$
Fe	pyrite (FeS_2)	$[Fe^{2+}] = 5.75 \times 10^{-17}$
Pb	galena (PbS)	$[Pb^{2+}] = 2.42 \times 10^{-17}$
Zn	sphalerite (ZnS)	$[Zn^{2+}] = 2.37 \times 10^{-14}$
Ni	millerite (NiS)	$[Ni^{2+}] = 8.80 \times 10^{-11}$
Co	cobaltite (CoS)	$[Co^{2+}] = 7.80 \times 10^{-10}$
Mn	alabandite (MnS)	$[Mn^{2+}] = 3.97 \times 10^{-3}$

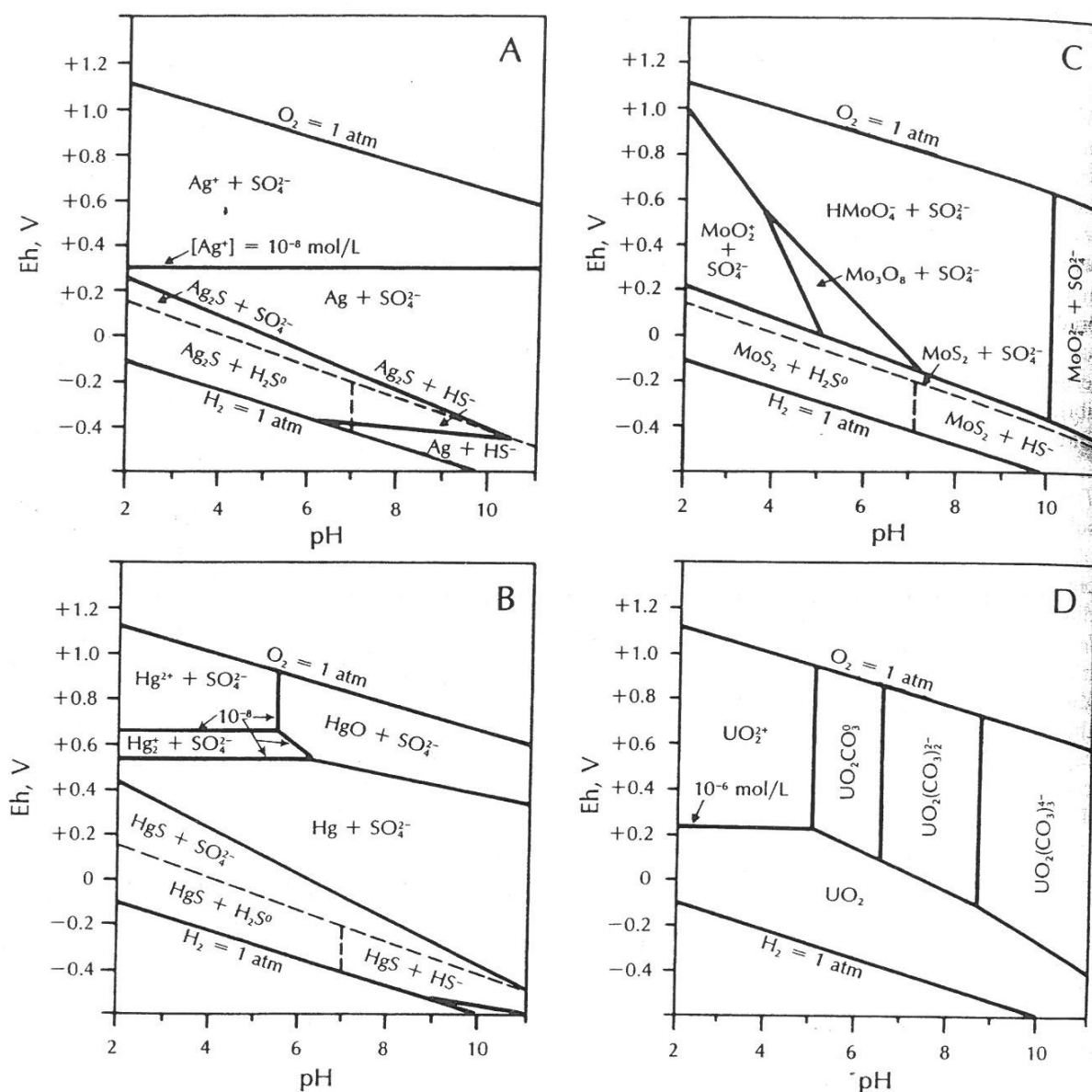


Figure 21.4 A. Eh-pH diagram for metallic Ag and its sulfide argentite in a system containing $\Sigma\text{S} = 10^{-3} \text{ mol/L}$ at 25°C and 1 atm. The solubility boundary is drawn at $[\text{Ag}^+] = 10^{-8} \text{ mol/L}$.

B. Eh-pH diagram for metallic Hg, the sulfide cinnabar and the oxide montroydite in a system containing $\Sigma\text{S} = 10^{-3} \text{ mol/L}$ at 25°C and 1 atm. The solubility boundaries are drawn at $[\text{Hg}^{2+}]$ and $[\text{Hg}_2^{2+}] = 10^{-8} \text{ mol/L}$.

C. Eh-pH diagram for molybdenite (MoS_2) and ilsemanite (Mo_3O_8) in a system containing $\Sigma\text{S} = 10^{-3} \text{ mol/L}$ at 25°C and 1 atm. The solubility boundaries are drawn at $[\text{MoO}_4^{2-}]$, $[\text{HMoO}_4^-]$, and $[\text{MoO}_4^{2-}] = 10^{-8} \text{ mol/L}$.

D. Eh-pH diagram for uraninite (UO_2), the uranyl ion (UO_2^{2+}), and its carbonate complexes in a system containing $\Sigma\text{C} = 10^{-3} \text{ mol/L}$ and $\Sigma\text{S} = 10^{-3} \text{ mol/L}$ at 25°C and 1 atm. The solubility boundaries are at 10^{-6} mol/L of the respective ions and molecules (after Brookins, 1988).

(epithermal) and thereby become separated from the sulfides of Fe, Cu, Mo, and other metals that are deposited at higher temperatures (hypothermal-mesothermal).

Molybdenum is an important element that occurs as the sulfide molybdenite (MoS_2) and is commonly associated with Cu sulfides. Molybdenum is a member of the Cr group (group VIB, Figure 8.3), which also includes W and U. These elements may be oxidized to the +6 state and then combine with O to form oxy ions. Molybdenite dissolves under oxidizing conditions to form the bimolybdate (HMoO_4^-) ion, which gives way to the molybdate (MoO_4^{2-}) ion at a pH above ~ 10 (Brookins, 1988). In addition, Mo forms MoO_2^+ ions under strongly acidic conditions in which Mo has a valence of +5. Consequently, Mo ions released by the oxidation of molybdenite tend to be dispersed, but may be reprecipitated under reducing conditions with secondary U minerals. The mobility of Mo under oxidizing conditions makes it useful in geochemical exploration surveys as an indicator of both Cu-Mo and secondary U deposits. The bimolybdate ion reacts with Pb^{2+} to form the mineral wulfenite (PbMoO_4), which is much less soluble than the molybdates of other metals (Landergrén and Manheim, 1978).

The aqueous geochemistry of U and its deposits has been studied intensively because of the importance of this element as a source of energy and as an explosive based on induced fission of ^{235}U (Rich et al., 1977). All aspects of the geochemistry and technology of U are the subject matter of the scientific journal *Uranium*. The element forms complex ions with O, hydroxyl, carbonate, phosphate, and other ions under oxidizing conditions where U assumes a valence of +6 (Langmuir, 1978). Therefore, U is *mobile* under oxidizing conditions but can be precipitated in the tetravalent state as *uraninite* (UO_2), *coffinite* (USiO_4), and a few other compounds not all of which have mineral names. In addition, the uranyl ion (UO_2^{2+}) forms a very large number of insoluble oxides, carbonates, sulfates, phosphates, arsenates, vanadates, silicates, and molybdates, including *rutherfordine* (UO_2CO_3), *autunite* ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12\text{H}_2\text{O}$),

and *carnotite* ($\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3\text{H}_2\text{O}$) (Rogers and Adams, 1969).

21.7 Geochemical Exploration

When certain kinds of mineral deposits weather, ions may be released into the ambient groundwater or saprolite in unusual concentrations. The resulting geochemical anomalies can be detected by analyzing systematically collected samples of water, soil, colluvium, or plants. Once geochemical anomalies have been located, they become the targets for more detailed exploration based on geological, geophysical, and additional geochemical methods. The ultimate objective is to discover the sources of the geochemical anomalies and to determine the economic potential of the mineral deposits. Therefore, geochemical exploration is one of the techniques geologists use in their quest to discover new ore deposits (Chapter 1).

Geochemical prospecting requires an understanding of the geological processes that apply to the formation of mineral deposits and that come into play during their eventual alteration at the surface of the Earth. In addition, information is required regarding the chemical properties of the elements and how these properties affect the migration and dispersion of selected elements under a given set of environmental circumstances.

Geochemical exploration is the principal occupation of a large number of geologists and geochemists working in the mineral industry. They have organized several professional societies, hold national and international symposia, and publish the results of their research in specialized journals, including the *Journal of Geochemical Exploration*, *Mineralium Deposita*, and *Economic Geology*. The principles of geochemical exploration have been summarized in many textbooks and monographs, e.g. Hawkes and Webb (1962), Brooks (1972), Levinson (1974), Fletcher (1981), Boyle (1982), Howarth (1982), Govett (1983), Davy and Mazzucchelli (1984), Thornton and Howarth (1986), and Wignall and de Geoffrey (1987). In addition, the *Proceedings of the International*

Geochemical Exploration Symposia have been reprinted from the *Journal of Geochemical Exploration* under the general title: *Geochemical Exploration . . .* published annually by Elsevier Science Publishers in Amsterdam.

Geochemical methods of exploration are appropriate in areas where the bedrock is not exposed because of the accumulation of weathering products or because of the presence of alluvial sediment or till. In addition, these methods can be used in areas that are inaccessible because of rugged topography, heavy vegetation, or the absence of adequate roads. Such conditions prevail in many areas of the world, including some parts of Africa, South America, Asia, Australia, and Antarctica. Geochemical surveys are relatively inexpensive and can be adapted to achieve specific objectives under a given set of circumstances.

Before any work is done in the field, available sources of information should be thoroughly studied to determine the bedrock geology and overburden of the area to be investigated, as well as its vegetation and climate, roads and settlements, existing mines and smelters, legal requirements to obtain permits, and the availability of housing, food, and fuel. Such preliminary work is necessary not only because the study area may be in a remote location in a foreign country, but also because the most appropriate method of collecting and analyzing samples must be selected.

The preliminary study of the geology of the area to be surveyed will suggest what kinds of deposits may be present and what minerals they may contain. For example, low-Ca granites are enriched in Sn, Hg, Li, and Be, whereas Fe, Co, Ni, and Cr are associated with ultramafic rocks. Sedimentary rocks may contain fossil fuels as well as deposits of Fe, Mn, P, U, and more rarely Cu, Pb, or Zn. All of the information gathered by geochemists about the chemical compositions of different kinds of rocks finds direct practical application when it becomes necessary to predict the composition of potential mineral deposits in an area.

After the metals to be searched for have been identified, the solubility of the minerals in

which they occur and the properties of their ions and molecules that form during dissolution of these minerals need to be reviewed. According to information in Chapter 19, some minerals resist chemical weathering and are ultimately concentrated in deposits of sand and gravel. The valuable minerals in this category include Au, Pt group metals, diamonds, rutile, various phosphate minerals, magnetite, corundum, and others. The mobility of some elements is limited by the formation of secondary minerals and the extent to which their ions may be adsorbed on clay minerals, oxide and hydroxide particles or grain coatings, and organic matter.

The geochemical properties of the elements to be included in a survey must also be considered in choosing appropriate methods of sampling and analysis. In addition, the geochemist planning a survey must consider the objectives and budgetary limitations when deciding what kinds of samples to collect. In general, a wide variety of materials can be collected for study:

1. Rock samples from outcrops or boulders embedded in the regolith.
2. Soil in bulk or from specific horizons in which the elements of interest may be concentrated.
3. Stream or lake water.
4. Sediment carried in suspension in the water or from the bottom of streams or lakes.
5. Organic matter in streams or lakes including molluscs, fish, larvae, and aquatic plants in bulk, or selectively.
6. Water from springs and water wells.
7. Land plants, including leaves, pine needles, twigs, seeds, or soil humus.
8. Selected land animals, their feces, and solid body parts such as antlers, bones, or hair.
9. Soil gases and air.

Each of these is appropriate for certain elements, represents a different part of the environment, and can be collected in ways that reflect the scope of the survey to be undertaken.

Geochemical methods of exploration may be used to evaluate the resource potential of an area in a *preliminary manner*. In this case, water and/or sediment samples can be collected from streams in existing drainage basins. Metal ions may enter a stream through its tributaries or as effluent from the groundwater. Therefore, samples should be taken at the confluence of each tributary and along the main stream. Alternatively, preliminary surveys may be carried out by sampling soil along the existing network of roads. In both cases, the objective is to identify areas that warrant more detailed investigation.

For a *detailed survey*, samples are collected at regular intervals either based on surveyed lines or by reference to topographic maps or aerial photographs of the area. The spacing of sampling sites must reflect the size of the deposit being searched for. Samples may consist of soil, vegetation, or soil gases, as appropriate for the elements being sought. If the bedrock is well exposed, rock samples can also be taken. The samples collected in the field should be analyzed while the survey is still in progress so that the sampling can be extended based on the initial results.

The analysis of the samples should be done by experts, but the pretreatment of the samples requires careful consideration by the geochemists in charge of the survey. For example, soil samples may be collected selectively from the A, B, or C horizons, they may be analyzed by complete dissolution of the bulk sample or of a selected grain-size fraction, or they may be leached with acids or other solvents to selectively extract elements that are adsorbed or exist in secondary acid-soluble compounds. In some cases, certain minerals may be selectively concentrated prior to analysis based on differences in specific gravity, magnetic susceptibility, or electrical conductivity. Whatever pretreatment procedure and analytical method is chosen, must be applied uniformly to all samples in order to generate an internally consistent data set.

The interpretation of the results of a systematic geochemical survey usually *starts* with the preparation of a contoured map for each of the elements included in the survey. In the ideal case, such a map

describes a *geochemical landscape* within which may occur *geochemical anomalies*. An anomaly is an area on the contoured geochemical map in which the concentration of a selected element is consistently and significantly above the background based on systematically collected and analyzed samples of a certain kind. Therefore, the *background* must be defined for each element included in the survey.

The geochemical background depends on the lithologic composition of the bedrock in the study area and therefore may change at geological contacts. This principle has been used in geologic mapping of areas where bedrock is covered by overburden that formed in place. Certain kinds of igneous or sedimentary rocks may give rise to high geochemical backgrounds in surficial deposits because the rocks are enriched in certain elements. For example, carbonaceous shales and phosphate rocks commonly produce high geochemical backgrounds in saprolite or soil formed from them. Ultramafic igneous rocks and certain syenites also give rise to high background values of elements that are concentrated in them (Table 4.5). Therefore, such elevated local backgrounds must be distinguished from the somewhat lower regional background. In addition, the *range* of random variations of the concentrations of elements in the background must be known.

Large geochemical anomalies have resulted from the dispersal of contaminants released as a consequence of human activity. Some common sources of such anthropogenic contamination of the environment include:

1. Effluent from piles of waste rock or tailings ponds associated with mining operations.
2. Particles deposited from plumes of smoke and gases emitted by smelters.
3. Effluent from chemical or manufacturing plants.
4. Leachate from municipal landfills and effluent from sewage-treatment facilities.

The geochemical anomalies that can be attributed to anthropogenic causes must be identified and removed from further consideration. The

remaining *natural* anomalies become targets for further evaluation.

Natural geochemical anomalies can be classified on the basis of their formation into *clastic*, *hydromorphic*, and *biogenic* dispersion patterns. However, all three processes of dispersal may contribute to the formation of a particular geochemical anomaly (Hawkes and Webb, 1962). *Clastic* dispersion patterns result primarily from the movement of solid particles under the influence of gravity or by entrainment in moving water or ice. *Hydromorphic* dispersal is caused by the transport of ions and molecules in solution and their ultimate deposition by adsorption on solid particles or by precipitation of compounds. *Biogenic* patterns result from the absorption of ions by plant roots, the accumulation of metals in leaf litter and soil humus, or from the dispersal of elements in the metabolic products of animals.

The *contrast* between an anomaly in the concentration of a particular element in soil samples and the local background or *threshold* depends on the geochemical properties of the element and the environmental conditions in the soil. *High* contrast between anomalies and the background result from the following conditions occurring singly or in combination:

1. Shallow depth of chemical weathering.
2. Incomplete soil development.
3. Basic conditions ($\text{pH} > 7$).
4. Presence of carbonates and/or Fe oxides.
5. Presence of clay minerals and other adsorbents of ions.
6. Low rainfall.
7. Poor drainage.
8. Rapid erosion.

Conversely, the opposite conditions promote the *mobility* of ions and result in *low* contrast between anomalies and the local background.

Differences in the geochemical properties of metals occurring together in a deposit may affect the contrast of the anomalies they cause in soil. In general, metals whose compounds are soluble are *more mobile* under a given set of environmental

conditions than metals whose compounds are insoluble. Such metals therefore form large, but low-contrast, anomalies compared to the more insoluble metals with whom they may be associated in the deposit. For example, when Cu, Zn, and Pb occur together in a mineral deposit, the contrast of the resulting anomalies in soil may be $\text{Pb} > \text{Zn} > \text{Cu}$, regardless of their abundances in the deposit. Similarly, when Cu and Mo occur together, the contrast of the Cu anomaly is commonly greater than that of Mo because the latter is more mobile under oxidizing conditions than Cu. However, Mo is dispersed *more widely* in a low-contrast anomaly that can be found more easily by a geochemical survey than the high-contrast more localized Cu anomaly. Therefore, Mo acts as a *pathfinder* for deposits that contain both Cu and Mo.

In general, pathfinders are elements that are more easily detected in geochemical surveys than the valuable metals with which they are commonly associated in different kinds of mineral deposits. The list of pathfinders in Table 21.2 includes not only Mo, but also SO_4 , As, Hg, Se, and Ag.

One of the most important aspects of the evaluation of geochemical anomalies is to discover their *sources*, which, in many cases, are not exposed to direct observation. The first step toward that objective is to recognize the process by which an anomaly was produced. In general, the sources of *clastic* dispersal patterns are located upslope of the anomaly, whereas the sources of hydromorphic patterns lie upstream or in the up-gradient direction of the water table. Consequently, the sources of geochemical anomalies are commonly *not* located in the rocks that *underlie* them.

This insight is helpful in planning the evaluation of geochemical anomalies by means of more detailed geochemical surveys, by geophysical methods, and ultimately by core drilling. If the further exploration of a deposit yields positive results, a thorough drilling program is undertaken to determine its volume and tenor, which must be known in order to determine whether the deposit can be mined at a profit. Most natural geochemical anomalies do *not* result in the discovery of a

Table 21.2 Pathfinders of the Ore Deposits from Which They Originate

<i>Pathfinder</i>	<i>Samples taken</i>	<i>Type of mineral deposit</i>
SO ₄ ²⁻	water	all sulfide deposits
Mo	water, sediment, soil	porphyry Cu deposits
As	soil, sediment	Au-bearing veins
Hg	soil	Pb-Zn-Ag deposits
Se	soil	hydrothermal sulfide deposits (epithermal)
Ag	soil	Au-Ag deposits

SOURCE: Hawkes and Webb (1962).

minable deposit because the volume of mineralized rock, or the concentrations of metals, or both, are insufficient to warrant the expense of bringing the deposit into production. However, some large but low-grade deposits may ultimately become minable if the market value of the metals it contains rises or if large-scale surface mining methods are adopted.

21.8 Production and Consumption of Mineral Resources

At the *start* of the 20th century, when the population of the Earth was 1.6 billion, the natural resources of the world appeared to be inexhaustible. As we approach the end of this century, the situation has changed dramatically. The world population is rapidly approaching 6.0 billion, and serious questions have been raised about the future availability of adequate natural resources. Alarming predictions have been made about the decline of living standards based on extrapolations of present rates of consumption of natural resources. These concerns are based in part on our instinctive urge to assure the survival of the human species on Earth, not just for another century, but for all time.

Ore deposits, in the present sense of the term, are rocks whose chemical composition differs greatly from that of the average continental crust.

Consequently, such rocks are relatively *rare* and their total volume, in that part of the crust that is accessible to us, is *small*. In addition, metallic and nonmetallic deposits are *nonrenewable*. These facts combine to confront geologists with the challenging task of finding new deposits to replace those that have been mined out and thereby to assure an adequate supply of all kinds of natural resources for the future.

The limited volume and the nonrenewable character of metallic and nonmetallic mineral deposits affect the way in which the rate of production can vary as a function of time. The rates of production of all mineral commodities have increased with time since the middle of the 19th century. When these rates are projected into the future, the total amount produced increases and approaches infinity, which is obviously inconsistent with reality. Therefore, the *rates* of production of mineral commodities cannot continue to increase indefinitely, but eventually must reach a peak and must then *decline*. In spite of short-term fluctuations, a plot of annual production versus time must form a bell-shaped curve, sometimes irreverently called Hubbert's pimple after M. King Hubbert, who first drew attention to these essential facts of mineral economics (Hubbert, 1969; 1973).

Hubbert was concerned primarily with the production of fossil fuels at a time when the energy supply of the United States had become a matter of

growing concern. He prefaced one of his papers with a quotation from James B. Cabell (1926, p. 129).

The optimist proclaims that we live in the best of all possible worlds; and the pessimist fears that this is true.

Hubbert (1969) estimated that the total amount of petroleum that will ultimately be produced in the United States (excluding Alaska) is about 165×10^9 barrels and used this result to predict

the complete cycle of petroleum production in the United States. Figure 21.5 shows that 80% of all recoverable petroleum will be consumed in 65 years between 1934 and 1999 and that the highest production rate occurred around 1970. The decline of the rate of petroleum production in the United States was slowed temporarily by the discovery of oil on the North Slope of Alaska in 1968 and may be further slowed by improvements in the efficiency of oil recovery, which presently is less than 50%. However, Hubbert's

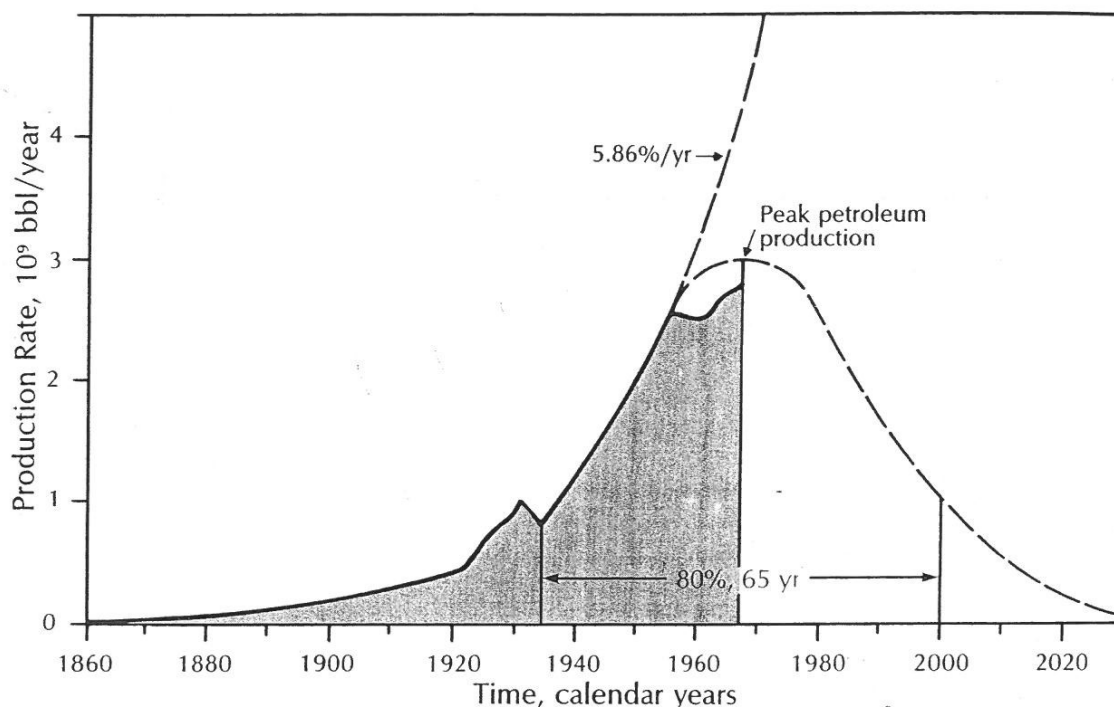


Figure 21.5 Forecast of petroleum production in the United States and its continental shelf excluding Alaska based on the estimate that the total amount of recoverable petroleum in the United States is 165×10^9 barrels (bbl). Therefore, the annual production rate must reach a peak and subsequently decline so that the area under the curve equals the total amount of available petroleum. Adding the expected production in Alaska raises the total amount of recoverable petroleum to about 190×10^9 bbl, which slows the rate of decline, but does not alter the forecast significantly. The shape of the annual production curve indicates that the United States will consume 80% of the available petroleum in 65 years and that by the year 2000 only 10% of the original amount will remain. The dashed line rising from the bell-shaped curve indicates the increase of the production rate based on an annual growth rate of 5.68%, which occurred between 1935 and 1955. This rate of growth cannot be sustained because it allows the total amount of petroleum to approach infinity (based on Hubbert, 1969).

model predicts the ultimate exhaustion of this and other nonrenewable natural resources.

The implications of the requirement that the rates of production of all nonrenewable mineral commodities must ultimately decline has given rise to a new genre of books on mineral economics. Some of these have quite alarming titles, as, for example, *Affluence in Jeopardy* (Park, 1968), *Earthbound* (Park, 1975), and *At the Crossroads* (Cameron, 1986). However, the basic facts regarding production and consumption of metals, nonmetallic minerals, and fossil fuels can be found in the *Minerals Yearbook* published annually in three volumes by the U.S. Bureau of Mines. In addition, the Bureau issues annual summaries of production and consumption of nonfuel mineral commodities (Bureau of Mines, 1988).

An important aspect of mineral economics is the extent to which the demand for mineral commodities can be met by *domestic* sources. Since no country is entirely self-sufficient, trade with other nations is required. Consequently, mineral economics affects foreign policy as nations develop alliances with trading partners who can provide the raw materials needed for industrial development. The position of the United States in this regard is shown in Table 21.3, which indicates that in 1987 more than 50% of the demand for 24 commodities was met by *imports* from other countries. In addition to the 37 metals and industrial minerals listed in Table 21.3, the United States also imported significant amounts of andalusite, Sb, Bi, Ga, Ge, I, ilmenite, Hg, Re, rutile, and V. The imports originated from 50 countries, 11 of which contributed 5 or more commodities. The list is led by Canada (24 commodities), Mexico (16), Republic of South Africa (13), Australia (9), Brazil (9), China (9), United Kingdom (6), Spain (6), Japan (5), Belgium (5), and Peru (5). The value of imports of mineral commodities in 1987 was \$4 billion for ores and raw materials and \$33 billion for metals and processed compounds. *Exports* from the United States in 1987 of raw materials, metals, and processed compounds were valued at \$24 billion, which resulted in a *trade imbalance* of about \$13 billion (Bureau of Mines, 1988).

The consumption of metals and industrial minerals has increased throughout most of the 20th century following the rise of the world's population and increases in per capita consumption (Park, 1968). However, between 1964 and 1985 the annual rates of production of most metals and industrial minerals in Table 21.4 *declined* in spite of the continuing growth of the population (Figure 19.6). The changes in production rates take the form of progressively smaller gains (Al, Cr, Fe, Ni, cement, phosphate, and potash), as well as actual reductions in the amounts produced, especially in the period 1981–1985 (Co, Mo, Sn, Hg, W, barite, fluorite, ilmenite/rutile, bauxite, and salt). Such declines in the amounts of these commodities may represent short-term fluctuations that will reverse in the future. Some evidence of such fluctuations can be seen in the production rates of Cu, Pb, Mn, Hg, W, barite, and feldspar. Nevertheless, fluctuations in the production of metals and industrial minerals are partly driven by prices and reflect the state of the balance between supply and demand. Such short-term fluctuations are a property of the world mineral economy and do not provide a reliable basis for predicting the availability of mineral resources in the distant future.

Even the rational analysis of the *petroleum production* in the United States by Hubbert (1969) *cannot* be used to predict the future availability of *metals* because the definition of what constitutes an *ore deposit* has changed and is continuing to do so. In the past, the nonferrous metals were typically recovered from high-grade deposits mined by underground methods. Most of the richest deposits have been mined out or are becoming unprofitable because the cost of underground mining has increased, whereas the prices of metals fluctuate and were depressed in the 1980s because of overproduction. Consequently, the industry has concentrated on mining low-grade deposits at shallow depth that can be recovered by less expensive open-pit methods. The trend toward large-scale mining of low-grade deposits began in 1907 when D. C. Jackling and R. C. Gemmell began open-pit mining of the porphyry-copper deposit in Bingham Canyon in Utah (Skinner, 1987).

As a result of the decrease in the minimum tenor of ore deposits, the *volume* of ore available

Table 21.3 Imports of Mineral Commodities to the United States in 1987 Expressed as Percent of Apparent Consumption

<i>Commodity</i>	<i>Imports, %</i>	<i>Sources</i>
Arsenic	100	Sweden, Canada, Mexico
Niobium	100	Brazil, Canada, Thailand, Nigeria
Graphite	100	Mexico, China, Brazil, Madagascar
Manganese	100	S. Africa, France, Gabon, Brazil
Mica	100	India, Belgium, Japan, France
Celestite	100	Mexico, Spain, China
Yttrium	100	Australia
Gem stones	99	Belgium, Luxembourg, Israel, India, S. Africa
Bauxite	97	Australia, Guinea, Jamaica, Suriname
Tantalum	92	Thailand, Brazil, Australia, Canada
Diamond (industrial)	89	S. Africa, United Kingdom, Ireland, Belgium, Luxembourg
Fluorite	88	Mexico, S. Africa, Spain, Italy, China
Platinum group metals	88	S. Africa, United Kingdom, Russia
Cobalt	86	Zaire, Zambia, Canada, Norway
Tungsten	80	China, Canada, Bolivia, Portugal
Chromium	75	S. Africa, Zimbabwe, Turkey, Yugoslavia
Nickel	74	Canada, Australia, Norway, Botswana
Tin	73	Brazil, Thailand, Indonesia, Bolivia
Potassium salts	72	Canada, Israel, Germany, Russia
Zinc	69	Canada, Mexico, Peru, Australia
Cadmium	66	Canada, Australia, Mexico, Germany
Barite	63	China, Morocco, India
Silver	57	Canada, Mexico, United Kingdom, Peru
Asbestos	51	Canada, S. Africa
Gypsum	37	Canada, Mexico, Spain
Silica	33	Brazil, Canada, Norway, Venezuela
Fe ore	28	Canada, Brazil, Venezuela, Liberia
Copper	25	Canada, Chile, Peru, Zaire, Zambia, Mexico
Aluminum	24	Canada, Japan, Venezuela, Brazil
Cement	20	Canada, Mexico, Spain
Iron + steel	19	Europe, Japan, Canada, Rep. Korea
Lead	15	Canada, Mexico, Peru, Australia, Honduras
Salt (NaCl)	12	Canada, Mexico, Bahamas, Chile, Spain
Beryllium	11	Brazil, China, Switzerland, S. Africa
Titanium	8	Japan, Russia
Nitrogen	7	Canada, Russia, Trinidad and Tobago, Mexico
Sulfur	6	Canada, Mexico

SOURCE: Bureau of Mines (1988).

Table 21.4 Annual Growth Rates of Production of Selected Mineral Commodities in Percent per Year

Commodity	1964-1973	1973-1980	1981-1985
Metals			
Al	8.12	3.45	0.28
Cr	5.21	5.17	1.86
Fe (steel)	5.37	0.24	0.24
Co	5.96	0.87	-0.14
Cu	4.87	1.01	4.33
Pb	3.87	0.13	0.53
Mn	3.36	-1.85	1.00
Mo	7.74	4.2	-2.07
Ni	6.5	2.36	1.42
Sn	2.21	0.48	-3.58
Hg	0.88	-5.13	-1.39
W	3.43	5.23	-0.29
Industrial Minerals			
Barite	3.96	7.33	-5.27
Cement	5.99	3.44	1.92
Feldspar	4.26	3.12	4.11
Fluorite	6.55	0.29	-1.24
Ilmenite/rutile	4.27	2.91	-1.64
Bauxite	9.73	4.25	-0.05
Phosphate	6.24	4.88	1.64
Salt	5.13	0.91	-0.13
Potash	6.26	4.01	1.13
(K ₂ O eq.)			

SOURCE: Cameron (1986), Table 6.2; Bureau of Mines (1985).

for mining has increased and continues to grow. Therefore, predictions based on the ore reserves available at one time must be revised later when large amounts of previously unprofitable deposits are reclassified as ore. Mining technology has changed greatly during the 20th century and is likely to continue to develop methods that are relatively inexpensive, can recover *groups* of metals from low-grade deposits, and do not alter the environment irreversibly. Such methods may include *solution mining* of artificially fractured

rocks aided by *bacteria* that decompose sulfide minerals and thereby increase their solubility in aqueous solutions.

The long-range outlook for the availability of metals and industrial minerals depends more on the *cost* and *availability* of the *energy* required for mining and processing of ore than on the volume of minable rocks. The mineral resources of the Earth become very large if metals and industrial compounds can be recovered from certain kinds of sedimentary rocks such as carbonaceous shale, phosphorite, or carbonate rocks of marine and nonmarine origin.

21.9 Summary

The principles of geochemistry and the accumulated information about the properties of the elements and their compounds are applied in the search for ore deposits from which metals can be extracted at a profit. The applicable principles concern the oxidation-reduction reactions that occur during the chemical weathering of sulfide minerals of the transition metals, including those of Fe, Cu, Pb, Zn, Hg, Ag, and Mo.

The oxidation of pyrite and the subsequent formation of solid Fe(OH)₃ causes acidification that enhances the solubility of the compounds of other metals. The process is greatly accelerated by the metabolic activities of certain bacteria, some of which can also attack sulfide minerals.

Copper is commonly associated with Fe either in the form of discrete sulfide minerals, such as chalcocite and pyrite, or in mixed compounds, such as chalcopyrite, bornite, or cubanite. Under acidic and oxidizing conditions, these minerals dissolve to form solutions of Cu²⁺ and SO₄²⁻, which percolate downward towards the water table. If the solutions encounter basic environments, they may precipitate Cu oxides (cuprite or tenorite) or the carbonates (malachite or azurite). However, if the Cu²⁺ ions reach the reducing environment below the water table, they are reduced to Cu⁺ and may replace Fe²⁺ in pyrite. As a result of the formation of secondary chalcocite

by replacement of pyrite, the concentration of Cu in the rock is increased.

This process of supergene enrichment has played an important role in the formation of minable deposits of Cu and Ag. In principle, one can rank the sulfides of different metals in terms of *increasing* solubility and predict, on that basis, that the ions of one metal can replace the ions of another in a mineral that is *more* soluble. The effectiveness of supergene enrichment is enhanced when the water table is low, the rocks are permeable, hydrologic gradients and erosion rates are low, and carbonate rocks are absent. Supergene enrichment is ineffective for Pb and Zn, because these metals form insoluble sulfates and carbonates, and for Mo because its ions remain in solution over a wide range of environmental conditions.

The mobility of ions released by oxidation of sulfide deposits determines their dispersion and hence the contrast of the geochemical anomaly they form in surficial deposits. Geochemical exploration, which is based on this phenomenon, is an effective and widely practiced technique for locating mineral deposits. However, some of the anomalies identified by such surveys may be of

anthropogenic origin and most of the natural anomalies do not actually result in the discovery of minable deposits because either the tenor or the volume of the deposit, or both, are insufficient to warrant the expense of bringing it into production.

The consumption of mineral resources has increased historically in step with the growing population of the world. However, the average annual rates of production of some important metals and industrial minerals decreased in the second half of the 20th century and some have actually become negative. The shortages that may occur in the future may spur production, thereby contributing to the fluctuations in supply and demand that are characteristic of the mining economy of the world. The trend appears to be toward mining of low-grade near-surface deposits that can be worked by open-pit methods and by leaching metals from rocks either on the surface or below it. As a result of the changing definition of what constitutes a minable deposit, the volume of ore reserves is expanding. The ultimate limitation on the production of natural mineral resources is the cost of the necessary energy.

Problems

1. Derive the Eh-pH equation for the dissolution of cuprite (Cu_2O) to Cu^{2+} .
2. Derive the Eh-pH equation for the dissolution of tenorite (CuO) to Cu^{2+} .
3. Calculate the ration of $[\text{Cu}^{2+}]/[\text{Cu}^+]$ in an aqueous solution at Eh = +0.80 V.
4. Derive an Eh-pH diagram for sphalerite (ZnS) and zincite (ZnO) and their ions Zn^{2+} and ZnO_2^{2-} in a system at 25°C and 1 atm, where $\Sigma S = 10^{-3}$ mol/L (i.e., native S does not occur). Draw the solubility limits at activities of 10^{-8} mol/L (see Brookins, 1988, p. 55).
5. Calculate the solubility of molybdenite (MoS_2) dissolving to form HMoO_4^- at Eh = -0.20 V, pH = 5.0, $\Sigma S = 10^{-1}$ mol/L, 25°C at 1 atm.
6. Calculate the solubility of wulfenite (PbMoO_4) in pure water at pH = 7 and express it in terms of $[\text{Pb}^{2+}]$ at equilibrium (check Figure 21.4C).
7. If the system is open to the atmosphere ($[\text{CO}_2] = 3 \times 10^{-4}$ atm), would cerussite (PbCO_3) replace wulfenite assuming pH = 7.0 and $[\text{HMoO}_4^-]$ as calculated in Problem 6?
8. If the activity ratio $[\text{Ag}^+]/[\text{Pb}^{2+}] = 10^{-2}$ in contact with galena, how many moles of Ag_2S will form per liter of solution before equilibrium is restored? (Assume that the data in Table 21.1 apply.)
9. Consider whether supergene enrichment of Cd can occur by replacement of Zn in sphalerite in systems having $\Sigma S = 10^{-3}$ mol/L, if pH = 5.0, Eh = -0.20 V, 25°C and 1 atm (consult Brookins, 1988).

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Geochemical Cycles

The geochemical processes on the surface of the Earth work like a machine through which matter is cycled continuously (Section 4.3). The plumbing system of the machine consists of several reservoirs of different volumes connected by pipes through which matter moves from one reservoir to another. All chemical elements are continually being processed by this geochemical machine. However, the volumes of the reservoirs and the period of time a particular element resides in each reservoir depend on the geochemical properties of the element. Therefore, each element has a characteristic geochemical cycle that reflects its particular set of geochemical properties. The geochemical cycles of the elements have influenced the environment on the surface of the Earth and have, in turn, been affected by changes that have occurred on that surface. The most recent perturbation of geochemical cycles has been caused by human activities (Stumm, 1977).

The rock cycle in Figure 22.1 illustrates how the major rock types are related to each other by geological and geochemical processes. For example, chemical and mechanical weathering convert igneous rocks into sediment and ions in solution that are transported to the oceans where they are deposited (Sections 4.3 and 4.4). The resulting layers of sediment are lithified into sedimentary rocks that may be altered to metamorphic rocks or may be partially melted to form magma from which new igneous rocks crystallize. Since the rock cycle has operated throughout the history of the Earth, we can assume that it has achieved a *steady state*. Consequently, the chemical compositions of the conduits through which the ele-

ments pass and the reservoirs in which they reside for varying periods of time should have remained constant. This generalization is helpful because it implies that the chemical composition of sedimentary rocks, averaged over sufficiently long intervals of geologic time, is constant and that the chemical composition of seawater has likewise been constant.

The chemical composition of seawater and sedimentary rocks is, however, affected by *long-term* changes such as the evolution of life and the related changes in the chemical composition of the atmosphere (Holland, 1984). The reservoirs also respond to orogenies on continents, volcanic activity in subduction zones and along midocean ridges, and to the resulting chemical as well as isotopic exchange between seawater and basalt (Wolery and Sleep, 1988). Moreover, the geochemical differentiation of the mantle and continental crust in the course of geologic time has allowed differences to develop in the isotopic abundances of stable, *radiogenic* daughters of long-lived radioactive parents (Section 16.3). Consequently, the isotopic compositions of the nonvolatile elements Ca, Sr, Nd, Hf, Os, and Pb in the oceans and in clastic sedimentary rocks have changed over geologic time in response to variations in the inputs from the continental crust and the mantle of the Earth (Faure, 1986).

Some important contributions to the literature on geochemical cycles include the books by Garrels and Mackenzie (1971), Garrels et al. (1975), Salomons and Förstner (1984), Berner and Berner (1987), Gregor et al. (1988), and Lerman and Meybeck (1988).

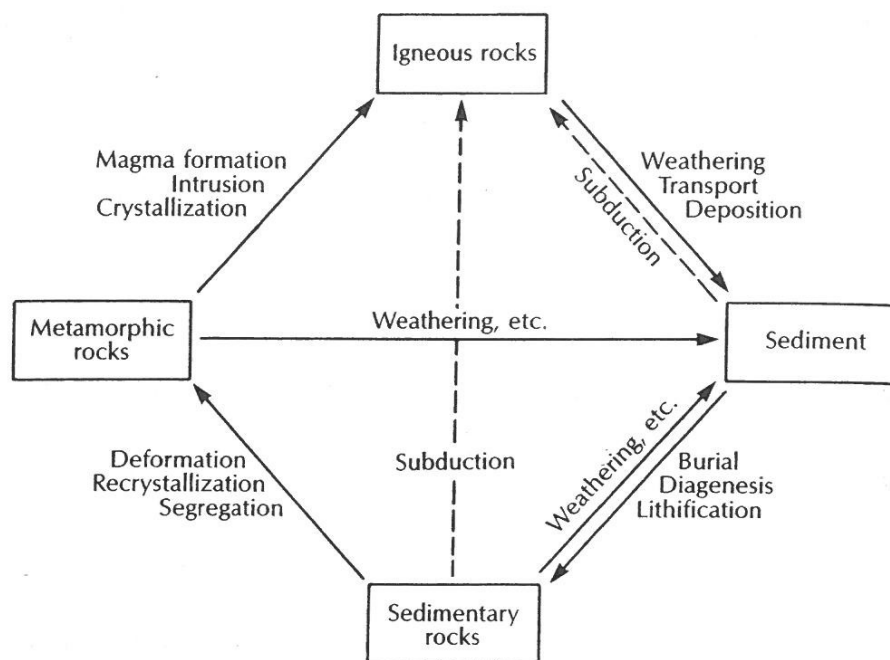


Figure 22.1 The rock cycle consisting of igneous, sedimentary, and metamorphic rocks. The arrows indicate the geological and geochemical processes that cause the required transformations of matter.

22.1 The Principle of Mass Balance

If the geochemical cycles of the elements are in a steady state, the total mass of a nonvolatile element released by weathering of igneous rocks must be equal to its mass in sedimentary rocks and in the oceans. This postulate is expressed by the equation (Drever et al., 1988):

$$M_{ig} C_{ig}^i = M_{sed} \sum a_j C_{sed}^i + M_{sw} C_{sw}^i \quad (22.1)$$

where M_{ig} = mass of all igneous rocks in the continental crust that have weathered
 C_{ig}^i = concentration of element i in igneous rocks of the crust
 M_{sed} = mass of all sedimentary rocks in existence at the present time, including sediment in the oceans
 C_{sed}^i = concentration of element i in sedimentary rocks and sediment in the oceans

M_{sw} = mass of water in the oceans

C_{sw}^i = concentration of element i in seawater

a_j = mass fractions of different kinds of sedimentary rocks and sediment in the oceans

Equation 22.1 neglects groundwater, surface water, and ice sheets because together they constitute only 2.75% of the water in the hydrosphere (Table 4.6) and because the concentrations of most elements they contain are low compared to seawater (Table 4.7). The equation *does* include the clay minerals, oxides, and hydroxides that form during incongruent dissolution of aluminosilicate minerals because they are ultimately incorporated into sedimentary rocks. The equation can be expanded to include saprolite, till, and soil on the continents and sediment in suspension in rivers, lakes, and in the oceans, if desired.

The masses of the various reservoirs have been estimated as follows:

$$M_{\text{sed}} = 2.5 \pm 0.4 \times 10^{24} \text{ g (Li, 1972; Ronov and Yaroshevsky, 1976)}$$

$$M_{\text{ig}} = 0.88 M_{\text{sed}}, \text{ where } M_{\text{sed}} \text{ includes volatile elements and compounds degassed from the interior of the Earth, such as } \text{H}_2\text{O, CO}_2, \text{ and the noble gases (Li, 1972)}$$

$$M_{\text{sw}} = 1.4 \times 10^{24} \text{ g (Sverdrup et al., 1942)}$$

The mass of sediment in the oceans is about $0.12 \times 10^{24} \text{ g}$ (Drever et al., 1988) distributed in approximately equal proportions between pelagic clay (deep-sea sediment) and calcareous ooze. The abundances of the different kinds of sedimentary rocks have been estimated in various ways with somewhat different results (Sections 4.2 and 4.3). Garrels and Mackenzie (1971) estimated the proportions of shale/sandstone/carbonates/evaporites to be 74:11:15:2. These proportions indicate that the mass fractions (a_i) are:

$$a_{\text{sh}} (\text{shale}) = 0.725 \quad a_{\text{cc}} (\text{carbonate}) = 0.147$$

$$a_{\text{ss}} (\text{sandstone}) = 0.108 \quad a_{\text{ev}} (\text{evaporite}) = 0.020$$

Drever et al. (1988) treated oceanic pelagic (op) and oceanic carbonate (oc) separately and adjusted the mass fractions in equation 22.1 accordingly:

$$\begin{aligned} M_{\text{ig}} C_{\text{ig}}^i = M_{\text{sed}} (0.702 C_{\text{sh}}^i + 0.108 C_{\text{ss}}^i \\ + 0.122 C_{\text{cc}}^i + 0.02 C_{\text{ev}}^i + 0.024 C_{\text{op}}^i \\ + 0.024 C_{\text{oc}}^i) + M_{\text{sw}} C_{\text{sw}}^i \end{aligned} \quad (22.2)$$

Since $M_{\text{sed}} = M_{\text{ig}}/0.88 = 2.5 \pm 0.4 \times 10^{24} \text{ g}$, we divide equation 22.2 by M_{sed} :

$$\begin{aligned} 0.88 C_{\text{ig}}^i = 0.702 C_{\text{sh}}^i + 0.108 C_{\text{ss}}^i \\ + 0.122 C_{\text{cc}}^i + 0.02 C_{\text{ev}}^i + 0.024 C_{\text{op}}^i \\ + 0.24 C_{\text{oc}}^i + 0.56 C_{\text{sw}}^i \end{aligned} \quad (22.3)$$

This equation can be used to calculate the chemical composition of seawater or to assess the geochemical balance of individual elements by substituting appropriate estimates of the concentrations in the different kinds of rocks and in seawater. In doing so, we make use of all of the accumulated informa-

tion about the chemical composition of terrestrial rocks summarized in Chapter 4.

In order to assess the state of the mass balance of the elements, it is convenient to evaluate each side of equation 22.3 separately and then to form the ratio of the results. If the right side of equation 22.3 is represented by $\bar{C}_s$, a perfect balance is indicated when the ratio:

$$\frac{\bar{C}_s}{0.88 C_{\text{ig}}^i} = 1.00 \quad (22.4)$$

However, because of the uncertainties in the magnitudes of the concentrations and mass fractions in equation 22.3, we can be satisfied with values between 0.8 and 1.30, as suggested by Drever et al. (1988).

The state of the mass balance for Mg can be evaluated by using data from Table 4.5. For this purpose we estimate the average Mg concentration of igneous rocks by combining low-Ca and high-Ca granites in equal proportions to obtain an average value for *granite* and by defining C_{ig}^i as follows:

$$C_{\text{ig}}^i = 0.35 C_{\text{basalt}}^i + 0.65 C_{\text{granite}}^i \quad (22.5)$$

The necessary data for the assessment of the Mg balance based on Table 4.5 (rocks) and Table 4.7 (seawater) are:

	%		%
$C_{\text{ig}}^{\text{Mg}}$	1.95	$C_{\text{ev}}^{\text{Mg}}$	4.70 (?)
$C_{\text{sh}}^{\text{Mg}}$	1.50	$C_{\text{op}}^{\text{Mg}}$	2.10
$C_{\text{ss}}^{\text{Mg}}$	0.70	$C_{\text{oc}}^{\text{Mg}}$	4.70 (?)
$C_{\text{cc}}^{\text{Mg}}$	4.70		

Based on these data, $C_s^{\text{Mg}} = 1.645\%$, $0.88 C_{\text{ig}}^{\text{Mg}} = 1.716\%$, and the ratio:

$$\frac{C_s^{\text{Mg}}}{0.88 C_{\text{ig}}^{\text{Mg}}} = \frac{1.645}{1.716} = 0.96 \quad (22.6)$$

which confirms the mass balance for this element.

The result for Ca does not work out this well. Using the data listed below from Tables 4.5 and 4.7 we find *excess* Ca in sedimentary rocks and seawater:

	%		%
C_{ig}^{Ca}	3.51	C_{ev}^{Ca}	30.23
C_{sh}^{Ca}	2.21	C_{op}^{Ca}	2.90
C_{ss}^{Ca}	3.91	C_{oc}^{Ca}	30.23
C_{cc}^{Ca}	30.23		

$$\frac{C_s^{Ca}}{0.88C_{ig}^{Ca}} = \frac{7.061}{3.088} = 2.3 \quad (22.7)$$

The Ca imbalance can be resolved either by questioning the validity of the data used in the calculation or by postulating the existence of additional sources for Ca that are not represented in equation 22.3, such as:

1. Leaching of Ca from volcanogenic sediment (Garrels and Mackenzie, 1971).
2. Preferential exchange of Mg^{2+} and Na^+ in seawater with Ca^{2+} in basalt in convecting hydrothermal systems along midocean ridges (Wolery and Sleep, 1976; Edmond et al., 1979), followed by precipitation of the Ca as calcite.

These and other suggestions were evaluated by Drever et al. (1988) without resolving the dilemma. Nevertheless, 43 elements listed in Table 22.1 have acceptable mass balances, whereas 18 elements do not. The balance ratios of these elements range from ~1.5 for U to 151 for Cl. Evidently, there is much more Cl in the oceans and in sedimentary rocks than can be accounted for by weathering of igneous rocks in the crust.

22.2 Mass Balance for Major Elements in the Ocean

The ocean plays an important role in the operation of geochemical cycles because both solid particles and ions/molecules pass through it. In Section 4.4, we calculated the mean oceanic residence times (MORT, Table 4.7) of the elements and discussed the importance of solid particles in selectively removing the ions of some elements

Table 22.1 State of the Geochemical Mass Balance for the Chemical Elements (Based on the requirement that the amount supplied by weathering of igneous rocks is equal to the amounts in sedimentary rocks and in the oceans.)

Element	Balance ratio ^a	Element	Balance ratio
A. Satisfactory balance			
Be	1.26	Y	1.05
F	1.24	Zr	1.07
Na	0.84	Nb	0.81
Mg	1.02	Pd	~1
Al	0.91	Ag	0.92
Si	0.94	Cd	1.29
P	0.81	In	0.91
K	0.96	Ba	1.02
Sc	0.81	La	1.01
Ti	0.87	Ce	1.13
V	0.88	Nd	1.24
Cr	1.18	Sm	0.97
Mn	1.27	Eu	1.25
Fe	0.94	Tb	1.00
Co	0.90	Yb	1.11
Ni	1.24	Hf	1.02
Cu	1.02	Ta	0.99
Zn	1.25	W	1.26
Ga	1.06	Au	0.98
Ge	1.13	Tl	1.17
Rb	1.20	Th	1.05
Sr	1.15		
B. Unsatisfactory balance			
Li	2.12	Sn	2.44
B	11.9	Sb	6.28
S	16.5	Te	10.4
Cl	151	I	7.52
Ca	2.1	Cs	1.79
As	6.1	Hg	15.1
Se	10.1	Pb	1.55
Br	12.7	Bi	8.5
Mo	2.34	U	1.47

^aThe balance ratio is defined in equation 22.4. A value between 0.80 and 1.30 implies a satisfactory mass balance, whereas a value >1.30 implies an imbalance between the mass of an element in sedimentary rocks (including the oceans) and crustal igneous rocks that have weathered.

SOURCE: Drever et al. (1988).

from seawater. We now return to this subject in order to assess the mass balance of elements entering and leaving the oceans by considering the relevant inputs and outputs of both major and trace elements.

The *major elements* enter the oceans primarily by discharge of river water and to some extent by ion exchange reactions between seawater and suspended sediment, and between seawater and hot basalt along midocean ridges. The input of major elements to the ocean by rivers has been evaluated by Meybeck (1979) based on estimates of the average chemical compositions and discharges of the rivers of the world (Sections 20.1 and 20.2 and Table 20.1). The amounts of each element discharged into the oceans as a result of chemical weathering of rocks on the continents must be reduced by subtracting cyclic marine salts and anthropogenic contaminants as shown in Table 22.2. Note that anthropogenic contamination contributes ~30% of the Na^+ , Cl^- , and SO_4^{2-} and from 7 to 10% of the Mg^{2+} , Ca^{2+} , and K^+ dissolved in rivers at the present time (Section 20.2). In addition, marine salts represent an additional 32% of the Cl^- and 20% of Na^+ dissolved in rivers, which means that only ~40–50% of the Cl^- and Na^+ in solution in river water was released by chemical weathering.

If the ocean is in a *steady state*, the inputs must be equal to the outputs for each element. The principal outputs of major elements from the ocean include:

1. Burial of pore water.
2. Ion exchange reactions and water-rock interactions.
3. Diagenesis.
4. Chemical precipitates of carbonates, sulfides, oxides, phosphates, silica, sulfates, and chlorides.

Each year a certain amount of seawater is removed from the oceans because it occupies pore spaces in sediment. The porosity of the sediment decreases as a result of compaction and therefore cannot be stated precisely. Drever et al. (1988) adopted a value of 30%, but considered

Table 22.2 Inputs of Major Elements in Solution in River Water That Enter the Oceans Each Year in Units of 10^{12} mol/yr Based on a Total Discharge of 37.4×10^{15} L/yr

<i>Ion or compound</i>	<i>Total flux</i>	<i>Marine salt</i>	<i>Anthropogenic contaminant</i>	<i>Net flux</i>
Na^+	11.7	2.39	3.39	5.91
K^+	1.36	0.05	0.13	1.17
Mg^{2+}	5.59	0.29	0.41	4.85
Ca^{2+}	13.7	0.05	1.18	12.36
Cl^-	8.69	2.82	2.63	3.27
SO_4^{2-}	4.49	0.16	1.29	3.07
HCO_3^-	33.4	—	1.64	32.09
H_4SiO_4	6.47	—	—	6.47

SOURCE: Drever et al. (1988); Meybeck (1979).

that it could range up to 50%. Ion exchange of suspended clay minerals entering the oceans is relatively unimportant for the major elements and involves primarily Na^+ replacing Ca^{2+} on adsorption sites. However, water-rock interaction may be a source for some elements and a sink for others. Chemical reactions between mineral particles in the sediment and trapped seawater (diagenesis) also release some ions while consuming others. An evaluation by Sayles (1979) indicated that K^+ and Mg^{2+} are consumed, whereas Na^+ , Ca^{2+} , and HCO_3^- are released by diagenetic reactions. Seawater is close to being saturated with respect to several types of compounds (listed above), which may precipitate from it under favorable physical/chemical conditions or as a result of biological activity.

The quantitative estimates of outputs from the oceans in Table 22.3 (Drever et al., 1988) can be compared to the inputs by rivers to test the balance for each major element. For example, Na^+ is removed from seawater by burial of pore water and by ion exchange reactions, but is added by diagenetic reactions in the sediment. The sum of the inputs and outputs for Na^+ is $+5.9 \pm 2.4 \times 10^{12}$ mol/yr, where the uncertainty is the sum of the errors of the estimated fluxes in

Table 22.3 Inputs and Outputs of Major Elements in Solution in the Ocean^a in Units of 10^{12} mol/yr

<i>Ion or compound</i>	<i>River^b input</i>	<i>Burial, pore water</i>	<i>Ion exchange</i>	<i>Diagenetic reactions</i>	<i>Precipitates</i>	<i>Net balance</i>
Na ⁺	+5.91	-0.96 ± 0.64	-1.53 ± 0.06	+2.5 ± 1.7	—	+5.9 ± 2.4
K ⁺	+1.17	-0.02 ± 0.01	-0.20 ± 0.08	-0.9 ± 0.5	—	+0.05 ± 6
Mg ²⁺	+4.85	-0.09 ± 0.04	-0.32 ± 0.08	-2.3 ± 1.6	-0.26 ± 0.02	+1.9 ± 1.7
Ca ²⁺	+12.36	-0.02 ± 0.01	-0.96 ± 0.10	+3.6 ± 3.0	-12.5 ± 1.8	+4.5 ± 4.9
Cl ⁻	+3.27	-1.07 ± 0.71	—	—	—	+2.2 ± 0.7
SO ₄ ²⁻	+3.07	-0.06 ± 0.04	—	—	-0.60 ± ?	+2.4
HCO ₃ ⁻	+32.09	—	-0.42 ± 0.16	+4.7 ± 4.0	-24.2 ± 3.6	+11.6 ± 7.8
H ₄ SiO ₄	+6.47	—	—	—	-7.0 ± 0.09	-0.5 ± 0.09

^aA plus sign indicates gain by and a minus sign means loss from the ocean.^bFrom Table 22.2.

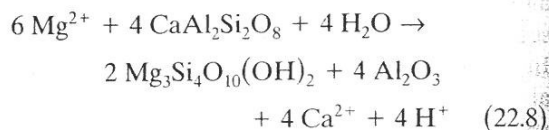
SOURCE: Drever et al. (1988).

Table 22.3. Evidently, more Na⁺ appears to be entering the ocean than is leaving it, which may indicate either that the estimates of the input or output fluxes are incorrect or that the ocean is not in a steady state with respect to Na⁺; that is, the Na⁺ concentration of seawater is increasing. Similar positive imbalances exist for Ca²⁺, Cl⁻, HCO₃⁻, SO₄²⁻, and Mg²⁺, whereas K⁺ and H₄SiO₄ appear to be in balance.

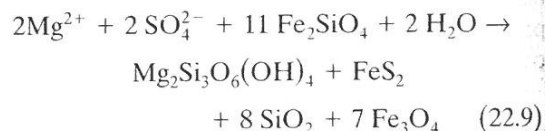
The excess Ca²⁺ in the ocean is partly matched by an excess of SO₄²⁻, whereas the Na⁺ excess correlates with the excess in Cl⁻. Therefore, we may conclude that the concentrations of these elements in seawater are rising in preparation for the next episode of deposition of CaSO₄ and NaCl in marine evaporite basins. The last such episode occurred $\sim 5.5 \times 10^6$ yr ago when the Mediterranean basin was isolated from the Atlantic Ocean (Hsü, 1983). However, the imbalances for Na⁺ and Ca²⁺ persist even after allowances are made for the future precipitation of gypsum and halite.

This difficulty serves as a reminder that the estimates of inputs and outputs in Table 22.3 do not include the interactions of seawater with hot basalt along midocean ridges. According to studies cited by Drever et al. (1988), these reactions involve the conversion of anorthite (CaAl₂Si₂O₈)

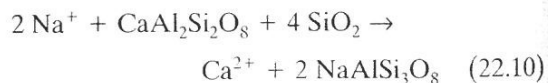
to talc (Mg₃Si₄O₁₀(OH)₂) by the uptake of Mg²⁺ from seawater:



Complex interactions of fayalite (Fe₂SiO₄) with SO₄²⁻ and Mg²⁺ form sepiolite (Mg₂Si₃O₆(OH)₄), pyrite, amorphous silica, and magnetite:



In addition, Na⁺ replaces Ca²⁺ and K⁺ as a result of the albitization of Ca-plagioclase and K-feldspar, respectively:



and:



These reactions *reduce* the concentrations of Mg²⁺, SO₄²⁻, and Na⁺ in seawater and *increase* the concentrations of Ca²⁺ and K⁺. However, the

Ca^{2+} released by this process precipitates as calcite in fractures and cavities in the basalt and does not remain in seawater. Moreover, the fluxes of the major elements leaving and entering the ocean as a result of water-rock interactions have not been quantified. Therefore, we can say only that these reactions probably remove Na^+ , Mg^{2+} , and SO_4^{2-} from the oceans and that some K^+ may be released. However, water-rock interaction does *not* help to explain the apparent excess of Ca^{2+} in the oceans.

The attempt to balance inputs and outputs of major elements in the oceans is only partly successful. This could mean that the ocean is not in a steady state and that the composition of seawater is changing due to natural causes and probably has done so in the geologic past. The imbalances discussed above become *larger* when anthropogenic contamination of rivers is included. For example, the riverine Na^+ flux to the ocean at the *present time* is not 5.91×10^{12} mol/yr (Table 22.2) but is actually 9.30×10^{12} mol/yr when the anthropogenic input of 3.39×10^{12} mol/yr is added to the natural flux. However, anthropogenic contamination has a *negligible* effect on the concentrations of the *major elements* in the ocean. For example, Drever et al (1988) reported that it would take 300×10^6 yr before the anthropogenic input of SO_4^{2-} (1.29×10^{12} mol/yr) would saturate seawater with respect to gypsum, assuming that the concentration of Ca^{2+} in the ocean remains constant. The ocean resists change because it is a very large reservoir of the major elements compared to the annual inputs by rivers.

22.3 Mass Balance for Trace Elements in the Ocean

Trace elements in solution in river water and adsorbed on suspended particles are generally deposited in estuaries and on the continental shelves or accumulate in deep-sea clay (Sections 4.3 and 4.4). Therefore, the annual riverine input of a trace element to the oceans must be equal to the output of that element associated with marine

muds. The annual input of trace element i by rivers can be represented by:

$$\text{input}_i = M_{\text{sp}} C_{\text{sp}}^i + M_{\text{rw}} C_{\text{rw}}^i \quad (22.12)$$

where M_{sp} = mass of suspended sediment transported annually by rivers into the ocean

M_{rw} = mass of river water entering the ocean annually

C_{sp}^i = concentration of element i in suspended particles

C_{rw}^i = concentration of element i in river water

The output from the oceans is given by:

$$\text{output}_i = M_{\text{ds}} C_{\text{ds}}^i + M_{\text{sh}} C_{\text{sh}}^i \quad (22.13)$$

where M_{ds} = mass of deep-sea clay deposited annually

M_{sh} = mass of mud deposited annually in estuaries and on continental shelves

C_{ds}^i = concentration of element i in deep-sea clay

C_{sh}^i = concentration of element i in shelf sediment (shale)

The mass of sediment deposited near shore each year is equal to the input by rivers in the form of suspended particles and dissolved ions minus the mass of deep-sea clay:

$$M_{\text{sh}} = M_{\text{sp}} + M_{\text{rw}} \sum C_{\text{rw}}^i - M_{\text{ds}} \quad (22.14)$$

The term $\sum C_{\text{rw}}^i$ in equation 22.14 is the sum of the concentrations of all ions in river water, excluding Ca^{2+} and HCO_3^- , after reducing the concentrations by the amount of recycled marine chloride. Drever et al. (1988) excluded Ca^{2+} and HCO_3^- because they precipitate as calcite in the ocean and because calcite concentrates only a few of the trace elements.

By substituting equation 22.14 in equation 22.13 and by letting $\text{input}_i = \text{output}_i$, we obtain the complete mass balance equation (Drever et al., 1988):

$$M_{\text{sp}} C_{\text{sp}}^i + M_{\text{rw}} C_{\text{rw}}^i = M_{\text{ds}} C_{\text{ds}}^i + \left(M_{\text{sp}} + M_{\text{rw}} \sum C_{\text{rw}}^i - M_{\text{ds}} \right) C_{\text{sh}}^i \quad (22.15)$$

The masses of sediment entering and leaving the ocean annually have been estimated and can be specified as follows:

$$M_{sp} = 18 \pm 3 \times 10^{15} \text{ g/yr} \\ (\text{Holeman, 1968; Meybeck, 1979})$$

$$M_{ds} = 1.1 \pm 0.4 \times 10^{15} \text{ g/yr} \\ (\text{Ku et al., 1968})$$

$$M_{rw} = 33 \pm 3 \times 10^{18} \text{ g/yr} \\ (\text{Garrels and Mackenzie, 1971})$$

$$M_{rw} \sum C_{rw}^i = 0.92 \times 10^{15} \text{ g/yr} \\ (\text{Drever et al., 1988})$$

Substituting these values into equation 22.15 yields:

$$(18 \times 10^{15})C_{sp}^i + (33 \times 10^{18})C_{rw}^i \\ = (1.1 \times 10^{15})C_{ds}^i + [(18 \times 10^{15}) \\ + (0.92 \times 10^{15}) - (1.1 \times 10^{15})]C_{sh}^i \quad (22.16)$$

which reduces to:

$$C_{sp}^i + (1.8 \times 10^3)C_{rw}^i = 0.06C_{ds}^i + 0.99C_{sh}^i \quad (22.17)$$

where the concentrations are expressed in parts per million. We now define the input (M_{in}^i) as:

$$M_{in}^i = C_{sp}^i + (1.8 \times 10^3)C_{rw}^i \quad (22.18)$$

and the output M_{out}^i as:

$$M_{out}^i = 0.06C_{ds}^i + 0.99C_{sh}^i \quad (22.19)$$

If the ocean is in a steady state with respect to a particular element, the ratio of its output and input functions must be:

$$\frac{M_{out}^i}{M_{in}^i} = 1.00 \quad (22.20)$$

As before, we accept values of this ratio between 0.80 and 1.30 as evidence of a satisfactory balance between output and input and use this criterion to classify the elements.

Data assembled from the literature by Drever et al. (1988) indicate that 30 elements identified in Table 22.4A have satisfactory input-output balances. Lithium, As, and Rb, whose output/input

Table 22.4 Mass Balance of Elements (Equation 22.20) Entering the Ocean by Discharge of Rivers (in Solution and in Suspended Particles) and Leaving the Ocean by Deposition of Sediment (as Shale and Deep-Sea Clay)

Element	Output/input	Element	Output/input
A. Satisfactory Balance (Output $\approx$ Input)			
Li	2.26	Ga	0.80
B	1.3	As	1.58
Mg	0.83	Rb	1.43
Al	0.89	Sr	1.07
Si	0.97	Mo	1.0
K	1.14	Cs	0.89
Ca ^a	1.02	Ba	1.1
Sc	0.78	La	0.96
Ti	0.86	Ce	0.93
V	0.79	Nd	1.14
Cr	0.93	Sm	1.13
Mn	1.2	Eu	1.13
Fe	1.05	Lu	1.27
Co	1.2	Th	0.90
Ni	0.89	U	1.02
B. Unsatisfactory Balance (Input > Output)			
Na	0.65	Ag	0.11
F	0.66	Cd	0.29
S	0.37	Sb	0.25
Cl	0.10	I	0.30
Cu	0.53	Au	0.026
Zn	0.27	Hg	0.52
Br	0.20	Pb	0.16
C. Not Classified (Nonvolatile)			
Be	Pd	Ho	Re
F	In	Er	Os
Ge	Te	Tm	Ir
Zr	Pr	Yb	Pr
Nb	Gd	Hf	Tl
Ru	Tb	Ta	
Rh	Dy	W	

^aOceanic carbonate included by adding $0.08 C_{oc}^i$ to the right side of equation 22.17 (Drever et al., 1988).

SOURCE: Drever et al. (1988).

ratios (equation 22.20) are actually greater than 1.30 are, nevertheless, included in this group. A second group of 14 elements are out of balance because their *inputs* to the ocean are significantly *greater* than their outputs. A large number of elements are not listed at all, either because they are volatile or because the information necessary for an evaluation is lacking. Table 22.4 contains 26 unclassified nonvolatile elements without including the noble gases, C, H, N, O, and the radioactive elements in the decay chains of U and Th: Po, At, Fr, Ra, Ac, and Pa.

The apparent imbalance of the inputs and outputs of elements in Table 22.4B may be caused by *inaccurate* analytical data or by the existence of outputs that are not included in equation 22.17. Drever et al. (1988) considered the possible removal of these elements from the ocean by *water-rock interactions* in the hydrothermal systems along midocean ridges. However, they concluded that only a small fraction of the excess can be removed in this way.

Another possibility is that the apparent *excess* in the riverine *input* may be caused by the recycling of marine aerosols. In other words, elements are removed from the ocean in aerosols, are washed out of the atmosphere by rain or snow deposited on the continents, and are then returned to the oceans in solution in river water. Additional sources of the excess riverine input of some of the Table 22.4B elements may be volcanic gases, exhalations by plants, and anthropogenic contamination. Drever et al. (1988) concluded that the apparent excess of Cl, Br, I, Na, Cd, and Hg *can* be accounted for by recycling of marine aerosols.

However, the apparent excess in the riverine input of Na and Cl may also be an indication, already suggested by the data in Table 22.3, that these elements as well as Br, I, and S are actually *accumulating* in the ocean. Therefore, the mass balance on the basis of particulate fluxes through the ocean (equation 22.17) confirms conclusions regarding these elements based on the rock cycle (equation 22.3; i.e., weathered igneous rocks = sedimentary rocks + seawater). Moreover, these elements all have long oceanic residence times expressed in years (Table 4.7):

Na	2.0×10^8
S	5.0×10^8
Cl	6.3×10^8
Br	7.8×10^8
I	$<4.0 \times 10^6$

as expected, if they are accumulating in the ocean.

Although Hg and Cd may be supplied to the rivers by marine aerosols, the excess may also originate from exhalations by volcanoes and plants on the continents. In this case, they should have been accumulating in the ocean because the known outputs are unable to remove them completely. However, their short oceanic residence times (Cd, 7.9×10^4 yr; Hg, 7.9×10^3 yr, Table 4.7), indicate that the apparent excess input is probably caused by anthropogenic contamination or by bad data.

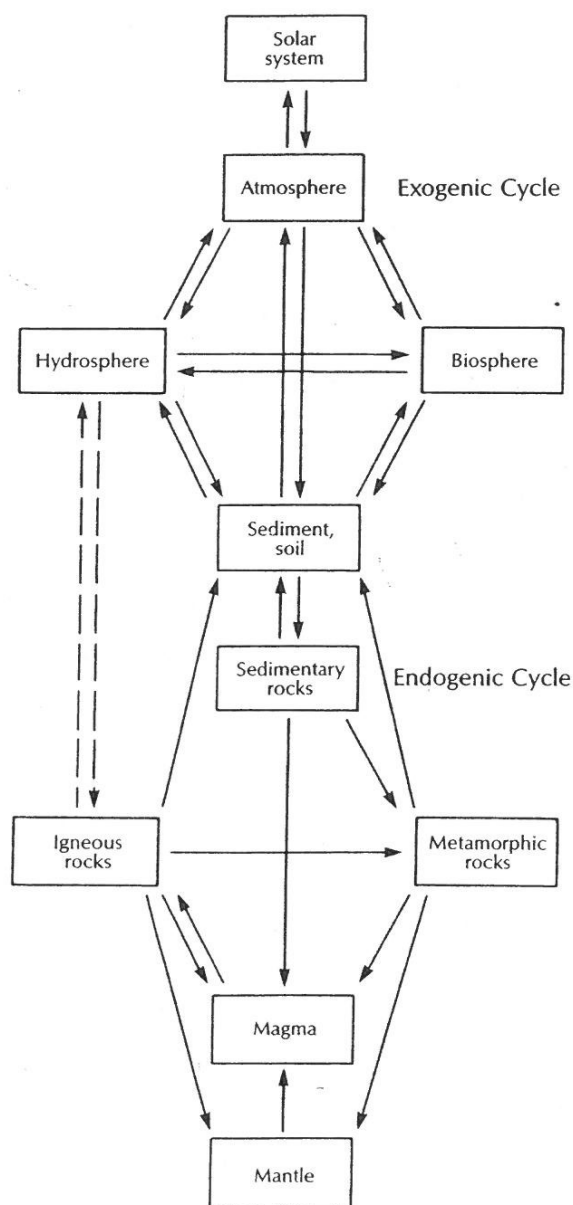
The other elements of Table 22.4B (P, Cu, Zn, Ag, Sb, Au, and Pb) are not explainable by recycling of marine aerosols or by natural emissions by volcanoes and plants. Moreover, only Sb and Au have long oceanic residence times of 1.3×10^5 yr and 1.6×10^6 yr, respectively. Drever et al. (1988) concluded that the apparent excess of the riverine inputs of all of these elements is caused either by anthropogenic contamination of streams or by inaccurate data.

22.4 The Cycles of C-H-O-N

The geochemical cycles of the volatile elements, including C-H-O-N and the noble gases, cannot be represented adequately in terms of solids and ions in solution because these elements occur in the gas phase and together constitute the atmosphere, the biosphere, and the hydrosphere of the Earth. The geochemical cycles of these elements are therefore of paramount importance because they create the environment in which we live and of which we are an integral part.

The C-H-O-N elements dominate the *exo-genic cycle*, which operates on the surface of the Earth. Their principal reservoirs and the processes that move them from one reservoir to another are

depicted in Figure 22.2 by boxes and arrows, respectively. The resulting "plumbing system" shows that the exogenic cycle is connected to the *endogenic cycle*, which operates in the interior of the Earth and involves magma, igneous rocks, sedimentary rocks, and metamorphic rocks



(Wolery and Sleep, 1976). The principal connection between the cycles occurs in sediment and soil because both are the result of weathering of endogenic rocks and also interact with the biosphere, the hydrosphere, and the atmosphere. Additional connections take the form of water-rock interactions along midocean ridges and the exhalation of volcanic gases.

The nonvolatile elements tend to reside preferentially in the reservoirs of the *endogenic cycle*, whereas the volatile and the water-soluble elements occupy reservoirs in the *exogenic cycle*. However, all elements occur in all of the available reservoirs even though their residence times may be short and their concentrations may be low.

We have already considered parts of this geochemical machine by evaluating the rates at which nonvolatile elements enter and leave the ocean and by calculating their mean oceanic residence times (Table 4.7). We have also specified the volumes of the reservoirs of the hydrologic cycle (Table 4.6) and made an inventory of the composition of the atmosphere (Table 4.8).

The geochemical cycles of C-H-O-N are interconnected because these elements form compounds involving two or more of the elements in

Figure 22.2 Interactions between the exogenic and endogenic cycles of the elements. The boxes are reservoirs in which elements reside for varying periods of time depending on their geochemical properties. The arrows are processes that move elements from one reservoir to another. The two cycles are connected primarily through sediment and soil, which interact directly with the atmosphere, the biosphere, and the hydrosphere. Other connections take the form of subduction and partial melting of sedimentary rocks or their metamorphic descendents and the exchange of elements between hot basalt and seawater. The mantle of the Earth is the ultimate source of all matter in the two cycles except for a small amount derived from the solar system as meteorites, interplanetary dust, and the solar wind. Some of the processes that make the geochemical cycles work are *reversible* as indicated by double arrows, whereas others are *unidirectional* and are *irreversible*.

this group, such as H_2O , CO_2 , CH_4 , CH_2O , and NO_2 . These elements also occur in minerals and therefore participate in the *endogenic* cycle. For example, O is the most abundant chemical element in the rocks of the continental crust (Table 4.3), whereas C occurs in mantle-derived kimberlites as diamond.

a. The Carbon Cycle

The geochemistry of C is dominated by the reduction of C in CO_2 during photosynthesis and by its eventual reoxidation to CO_2 , some of which may react with water to form bicarbonate ions and hence CaCO_3 . The movement of C through the *endogenic* and *exogenic* cycles can be traced in Figure 22.3. The amounts of C in the reservoirs and the magnitudes of the fluxes are listed in Table 22.5.

Reduced C enters the crust from the mantle by the intrusion of magma and resides in igneous rocks or is exhaled through volcanoes directly into the atmosphere primarily as CO_2 . The CO_2 of the atmosphere dissolves in the water of the hydrosphere and also enters the biosphere by photosynthesis and by absorption of carbonate ions through plant roots. The hydrosphere and biosphere in Figure 22.3 are each divided into oceanic and continental reservoirs. The bicarbonate ions of the hydrosphere are incorporated into sediment in the form of CaCO_3 , whereas a fraction of the biospheric C is deposited as organic matter in sediment and soil. Sediment composed primarily of CaCO_3 forms *limestone*, whereas sediment composed of plant debris forms *coal*. In addition, the organic matter in shale may alter to *kerogen* from which *petroleum* and *natural gas* may form.

Once it has entered the *endogenic* cycle, the C in sedimentary rocks may be transformed into anthracite or graphite by thermal metamorphism of its sedimentary host, whereas limestones may recrystallize to form marble. Some C in sedimentary rocks may be incorporated into magma during partial melting and thus enters igneous rocks of the crust. In addition, C may return to the mantle by subduction of sedimentary and volcanic rocks.

The pathways of C in the exogenic cycle are *reversible*, whereas those of the endogenic cycle are generally *unidirectional* and *irreversible*. Once C has become enclosed in sedimentary, igneous, or metamorphic rocks, it can return to the exogenic cycle only as a result of weathering of its host, by venting of magma through volcanoes, or by decarbonation reactions of carbonate rocks at elevated temperatures.

If the geochemical machine in Figure 22.3 is in a steady state, the amounts of C in the various reservoirs and the fluxes between them are invariant with respect to time, with the exception of the long-term changes discussed before. Therefore, the present magnitudes of these reservoirs and fluxes can provide a valid description of how the C-cycle works at the present time and how it has worked in the not-too-distant geologic past. The data listed in Table 22.5 indicate that sediment in the oceans and on the continents, and the sedimentary rocks derived from them, together form the largest reservoir with 7643×10^{18} moles of C. The ocean contains only 3.3×10^{18} moles of C, whereas the oceanic and continental biospheres together contain even less at $\sim 0.39 \times 10^{18}$ moles of C. The atmosphere, with only 0.058×10^{18} moles of C, nevertheless plays an important role in the C-cycle because it allows C to pass between the hydrosphere and the biosphere. Therefore, it acts more as a conduit of C than as a reservoir and is the point of entry of C released into the atmosphere by volcanoes and by the combustion of fossil fuel by humans.

The fluxes of C between the atmosphere and the ocean are very large ($\sim 8000 \times 10^{12}$ mol/yr), which favors the establishment of a steady state. Similarly, the fluxes between the atmosphere and the continental biosphere ($\sim 4800 \times 10^{12}$ mol/yr) and between the ocean and the marine biomass ($\sim 3100 \times 10^{12}$ mol/yr) are quite large and likewise permit C to move freely among these reservoirs. As a result, changes in the C-content of one reservoir are rapidly transmitted to the others. For example, a reduction of the continental biomass releases C into the atmosphere as a result of bacterial degradation of organic matter. Consequently, the C-content of the atmosphere rises temporarily

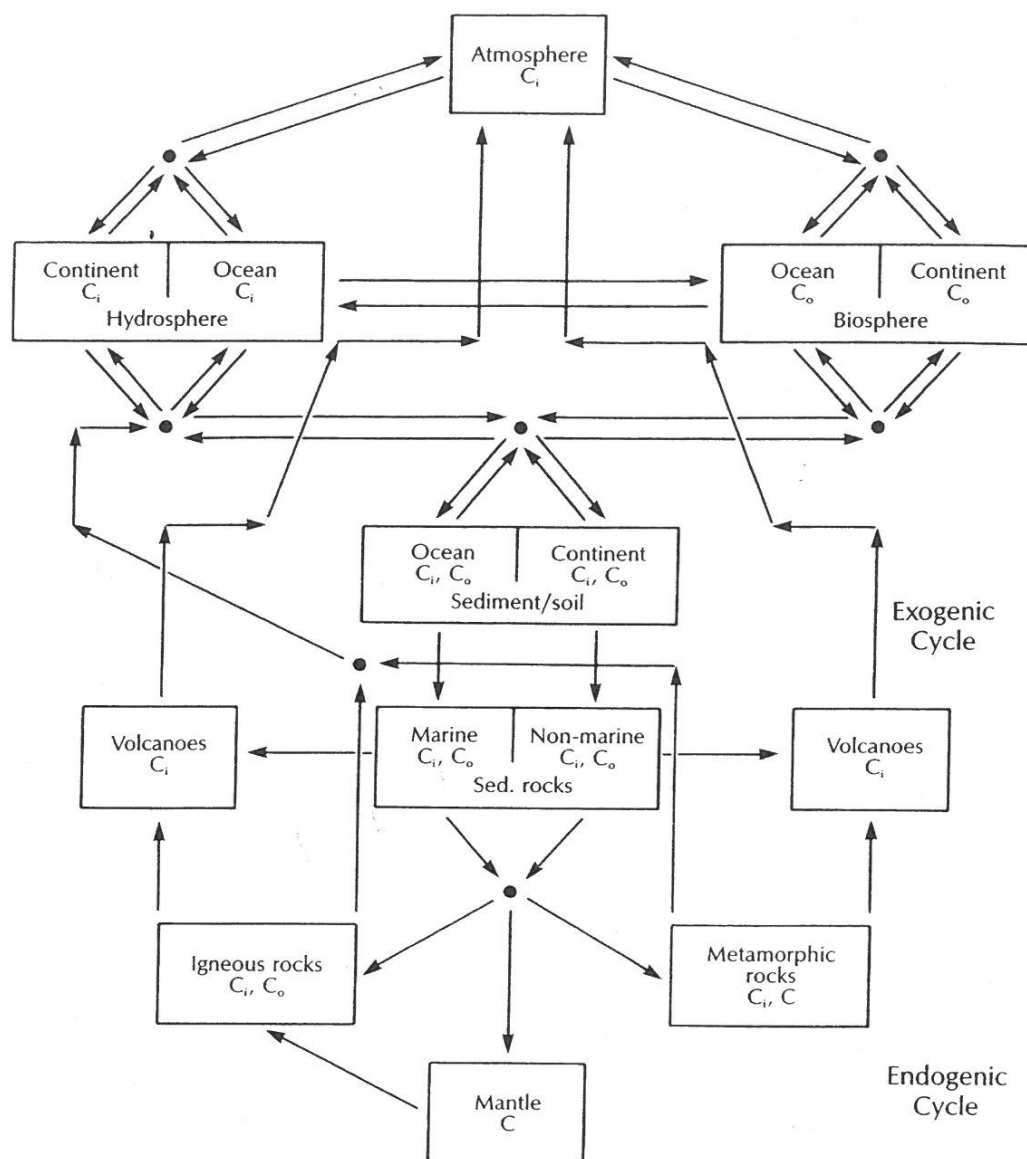


Figure 22.3 Geochemical cycle for carbon. The boxes identify the major reservoirs, and the arrows are the fluxes of C moving between them annually. The magnitudes of the C-reservoirs and fluxes are stated in Table 22.5. C_i = inorganic C (carbonate and CO_2), C_o = organic C (hydrocarbons, carbohydrates, etc.), C = native C (diamond and graphite). All other elements circulate through the exogenic and endogenic cycles in a similar way as C, except that the amounts in the reservoirs and the fluxes of other elements may be very different from those of C (adapted from Holser et al., 1988).

Table 22.5 Reservoirs and Fluxes of the Natural Carbon Cycle^a

Reservoir		Flux		
Name	Amount, mol	From	To	Amount, 10 ¹² mol/yr
Atmosphere	58 × 10 ¹⁵ C _i	atmosphere	ocean	8000 C _i
		atmosphere	biosphere (cont.)	4800 C _i
		atmosphere	sed. and soil (cont.)	35 C _i
Hydrosphere (ocean)	3.3 × 10 ¹⁸ C _i	ocean	atmosphere	8042 C _i
		ocean	biosphere (ocean)	3100 C _i
		ocean	sediment (ocean)	5 C _i
		ocean	sediment (cont.)	46 C _i
				8 C _o
Hydrosphere (continent)	2 × 10 ¹² C _o	hydrosphere (cont.)	ocean	86 C _i
				18 C _o
Biosphere (ocean)	130 × 10 ¹⁵ C _o	biosphere (ocean)	ocean	3090 C _o
		biosphere (ocean)	sediment (ocean)	0.2 C _o
		biosphere (ocean)	sediment (cont.)	10 C _o
Biosphere (continent)	260 × 10 ¹⁵ C _o	biosphere (cont.)	hydrosphere (cont.)	10 C _o
		biosphere (cont.)	atmosphere	4790 C _i
Sediment/soil (ocean)	1290 × 10 ¹⁸ C _i	sediment (ocean)	mantle	5 C _i
	63 × 10 ¹⁸ C _o	sediment (ocean)	volcanoes	0.2 C _o
		sediment (ocean)	met. and igneous rocks	0.02 C _i
Sediment/soil (continent)	5170 × 10 ¹⁸ C _i	sediment (cont.)	hydrosphere (cont.)	86 C _i
	1120 × 10 ¹⁸ C _o			8 C _o
		sediment (cont.)	volcanoes	3 C _i
		sediment (cont.)	met. and igneous rocks	?
Metamorphic and igneous rocks	?	met. and igneous rocks	hydrosphere (cont.)	?
Volcanoes	?	volcanoes	atmosphere	3 C _i
Mantle	?	mantle	hydrosphere (ocean)	6 C _i

^aC_i means inorganic C in carbonate or carbon dioxide; C_o means organic carbon.

SOURCE: Holser et al. (1988).

until some of the excess is transferred to the ocean. Carbon dioxide entering the ocean forms bicarbonate ions, which may cause CaCO₃ to precipitate. Therefore, a fraction of the C released by the continental biosphere is put in storage as CaCO₃ in marine sediment. This C could be retrieved by dissolution of carbonate sediment in the ocean in response to a decrease in the atmospheric C-content.

The rapid exchange of C among the exogenic reservoirs stabilizes the C-cycle by preventing excessive concentrations from building up in any one of the major reservoirs. This fact may moderate the release of CO₂ into the atmosphere by combustion of fossil fuel and may reduce the severity of the resulting changes in the atmospheric circulation and climatic conditions of the world.

b. The Water Cycle

Hydrogen and O are combined in the molecules of water in the hydrologic cycle, which operates primarily on the surface of the Earth (Section 4.4). In addition, O is the most abundant element in the continental crust (45.5%) and mantle of the Earth (44.1% in pyroxite, Table 4.2). Water not only makes up the hydrosphere but also occurs in common minerals, including amphiboles, micas, clay minerals, and in the oxides, sulfates, and carbonates of some of the abundant elements in the crust (Na, Mg, Al, Ca, Mn, Fe, etc.). In this section we consider only the water in the exogenic cycle of the hydrosphere. The presence of water on the surface of the Earth is an essential prerequisite to life, and its movement permits transport of sediment and ions produced by chemical reactions that can occur only in its presence.

The history of the atmosphere and oceans of the Earth has been discussed by many authors including Rubey (1951) whose work was a milestone in the solution of the problem of their origin. Most of the proposed models for the formation of the atmosphere and oceans have been based on the abundances of the noble gases in the atmosphere, including particularly Ar, which has a radiogenic isotope (^{40}Ar) that forms by decay of ^{40}K (Section 16.3a). Important contributions to the history of outgassing of the Earth are by Damon and Kulp (1958), Turekian (1959, 1974), Fanale (1971), Hamano and Ozima (1978), Fisher (1978), Hart and Hogan (1978), Schwartzman (1978), and Holland (1984). The continuing quest for understanding indicates that the history of the oceans and atmosphere of the Earth is one of the most fundamental questions in the Earth Sciences.

Water was an original constituent of the planetesimals as water of hydration of certain minerals and as ice. Water was probably also contributed to the Earth by impacting comets or the so-called cometesimals (Section 2.2). Most of the water and other volatiles were initially in the interior of the Earth and may have been dissolved in a magma ocean during the early molten stage of the Earth.

Most evidence supports the conclusion that the volatile elements and compounds were out-

gassed very early in the history of the Earth. A model by Holland (1984) indicates that about two thirds of the atmosphere was released at the time of accretion or very soon thereafter. About 30% of the water was subsequently consumed by chemical weathering and now resides in the continental crust. Nevertheless, Holland (1984) concluded that large bodies of water existed on the surface of the Earth more than ~ 4 billion years ago. This conclusion is strongly supported by the presence of (3.7×10^9) -year-old sedimentary rocks, including chemically precipitated carbonate rocks, at Isua in Greenland (Schidlowski et al., 1979; Appel, 1990; Baadsgaard et al., 1986).

The geochemical cycle of water therefore started more than 4×10^9 years ago with the release of water during cooling and crystallization of the mantle and later by the formation and subsequent upward movement of magma. Some water was trapped in igneous rocks, but most of it was initially discharged into the atmosphere by volcanic activity. Outgassing of the Earth has continued to the Present, but at a greatly diminished rate, as indicated by the discharge of primordial ^3He by submarine volcanic activity (Kurz et al., 1982).

The movement of water through the exogenic and endogenic cycle at the present time is outlined in Figure 22.4. Volcanoes still discharge water vapor, but almost all of it now originates from groundwater and by dehydration of crustal rocks. A small fraction of water in the upper atmosphere ($4.8 \times 10^{-4} \text{ km}^3/\text{yr}$, Walker, 1977) dissociates into its constituent gases and the H_2 subsequently escapes into space. The biosphere occupies a central place in the hydrologic cycle because it depends on the presence of water for its existence and because it receives and discharges water to the other reservoirs on the surface of the Earth. Figure 22.4 does *not* show that water contained in crustal rocks may be released during chemical weathering and that water may also return to the mantle by the subduction of wet sediment and hydrated volcanic rocks.

The ocean is by far the largest reservoir, containing 95.25% of all the water in the hydrosphere (Tables 4.3 and 22.6). Glaciers and continental ice sheets make up 2.05%, whereas groundwater

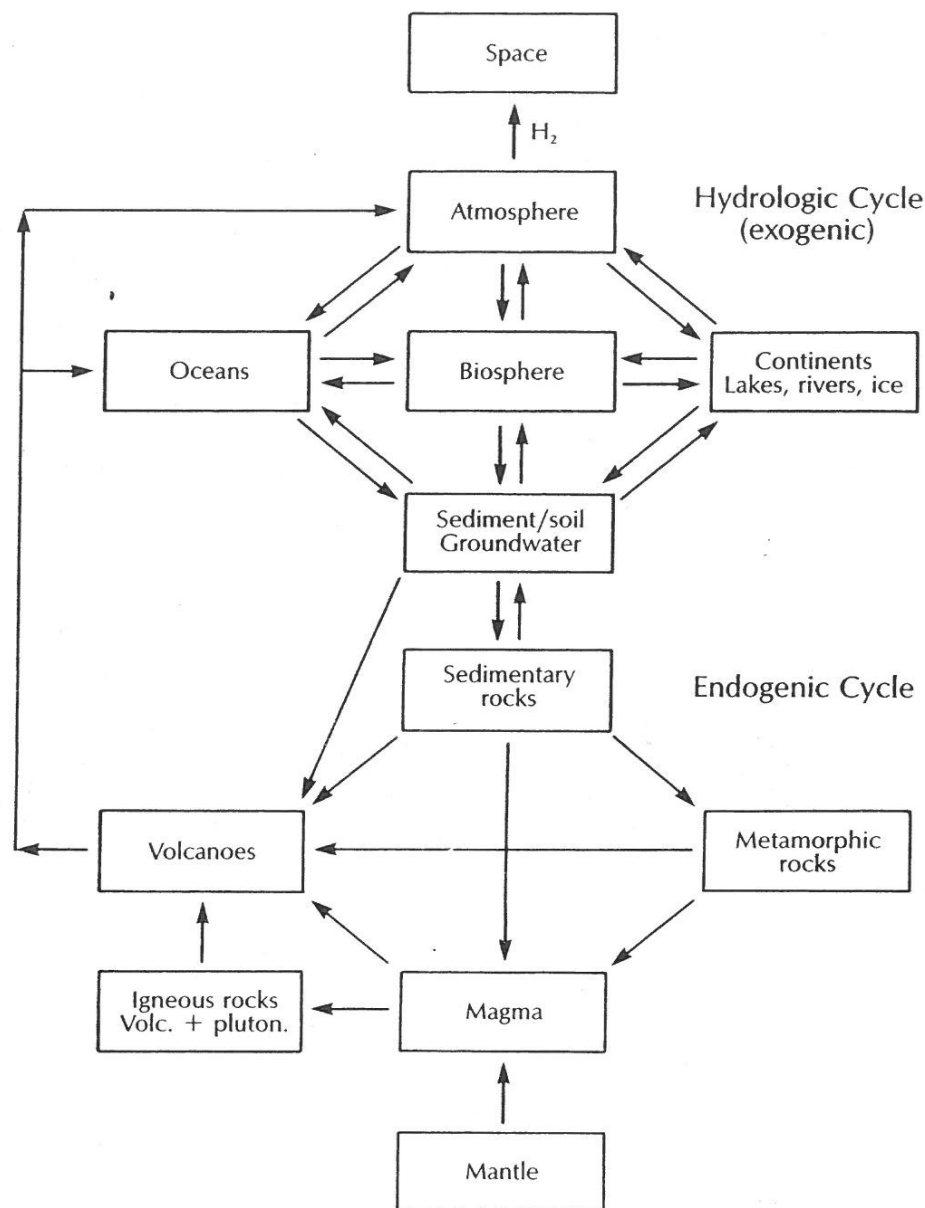


Figure 22.4 Geochemical cycle of hydrogen and oxygen in the form of H_2O . The water on the surface of the Earth was outgassed from the mantle by volcanic activity in Early Archean time. Since then, most of it has been circulating through the reservoirs of the *hydrologic cycle*. The biosphere occupies a central position in the cycle of water because it communicates with all other surface reservoirs and because it depends on water for its existence. Water enters the *endogenic cycle* via sedimentary rocks and may be stored in hydrous minerals of metamorphic and igneous rocks. Volcanoes continue to vent groundwater and water derived from sedimentary, igneous, and metamorphic rocks back into the atmosphere. The diagram does not show that water may return to the mantle by subduction of crustal rocks and that water in these rocks may be released into the hydrologic cycle by chemical weathering.

(shallow and deep), lakes, and rivers together contain only $\sim 0.70\%$ of the water on the surface of the Earth. The actual volume of fresh water that is available for domestic, agricultural, and industrial use is about $9.86 \times 10^6 \text{ km}^3$.

Data cited by Berner and Berner (1987) indicate that the hydrologic cycle is driven largely by solar energy ($0.5 \text{ cal cm}^{-2} \text{ min}^{-1}$, 99.98%), with much smaller contributions by heat flow from the interior of the Earth ($0.9 \times 10^{-4} \text{ cal cm}^{-2} \text{ min}^{-1}$, 0.018%), and from tides ($0.9 \times 10^{-5} \text{ cal cm}^{-2} \text{ min}^{-1}$, 0.0012%). The amount of heat received by the Earth from the Sun must be equal to heat losses in order to maintain the thermal balance. According to Berner and Berner (1987), $\sim 30\%$ of the solar energy received by the Earth is reflected back into space as short-wave radiation ($\lambda < 4 \text{ }\mu\text{m}$). The remainder is absorbed by the surface (51%) and by the atmosphere (water vapor, dust, ozone, CO_2 , 16%; clouds, 3%). The amount of heat absorbed by the atmosphere depends on its chemical composition, including primarily the concentrations of CO_2 , H_2O , CH_4 , and certain fluorocarbon gases used as

refrigerants and propellants in aerosol cans. (See Chapter 23.)

The input of energy from the Sun causes water to evaporate from the surface of the ocean. Some of that water is returned to the ocean by direct precipitation. However, the data in Table 22.6 indicate a net flux of $37,400 \text{ km}^3/\text{yr}$ of water from the oceans to the continents in the form of atmospheric water vapor. This amount of water must return to the oceans annually in order to balance the cycle. The atmosphere over the continents also receives $72,900 \text{ km}^3/\text{yr}$ of water by evaporation from the continents, so that the total amount of precipitation over the continents is $110,300 \text{ km}^3/\text{yr}$. Some of this water is stored temporarily in the polar ice sheets or glaciers and as groundwater. However, $\sim 6\%$ of the return flow to the oceans is by discharge of groundwater directly into the ocean (Berner and Berner, 1987, Table 2.2).

The ocean acts as a giant heat reservoir that moderates temperature fluctuations of the atmosphere. Therefore, the climate of the Earth, both

Table 22.6 Volumes and Fluxes of Water Within the Hydrologic Cycle

<i>Reservoir</i>		<i>Flux</i>		
<i>Name</i>	<i>Amount, 10^6 km^3</i>	<i>From</i>	<i>To</i>	<i>Amount, km^3/yr</i>
Ocean	1370	ocean	atmosphere	423,100
Ice sheets, glaciers	29	atmosphere	ocean	385,700
Groundwater (750–4000 m)	5.3	ocean	continents (water vapor)	37,400
Groundwater (<750 m)	4.2	continents	atmosphere	72,900
Lakes	0.125	atmosphere	continents	110,300
Soil moisture	0.065	continents	ocean	37,400
Atmosphere (liquid equivalent)	0.013	whole Earth	atmosphere	496,000
Rivers	0.0017	atmosphere	whole Earth	496,000
Biosphere	0.0006			
Total	1408.7			

SOURCE: Berner and Berner (1987).

globally and locally, depends on complex interactions between the atmosphere and the oceans. These interactions include feedback mechanisms, which may amplify small random perturbations into major events that affect global weather patterns. These events are virtually impossible to predict because they result from the *chaotic* behavior of the ocean-atmosphere system.

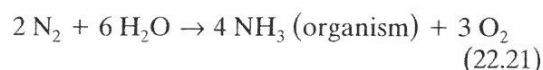
c. The Nitrogen Cycle

Nitrogen is strongly concentrated in the atmosphere, which contains 78.084 volume % (Table 4.8) or 2.82×10^{20} moles of nitrogen as $N_2(g)$ and much smaller amounts ($\sim 10^{12}$ moles) of six other molecular species: NH_3 , NH , N_2O , NO , NO_2 , and HNO_3 (Table 22.7). The biosphere in the oceans and on the continents contains 6.40×10^{16} and 5.52×10^{16} moles of N, respectively. In addition, the oceans contain 2.40×10^{16} moles of N in dissolved organic

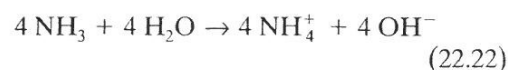
compounds but only 1.57×10^6 moles of N as dissolved N_2 . Sediment and sedimentary rocks are a major sink for N containing 14.2×10^{18} moles of inorganic N and 57.2×10^{18} moles of N in organic compounds.

Nitrogen is an important element in the biosphere and its geochemical cycle (Delwiche, 1970) reflects the metabolic activity of bacteria (Section 19.7). In addition, the combustion of fossil fuel at high temperatures causes atmospheric N_2 to be converted to oxides, including NO_2 , which is a toxic constituent of urban smog. Atmospheric N_2 is also used to make fertilizer containing NO_2^- or NO_3^- . However, the removal of N_2 from the atmosphere by this process does not threaten to reduce the atmospheric reservoir appreciably.

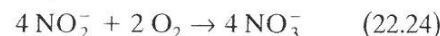
The geochemical cycle, outlined in Figure 22.5, starts with the "fixation" of atmospheric N_2 by bacteria, including *Azotobacter*:



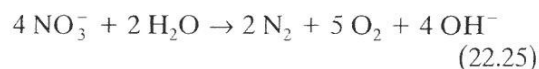
The NH_3 is released following the death of the organism. Subsequent hydrolysis of NH_3 produces NH_4^+ :



The NH_4^+ is oxidized to NO_2^- and NO_3^- by nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*):



The NO_2^- and NO_3^- as well as NH_4^+ are assimilated by plants through their roots and are incorporated into cell material as the amino radical NH_2 . However, NO_3^- may also be reduced to N_2 by *denitrifying* bacteria (e.g., *Pseudomonas*):



This process is a form of anaerobic respiration from which bacteria derive O_2 .

The biological cycling of N_2 is augmented by *abiologic* processes in the troposphere (<17 km

Table 22.7 Inventory of Nitrogen Compounds in the Major Exogenic Reservoirs

Reservoir	Amount, mol N	Residence time
Atmosphere		
N_2	2.82×10^{20}	44×10^6 yr
NH_3	1.83×10^{12}	3–4 mo
NH	0.29×10^{12}	2–3 wk
N_2O	91×10^{12}	12–13 yr (?)
NO	0.22×10^{12}	1 mo (?)
NO_2	0.22×10^{12}	1–2 mo
HNO_3	small	2–3 wk
Biosphere		
Continents	5.52×10^{16}	
Ocean	6.40×10^{16}	
Hydrosphere (oceans)		
Dissolved N_2	1.57×10^6 (N)	
Dissolved organic	2.40×10^{16} (N)	
Sediment		
Inorganic N	14.2×10^{18}	
Organic N	57.2×10^{18}	400×10^6 yr

SOURCE: Garrels et al. (1975).

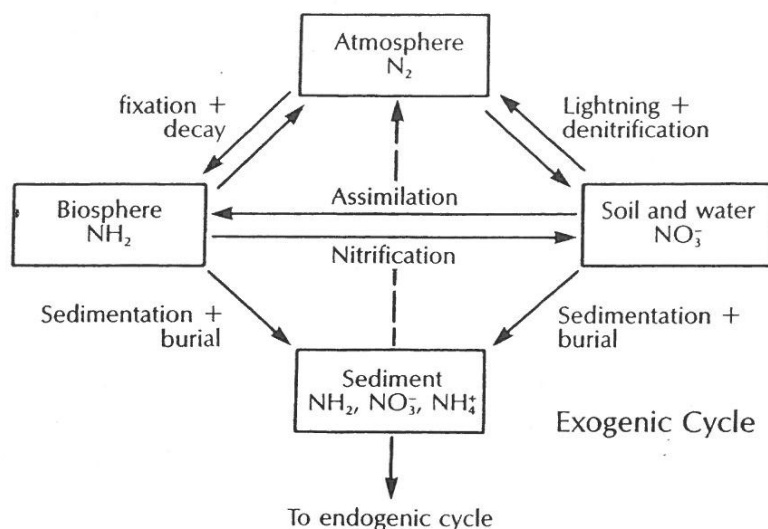


Figure 22.5 Exogenic cycle of nitrogen. The N₂ of the atmosphere is *fixed* by bacteria as NH₃, which hydrolyzes to NH₄⁺, and is converted to NO₂⁻ and NO₃⁻ by *nitrification*. Nitrite and nitrate ions are *assimilated* by plants through their roots and are incorporated into plant tissue as NH₂. Nitrogen is also fixed by the conversion of N₂ to NO₃⁻ during lightning discharge. Some of the nitrogen is incorporated into sediment in the form of organic matter and as NH₄⁺, which substitutes for K⁺ in clay minerals and mica. Nitrogen returns to the atmosphere by decay of organic matter, which releases NH₃ and NH₄⁺, and by the action of denitrifying bacteria in the soil, which convert NO₃⁻ to N₂ (adapted from Walker and Drever, 1988).

above the equator), which are initiated by the formation of nitric oxide (NO) during lightning discharge. The NO is subsequently converted to NO₃⁻ by photochemical reactions and is removed from the atmosphere in rain or snow. The nitrate produced by lightning in the atmosphere is assimilated by plants and thus enters the biosphere.

A small fraction of N in plant tissue enters the *endogenic cycle* when organic material is deposited in sedimentary basins and is ultimately buried and incorporated into sedimentary rocks by diagenesis and lithification. In addition, N may be present in sedimentary rocks as NH₄⁺, which replaces K⁺ in clay minerals and mica in accordance with Goldschmidt's rules (Section 8.1). The concentration of N in sedimentary rocks (200–4000 ppm), results primarily from the pres-

ence of organic matter. Igneous and metamorphic rocks contain even less N (1–20 ppm), presumably in mica minerals (Wlotzka, 1972).

The return flow of N from the biosphere to the atmosphere takes place during decay of organic matter, which releases NH₃. The fluxes of NH₃ to the atmosphere are about 5.4×10^{12} mol/yr from the continental biosphere and 2.9×10^{12} mol/yr from the oceans (Garrels et al., 1975). The concentration of NH₃ in the atmosphere is about 6 ppb, which gives a total NH₃ inventory of 1.83×10^{12} moles. The NH₃ is hydrolyzed to NH₄⁺, which is rapidly removed from the atmosphere. Once the atmospheric NH₄⁺ has entered the soil, it may be converted to NO₂⁻ and NO₃⁻ by nitrifying bacteria (equations 22.23 and 22.24), or it is assimilated by plants.

The release of nitric oxide (NO) into the atmosphere by high-temperature combustion of fossil fuel has undesirable environmental consequences because NO reduces the *ozone* concentration of the stratosphere located between 17 and 50 km above the surface of the Earth at the equator (Chapter 23).

22.5 The Sulfur Cycle

The geochemistry of S on the surface of the Earth is dominated by the activity of the anaerobic bacteria *Desulfovibrio desulfuricans*, which reduce sulfate to sulfide or, more rarely, to native S (Section 17.9). These bacteria occur widely in marine as well as lacustrine sediment and may also occur in the overlying water column, provided conditions are sufficiently anoxic ($E_h < +0.100$ V), as in the Black Sea and in the water of the Carioca Trench (Holser et al., 1988). In order to survive, the bacteria require a food supply, which they derive from the organic matter that is deposited with the sediment. The bacteria prefer simple hydrocarbons and short-chain carboxylic acids and may enter into symbiotic relationships with fermentative bacteria that break down complex organic molecules into edible form.

The S-reducing bacteria can tolerate a wide range of pH conditions and salt concentrations and are not poisoned by the sulfide they excrete. The reduction of sulfate takes place primarily a few centimeters below the sediment-water interface, but may continue to a depth of several meters. The sulfate is supplied by seawater trapped in the pores of marine sediment and by diffusion from the overlying water column. In lacustrine environments the sulfate originates by dissolution of marine evaporite deposits and by oxidation of sulfide minerals in the drainage basin.

The sulfide ions produced by the bacteria precipitate as iron sulfide, which recrystallizes to pyrite. The necessary Fe is derived from Fe-oxide coatings of detrital mineral particles, which release Fe^{3+} that must be reduced to Fe^{2+} by oxidation of organic carbon or sulfide. Therefore, the

accumulation of pyrite in the sediment depends not only on the availability of HS^- but also on the availability of Fe^{2+} . When the supply of Fe^{2+} is inadequate to precipitate all of the sulfide that is produced, the bacteria may manufacture native S, as they seem to do in the caprock of salt domes.

The ratio of organic C to pyrite S in marine shales of different ages has varied with time, but shales from a particular period of geologic time tend to have similar C/S ratios (Raiswell and Berner, 1986). This relationship presumably arises because the rate of pyrite production depends on the supply of edible C-compounds, which make up a certain fraction of the total organic matter in the sediment (Goldhaber and Kaplan, 1974). As a result, the amount of S in pyrite and the amount of residual inedible C in marine shale are correlated. Unaltered and unmetamorphosed marine shales of Cambrian and Ordovician age have significantly lower average C/S ratios (0.5 ± 0.1) than shales of Devonian to Tertiary age (1.8 ± 0.5), presumably because of the absence of vascular land plants in early Paleozoic time. Vascular plants produce lignin and therefore are a major source of refractory C in shale of post-Ordovician age. Marine sediment of Holocene age has a mean C/S ratio of 2.8 ± 0.2 .

The preanthropogenic S cycle depicted in Figure 22.6 has many reservoirs whose S contents are listed in Table 22.8. We start the cycle with the bacterial reduction of sulfate in the ocean and in bodies of fresh water. The reduced S is deposited as pyrite in marine and nonmarine shales. In addition, sulfate salts may be precipitated episodically in marine and nonmarine evaporite basins. The S sequestered in sedimentary rocks returns to the hydrosphere in the form of dissolved sulfate when the sedimentary rocks are exposed to chemical weathering.

Sulfur from the mantle may enter the hydrosphere as a result of alteration of basalt in the ocean, as a result of chemical weathering of mafic igneous rocks, and by the emission of SO_2 by volcanoes. However, the S discharged by volcanoes is partly derived from sedimentary rocks as well as from igneous and metamorphic rocks of the crust.

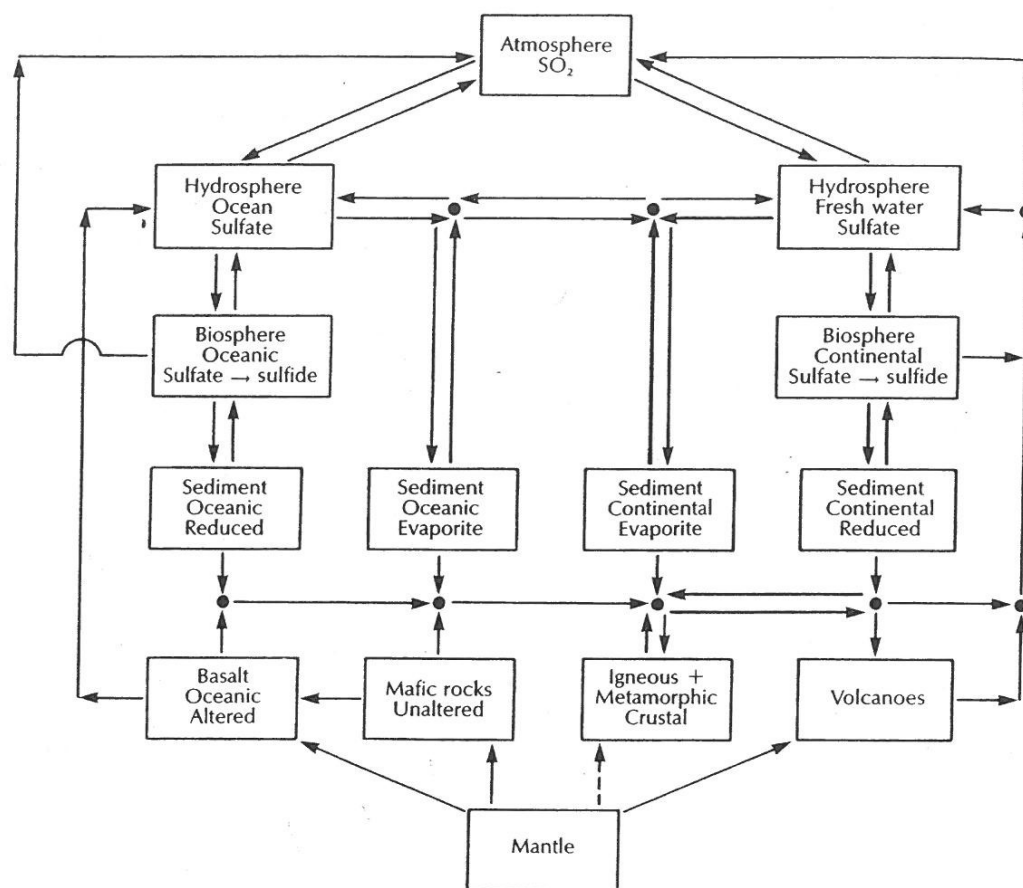


Figure 22.6 The natural geochemical cycle of sulfur. The exogenic cycle of S is dominated by the reduction of dissolved sulfate to sulfide by anaerobic bacteria (*Desulfovibrio*) living just below the sediment–water interface in the oceans and in bodies of fresh water. The sulfide is precipitated as pyrite in the presence of an adequate supply of Fe^{2+} . In addition, sulfate salts may form in marine and continental evaporite basins. The return flow of the S from sedimentary rocks to the hydrosphere takes place by chemical weathering. In the endogenic cycle, S from the mantle is brought into the crust by basalt and other mafic rocks from which it may be released by weathering and by alteration of basalt on the floor of the ocean. A third outlet for S from the interior of the Earth is by volcanic activity that may release a mixture of S derived partly from the mantle and partly from igneous, sedimentary, and metamorphic rocks of the continental and oceanic crust. The S released by volcanic activity may enter the hydrosphere directly or may enter the atmosphere first and be subsequently removed as sulfate in meteoric precipitation. The igneous and metamorphic rocks contain S derived primarily from oceanic or continental sediment with contributions from the mantle via volcanic rocks of basaltic composition. Anthropogenic effects on the S cycle are not shown here.

Table 22.8 Principal Reservoirs of Sulfur in the Endogenic and Exogenic Cycles

<i>Reservoir</i>	<i>Moles of S</i>	<i>Principal form</i>
Ocean	40×10^{18}	sulfate
Atmosphere	56×10^9	SO ₂
Fresh water	40×10^{15}	sulfate
Sediment		
Oceanic	8×10^{18}	sulfide
Continental, reduced	145×10^{18}	sulfide
Continental, oxidized, evaporite	192×10^{18}	sulfate
Oceanic basalt, altered	25×10^{18}	sulfide
Mafic rocks, unaltered	106×10^{18}	sulfide
Igneous and metamorphic rocks	430×10^{18}	sulfide

SOURCE: Holser et al. (1988).

Figure 22.6 does not show that even seawater or continental brines may contribute part of the S that is recycled by volcanic activity. Volcanic emissions of S may contain H₂S, but it is rapidly oxidized during the eruption and enters the atmosphere as SO₂.

The atmosphere contains S derived primarily by volcanic activity, by exhalation from the biosphere, and by recycling of sulfates from the surface water of the ocean, from surficial salt deposits, and from brine lakes. Sulfur compounds of volcanic or biogenic origin are oxidized by reactions with O₂ and H₂O in the atmosphere to form sulfuric acid. The resulting acidification of rain and snow is a natural phenomenon that commonly follows large volcanic eruptions. Evidence for this process is preserved in the ice sheets of Antarctica and Greenland in the form of layers of ice containing tephra overlain by ice containing excess sulfate. Evidently, the S emitted by major volcanic eruptions remains in the atmosphere somewhat longer than the tephra, which are deposited downwind from their source (Pal  is and Kyle, 1988).

The S cycle has been significantly disturbed by the emission of SO₂ into the atmosphere from coal-burning electric power plants and by roasting

of sulfide ores. In addition, mining operations and construction projects cause exposure of sulfide-bearing rocks, which accelerates chemical weathering and causes localized release of H₂SO₄ into streams, lakes, and groundwater (Sections 14.5d and 21.2).

The isotope composition of S processed by bacteria is altered because of the preferential enrichment of the metabolic H₂S in ³²S (Section 17.9). As a result, sedimentary sulfide deposits may be variably enriched in ³²S, whereas marine sulfate deposits are enriched in ³⁴S and depleted in ³²S. The δ³⁴S values of marine sulfate deposits have varied systematically throughout geologic time (Figure 17.6) in response to secular variations in the isotope compositions of the inputs and outputs of S to and from the ocean. The models that have been proposed to account for the observed variation of the δ³⁴S value of marine sulfate deposits were reviewed by Holser et al. (1988). We focus attention here on the possibility that the alteration of the isotope composition of S by bacteria can be used to detect the first appearance of S-reducing bacteria on the Earth in Early Archean time.

Measurement by Monster et al. (1979) indicate that sulfide minerals in different facies of the banded iron formation at Isua in Greenland have an average δ³⁴S value of $+4.5 \pm 0.90\%$ relative to S in the Canyon Diablo troilite. Associated tuffaceous amphibolites have δ³⁴S = $+0.27 \pm 0.91\%$, and sulfide veins in the iron formation and amphibolite yielded δ³⁴S = $+0.78 \pm 0.63\%$. These values are *indistinguishable* from each other and from meteoritic S, which represents S in igneous rocks derived from the mantle. Therefore, Monster et al. (1979) concluded that sulfate-reducing bacteria had *not* yet evolved 3.7×10^9 years ago. The reason may be that these bacteria require an ample supply of sulfate, which was not available until photosynthetic organisms had begun to release O₂ into solution in standing bodies of water. The first appearance of S-reducing bacteria occurred prior to about 2.0 billion years ago, but the precise timing of this event is still controversial (Schidlowski, 1979; Cameron, 1983).

22.6 Summary

Geological and geochemical processes have been operating on the surface of the Earth throughout geologic time. Therefore, we may assume that these processes are in a steady state such that the chemical compositions of the major reservoirs have remained constant except for long-term changes caused by the evolution of life, convection in the mantle, and the decay of long-lived radioactive nuclides to stable daughters.

The assumptions can be tested by equating the mass of an element released by chemical weathering of igneous rocks with the sum of its masses in sedimentary rocks and in the ocean at the present time. The resulting mass-balance equation can be evaluated for each element using its average concentrations in the three principal reservoirs. The results yield satisfactory balances for many elements with some notable exceptions, including S, Cl, Ca, F_2 , and 14 other elements. All of these elements have *higher* concentrations in the oceans and in sedimentary rocks than can be accounted for by the mass of igneous rocks that has weathered.

Another kind of balance involves a comparison of the mass of an element entering the ocean annually and its rate of removal from the ocean. The annual inputs by rivers must be corrected for recycling of marine salts, which are transported to the continents as atmospheric aerosols, and for anthropogenic contamination of river water. Outputs from the ocean take the form of burial of pore water, ion exchange reactions, diagenesis and precipitation of salts all of which are difficult to evaluate quantitatively. Nevertheless, satisfactory input-output balances can be demonstrated for 30 elements, whereas 14 elements have *larger inputs* than outputs.

The group of elements with unsatisfactory oceanic input-output balances includes some of the same elements that have unsatisfactory mass balances (weathered granite = sedimentary rocks + oceans): S, Cl, Hg, as well as Na, P, Cd, and Pb. These results suggest that the concentrations of Na, Cl, and S in seawater are actually

increasing at the present time. The excess inputs of other elements may only be apparent because they may be caused by recycling of marine salt (Hg and Cd), by anthropogenic contamination of river water, or by bad data.

The geochemical balances of the volatile elements (C-H-O-N and noble gases) cannot be evaluated in terms of their concentrations in rocks or water alone because significant proportions of these elements reside in the atmosphere and in the biosphere. Their complete geochemical cycles include both an *endogenic* (magma, igneous, sedimentary, and metamorphic rocks) and an *exogenic* (atmosphere, biosphere, ocean, sediment/soil) subcycle. If the amounts of an element in all of the available reservoirs and the fluxes between them are known, then it is possible to describe the complete geochemical cycle of that element and to calculate residence times in each reservoir. Such complete descriptions of geochemical cycles are difficult to achieve partly because of the complex interactions among reservoirs and partly because of anthropogenic intervention in the natural operation of the geochemical cycles of many elements. Nevertheless, even qualitative descriptions of the circulation of an element among its exogenic and endogenic reservoirs promote *understanding* of the interactions among the reservoirs.

The discussion of the exogenic cycles of the C-H-O-N group of elements leads to important questions about the CO_2 content of the atmosphere, the history of outgassing of the Earth, and the role of bacteria in the global circulation of N. The exogenic cycle of S is likewise dominated by the bacterial reduction of sulfate to sulfide, which is accompanied by significant fractionation of the stable isotopes of S. A study of the isotope composition of S in pyrite in rocks of Archean age indicates that bacterial reduction of sulfate *post-dates* photosynthesis because the bacteria require sulfate ions that could not form until after green plants had begun to release O_2 into solution in standing bodies of water on the surface of the Earth.

Problems

1. Check equation 22.9 for proper exchange of electrons and material balance.
2. Determine whether this reaction can be in equilibrium in seawater at 25°C and 1 atm pressure (use data from Table 4.7 and Appendix B).
3. Calculate the total amount of Na^+ in the ocean (Table 4.7), mass of seawater = 1.4×10^{24} g).
4. How long would it take to increase the concentration of Na^+ in seawater by 10% based on the present anthropogenic flux (Table 22.2), assuming that the increase was not counteracted by increases in the output?
5. Calculate the average residence time of water (liquid equivalent) in the atmosphere based on data in Table 22.6.
6. Calculate a mass balance for K using data from Tables 4.5 and 4.7. Assume that average granitic rocks consist of 35% basalt and 65% granite and that granite is the average of high-Ca and low-Ca granite.
7. Calculate the output/input ratio for Fe entering and leaving the ocean using equations 22.18 and 22.19 and the following data (Drever et al., 1988):

	ppm
Fe_{sp}	48,000
Fe_{rw}	0.0388
Fe_{ds}	65,000
Fe_{sh}	47,272

8. Draw the endogenic and exogenic cycles of P including its major reservoirs and pathways.

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Chemistry of the Atmosphere

Until recently, the atmosphere of the Earth has not received the attention from geochemists it deserves, even though our very lives depend on the availability of oxygen in the air we breathe. Our complacency about the atmosphere was shattered by the publication of a paper by Farman et al. (1985) in which they reported a drastic decline in the ozone (O_3) content of the stratosphere in the austral spring (October to November) at Halley Bay in Antarctica. This discovery raised worldwide concern because ozone contributes significantly to the absorption of ultraviolet light, which can cause skin cancer in humans and may have other harmful biological effects.

Another danger signal is the steady increase of the carbon dioxide (CO_2) concentration of the atmosphere recorded continuously since 1958 at the Mauna Loa observatory in Hawaii (Keeling et al., 1982). Ice cores collected at Siple Station in Antarctica (Friedli et al., 1986) extended this geochronological record to about 1750 A.D. and demonstrate that the concentration of carbon dioxide in the atmosphere has been rising at an accelerating rate from about 275 ppmv (parts per million by volume) in 1750 A.D. to about 350 ppmv in 1988. Increases have also been recorded in the concentrations of methane (CH_4) (Khalil and Rasmussen, 1987), carbon monoxide (CO) (Zander et al., 1989), and nitrous oxide (NO_x) (Pearman et al., 1986). These gases, as well as water vapor and ozone, absorb infrared radiation ($\lambda > 750$ nanometers)

emitted by the surface of the Earth, thus causing the atmosphere to heat up in the so-called greenhouse effect.

A third reason for the rising interest in the atmosphere of the Earth is the exploration of the earthlike planets and the satellites of the gaseous planets of the solar system. The atmospheres of Venus and Mars are different from that of Earth in composition, temperature, and density, whereas Mercury and the Moon lack atmospheres altogether (excluding very small concentrations of He on the former, Lewis and Prinn, 1983, p. 121). The exploration of the solar system has therefore focused attention on the evolution of planetary atmospheres (Lewis and Prinn, 1983; Chamberlain and Hunten, 1987) and on the origin of the atmosphere of Earth (Holland, 1979, 1984; Holland et al., 1986).

Our increased awareness of the place of the Earth in the solar system has added urgency to the study of impacts by meteoroids, asteroids, and comets on the Earth. The energy released by such events cause catastrophic temporary changes in the atmosphere, including an increase in the dust content, global fire storms, and acid rain (Prinn and Fegley, 1987). The traumatic effect on the biosphere of such sudden environmental changes may have been responsible for large-scale extinctions of species that were unable to cope with the environmental consequences of these celestial accidents. (Silver and Schultz, 1982; Alvarez et al., 1984; Fassett and Rigby, 1987).

The growing realization of the importance of atmospheric processes is reflected in the publication of monographs on the chemistry of the atmosphere (Warneck, 1988) and of interdisciplinary textbooks concerned with climate change on the Earth (Graedel and Crutzen, 1993).

23.1 Structure and Composition

The vertical structure of the atmosphere in Figure 23.1 is based on the observed variation of the temperature as a function of altitude above sea level and consists of the troposphere (0–12 km), stratosphere (12–50 km), mesosphere (50–100 km), and

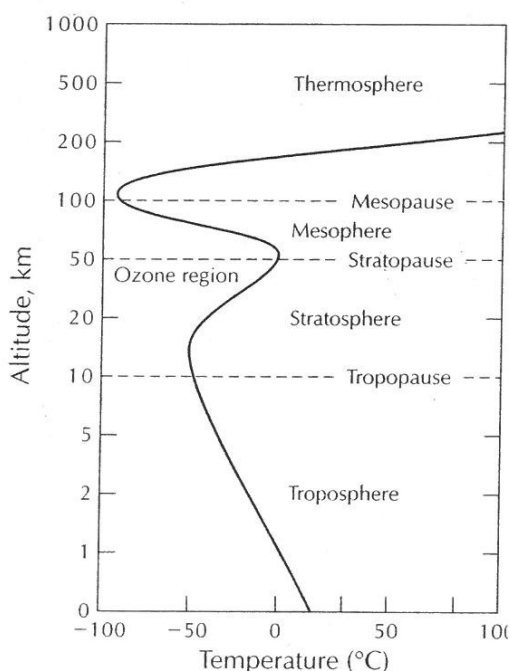


Figure 23.1 The structure of the atmosphere based on the variation of the temperature ($^{\circ}\text{C}$) with altitude (km) above the surface of the Earth. Note that the boundaries between the major units are placed at or close to reversals in the temperature gradient and that the altitude scale is logarithmic rather than linear. [Modified from Graedel and Crutzen (1993) who adapted it from Chameides and Davis (1982).]

the thermosphere (100 to >1000 km). The boundaries between these atmospheric shells are called the tropopause, stratopause, etc. The chemical compositions of the troposphere and the stratosphere affect the climate and hence the living conditions on the surface of the Earth in ways to be discussed in this chapter.

The temperature in the troposphere decreases with altitude from 288.15 K (15.0°C) at the surface to 216.65 K (-56.5°C) at the tropopause (12 km) (Anonymous, 1976). The temperature in the stratosphere actually *increases* with altitude and reaches 270.65 K (-2.5°C) at the stratopause 50 km above the surface of the Earth. In the overlying mesosphere the temperature decreases again to 186.87 K (-86.28°C), but rises in the thermosphere to values in excess of 373.15 K (100°C). However, the thermosphere contains very little heat because of its low density.

The pressure of the atmosphere decreases with altitude from 1010 millibars (mbar) at the surface to 194 mbar at 12 km (tropopause), to 0.800 mbar at 50 km (stratopause), and to 0.00184 mbar at 90 km (mesopause). Therefore, the pressure range of the stratosphere (194 to 0.800 mbar) includes the atmospheric pressure on the surface of Mars of about 8 mbar.

The atmospheric pressure can also be expressed as the “number density” in terms of the number of molecules per cubic centimeter of space. The number density of the atmosphere decreases from 2.55×10^{19} molecules/ cm^3 at the surface to 6.49×10^{18} molecules/ cm^3 at the tropopause (12 km) and to 2.14×10^{16} molecules/ cm^3 at the stratopause (50 km). In other words, the number of molecules in a cubic centimeter of space 50 km above the surface of the Earth is about 1200 times smaller than at the surface of the Earth. The lower number density of the stratosphere reduces the frequency of molecular collisions and hence affects the rates of chemical reactions.

The chemical composition of the atmosphere can be described in terms of only 10 constituents listed in Table 23.1. (See also Table 4.8.) The data indicate that N_2 and O_2 make up 99.0% of the atmosphere followed by the noble gases at

Table 23.1 Chemical Composition of Dry Air at the Surface in Remote Continental Areas

Constituent	Symbol or formula	Concentration, %
Nitrogen	N ₂	78.1
Oxygen	O ₂	20.9
Argon	Ar	0.93
Carbon dioxide	CO ₂	0.035
Neon	Ne	0.0018
Helium	He	0.0005
Methane	CH ₄	0.00017
Krypton	Kr	0.00011
Hydrogen	H ₂	0.00005
Ozone	O ₃	0.000001–0.000004

SOURCE: Graedel and Crutzen (1993).

0.932% and CO₂ with 0.035%. These gases together amount to 99.967% of the atmosphere, leaving only 0.0326% for methane, hydrogen, and ozone. The compounds in the atmosphere participate in chemical reactions when molecules are energized or broken up by ultraviolet radiation from the Sun. Therefore, chemical reactions in the stratosphere reduce the amount of ultraviolet radiation that reaches the surface of the Earth and thus protect the biosphere from the harmful effects of this radiation.

23.2 Ultraviolet Radiation

The Sun emits electromagnetic radiation having a wide range of wavelengths (λ) consistent with its surface temperature of 5780 K. The peak intensity occurs at $\lambda \sim 500$ nanometers (nm; $1\text{ nm} = 10^{-9}\text{ m}$). The wavelength spectrum of solar radiation consists of three types of radiation:

ultraviolet, $\lambda < 400\text{ nm}$

visible light, $\lambda = 400\text{ to }750\text{ nm}$

infrared, $\lambda > 750\text{ nm}$

The energy (E) transmitted by electromagnetic radiation is related to its wavelength through the equation:

$$E = h\nu \quad (23.1)$$

where h is Planck's constant ($6.626 \times 10^{-34}\text{ J s}$) and ν is the frequency, equal to c/λ , where c is the speed of light ($2.998 \times 10^8\text{ m/s}$). Therefore, the energy of electromagnetic radiation of wavelength λ , stated in Chapter 5 equation 5.16, is:

$$E = \frac{hc}{\lambda} \quad (23.2)$$

Ultraviolet radiation is further subdivided into UV-A (400–320 nm), UV-B (320–290 nm), and UV-C (<290 nm). The most energetic ultraviolet light (UV-C) is absorbed primarily by N₂O (20–100 nm), O₂ (80–210 nm), and O₃ (ozone) (200–290 nm). The presence of these molecules in the stratosphere therefore prevents UV-C from reaching the surface of the Earth.

The efficiency with which molecules absorb ultraviolet radiation is expressed by the absorption cross section, defined as a quantitative measure of the absorption of ultraviolet light at a specified wavelength by atoms or molecules in the atmosphere. Ozone plays an important role in absorbing UV-C because its absorption cross section for ultraviolet light (Figure 23.2) rises to a maximum at $\lambda = 250\text{ nm}$ (Hartley band) and then declines to low values above $\lambda = 290\text{ nm}$. The decrease of the absorption cross section of ozone for wavelengths between 290 and 320 nm causes the magnitude of the UV-B flux received by the surface of the Earth to increase with increasing wavelength by a factor of about 10^4 . Since the least energetic form of ultraviolet light (UV-A) is not significantly absorbed by the atmosphere, most incident UV-A reaches the surface. The biosphere has evolved a tolerance for UV-A, but the sensitivity of DNA increases rapidly with decreasing wavelength of UV-B. Therefore, the reduction of the ozone concentration in the stratosphere increases the exposure of the biosphere to the harmful effects of UV-B.

Research results summarized by Graedel and Crutzen (1993, p. 262) indicate that many plants

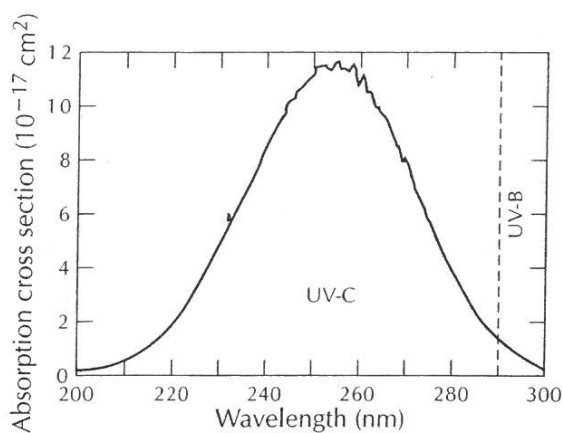


Figure 23.2 Efficiency of absorption of the most energetic ultraviolet light (UV-C) by ozone expressed here as the absorption cross section. The diagram demonstrates that the ozone of the stratosphere helps to shield the surface of the Earth from UV-C. The efficiency of ozone as an absorber of UV-B (290–320 nm) is much less than for the more damaging UV-C. [Modified from Graedel and Crutzen (1993) who reproduced it from Brasseur and Solomon (1986).]

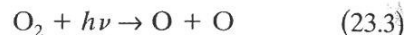
are adversely affected by exposure to UV-B, showing reductions in the size of leaves, in the length of shoots, and in the rate of photosynthesis. For example, a 25% reduction in the concentration of stratospheric ozone is projected to cause a 50% reduction in soybean yields. Since planktonic organisms in the oceans are likewise sensitive to UV-B, they live at a depth below the surface that permits only long-wave UV radiation needed for photosynthesis to penetrate. An increase in the UV-B flux may force plankton to live at greater depth, thereby causing a reduction of the food supply for organisms higher in the food chain, including invertebrates, fish, and whales. Whether the increase in UV-B radiation caused by the present ozone depletion of the stratosphere over Antarctica has affected plankton in the Southern Ocean is not yet known.

Exposure of unprotected humans to UV-B causes cancer, increases the occurrence of cataracts, and weakens the immune system. According to Graedel and Crutzen (1993, p. 262), a 1% reduction in the concentration of stratospheric ozone

increases the UV-B flux at the surface of the Earth by 2% which raises the incidence of basal-cell carcinomas by 4% and the occurrence of squamous-cell carcinomas by 6%. In addition, exposure to UV-B also causes the more dangerous melanoma skin cancers.

23.3 Ozone in the Stratosphere

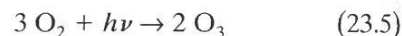
When molecular O_2 in the stratosphere absorbs UV-C, it dissociates into two atoms of O:



where $h\nu$ is the energy of the UV radiation having $\lambda < 240$ nm. Each of the two free oxygen atoms then reacts with diatomic oxygen molecules to form ozone (O_3):

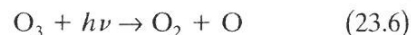


resulting in a net transformation of:



Reaction 23.4 requires the presence of a molecule (M), such as N_2 or O_2 , that absorbs the energy liberated by this reaction and disperses it by collisions with other molecules in the surrounding space.

The ozone produced by this process absorbs UV-C most effectively at $\lambda \approx 250$ nm (Hartley band). As a result, the ozone dissociates:



followed by:

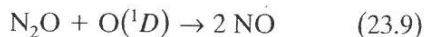


for a net change of:



The process outlined above is modified by the catalytic destruction of ozone in the stratosphere caused by the presence of certain trace constituents, symbolized by $X\cdot$ and $XO\cdot$, where $X = NO, HO,$ or Cl . For example, N_2O emitted by soil bacteria passes through the troposphere with a residence time of 150–200 years. Once it reaches

the stratosphere, the N_2O molecules are decomposed into NO by several processes, including:

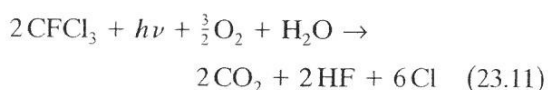


where $\text{O}(^1\text{D})$ is an oxygen atom that has been energized by ultraviolet radiation.

The NO radical then reacts with ozone in a sequence of steps that transform it into diatomic oxygen"

1. $\text{NO} \cdot + \text{O}_3 \rightarrow \text{NO}_2 \cdot + \text{O}_2$
2. $\text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2$
3. $\text{O} + \text{NO}_2 \rightarrow \text{NO} \cdot + \text{O}_2$
4. $2\text{O}_3 + h\nu \rightarrow \text{NO} \cdot + 3\text{O}_2 \quad (23.10)$

The net result (step 4) is the same as that of reactions (23.6–23.8). Although the catalysts listed above (NO, HO, and Cl) are present in the stratosphere in very small concentrations under natural conditions, the destruction of ozone in the stratosphere is accelerated when the concentrations of these catalysts are increased as a result of anthropogenic activities. For example, NO may be injected into the stratosphere by high-flying aircraft or by nuclear explosions in the atmosphere. In addition, the catalytic destruction of ozone in the stratosphere is linked to the release of chlorofluorocarbon gases used in refrigerators and as propellants in aerosol spray cans. These compounds, exemplified by CFCl_3 and CF_2Cl_2 , are very stable and are not soluble in water. The so-called "CFCs" are not removed from the troposphere by meteoric precipitation, but rise to altitudes of about 25 km in the stratosphere where they are decomposed by UV-C in reactions such as:

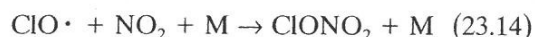
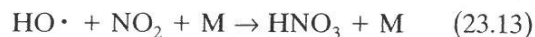


The Cl acts as a catalyst in the destruction of ozone by the sequence of reactions:

1. $\text{Cl} \cdot + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2$
2. $\text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2$
3. $\text{ClO} \cdot + \text{O} \rightarrow \text{Cl} \cdot + \text{O}_2 \quad (23.12)$

thereby causing the conversion of 2O_3 into 3O_2 (Molina and Rowland, 1974).

The catalytic "ozone killers" may be neutralized in reactions such as:



where ClONO_2 is a molecule of chlorine nitrate. However, these compounds are short-lived reservoirs of $\text{HO} \cdot$ and $\text{ClO} \cdot$ because the HNO_3 and ClONO_2 molecules are decomposed by ultraviolet radiation.

Chlorine is supplied to the stratosphere by sea spray, volcanic eruptions, and in the form of methyl chloride gas (CH_3Cl) released by seaweed. According to Graedel and Crutzen (1993, p. 143), the Cl concentration of the stratosphere has increased by a factor of five, from 0.6 to about 3 ppbv (parts per billion by volume), as a consequence of anthropogenic emissions of CFCs and other Cl-bearing industrial gases. The increase in the Cl concentration of the stratosphere caused by the release of CFC gases has contributed to a decrease of the ozone concentration of the atmosphere, especially over Antarctica.

23.4 Ozone Hole Above Antarctica

The abundance of ozone in a column of air having a diameter of 1.0 cm^2 varies seasonally and with latitude. In the equatorial region of the Earth, the ozone content of the atmosphere is about 250 Dobson units (DU), where:

$$1\text{ DU} = 2.69 \times 10^{16} \text{ molecules of } \text{O}_3/\text{cm}^2$$

The DU is defined by the statement that 100 DU corresponds to a layer of ozone 10 mm thick at a pressure of 1.0 atmosphere and a temperature of 0°C .

The amount of ozone in the polar regions varies seasonally. In the Arctic the range is from about 300 DU in the early fall up to about 460 DU in the spring. In the Antarctic the ozone levels in the spring reach only about 400 DU under natural

conditions. However, the measurements by Farman et al. (1958) shown in Figure 23.3 demonstrated that the average ozone concentration in October over Halley Bay, Antarctica, declined from about 330 DU in 1957 to about 200 DU in 1984. The monthly average ozone content for October has continued to decline since then and fell to just over 120 DU in 1989.

The cause for this alarming phenomenon was ultimately deduced from the following observations: (1) Direct measurements by a high-flying ER-2 plane on September 21, 1987 (Anderson et al., 1989), demonstrated a strong anticorrelation between the concentrations of ClO and O₃ in the stratosphere over Antarctica at latitudes greater than about 70°S; (2) a balloon launched from McMurdo on October 27, 1987, detected a significant decrease in the ozone profile in the lower stratosphere between altitudes of about 12 and 21 km (Hofmann et al., 1989); (3) balloon

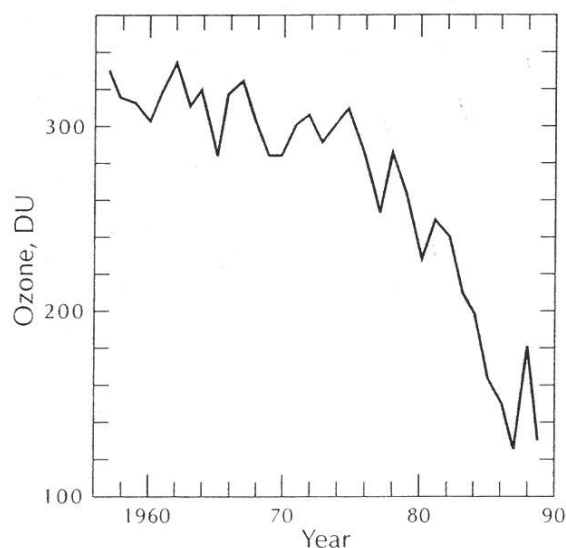
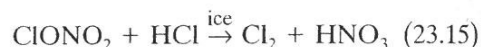


Figure 23.3 Average ozone concentrations of the stratosphere during the month of October over Halley Bay, Antarctica, from 1957 to 1989. The data show that the average ozone concentrations for October at this site declined from 330 DU in 1957 to about 120 DU in 1989, or about 64% in 33 years. [Modified from Graedel and Crutzen (1993) who adapted it from Farman et al. (1985).]

launches demonstrated a 20-degree increase in the temperature at 21 km in the stratosphere over McMurdo between August 29 and October 27, 1987. These direct observations indicated that the reduced ozone concentrations in Antarctica occur in the early austral spring (September–October), coincide with elevated concentrations of ClO, and are associated with an increase in the temperature of the lower stratosphere. These are the principal clues that were used to explain the development of the ozone hole over Antarctica.

During the austral winter months (June–September), the atmosphere over Antarctica is isolated from the global circulation by the polar vortex and the stratosphere receives no direct sunlight. As a result, the temperature of the stratosphere over Antarctica declines to -80°C . This permits the formation of ice crystals composed of a mixture of water and nitric acid. The absence of UV radiation caused by the absence of solar radiation retards the reactions that produce and destroy ozone in the stratosphere. Under these conditions, chlorine nitrate (ClONO₂) is incorporated into the ice crystals and is adsorbed on their surfaces where it reacts with HCl to form Cl₂ and HNO₃:



The Cl₂ molecules are released into the air of the stratosphere, whereas the HNO₃ remains in the ice crystals. When sunlight returns to Antarctica in the early spring, the ice crystals sublime and the chlorine molecules are dissociated by UV ($\lambda < 450 \text{ nm}$), thus releasing the Cl catalyst:



Consequently, the return of the Sun to Antarctica triggers rapid catalytic destruction of ozone by the Cl· stored in the stratosphere. However, as the stratosphere warms up, the circumpolar circulation breaks down and the ozone-depleted air over Antarctica mixes with ozone-rich air at lower latitudes. This phenomenon causes the “ozone hole” to spread to populated areas in the southern hemisphere until normal transport

processes in the stratosphere restore the global distribution of ozone.

The potential hazard to the biosphere of increased exposure to UV-B caused by the large-scale destruction of ozone by CFCs was considered in 1987 by an international conference in Montreal (Graedel and Crutzen, 1993, p. 372). The protocol arising from that conference called for a voluntary 50% reduction in the manufacture of CFCs by 1998. This recommendation was strengthened at a subsequent conference in 1990 in London by specifying maximum allowable production of CFCs relative to 1986: 80% by 1993; 50% by 1995; 15% by 1997; and 0% by 2000. In addition, the production of methylchloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) is to end in 2005. Although the production of CFCs in Europe and North America has been reduced, the targets have not been met by some major industrial nations.

Model calculations by Brühl and Crutzen (1988) predict a significant 28% reduction of stratospheric ozone (relative to 1965) in the southern hemisphere by the year 2030 even if the production targets of London are actually realized. However, if CFC production continues at 1974 levels, the ozone depletion of the southern hemisphere will reach 48% of the 1965 level in 2030. If the recommendations for reduced production of CFCs are not implemented and production rises above 1974 levels, the ozone depletion will be greater than 48% and the resulting health hazard to humans may become quite serious.

For this reason, Cicerone et al. (1991) considered the feasibility of reducing the chlorine content of the stratosphere over Antarctica by injecting ethane (C_2H_6) and propane (C_3H_8). These gases react with $\text{Cl}\cdot$ to form HCl , thus sequestering it and preventing the destruction of ozone:



Unfortunately, a fleet of high-flying aircraft would be required to disperse about 50,000 tons of the hydrocarbons annually. In addition, the gas must be dispersed widely within the atmosphere

encompassed by the polar vortex whose position and integrity vary unpredictably. It is probably better to stop production of chlorine-bearing gases worldwide than to attempt to repair the atmosphere. However, even in the unlikely event that production of these gases is actually stopped in 2005, ozone depletion in the southern hemisphere will continue for many decades until the atmosphere gradually cleans itself up.

Ozone depletion by CFCs is, of course, a world-wide phenomenon that is aggravated in the Southern Hemisphere because of the isolation of Antarctica during the winter months by the polar vortex. In the Northern Hemisphere the problem is not as severe because the Arctic region does not develop a polar vortex. Consequently, the ozone content of the stratosphere in the Arctic is reduced by only 10–20% of normal levels when the sun returns at the end of the winter.

23.5 Infrared Radiation and the Greenhouse Effect

Ninety percent of the sunlight reaching the Earth is in the visible (λ 400–750 nm) and infrared ($\lambda > 750$ nm) part of the spectrum. The radiation that reaches the surface is converted into heat and causes the surface to emit infrared radiation consistent with its temperature. This radiation is not sufficiently energetic to break chemical bonds, but it is absorbed by molecules of the air and increases their vibrational and rotational energies. The excess energy is transformed into kinetic energy and results in an increase in the frequency of molecular collisions (heat). The principal constituents of the atmosphere, O_2 and N_2 , are not efficient absorbers of infrared radiation. Instead, minor constituents including H_2O , CO_2 and O_3 are primarily responsible for absorption of infrared radiation emitted from the surface of the Earth.

The radiation budget of the Earth indicates that almost 30% of the incoming solar radiation is reflected back into space, approximately 25% is absorbed by the atmosphere, and the rest (about 47%) is absorbed at the surface. Most of that radiation is consumed as latent heat of evaporation of

water and is released back into the atmosphere when water vapor condenses in the troposphere. In addition, some of the secondary infrared radiation is absorbed by H_2O and CO_2 . The recycling of solar energy between the surface of the Earth and its atmosphere increases the temperature of the surface quite significantly compared to what it would be without this natural greenhouse effect.

Certain trace constituents of the atmosphere (O_2 , N_2O , CH_4 , CFCl_3 , etc.) play a sensitive role in the heat budget of the atmosphere because they absorb infrared radiation in the wavelength band 8000–12,000 nm where H_2O and CO_2 are not effective. Therefore, these trace gases trap some of the infrared radiation that would otherwise escape and thereby enhance the greenhouse warming of the atmosphere.

The effective radiation temperature of the Earth (T_E) depends on the amount of solar energy the Earth receives from the Sun (E_S) and the amount of energy emitted by the Earth as infrared radiation. This balance is expressed by the equation:

$$\frac{E_S}{4} (1 - \alpha) = \sigma T_E^4 \quad (23.19)$$

where $E_S = 1380 \text{ W m}^{-2}$ (solar constant) is the solar energy received by the Earth at the average Sun–Earth distance in units of watts per square meter; $\alpha = 0.28$ (planetary albedo) is the fraction of solar radiation reflected into space; $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ (Stefan–Boltzmann constant); and the factor $1/4$ is the ratio of the planetary disk to its surface area, required because the solar radiation is intercepted by the area of the disk. Substituting the appropriate values into equation 23.19:

$$\frac{1380}{4} (1 - 0.28) = 5.67 \times 10^{-8} T_E^4$$

yields:

$$T_E = 257 \text{ K or } -16^\circ\text{C}$$

The recycling of infrared radiation emitted by the surface of the Earth can be taken into account by means of the effective atmospheric infrared transmission factor, $f = 0.61$; that is, only about 61% of the secondary infrared radiation actually escapes

from the Earth. Therefore, equation 23.19 is modified to include the infrared transmission factor:

$$\frac{E_S}{4} (1 - \alpha) = f \sigma T_S^4 \quad (23.20)$$

where T_S is the temperature of the Earth's surface as before. The result is:

$$T_S = 291 \text{ K or } 18^\circ\text{C}$$

which is close to the observed global temperature of about 15°C . This calculation demonstrates the importance of the greenhouse effect of the natural atmosphere, which increases the average global surface temperature of the Earth by 34°C compared to what it would otherwise be.

The beneficial effects of energy recycling in the atmosphere are amplified by increases in the concentrations of the so-called greenhouse gases. These gases have different heating powers depending partly on their concentrations in the natural atmosphere. For example, an increase in the concentration of methane from 0 to 2 ppmv adds about the same amount of heat to the atmosphere as an increase in the CO_2 content from 275 to 375 ppmv. The reason is that CO_2 is already absorbing most of the infrared radiation in its spectral region because of its high natural concentration. Therefore, the heating power of the greenhouse gas (called radiative forcing) can be expressed in terms of the reduction of the amount of infrared radiation leaving the Earth caused by a unit increase in the concentration of the gas in the atmosphere. A comparison by Houghton et al. (1990) of atmospheric heating by greenhouse gases indicates that the effect of CFCs, CH_4 , N_2O , and stratospheric water vapor has been rising and nearly equalled the heating caused by CO_2 in the decade of the 1980s.

The climatic consequences of the release of different greenhouse gases into the atmosphere depend not only on their concentration and hence on their radiative forcing but also on their residence time in the atmosphere. Therefore, the global warming potential (GWP) of a greenhouse gas is computed by including its atmospheric lifetime and by comparing the resulting heating function to that of CO_2 . Houghton et al. (1990) listed

values of the global warming potentials per kg of the principal greenhouse gases relative to CO_2 :

Greenhouse gas	GWP
CO_2	1
CH_4	21
N_2O	290
CFCs	3000–8000

The global warming potential of 1 kg of CH_4 causes 21 times as much absorption of infrared radiation as the release of 1 kg of CO_2 . The heating potentials of the CFCs are obviously very large compared to that of CO_2 because their concentration in the natural atmosphere is zero, because they absorb infrared radiation in the wavelength band between 8000 and 12,000 nm where CO_2 is ineffective, and because they have long atmospheric residence times.

The global warming potentials of greenhouse gases help to quantify the effect these gases have on the average global temperature. Predictions of the increase in the surface temperature to be expected during the 21st century vary depending on the assumed rate of release of greenhouse gases, on the uptake of the resulting heat by the oceans, and on other factors such as changes in the planetary albedo caused by increased cloudiness, etc. Nevertheless, virtually all models predict an increase in the average global surface temperature during the 21st century (Houghton et al., 1990):

	Temperature increase, °C	
	by 2050 A.D.	by 2100 A.D.
High estimate	3.75	6.25
Best estimate	2.75	4.25
Low estimate	1.75	3.00

Even the lowest estimate predicts an increase of 1.75°C in the average global temperature by the year 2050.

Changes in the surface temperature of the Earth have certainly occurred in the past. For example, the Little Ice Age (1450–1890) was caused by a *decrease* in the average global tem-

perature of about 1°C , and the end of the last ice age about 15,000 years ago was accompanied by an *increase* in the average global temperature of about 3°C . However, the warming at the end of the last ice age occurred gradually over a period of many centuries, whereas the expected global warming caused by the release of greenhouse gases will take only a few decades.

23.6 Prediction of the Future Global Climate

The geological record contains clear evidence that the global climate has changed significantly during the Earth's history as a result of both terrestrial and extraterrestrial factors. The extraterrestrial causes of global climate change include:

1. The variation of the luminosity of the Sun in the past 4.5×10^9 years (Graedel et al., 1991).
2. Periodic changes in the celestial mechanics of the Earth (Milankovitch theory) that affect the amount of sunlight it receives (Berger, 1988).

The terrestrial causes of climate change include:

1. The chemical evolution of the atmosphere.
2. The amount of dust emitted by volcanic eruptions and meteoroid impacts.
3. Changes in the circulation pattern of the oceans.
4. Changes in the albedo caused by the formation of continental ice sheets.
5. Anthropogenic emissions of CO_2 and other gases.

However, even though the average global temperature has undoubtedly changed significantly in the course of geologic time, life on the Earth has continued without interruption since its first recorded presence about 3.5×10^9 years ago.

The extraterrestrial factors affecting the average global temperature (solar luminosity and celestial mechanics) will continue to do so in the future. Volcanic eruptions and infrequent meteoroid impacts will also continue to cause

short-term catastrophic climate perturbations. An evaluation by Lamb (1977) of the effects of orbital changes on the amount of solar radiation reaching the top of the atmosphere of the Earth suggests that episodic decreases in the winter temperatures will occur during the next several tens of thousands of years. The effectiveness of celestial mechanics to cause global temperature fluctuations was clearly demonstrated by Prell and Kutzbach (1987). Therefore, the orbital parameters are likely to cause a decrease in the average global temperature with minima at 5 and 22 kyr after the present (AP), leading to continental glaciation at about 50 kyr AP (Berger, 1987).

However, the climate predictions based on Milankovitch theory (celestial mechanics) must be modified to include the anthropogenic emission of greenhouse gases. Continued combustion of fossil fuel, deforestation, and other factors may increase concentrations of CO_2 and other greenhouse gases in the atmosphere by up to a factor of four in the next 1000 years or less. Broecker (1987) in his book *How to Build a Habitable Planet* predicted that in the next 5000 years global temperature could rise by about 4.5°C above normal values, but would then decline as predicted by Milankovitch theory.

The extent of global warming depends significantly on the response of the C-cycle (Section 22.4, Figure 22.3) to the release of greenhouse gases. If the increase in the concentration of atmospheric CO_2 stimulates the growth of marine organisms, the increase in the oceanic biomass will result in the burial of a portion of the carbon in marine sediment, thus taking it out of circulation for long periods of geologic time. Therefore, the anthropogenic greenhouse warming of the Earth may be a short-lived episode on the geological time scale, producing an "anthropogenic superinterglacial" epoch to be followed by the next glaciation mandated by celestial mechanics (Broecker, 1987). However, this long-range prediction provides little comfort to humans who must cope with the effects of global warming and increased sea level in the next several centuries.

23.7 Summary and Prognosis for the Future

The atmosphere of the Earth is composed primarily of N_2 and O_2 with minor concentrations of Ar, CO_2 , Ne, He, CH_4 , Kr, H_2 , and O_3 . The structure of the atmosphere consists of the troposphere (0–10 km), stratosphere (10–50 km), mesosphere (50–100 km), and the thermosphere (100–1000 km). The pressure of the atmosphere decreases exponentially from 1.0 atmosphere at sea level to 10^{-4} atmospheres close to 70 km above the surface of the Earth. The temperature in the troposphere decreases with increasing altitude and reaches about -50°C at the tropopause located at an altitude of 10 km at the equator. Subsequently, the temperature rises in the stratosphere, decreases in the mesosphere, but rises again in the thermosphere.

The gases of the atmosphere absorb ultraviolet radiation and thereby protect the surface of the Earth from it. The wavelength spectrum of ultraviolet radiation includes UV-C ($\lambda < 290\text{ nm}$), UV-B (290–320 nm), and UV-A (320–400 nm). The most energetic form of ultraviolet radiation (UV-C) is absorbed by N_2O , O_2 , and O_3 in the stratosphere. However, UV-B does reach the surface and can cause biological damage unless precautions are taken to limit exposures.

Ozone plays an important role in reducing the fluxes of UV-C and UV-B that reach the surface of Earth. Ozone is produced in the stratosphere when UV-C breaks the bond of O_2 molecules. The resulting oxygen atoms then react with O_2 to form ozone (O_3). Under natural conditions the inventory of O_3 in the stratosphere is maintained in a steady state by the production and destruction of this molecule.

The introduction into the atmosphere of Cl-bearing anthropogenic gases (CFCs and others) has resulted in an acceleration of the destructive reactions causing the ozone content of the stratosphere to decline. The effect is especially severe over Antarctica during the spring (September–October) because of the combination of factors related to the geographic location and atmospheric circulation during the austral winter.

The reduction in the ozone content of the stratosphere over Antarctica (ozone hole) has caused an increase in the UV-B flux to that region, and this increase endangers all life forms that are exposed to it. The increase in the flux of UV-B also raises concerns about the increased risk to life on a global scale.

The release of excess amounts of CO_2 , CH_4 , and certain other gases (e.g., CFCs) has increased the ability of the atmosphere to absorb infrared radiation ($\lambda > 750 \text{ nm}$) emitted by rocks and soil on the surface of the Earth. The expected increase in the average annual global temperature will change weather patterns and may increase the frequency and severity of storms. Global warming may also lead to an increase in sea level caused by

the recession of glaciers and polar ice sheets and by an increase in the temperature of seawater. Existing models all predict an increase in the average annual global temperature, but differ in the effect that the increase in temperature will have on the albedo of the Earth and the response of the polar ice sheets.

Long-range predictions suggest that global warming will be a relatively short-lived phenomenon on a time scale of 10^4 years because the excess C in the atmosphere will be buried in marine sediment. Subsequently, changes in the celestial mechanics of the Earth will cause cooling, leading to another ice age at about 50,000 years after the present.

Problems

1. Given that 100 Dobson units (DU) correspond to a layer of ozone 1 mm thick at atmospheric pressure and 0°C , demonstrate that $1 \text{ DU} = 2.69 \times 10^{16} \text{ molecules of O}_3 \text{ cm}^{-2}$.

2. Calculate the number density of air at 1 atm and 0°C assuming that it is composed of $\text{N}_2 = 78.15\%$, $\text{O}_2 = 20.95\%$. Express the result in molecules per cm^3 .
(Answer: $2.66 \times 10^{19} \text{ molecules/cm}^3$)

3. Using equation 23.2, calculate the energy of a photon of ultraviolet light (UV-C) having a wavelength of 250 nm ($= 250 \times 10^{-9} \text{ m}$).
(Answer: $7.94 \times 10^{-18} \text{ J}$)

4. Use equation 23.19 to calculate the effective radiation temperature of the Earth if the albedo of the Earth increases by 10% to 0.31, assuming that the solar constant remains 1380 W m^{-2} .

(Answer: -18.6°C)

5. Explain why the average annual global temperature at the surface of the Earth is significantly higher than the radiation temperature.

6. How will the atmosphere infrared transmission factor (f) change when anthropogenic emissions of greenhouse gases cause an increase in global temperatures?

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Environmental Geochemistry: Disposal of Radioactive Waste

We now return to the idea that geochemists have a role to play in the struggle of the human race to survive on the Earth. Although we have succeeded in controlling the environment on a local scale, we cannot escape the fact that the capacity of the Earth to support the human population is limited. Moreover, our efforts to improve the quality of life worldwide have unexpectedly caused the environment to deteriorate in ways that threaten the very quality of life we seek to improve. This dilemma can be avoided only by prudent management of all of the Earth's resources based on an understanding of the natural processes that make the Earth "an abode fitted for life."

24.1 The Big Picture

Life on the Earth has always been hazardous because of the occurrence of violent geological events, including volcanic eruptions, earthquakes, floods, and landslides. In addition, we are exposed to *geochemical hazards* associated with the ionizing radiation emitted by naturally occurring long-lived radionuclides, by the unstable daughters of U and Th, and by cosmogenic radionuclides including tritium, ^{10}Be , and ^{14}C (Faure, 1986). Other natural geochemical hazards consist of anomalous concentrations of certain elements whose presence or absence in our diet can cause medical problems (Cannon, 1974). In addition, our individual survival is endangered by toxins

generated by bacteria and by certain plants and animals of the biosphere. We even face danger from outer space in the form of meteorite impacts, ultraviolet radiation, and cosmic rays. All of these hazards are a natural property of the environment on the surface of the Earth and ultimately control our life expectancy. Some of these natural hazards can be minimized by a judicious choice of life style and habitat. However, all forms of life are exposed to these natural risks and have adapted themselves to survive as long as possible. The subject of this chapter concerns new anthropogenic hazards that threaten not only the human population but could affect the entire biosphere on the surface of the Earth.

Geologists and geochemists have studied the natural hazards of life for many years and have attempted to inform the public by pointing out that the loss of life and property resulting from natural disasters was predictable and *could* have been and therefore *should* have been avoided in many cases. Inevitably, the subject matter of environmental geology and environmental geochemistry has been presented in the form of case studies of natural disasters in the hope that the horror stories of the past will not be repeated in the future.

In addition to the natural geological and geochemical hazards, we now face threats that are a direct consequence of our own actions. These threats were not anticipated in many cases because we believed that the capacity of the Earth

to provide the resources we require and to absorb our waste products is virtually unlimited. We have begun to realize only recently that nonrenewable natural resources are limited (Section 21.8) and that the improper disposal of waste products can cause a deterioration of the environment in which we live. Instead of presenting the evidence for these newly recognized threats in another series of horror stories, we attempt here to integrate them into a big picture.

We begin by asserting that all human beings have a right to live and are therefore entitled to have access to the natural resources required to provide the necessities of life: food, water, air, housing, tools and utensils, transportation, and energy. The consumption of natural resources inevitably creates waste products, which must be disposed of in such a way that they do not threaten the quality of life of future generations. Therefore, the problem to be addressed includes both the *supply* of natural resources and the *disposal* of the resulting waste products. The severity of the problem we face is increased by the rapid increase of the population during the 20th century, by the uneven distribution of natural resources, and by the need to transport food products and mineral commodities to population centers. All of these activities require the use of *energy*, which also must be provided from natural sources, resulting in additional waste products that aggravate the potential for environmental degradation. The role of *geochemists* in this formidable task centers increasingly on evaluations of the environmental consequences arising both from the *exploitation* of natural resources and from the *disposal* of waste products.

We have already considered some aspects of the production of food (Section 19.8), water (Section 20.6), and mineral resources (Section 21.8). These can be treated as *global abstractions* but are expressed directly at the *local level* where they affect the quality of life of the people and the environment in which they live. In this chapter we draw attention to problems of *waste disposal*, which can also be treated on a global scale as well as at the local level. We select for discussion the consequences of energy production by induced fission of ^{235}U because the resulting

waste products remain harmful to life for very long periods of time. The uncontrolled dispersal of radioactive isotopes on the surface of the Earth, and the safe disposal of nuclear waste have become important problems that require the attention of geochemists throughout the world.

24.2 High-Level Radioactive Waste

Nuclear power reactors generate heat by means of a controlled chain reaction based on the fission of ^{235}U by thermal neutrons (Section 16.1c). The resulting fission-product nuclides accumulate in the fuel rods of nuclear reactors together with transuranium elements, including plutonium (Pu), neptunium (Np), americium (Am), and curium (Cm), which are produced by neutron-capture reactions starting with ^{238}U and ^{235}U . The fuel rods of nuclear reactors therefore become highly radioactive as a result of the decay of the fission products, of the transuranium elements, and of their unstable daughters. The activity of spent fuel elements decreases *slowly* with time and reaches the level of U ore only after 10,000–100,000 years, depending on whether or not the fuel elements are reprocessed. The radioactive wastes generated by nuclear power reactors not only are highly *radiotoxic* but also release significant amounts of *heat*. For these reasons, such wastes must be isolated in repositories designed to contain them safely until the rate of decay has diminished to levels encountered in U ore.

The rate of decay of a radioactive nuclide is expressed in the *becquerel* (Bq), defined as one disintegration per second (dis/s). Alternatively, the rate of decay may be stated in *curies* (Ci), where $1 \text{ Ci} = 3.70 \times 10^{10} \text{ Bq}$. The decay rates encountered in nuclear waste are of the order of terabecquerels ($1 \text{ TBq} = 10^{12} \text{ Bq}$) and petabecquerels ($1 \text{ PBq} = 10^{15} \text{ Bq}$).

The exposure to ionizing radiation (α -, β -, γ -, and x-rays) is measured in terms of the energy that is released when the radiation interacts with a unit weight of the absorber such as biological

tissues. The basic unit of measurement of the *radiation dose* is called the *gray* (Gy), which is equal to 1 J/kg or to 100 *rad* (radiation absorbed dose). One rad is the amount of radiation required to liberate 1×10^{-5} J of energy per gram of absorbing material (Roxburgh, 1987, p. 18). In order to make the radiation dose relevant to humans, the *rem* (roentgen equivalent man) is defined as one rad of x-rays or γ -rays. The *sievert* (Sv) is defined as 100 rem.

All forms of ionizing radiation are harmful, but the amount of tissue damage depends on the intensity and energy of the radiation, on the distance between the source of the radiation and the object being irradiated, on the shielding provided by the matter between the source and the object, on the duration of the exposure, on the type of radiation, and on the tissue that is irradiated. The natural, whole-body, background radiation from rocks, cosmic rays, and atmospheric gases is ~ 0.1 rem per year, depending on the composition of the rocks, the elevation of the site, and other circumstances. Anthropogenic sources of radiation, such as medical or dental x-rays, just about double the average exposure to 0.2 rem per year, although wide variations occur here as well, depending on the circumstances. The physiological effects of full-body irradiations described in Table 24.1 require *much larger* doses than are provided by the natural environment. However,

high-level radioactive waste from nuclear reactors can administer large doses of ionizing radiation in a short time that severely affect tissues, the digestive system, and the nervous system. As a result, a deficiency of white blood cells (leukopenia) occurs, followed by hemorrhaging, fever, vomiting, and death.

The radioactive waste generated in the course of the fuel cycle is indicated in Figure 24.1. The waste rock and mineral residues produced during the mining and extraction of U from the ore are commonly stored at the mine in tailings ponds and piles of waste rock (Brookins, 1984, ch. 10). The mine tailings are radioactive because of the presence of the unstable daughters of U and Th, including the isotopes of the noble gas radon (Rn). In addition, the mine tailings may contain pyrite and other minerals that create an environmental hazard when they react with water and oxygen (Sections 14.1 and 21.2). Chemical weathering of mine tailings may also release potentially toxic elements into the local groundwater including Mo, Se, and As. The environmental hazards of mine tailings of any kind are magnified when such sites are later used to construct housing developments and shopping malls. The most dangerous high-level waste (HLW) in the U-fuel cycle is produced during the initial fabrication of the fuel elements, during their subsequent reprocessing after use in a reactor, and by discarding the spent fuel elements without reprocessing them.

When the U fuel of a nuclear reactor has been depleted in ^{235}U , the fuel rods are removed from the core of the reactor and are stored at the reactor site for up to five years in order to allow the intensity of the radioactivity to decrease. Subsequently, the fuel elements may be reprocessed to recover the U and Pu they contain. For this purpose, the U fuel is separated from the metal containers into which it is packed and is then dissolved in nitric acid. The U and Pu are separated from this solution by solvent extractions with tributyl phosphate (TBP) and odorless kerosene (OK). The residual nitric acid solution contains 99.9% of the non-volatile fission products, 0.1% of the U, <1% of the Pu, and most of the other transuranium elements that form in the reactor by neutron capture and

Table 24.1 Physiological Effects of Whole-Body Irradiation

<i>Dose, rem</i>	<i>Effects</i>
0–25	reduction of white blood cells
25–100	nausea, fatigue, changes in blood
100–200	nausea, vomiting, fatigue, susceptible to infection due to low count of white blood cells; death possible
200–400	fatal in 50% of cases, especially without treatment; damage to bone marrow and spleen
>600	fatal, even with treatment

SOURCE: Roxburgh (1987).

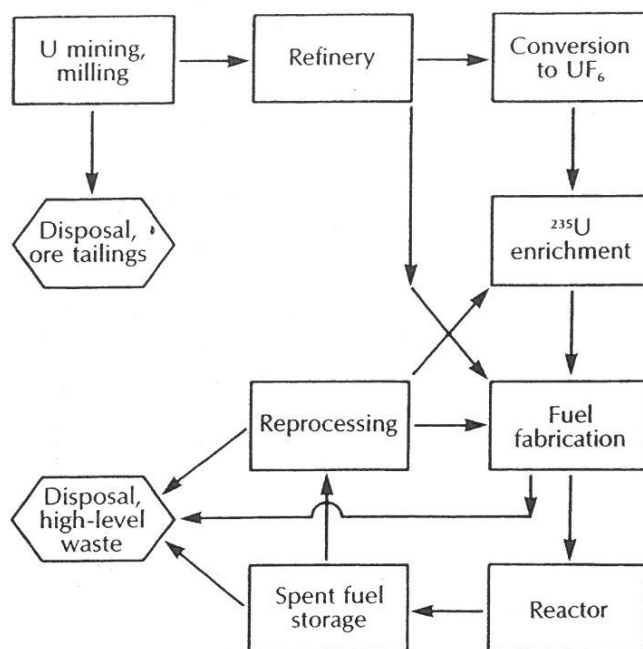


Figure 24.1 Nuclear fuel cycle starting with the mining and milling of U-ore leading to the fabrication of fuel elements and their use in nuclear power reactors. In the United States the spent fuel is stored at the reactor site for up to five years in order to allow the short-lived fission-product nuclides and some of the transuranium elements to decay. Subsequently, the spent fuel may be reprocessed or discarded. Radioactive waste products arise during the initial mining and milling of U-ore, during the reprocessing of spent fuel elements, and by discarding spent fuel without reprocessing. The spent fuel and high-level waste remain radiotoxic for more than 10,000 years.

β -decay (Roxburgh, 1987). The heat liberated by the decay of these radionuclides is used to remove excess water by boiling. After further cooling, the residue is converted into a borosilicate glass, which is poured into steel containers for ultimate disposal in a geological repository. The U recovered in this process can be reused after some additional enrichment of the remaining ^{235}U . The ^{239}Pu produced from ^{238}U during the operation of the reactor is itself fissionable and is used in nuclear weapons (Blasewitz et al., 1983).

The volume of HLW produced by reprocessing one metric ton ($1\text{ t} = 10^3\text{ kg}$) of spent fuel is about 5 m^3 , according to an estimate by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD) (Anonymous, 1984). To put it another way, the generation of 1 GW ($1\text{ GW} = 10^9\text{ W}$) of electric power (GWe) produces 6 m^3 of HLW in vitrified form and $\sim 50\text{ m}^3$ of additional highly radioactive waste containing high concentrations of alpha emitters. The NEA has estimated that the nuclear generating capacity of the world in

the year 2000 will be 600 GWe, which will result in the discharge of about 15,000 metric tons of spent fuel annually. If half of that is reprocessed, it would result in 750 m^3 of HLW per year worldwide. According to data cited by Roxburgh (1987, Table 1.9), the total amount of HLW in the United States by the year 2000 will have a volume of $10,500\text{ m}^3$ with an activity of 126,000 megacuries (MCi) or $4662 \times 10^{18}\text{ Bq}$. Various other forms of radioactive waste (*radwaste*) will have a volume of $2.28 \times 10^6\text{ m}^3$ and a total activity of 1980 MCi, which is equivalent to $73.26 \times 10^{18}\text{ Bq}$ and will raise the total accumulated radioactivity in the United States alone to $4735 \times 10^{18}\text{ Bq}$.

The radiochemical composition of the fission products in HLW can be predicted from the isotopic abundance of ^{235}U in the fuel, from the energy spectrum of the neutrons in the reactor, from possible neutron-capture reactions of product nuclides, and from the decay time since the fuel was removed from the reactor. The results of such a calculation are listed in Table 24.2 for a reactor that operated for one year at one MWe

Table 24.2 List of Fission-Product Nuclides and Their Activities in Terabecquerels (1 TBq = 10^{12} Bq) at Different Times After Removal from a Reactor That Operated for One Year at One MWe

Radionuclide	$t = 0$	$t = 100$ days	$t = 5$ years
^{85}Kr	7.07	6.92	4.88
^{89}Sr	1413.40	381.10	0
^{90}Sr	52.91	52.54	44.40
$^{90}\text{Y}^a$	52.91	52.54	44.40
^{91}Y	1809.30	536.50	0
^{95}Zr	1820.40	629.00	0
$^{95}\text{Nb}^a$	1783.40	1061.90	0
^{103}Ru	1143.30	219.04	0
$^{103\text{m}}\text{Ru}$	1143.30	219.04	0
^{106}Ru	80.66	66.60	2.59
$^{106}\text{Rh}^a$	80.66	66.60	2.59
^{131}I	932.40	0.15	0
^{133}Xe	2046.10	0	0
^{137}Cs	39.96	39.59	35.89
$^{137\text{m}}\text{Ba}^a$	38.11	37.74	34.04
^{140}Ba	1912.90	8.51	0
$^{140}\text{La}^a$	1912.90	9.99	0
^{141}Ce	1768.60	175.38	0
^{143}Pr	1676.10	10.73	0
^{144}Ce	987.90	769.60	9.99
$^{144}\text{Pr}^a$	987.90	769.60	9.99
^{147}Nd	806.60	1.48	0
$^{147}\text{Pm}^a$	181.30	177.60	50.32

^aDaughter of a fission-product nuclide.

SOURCE: Roxburgh (1987) after Pentreath (1980).

(Roxburgh, 1987, after Pentreath, 1980). The data indicate that the activity and hence the radiotoxicity of the principal fission-product nuclides and their daughters decrease rapidly with time. After a "cooling time" of 100 days, the total activity of the radionuclides decreases to about 23% of its original value and is further reduced to 0.84% of its initial value in 5 years when its activity is about 190 TBq.

The principal radionuclides remaining in HLW after a cooling period of 5 years are isotopes of some of the rare earth elements (Pm, Pr, and Ce), platinum group metals (Ru and Rh), the alkaline earths (Sr and Ba), plus Kr, Y, and Cs. In addition, *spent unprocessed fuel* (SURF) contains isotopes of the actinide elements, including specifically ^{239}Pu ($T_{1/2} = 2.44 \times 10^4$ yr), ^{240}Pu ($T_{1/2} = 6.54 \times 10^3$ yr), ^{241}Am ($T_{1/2} = 433$ yr), ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ yr), ^{238}U ($T_{1/2} = 4.47 \times 10^9$ yr), and residual ^{235}U ($T_{1/2} = 7.04 \times 10^8$ yr). All of these nuclides have long half-lives and give rise to series of unstable daughters whose decay augments the activity of their parents. As a result, SURF not only contains more radioactivity than HLW but also remains active longer than reprocessed HLW (Roxburgh, 1987). This point is illustrated in Figure 24.2, which shows that the fission-product nuclides of HLW and SURF decay to less than one TBq in 1000 years, whereas the actinides of SURF require more than 100,000 years to decay to the same level of activity.

The radioactivity of HLW, SURF, and of the cladding hulls of spent nuclear fuel elements releases very substantial amounts of heat for about 10,000 years after they were removed from a power reactor. The heat output decreases with time, as shown in Figure 24.3; but even after 100,000 years, HLW produces ~ 1 W/metric ton of nuclear fuel, whereas SURF gives off about six times that much heat. An even more graphic illustration of the thermal energy produced by SURF is to note that the spent fuel removed *annually* from the Pickering A power reactor in Canada produces the same amount of heat as the combustion of 25 million barrels of oil (Barnes, 1979).

24.3 Geological Disposal of Radioactive Waste

The radwaste that is accumulating at nuclear reactors is a threat to all life forms for more than 10,000 years after its removal from the reactor. Therefore, this material must be isolated from the biosphere in

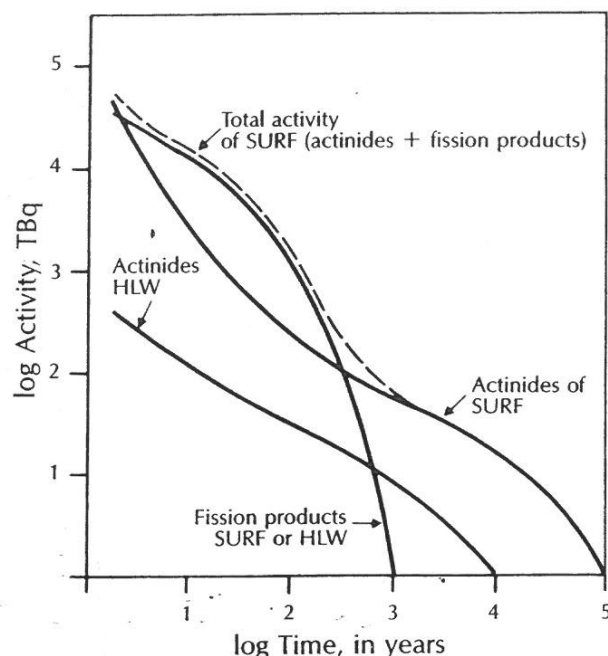


Figure 24.2 Decay rate of reprocessed high-level waste (HLW) and spent unprocessed fuel (SURF) in units of terabecquerels (1 TBq = 10^{12} dis/s) and time in years. The data pertain to a pressurized water reactor generating 33 GW day tonne^{-1} (1 GW = 10^9 W) after five years of cooling and are normalized to one metric tonne of heavy metal in the original fuel elements. The fission-product nuclides in both HLW and SURF decay to <1 TBq in ~ 1000 years, whereas U and the transuranium elements (^{238}U , ^{235}U , ^{237}Np , ^{239}Pu , ^{241}Am , and their daughters) in SURF require $>100,000$ years to decay to that level of activity (plotted from data listed in Roxburgh, 1987).

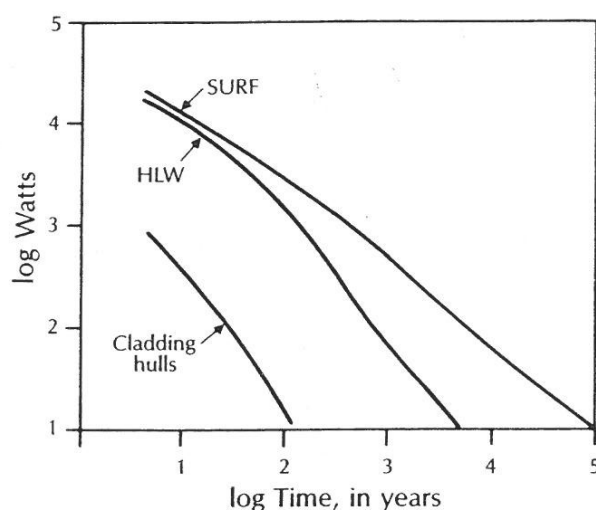


Figure 24.3 Heat output from spent unprocessed fuel (SURF), high-level waste (HLW), and cladding hulls as a function of time. The data pertain to a pressurized water reactor with a fuel consumption of 33 GW day tonne^{-1} followed by a 5-year cooling period. The thermal energy is expressed in watts per metric tonne of heavy metal in the original fuel elements. Note that SURF generates significantly more heat and does so for a longer period of time than HLW because of the presence of U and certain transuranium elements and their unstable daughters (data from Roxburgh, 1987).

such a way that all accidental contact with it is prevented (Blomke, 1976; Chapman and McKinley, 1987). In general, this can be achieved by storing the material in appropriately designed underground

repositories within certain kinds of rocks that can tolerate the heat generated by the radioactivity and are sufficiently impermeable to prevent the contamination of groundwater by radionuclides.

The design and construction of underground nuclear-waste repositories have been technically feasible for many years. Nevertheless, construction of such facilities has been delayed for a number of reasons:

1. The need to make detailed evaluations of proposed sites to determine the hydrologic conditions as well as the geochemical and structural stability of the rocks at these sites.
2. Reluctance by people living near proposed repositories to permit their construction because of potential hazards resulting from accidents during transport of radwaste to the site or from unforeseen problems with its containment within the repository.

The social and political resistance to the siting of repositories has given rise to the NIMBY complex (not in my back yard). Few people want their area to become the dumping ground of other people's radwaste. At the present time, each country with a significant nuclear industry is planning to build repositories for waste created within its own borders. These repositories will be constructed within different kinds of rocks, will be based on a variety of designs, and will use different packaging methods. The construction of a large number of radwaste repositories all over the world may increase the probability of accidents but may also reduce the severity of their consequences. Moreover, shorter transport distances from reactors to the national or regional disposal facilities may reduce the risk of accidents en route.

Underground storage of nuclear waste provides a number of important advantages compared to other disposal methods that have been considered, such as deposition in deep-sea trenches, burial in continental ice sheets, and injection into the Sun (Anonymous, 1981, 1983, 1984). Geological repositories of nuclear waste have the following desirable attributes:

1. They are *safe* because the host rock (if properly chosen) can absorb the radiation and dissipate the heat, and because acci-

dental or malicious intrusion can be prevented by the depth of the repository below the surface. The migration of certain radionuclides by diffusion or advection by groundwater can be minimized by the use of multiple barriers. Any future movement of radionuclides out of the repository can be predicted from the known properties of the nuclides, the hydrologic conditions in the host rock, and the mineral and chemical composition and ion-exchange properties of the rocks.

2. Underground repositories require *no maintenance* after they are filled and sealed. This is important because the time required to detoxify radioactive waste is longer than the rise and fall of most human civilizations in the past.
3. Geological repositories offer *flexibility* and *convenience* in site selection and construction because repositories can be constructed within different kinds of rocks, including granitic rocks, evaporites, shale, tuff, or basalt. Therefore, most nations wishing to build a repository can do so within their borders, and the repositories can be located so as to minimize transport distances from reactor sites.
4. The construction of underground repositories is *feasible* based on well-established methods of mining engineering. The cost of building such installations does not add significantly to the price of electricity generated by nuclear power reactors.
5. The radioactive waste is *retrievable* even though underground geological repositories are designed to contain the waste products indefinitely.

Several countries have made substantial progress toward the construction of underground repositories of nuclear waste in different kinds of rocks: the Federal Republic of Germany in salt; Canada, Finland, France, Sweden, and United Kingdom, granitic rocks; Belgium and Italy, clay; and the United States, tuff, basalt, and salt deposits.

The safety of underground nuclear repositories during the time interval in the future when the waste material remains toxic must be predicted by modeling. The validity of such predictions depends on factual information about the composition of the waste material and about the local and regional geologic environment of the site. The specific properties of the host rock to be evaluated include (Fried, 1979; Barney et al., 1984; Tsang, 1987):

1. The presence and movement of gases, water, and brine within the host rock at the site and in the surrounding area as well as above and below the repository.
2. The response of the host rock to the input of heat from the radwaste and the effect of the temperature increase on its mechanical and hydrologic properties.
3. The behavior of radionuclides within the host rock and their migration routes.
4. The degradation of the packaging of the radwaste and of the barriers designed to contain radionuclides.
5. Risk of disruption of the repository by geological events such as earthquakes, movement along faults, volcanic eruptions, formation of continental ice sheets, subsidence, or sea-level rise.

The role of *geochemists* in this enterprise is to obtain the information that is needed to predict the future safety of each proposed nuclear waste repository. The necessary information is partly site-specific, but also requires laboratory studies of basic properties and investigations of natural analogs in which the movement of radionuclides in the geologic past can be observed.

The future safety of a particular nuclear-waste repository depends not only on its geologic setting and on geochemical processes but also on its design and on the complementarity of various design features. These include the packaging of the waste material, the depth of the repository and the spacing of waste packages, use of buffers around individual packages, and backfilling of tunnels after the waste packages have been emplaced.

The packaging of nuclear waste must allow it to be transported and stored safely prior to being placed in its final repository. In addition, the form of packaging must contribute to the long-term containment of radionuclides by being mechanically strong and chemically stable. Canisters containing vitrified HLW will probably have overpacks that will enhance safety during transport, will assure their physical integrity for 1000 years or more, and will retard the release of radionuclides in combination with clay (bentonite) buffers placed around each canister.

The estimated release rates of radionuclides from repositories containing several thousand canisters after 10^5 years are listed in Table 24.3 (Anonymous, 1984). Most of the remaining activity is due to isotopes of Pu whose solubility in water is sufficiently low (~ 2.4 ppm) that only a small fraction ($\sim 2 \times 10^{-6}$) escapes annually. The *dilution* of the radionuclides released by repositories in the ambient groundwater is expected to reduce their environmental impact. The amount of ^{239}Pu that can be maintained in the human body without significant injury is $0.13 \mu\text{g}$ whose decay rate is $0.008 \mu\text{Ci}$ or $\sim 300 \text{ Bq}$.

24.4 Geochemistry of Plutonium

Plutonium and many other transuranium elements, some of which are shown in Figure 24.4, originally existed in the solar nebula, but subsequently decayed because all of their isotopes are radioactive and have short half-lives compared to the age of the Earth. Only ^{238}U ($T_{1/2} = 4.47 \times 10^9 \text{ yr}$) and ^{235}U ($T_{1/2} = 7.04 \times 10^8 \text{ yr}$) have survived to the present time, whereas ^{244}Pu ($T_{1/2} = 8.3 \times 10^7 \text{ yr}$) did not and ^{234}U ($T_{1/2} = 2.44 \times 10^5 \text{ yr}$) occurs only because it is a short-lived daughter of ^{238}U . The former presence of ^{244}Pu in meteorites was confirmed by Alexander et al. (1971) by the presence of fissionogenic xenon. However, a search by Wetherill et al. (1964) for ^{247}Cm ($T_{1/2} = 1.54 \times 10^7 \text{ yr}$) in the rare-earth concentrate of terrestrial *euxenite* (REE niobate and titanate) failed to confirm the pres-

Table 24.3 Estimated Rates of Leaching of Radioactive Isotopes of Actinide Elements from Repositories Containing Several Thousand Canisters of High-Level Waste (HLW) and Spent Unreprocessed Fuel (SURF) After 10^5 Years

Nuclide	Solubility, ppm	Leach rate, ^a fraction/yr		Activity released per year	
		HLW	SURF	HLW, Ci/3000 canister	SURF, Ci/7000 canister
^{238}U	485	1.4×10^{-4}	3.1×10^{-7}	129	948
$^{242}\text{Pu}^b$	2.4	1.3×10^{-6}	2.3×10^{-6}	3,940	29,500
$^{237}\text{Nb}^c$	0.007	1.2×10^{-9}	1.45×10^{-9}	2.1	16
$^{230}\text{Th}^d$	0.024	1.3×10^{-5}	1.68×10^{-7}	196	1,470
^{239}Pu	2.4	1.3×10^{-6}	2.3×10^{-6}	61,900	464,000

^aFlow of water assumed to be limited by diffusion through a bentonite buffer.

^bTable 7a of Anonymous (1984) lists ^{237}Pu for HLW, which may be a misprint because this isotope has a half-life of only 45.6 days.

^cReducing conditions.

^dDaughter of ^{238}U .

SOURCE: Anonymous (1984).

ence of this isotope. All of the other isotopes of Np, Pu, Am, and Cm in Figure 24.4 have shorter half-lives than ^{244}Pu and ^{247}Cm . Nevertheless, several of these do occur in small concentrations in terrestrial environments.

The presence of ^{239}Pu ($T_{1/2} = 2.44 \times 10^4$ yr) in U minerals was originally predicted by Goldschmidt (1942) based on the neutron capture of ^{238}U followed by β -decay of the resulting ^{239}U and ^{239}Np . Subsequently, Seaborg and Perlman (1948) and Garner et al. (1948) actually detected ^{239}Pu in pitchblende and carnotite. This and other isotopes of Np, Pu, Am, and Cm form not only in U minerals but also in nuclear reactors and during the explosion of nuclear fission devices. Consequently, the isotopes occupying the shaded squares in Figure 24.4 occur in radwaste and spent unreprocessed U-fuel and have been dispersed all over the Earth by fallout resulting from testing of nuclear weapons in the atmosphere and by the burnup of radioisotope thermoelectric generators (RTGs) fueled with ^{238}Pu and used in satellites and space probes. These anthropogenic sources now contribute more transuranium isotopes to the

environment than the natural neutron-capture reactions (Harley, 1980).

The discharge of various radionuclides into the environment by fallout from nuclear weapons tests and by reprocessing plants may be used to date marine and lacustrine sediment (Stanners and Aston, 1984) as well as ice in Greenland and Antarctica (Koide et al., 1985).

The Pu isotopes that have been identified in natural materials include ^{238}Pu ($T_{1/2} = 87.8$ yr), ^{239}Pu ($T_{1/2} = 2.44 \times 10^4$ yr), ^{240}Pu ($T_{1/2} = 6.54 \times 10^3$ yr), ^{241}Pu ($T_{1/2} = 15$ yr), and ^{242}Pu ($T_{1/2} = 3.87 \times 10^5$ yr). The atomic ratios of Pu isotopes in fallout from nuclear weapons tests are:

$$^{240}\text{Pu}/^{239}\text{Pu} = 0.18 \pm 0.01$$

$$^{241}\text{Pu}/^{239}\text{Pu} = 0.009 \pm 0.002$$

$$^{242}\text{Pu}/^{239}\text{Pu} = 0.004 \pm 0.001$$

whereas the activity ratio (in the radiological sense) of $^{240}\text{Pu}/^{239}\text{Pu}$ released by weapons tests is ~ 0.67 (Sholkovitz, 1983).

The concentrations of Pu are usually determined by separating and purifying the element

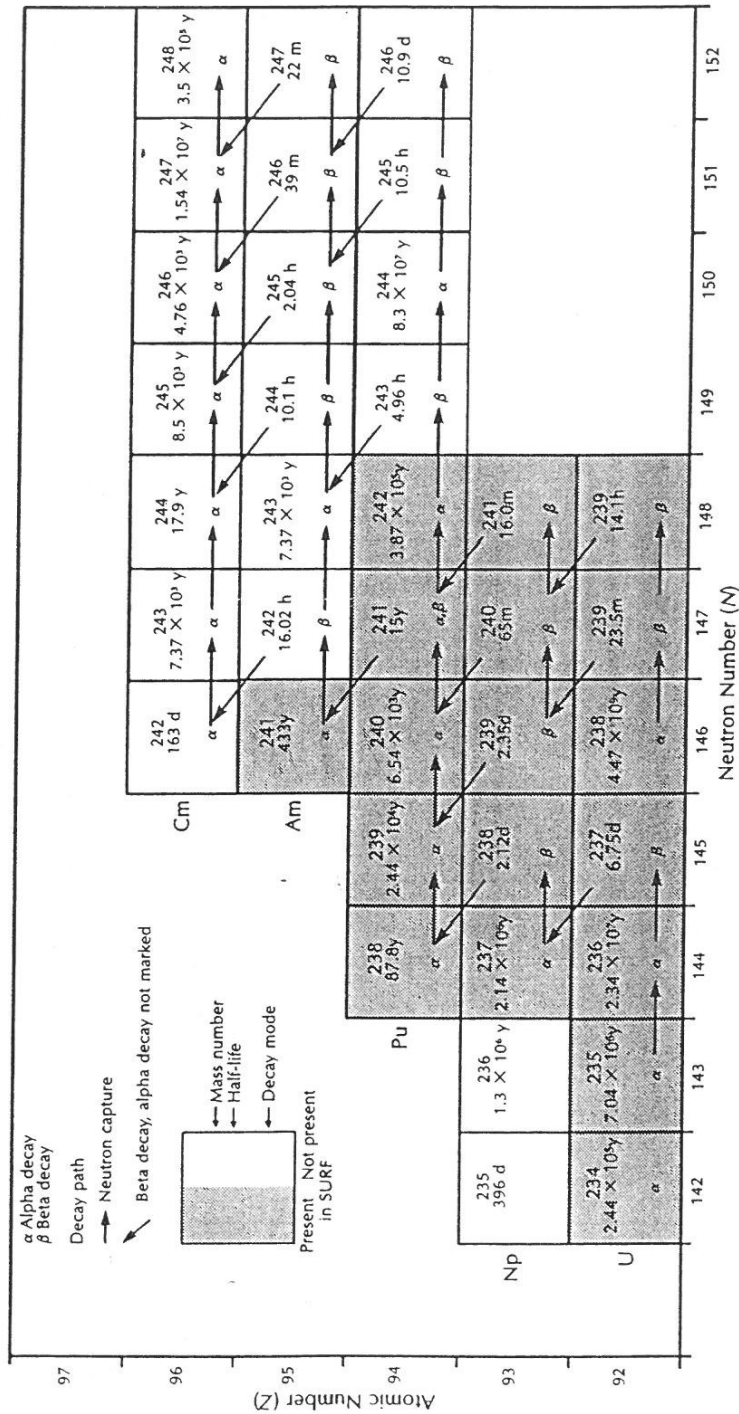


Figure 24.4 Partial chart of the nuclides showing the principal isotopes of U and of the transuranium elements neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm). Although all of the isotopes of these elements are radioactive, those that are shaded occur in spent unprocessed fuel elements (SURF) as a result of sequential neutron capture and β -decay starting with ^{238}U and ^{235}U . The isotope ^{234}U occurs because it is a daughter of ^{238}U . The neutron-capture reactions take place during the operation of nuclear reactors as well as during the explosion of nuclear fission devices. In addition, isotopes of Np and Pu form in U-rich rocks as a result of the neutron flux maintained by spontaneous fission of ^{238}U , by (α, n) reactions, and by cosmic-ray neutrons.

chemically and by measuring the rate of emission of α -particles by the isotopes of Pu. Unfortunately, the α -particles emitted by ^{240}Pu and ^{239}Pu have similar energies and cannot be resolved by this technique. Therefore, the two isotopes are determined together and the results are reported as $^{240,239}\text{Pu}$. Alternatively, both the isotope composition and the concentration of Pu in natural samples can be determined by mass spectrometry. However, this technique is time consuming and is therefore not used for studies of Pu concentrations requiring large numbers of analyses.

The occurrence of Pu in nature implies that short-lived ^{238}Np ($T_{1/2} = 2.12$ d), ^{239}Np ($T_{1/2} = 2.35$ d), ^{240}Np ($T_{1/2} = 65$ m), and ^{241}Np ($T_{1/2} = 16.0$ m) must also be present because they are intermediate products during the neutron-capture reactions that produce the Pu isotopes. However, they all decay rapidly as soon as the process stops, whereas ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ yr), ^{239}Pu , ^{240}Pu , and ^{242}Pu persist for tens of thousands of years because of their long half-lives.

The ^{241}Pu , formed by $^{240}\text{Pu}(n, \gamma)^{241}\text{Pu}$, decays by β -emission to ^{241}Am ($T_{1/2} = 433$ yr), which occurs in fallout and radwaste and is now widely distributed all over the Earth (Livingston and Bowen, 1976; Koide et al., 1980; Day and Cross, 1981). Americium is strongly adsorbed onto the surfaces of particles including crystals of calcite and aragonite (Shanbhag and Morse, 1982). The equilibrium constant ($K_d = \text{Am in solid}/\text{Am in solution}$) for calcite is $>10^5$ and the adsorption appears to be irreversible. Hence, ^{241}Am is scavenged rapidly from seawater and is incorporated into the sediment.

^{241}Am decays by α -emission to ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ yr), which grows in and becomes one of the dominant radionuclides in old radwaste. The ^{241}Am ($T_{1/2} = 433$ yr) may also capture a neutron to form ^{242}Am ($T_{1/2} = 16.02$ h), which decays by β -emission to ^{242}Cm ($T_{1/2} = 163$ d). This isotope emits an α -particle as it decays to ^{238}Pu ($T_{1/2} = 87.8$ yr). This sequence of events therefore contributes to the presence of ^{242}Am , ^{243}Cm , ^{237}Np , and ^{238}Pu in fallout and in radwaste from nuclear reactors. Figure 24.4 indicates that a multitude of other radionuclides may form both

by neutron capture and by subsequent decay depending on the magnitude of the neutron flux, the duration of the irradiation, and the time elapsed since the irradiation ended.

The natural neutron flux of U-bearing rocks also causes the formation of other radioactive isotopes including ^3H , ^{14}C , ^{36}Cl , ^{37}Ar , and ^{39}Ar , whereas induced fission of ^{235}U in rocks produces ^{81}Kr , ^{85}Kr , and ^{129}I (Andrews et al., 1989). The magnitude of the neutron flux in different kinds of rocks depends on the concentrations of U and Th in the rocks because the neutrons arise primarily by spontaneous fission of ^{238}U and by (α, n) reactions. Cosmic-ray neutrons also contribute to the neutron flux, depending on the depth below the surface, and are most effective in the atmosphere. The neutron flux in rocks is affected by their neutron-absorbing capacity, which arises from the presence of O, F, Na, Al, Si, K, and Mg. The neutron fluxes in different kinds of rocks in Table 24.4 range from $4.07 \times 10^{-4} \text{ n cm}^{-2} \text{ s}^{-1}$ in the U-rich Stripa granite in Sweden to $4.5 \times 10^{-8} \text{ n cm}^{-2} \text{ s}^{-1}$ in the salts formed by evaporating seawater.

The geochemistry of Pu in the oceans and on the continents was reviewed and reinterpreted by Sholkovitz (1983) based on the voluminous literature that has accumulated on this subject. Bowen et al. (1980) estimated that more than 400 kCi of ^{239}Pu and ^{240}Pu have been released by nuclear weapons tests in the form of about 3900 kg of ^{239}Pu and 700 kg of ^{240}Pu . About 70 kCi of the total amount of Pu remained close to the test sites, including the Bikini and Eniwetok atolls in the Pacific Ocean, which contain ~ 2.7 kCi of Pu in lagoonal sediment (Noshkin and Wong, 1979) in addition to ~ 2 kCi in sediment in the surrounding ocean (H. D. Livingston in Sholkovitz, 1983).

In addition to its dispersion in fallout, Pu has been injected into the Earth's surface environment as a result of accidents. These include the burnup over the Indian Ocean of the SNAP-9A navigational satellite, which contained an RTG fueled with 1 kg (17 kCi) of ^{238}Pu in April of 1964 (Hardy et al., 1973), the crash of a B-52 bomber at Thule, Greenland, which released weapons-grade Pu (Harley, 1980), and the explosion of the nuclear reactor in Chernobyl, Ukraine, on April 6, 1986.

Table 24.4 Calculated Neutron Flux in Rocks of Various Compositions

<i>Rock type</i>	<i>U, ppm</i>	<i>Th, ppm</i>	<i>Production n cm⁻³ y⁻¹</i>	<i>Absorption cross section, cm²/g</i>	<i>Neutron flux, n cm⁻² s⁻¹</i>
Granite, Stripa, Sweden	44.1	33.0	217.1	0.0065	4.07×10^{-4}
Ultramafic	0.001	0.004	0.004	0.0044	1.0×10^{-8}
Basalt	1.0	4.0	10.2	0.0073	1.6×10^{-5}
Granite	3.5	18.0	36.7	0.0069	6.4×10^{-5}
Clay, shale	3.2	11.0	17.6	0.0098	3.0×10^{-5}
Sandstone	0.45	1.7	2.0	0.0061	4.6×10^{-6}
Carbonates	2.2	1.7	5.45	0.0039	2.0×10^{-5}
Evaporite ^a	0.1	$<10^{-5}$	1.02	0.3260	4.5×10^{-8}

^aSalts formed by evaporation of seawater.

SOURCE: Andrews et al. (1989).

Other point sources of Pu and other radionuclides in the oceans are the reprocessing facilities at Windscale, United Kingdom (Aston and Stanners, 1981; Livingston et al., 1982), at LaHague near Cherbourg, France (Murray et al., 1979), at Savannah, Georgia (Hayes and Sackett, 1987), as well as dumping sites of low-level radwaste, especially in the northeastern Atlantic Ocean (Needler and Templeton, 1981). One reason for concern about the release of Pu into the oceans is the possibility that it can be remobilized from sediment after burial.

Plutonium can exist in four oxidation states (+3, +4, +5, and +6), it forms complex ions with both organic and inorganic ligands, and it can form colloidal suspensions (Cleveland, 1979). As a result, Pu is a *mobile* element under a wide range of environmental conditions and is therefore able to enter the food chain in the oceans. Consequently, fish and other kinds of seafood may become contaminated with Pu.

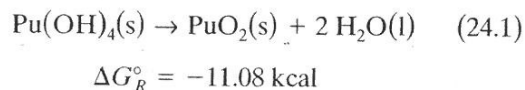
Noshkin and Wong (1979) reported that the concentration of Pu (²³⁹Pu and ²⁴⁰Pu) in the water of the lagoons of the Bikini and Eniwetok atolls ranges between 14×10^{-15} and 114×10^{-15} Ci/L, whereas that of the open ocean lies between 0.3×10^{-15} and 0.5×10^{-15} Ci/L. The Pu in the

lagoonal water constitutes only 0.08% of the Pu in the upper 60 cm of sediment in the lagoons. Noshkin and Wong (1979) therefore predicted that it will take between 400 and 500 years for all of the Pu in the sediment to be released into the lagoons and hence into the open ocean. Plutonium is also being released by sediment deposited west of the islands that contains close-in fallout.

When Pu first enters the ocean, it is rapidly scavenged by adsorption on biogenic particles. However, as the particles sink they decompose, thereby releasing the adsorbed Pu, which goes into solution in deep water. The Pu remains in solution until it is readsorbed onto another particle that may carry it all the way to the bottom of the ocean. In addition, Pu may be carried downward rapidly on large particles and may be released from them while still in the water column, at the sediment-water interface, or after burial (Sholkovitz, 1983; Bowen et al., 1980). Evidently, the geochemistry of Pu in the oceans involves complex processes reflecting not only the chemical properties of the element but also the biological productivity of the water and the input of sediment particles, both of which vary regionally within the ocean.

24.5 Eh-pH Diagrams for Neptunium and Plutonium

The geochemical properties of the transuranium elements can be presented in the form of Eh-pH diagrams (Brookins, 1988). The mobility of these elements, indicated by these diagrams, depends on whether the hydroxide or oxide is assumed to be the stable phase. For example, Np may form $\text{Np}(\text{OH})_4$, $\text{NpO}(\text{OH})_2$, or NpO_2 , all of which contain Np^{4+} . Similarly, Pu may exist as $\text{Pu}(\text{OH})_4$ or PuO_2 . The solid hydroxides transform spontaneously into the oxides when the water/rock ratio is reduced after initial precipitation of the hydroxide. In the case of Pu, the transformation is represented by the reaction:



Hence, PuO_2 is the stable phase in the standard state, although metastable $\text{Pu}(\text{OH})_4$ may initially precipitate from aqueous solution. When carbonate ions are present, the transuranium elements can form solid carbonates such as $\text{Np}(\text{CO}_3)_2$, $\text{Pu}_2(\text{CO}_3)_3$, and $\text{Am}_2(\text{CO}_3)_3$, as well as complex carbonate ions $\text{PuO}_2(\text{OH})\text{CO}_3^{2-}$ and $\text{NpO}_2(\text{OH})_2\text{CO}_3^{2-}$.

The transformation of $\text{Np}(\text{OH})_4$ to $\text{NpO}(\text{OH})_2$ and ultimately to NpO_2 is accompanied by a dramatic decrease in the solubility and hence in the mobility of this element at 25°C under conditions that prevail at the surface of the Earth or at shallow depth. The Eh-pH diagrams of Brookins (1988) in Figure 24.5 illustrates the progressive expansion of the stability fields of the solid phases $\text{Np}(\text{OH})_4$, $\text{NpO}(\text{OH})_2$, and NpO_2 , respectively. At pH values between 2 and 10 in Figure 24.5A, three ions [NpO_2^+ , $\text{Np}(\text{OH})_5^-$, and Np^{3+}] have equilibrium activities $>10^{-6}$ mol/L in contact with $\text{Np}(\text{OH})_4$. When $\text{NpO}(\text{OH})_2$ is the solid, only NpO_2^+ has equilibrium activities of that magnitude (Figure 24.5B). The solubility of NpO_2 to form NpO_2^+ is further restricted to environments having pH <8.0 and Eh >0.753 V (Figure 24.5C). Consequently, Np is *not* expected to be mobile in

groundwater under normal pH conditions (pH >3 but <7).

The mobility of Np in the oceans (pH ≈ 8.2) predicted from Eh-pH diagrams depends on the solid phase that actually forms in this environment. If $\text{Np}(\text{OH})_4$ is present (Figure 24.5A), Np can have activities $>10^{-6}$ mol/L both as $\text{Np}(\text{OH})_5^-$ and as NpO_2^+ depending on the Eh. However, if NpO_2 is present (Figure 24.5C), then NpO_2^+ , $\text{Np}(\text{OH})_5^-$, and $\text{NpO}_2(\text{OH})_2\text{CO}_3^{2-}$ all have equilibrium activities $<10^{-6}$ mol/L and Np is expected to remain immobile in the ocean and in marine sediment.

The solubility of the solids $\text{Pu}(\text{OH})_4$ and $\text{Pu}_2(\text{CO}_3)_3$ with respect to Pu^{3+} and $\text{Pu}(\text{OH})_5^-$ is depicted in Figure 24.6A, based on Brookins (1988). The ions PuO_2^+ and Pu^{4+} are dominant only at pH <2 and Eh $>+1.0$ V and therefore are rarely important in natural environments. When PuO_2 is the stable phase, only Pu^{3+} can have activities $>10^{-6}$ mol/L at pH <5.5 in systems represented by Figure 24.6B. Consequently, Pu may be *mobile* in acidic groundwaters under reducing as well as oxidizing conditions. As in the case of Np, the mobility of Pu in the oceans depends on whether solid $\text{Pu}(\text{OH})_4$ or PuO_2 is actually present.

In reality, the geochemistry of Pu in the oceans is more complicated than it appears to be, based on the Eh-pH diagrams in Figure 24.6, because Pu occurs in four oxidation states: Pu^{3+} , Pu^{4+} , Pu^{5+} , and Pu^{6+} . Nelson and Lovett (1978) reported that the ratio $(\text{Pu}^{5+} + \text{Pu}^{6+})/(\text{Pu}^{3+} + \text{Pu}^{4+})$ of dissolved $^{239,240}\text{Pu}$ in the Irish Sea (derived largely from the Windscale reprocessing plant) ranges from about 2.4 to 12, whereas Pu adsorbed on suspended particles has lower values of this ratio between 0 and 0.4. Evidently, Pu^{5+} and Pu^{6+} are concentrated in the *aqueous phase*, whereas Pu^{3+} and Pu^{4+} dominate on *suspended particles*. However, the opposite appears to apply to some lakes in central North America and Canada where the $(+5, +6)/(+3, +4)$ Pu ratio is <1 (Wahlgren et al., 1977). Evidently, the higher oxidation states dominate in the water of the Irish Sea, whereas the lower oxidation states are

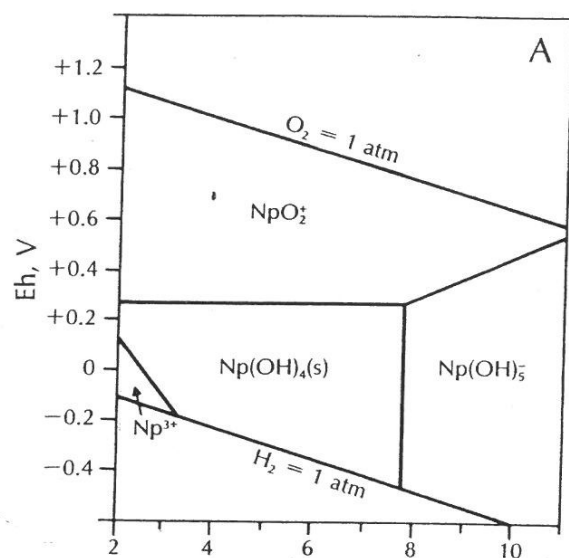
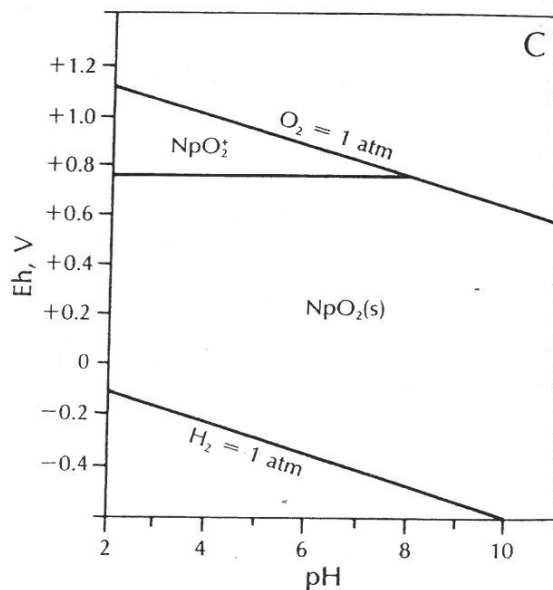
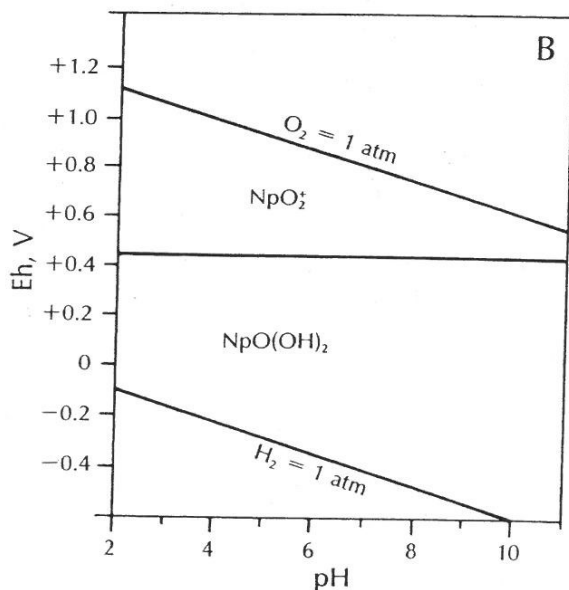


Figure 24.5 A. Eh-pH diagram for Np based on Np(OH)_4 as the solid phase in the presence of H_2O and containing $\Sigma(\text{carbonate}) = 10^{-3} \text{ mol/L}$. The solubility boundaries are drawn at activities of 10^{-6} mol/L of the ionic species, including NpO_2^+ , Np(OH)_5^- , and Np^{3+} . In addition, Np^{4+} is the dominant ion at $\text{pH} < 2.0$ and $\text{Eh} > 0.147 \text{ V}$ but is not shown here.

B. Eh-pH diagram for Np based on NpO(OH)_2 as the solid phase in the presence of H_2O and containing $\Sigma(\text{carbonate}) = 10^{-3} \text{ mol/L}$. Evidently, NpO(OH)_2 is less soluble than Np(OH)_4 , and NpO_2^+ is the only ion that can have activities $> 10^{-6} \text{ mol/L}$ in equilibrium with NpO(OH)_2 between $\text{pH} 2$ and $\text{pH} 10$.

C. Eh-pH diagram for Np based on NpO_2 as the solid phase in the presence of H_2O and containing $\Sigma(\text{carbonate}) = 10^{-3} \text{ mol/L}$. The Eh-pH conditions in which NpO_2^+ can have an activity $> 10^{-6} \text{ mol/L}$ in equilibrium with NpO_2 are further reduced. The equilibrium activity of the oxyhydroxycarbonate complex ($\text{NpO}_2(\text{OH})_2\text{CO}_3^{2-}$) is $< 10^{-6} \text{ mol/L}$ and does not appear on this diagram. (Adapted from Brookins, 1988.)



dominant in the water of some North American lakes. Actually, Pu^{5+} and Pu^{6+} also dominate in Lake Michigan and Clear Lake, which have $(+5, +6)/(+3, +4)$ Pu ratios between 4 and 6 like the Irish Sea.

Sholkovitz (1983) reviewed evidence that Pu^{4+} forms strong complexes with dissolved organic compounds, whereas Pu^{6+} forms carbonate complexes (Aston, 1980). Therefore, the concentration of dissolved Pu and the distribution of

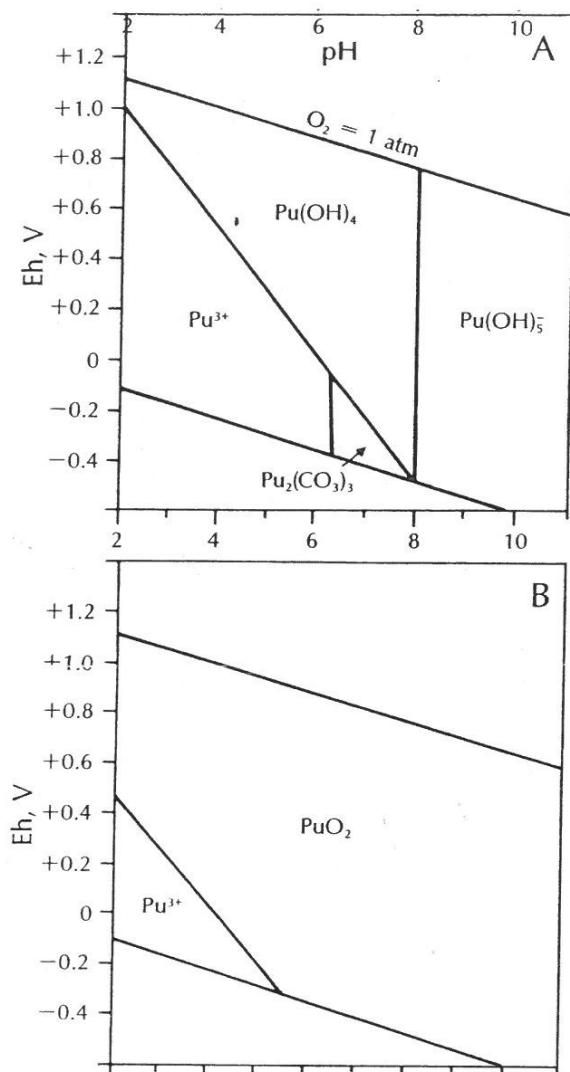


Figure 24.6 A. Eh-pH diagram for Pu based on the presence of $\text{Pu}(\text{OH})_4$ and $\text{Pu}_2(\text{CO}_3)_3$ in a system in which $\Sigma(\text{carbonate}) = 10^{-3} \text{ mol/L}$. The solubility boundaries are drawn at ion activities of 10^{-6} mol/L .

B. Eh-pH diagram for Pu based on the presence of PuO_2 in a system in which $\Sigma(\text{carbonate}) = 10^{-3} \text{ mol/L}$. Note that PuO_2 is much less soluble than $\text{Pu}(\text{OH})_4$, but that Pu^{3+} can have activities $>10^{-6} \text{ mol/L}$ in acidic environments. That the geochemistry of Pu is strongly affected by ion exchange equilibria is not apparent from these Eh-pH diagrams.

its oxidation states may depend on the abundances of dissolved organic compounds (fulvic acids) of low molecular weight (5000–10,000), on the carbonate content, and hence on the alkalinity of the water.

Some of the Pu in seawater is associated with suspended particles and can be removed from it by $0.45\text{-}\mu\text{m}$ filters. Sholkovitz (1983) estimated that from 5 to 20% of Pu in the open ocean occurs in particulate form. Nelson and Lovett (1978) reported that the distribution coefficients (solid/liquid) of “reduced” (+3, +4) Pu in the Irish Sea are consistently *larger* than those of “oxidized” (+5, +6) Pu. In fact, the values of K_d for reduced particulate Pu are from 21 times to 1000 times larger than the values of K_d for oxidized particulate Pu. Evidently, the particles suspended in the water of the Irish Sea preferentially scavenge reduced Pu from seawater and thereby concentrate the oxidized forms in the aqueous phase. However, the numerical values of K_d are probably variable because they depend on the character of the particles (inorganic, biogenic, and living organisms), on their composition (mineralogy and organic matter content), and on their size distribution. In addition, because the abundance of suspended particles varies regionally within the ocean, the fraction of adsorbed Pu also varies.

Sholkovitz (1983) expressed the fraction of adsorbed Pu as a function of the concentration of suspended particles in a system in which $K_d(\text{Pu}^{3+}, \text{Pu}^{4+}) = 25 \times 10^5 \text{ kg/L}$, whereas $K_d(\text{Pu}^{5+}, \text{Pu}^{6+}) = 0.15 \times 10^5 \text{ kg/L}$. The resulting graph in Figure 24.7 illustrates that ~95% of the “reduced” Pu is adsorbed when the suspended load is 10 mg/L , whereas only ~10% of the “oxidized” Pu is adsorbed under these conditions. Consequently, the ratio of “oxidized” to “reduced” Pu in solution *does* depend on the concentration of suspended particles and on their characteristic properties, which determine their ability to adsorb Pu ions.

The preceding discussion makes clear that Eh-pH diagrams are *incomplete* representations of the geochemistry of Pu in the ocean as well as in lakes and rivers. Presumably, ion exchange phenomena also affect the geochemical properties of

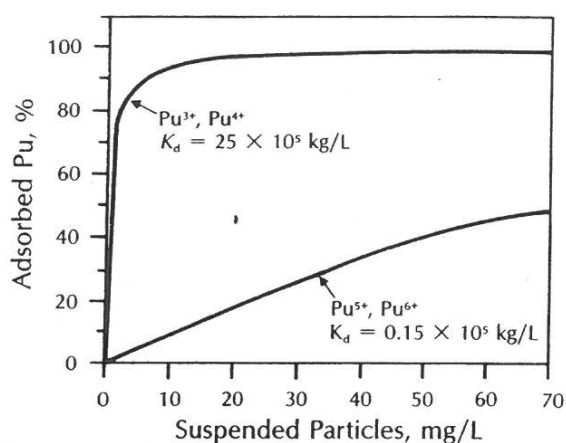


Figure 24.7 Fraction of Pu ions that are adsorbed onto suspended particles depending on their oxidation states, the concentration of suspended particles, and the values of the distribution constants (K_d) of the Pu^{3+} , Pu^{4+} (reduced) and Pu^{5+} , Pu^{6+} (oxidized) Pu. The graph illustrates the phenomenon that reduced Pu is scavenged more effectively than oxidized Pu and that the ratio of oxidized to reduced Pu remaining in solution can vary widely depending on the concentration of suspended particles and their compositions, which determine the magnitude of the distribution constants (adapted from Sholkovitz, 1983, Figure 9).

Pu ions in solution in groundwater. In addition, the study of dissolution, transport, and deposition of long-lived radionuclides, such as the isotopes of Pu, Np, and Am, in underground repositories must be coupled to other processes occurring at the same time.

The *coupling* of thermal, hydrological, mechanical, and chemical processes in predicting the long-term behavior of nuclear-waste repositories was the topic of an international conference in 1985 in Berkeley, California. The Proceedings of this conference were edited by Tsang (1987). It contains a paper by Langmuir (1987) in which he discussed the difficulties of predicting the outcome of geochemical processes in waste repositories because of the lack of sufficient thermodynamic and kinetic data at elevated temperature and pressure. In addition, even geochemical processes are *coupled*.

For example, the thermal gradient around a canister of HLW in a subsurface repository may cause silicate minerals to break down in its vicinity releasing silicic acid into the pore fluid which may transport it away from the canister to areas of lower temperature where the silicic acid precipitates as amorphous silica, thereby reducing the permeability of the rocks. Under the same set of circumstances, carbonates and sulfates, whose solubilities decrease with increasing temperature, may be deposited on the outer walls of the canister, thereby creating an additional barrier to the movement of radionuclides. Therefore, the escape of radionuclides from a canister of HLW is affected by geochemical processes that change the chemical composition and mechanical properties of the rocks surrounding the canister. The coupling of the process that may change the geochemical environment around an aging HLW repository makes it more difficult to predict the release of radionuclides and to evaluate its future safety. Consequently, such evaluations are not totally reliable and need to be confirmed by examining natural repositories of radioactive elements such as ore deposits of U in the form of veins or as mineral cements in sandstone (Brookins, 1984).

24.6 Analog Studies: The Natural Reactors at Oklo, Gabon

On September 25, 1972, the former chairman of the French High Commission for Atomic Energy, Dr. Francis Perrin, reported to the French Academy of Sciences that a uranium deposit in West Africa had undergone a chain reaction based on induced fission of ^{235}U (Section 16.1c). The deposit at Oklo, Gabon, had been put into production in the summer of 1970 and the U concentrate from the open-pit mine was shipped to Pierrelatte, France, for enrichment in ^{235}U prior to its use as reactor fuel. However, isotope analyses revealed that the U from Oklo was variably *depleted* in ^{235}U and that the abundance of ^{235}U in some batches of U concentrate was only 0.440 atom % compared to 0.720 atom % in normal terrestrial U. The

results also suggested that the abundance of ^{235}U decreased with increasing U content of the ore. In addition, analyses by Neuilly et al. (1972) at the French atomic center in Cadarach indicated that Nd, Sm, Eu, and Ce in the ore have anomalous isotope compositions. The scientists who had participated in these discoveries therefore concluded that ^{235}U in the orebodies at Oklo had fissioned in self-sustaining chain reactions with groundwater acting as the *moderator* of neutrons emitted by each fission event. The chain reaction probably operated intermittently because the reaction may have stopped when the rising temperature of the U-rich rocks caused the water to be converted to steam (Sullivan, 1972).

The discovery that natural chain reactions had occurred at Oklo was not entirely unexpected. Sixteen years earlier, Kuroda (1956) had demonstrated that 2100 million years ago a mass of pitchblende a few feet in diameter could have sustained a chain reaction in the presence of water because at that time the isotopic abundance of ^{235}U was 4.0% compared to 0.720% at the present time. Dr. Kuroda concluded that "The effect of such an event could have been a sudden elevation of the temperature, followed by a complete destruction of the critical assemblage." As a historical footnote let it be recorded that Dr. Kuroda obtained the analysis of the pitchblende (from Johanngeorgenstadt, Germany) out of F. W. Clarke's book, *The Data of Geochemistry* (see Chapter 1).

The unique natural reactors at the Oklo mine provide an opportunity to study the migration of fission-product nuclides in a natural setting. Consequently, the deposit has been studied intensively to determine its origin, to ascertain the conditions that permitted the occurrence of chain reactions, and to evaluate the mobility of long-lived radionuclides produced as fission products and by neutron capture (Brookins, 1978a,b; de Laeter et al., 1980; Loss et al., 1984). The initial results were summarized by Naudet (1974) and other French investigators in the June issue (No. 193) of the *Bulletin d'Informations Scientifiques et Techniques of the Commissariat à l'Energie Atomique*. Later, the International

Atomic Energy Agency in Vienna issued two reports on the Oklo reactors (IAEA, 1975, 1978). In addition, Kuroda (1982) included a description of the natural fission reactors at Oklo in his book on nuclear processes in nature.

The U ore at the Oklo mine occurs in sandstones of the Precambrian Francevillian Series. The U minerals were initially deposited syngenetically, but were subsequently remobilized during structural deformation of the host rocks and redeposited in small bodies containing between 50 and 70% U. The age of the U ore is 2.05×10^9 years based on the U-Pb method (Gancarz, 1978). As a result of the dissolution and reprecipitation, the remobilized U was not only concentrated but was also purified of certain elements (V, Se, Mo, and Fe) that could act as reactor poisons by absorbing neutrons.

The ore at the Oklo mine is composed of pitchblende (complex U-oxides, amorphous or cryptocrystalline), with impurities of chlorite and illite. Quartz is rare in the ore but common in the surrounding rocks. The ore also contains small amounts of pyrite, hematite, barite, chalcopyrite, and other minerals. Brookins (1984) pointed out that the presence of both pyrite and hematite fixes the range of Eh and pH conditions that existed in the ore at the time the chain reactions occurred (see Section 14.5d, Figure 14.11).

At the time of formation of the enriched orebodies at Oklo, the abundance of ^{235}U was 3.2%, which is within the range of modern reactor fuel. However, in order for a chain reaction to start based on *induced* fission of ^{235}U , groundwater must have been present in sufficient amounts to reduce the kinetic energies of neutrons to permit them to be absorbed by nuclei of ^{235}U , causing it to fission into complementary pairs of fission-product nuclides that subsequently decayed to stable daughters. About 17% of the time, the absorption of a slow neutron by ^{235}U leads to the formation of ^{236}U (Figure 24.4), which then decays by α -emission to long-lived ^{232}Th . Some of the ^{236}U atoms formed from ^{235}U may capture another neutron to form ^{237}U , which decays by a long series of α - and β -emissions to stable ^{209}Bi . Therefore, it is significant that Th and Bi occur in

the richest U ore at Oklo but not elsewhere in the deposit (Cowan, 1976).

Studies by many investigators have demonstrated that the stable daughters of about 30 fission-product nuclides are present in the natural reactors at Oklo in just about the expected amounts and proportions. This not only confirms the occurrence of chain reactions but also indicates that the fission-product nuclides in most cases did *not* migrate out of the volume of rock in which they were formed. Among the *immobile* elements are the REEs (La, Ce, Pr, Nd, Eu, Sm, and Gd) and the Pt group elements (Ru, Rh, and Pd), as well as Y, Zr, Nb, Th, and Bi. The REEs and Pt-group elements include the long-lived radionuclides that may survive in aging repositories of nuclear waste. Evidently, these potentially dangerous radionuclides did *not* migrate at Oklo. In addition, the transuranium elements Np, Pu, Am, and Cm were *not* mobile in the orebodies while the chain reactions were in progress or afterward (Brookins, 1984).

The elements that appear to have been only partially retained in the reactors at Oklo include Mo, Ag, I, Kr, and Xe. In addition, Rb, Cs, Sr, Cd, and Pb were either lost completely or show evidence of local migration (Cowan, 1976).

The chain reactions within the Oklo orebodies were based primarily on induced fission of the ^{235}U in the U ore. However, the indigenous ^{235}U was augmented by ^{235}U produced by decay of ^{239}Pu . The chain reactions were also based to some extent on induced fission of ^{239}Pu itself and on fission of ^{238}U caused by *fast* neutrons. Altogether, six tons of ^{235}U were consumed and 15,000 megawatt-years of energy were released by the chain reactions that occurred for at least 500,000 years (Cowan, 1976; Brookins, 1984).

During the period the chain reactions were occurring, the temperatures within the reactors probably exceeded 400°C , but the rocks did not melt and the deposit did not explode. The reason is that the chain reactions were controlled by the water content of the ore, which must have ranged from 12 to 15% to permit induced fission of ^{235}U to occur. When the temperature rose, the water content of the rocks was reduced, the flux of slow

neutrons was therefore decreased, and the chain reactions stopped. The evidence for relatively low temperatures in the reactor zones is supported by the fact that Bonhomme et al. (1965) obtained a Rb–Sr whole-rock isochron date of 1.85 ± 0.1 Ga for sedimentary rocks that overlie the U deposits at Oklo. Moreover, they reported a K–Ar date of 1.8 ± 0.1 Ga for concentrates of the 1M_d polymorph of illite from these rocks (Sections 16.3a, 16.3b, 13.2b.3, and 13.6). The 1M_d polymorph of illite does not retain radiogenic ^{40}Ar above $\sim 125^\circ\text{C}$ and is converted into the 2M polymorph between 150 and 250°C . Therefore, the survival of the 1M_d polymorph in the immediate vicinity of the reactors indicates that the chain reactions did not generate high temperatures in the surrounding rocks. In addition, these rocks could not have been buried more than a few hundred meters without destroying the 1M_d illite. However, the depth of the U ore at the time the natural reactors were operating is not known precisely.

The relevance of the natural reactors at Oklo to the evaluation of the safety of geological repositories of HLW is that the long-lived radionuclides of the REEs, the Pt-group metals, and the transuranium elements were quantitatively retained in rocks that have widely varying permeabilities and are also strongly jointed and fractured. Because of these properties, the Oklo site would *not* have been selected for the construction of a nuclear waste repository. Therefore, the evidence derived from studies of the natural reactors at Oklo indicates that rocks having low permeability and high thermal stability should retain radwaste even better than the rocks at Oklo.

24.7 Reactor Accidents: Chernobyl, Ukraine

The energy liberated by induced nuclear fission is very large compared to that of conventional energy sources, such as the combustion of fossil fuel or chemical explosives, including trinitrotoluene (TNT). Nevertheless, the process can be controlled by modulating the flux of thermal neutrons in the

core of the reactor. However, if for any reason the process goes out of control, the temperature in the reactor core can increase very rapidly, causing an explosion of the core and leading to the dispersal of radionuclides. Although the design of nuclear reactors is supposed to prevent such occurrences, several accidents have taken place since 1942, when the first reactor was built by Enrico Fermi and his associates in a squash court in the basement of the football stadium of The University of Chicago. The most recent reactor accident occurred on April 26, 1986, in Chernobyl, Ukraine.

The events leading up to this accident were described by Baier (1989) and Anspaugh et al. (1988). According to these sources, the Chernobyl Nuclear Power Station near the city of Kiev operated four power reactors of the "RBMK type" in which each fuel rod is contained within a pipe through which water is pumped at high pressure. The fuel assemblies were embedded in graphite, which served as the moderator. Reactor No. 4 at Chernobyl had 1659 fuel assemblies, each of which contained 114.7 kg of U. The fuel elements had been in the reactor for 610 days on average and had therefore accumulated more than 200 different fission-product nuclides including ^{90}Sr ($T_{1/2} = 29 \text{ yr}$) and ^{137}Cs ($T_{1/2} = 30.1 \text{ yr}$).

The power output of the reactor was controlled by means of 211 rods composed of neutron absorbers that could be inserted into the core to stop the chain reaction. Under normal operating conditions, 30 control rods had to be in place in the core of reactor No. 4 in order to keep the chain reaction under control. However, on the day before the accident the operators had reduced power to determine whether the heat in the graphite core of the reactor was sufficient to run the main electrical generator. While this experiment was in progress, the demand for electricity in the transmission lines fed by the generator suddenly increased. Therefore, the operators attempted to bring the reactor back to full power by withdrawing all but eight of the control rods, in violation of mandatory operating procedures. Consequently, the energy output rose within three seconds from 200 to 530 megawatts. In the next fraction of a second the reactor went out of

control. As the core temperature increased by 3000°C , Zr in the fuel elements reacted with water to form oxides, thereby releasing H_2 gas, which reacted explosively with O_2 and burst the steel housing containing the 2500 tons of graphite of the reactor core. The initial explosion caused a large-scale release of fission-product nuclides, including parts of the fuel elements, and resulted in the ultimate combustion of 250 tons of graphite.

After the initial explosive release of radionuclides, the temperature of the reactor core continued to rise for several days as a result of decay of radionuclides and because the cooling system had been destroyed in the explosion. The release of radionuclides, which had decreased drastically after the explosion, increased with the rising temperature and almost equaled the initial rate nine days earlier. The secondary release consisted primarily of the isotopes of volatile elements, including all of the noble gases, ^{131}I ($T_{1/2} = 8.041 \text{ d}$), ^{134}Cs ($T_{1/2} = 2.06 \text{ yr}$), and ^{137}Cs ($T_{1/2} = 30.1 \text{ yr}$), but only small amounts of nonvolatile radionuclides such as ^{89}Sr ($T_{1/2} = 50.59 \text{ d}$), ^{90}Sr ($T_{1/2} = 29 \text{ yr}$), ^{141}Ce ($T_{1/2} = 32.53 \text{ d}$), ^{144}Ce ($T_{1/2} = 284.44 \text{ d}$) and the Pu isotopes ^{238}Pu ($T_{1/2} = 87.8 \text{ yr}$), ^{239}Pu ($T_{1/2} = 2.439 \times 10^4 \text{ yr}$), and ^{240}Pu ($T_{1/2} = 6.54 \times 10^3 \text{ yr}$). The release was terminated nine days after the accident by corrective measures.

The plume of radionuclides emitted from Chernobyl moved northwest and reached Sweden and Finland, where it was quickly detected. Subsequently, the plume changed direction several times, resulting in the deposition of fallout over western Russia and most of Europe. The total amount of ^{137}Cs dispersed over the land areas of the northern hemisphere was about $10 \times 10^{16} \text{ Bq}$, of which western Russia and Europe received 79% and eastern Russia and Asia 20%, whereas the fallout over Canada and the United States amounted to 2.5×10^{14} and $2.8 \times 10^{14} \text{ Bq}$, respectively, or about 0.5% of the total. In addition to the former Soviet Union, the countries that were hardest hit by the fallout from the accident are identified in Table 24.5.

As a direct consequence of the accident, 31 persons in Ukraine died, 237 suffered acute radiation sickness, and more than 100,000 persons had

Table 24.5 Fallout of ^{137}Cs and Consequent Individual Radiation Dose of Persons in Selected Countries in Order of the Arrival of the Plume After the Reactor Accident in Chernobyl, Ukraine, on April 26, 1986

Country	Time of plume arrival, hr	Total ^{137}Cs deposition, Bq	50-year external dose, Gray/person
Finland	66	1.9×10^{15}	4.3×10^{-4}
Norway	78	1.1×10^{15}	2.1×10^{-4}
Sweden	78	3.4×10^{15}	5.8×10^{-4}
Poland	78	9.2×10^{15}	2.2×10^{-3}
Romania	90	6.7×10^{15}	2.1×10^{-3}
East Germany	102	5.8×10^{14}	4.0×10^{-4}
Switzerland	114	2.0×10^{14}	3.7×10^{-4}
Austria	114	1.1×10^{15}	9.5×10^{-4}
Bulgaria	132	2.7×10^{15}	1.8×10^{-3}
Czechoslovakia	132	5.9×10^{14}	3.5×10^{-4}
France	132	8.3×10^{14}	1.1×10^{-4}
Luxembourg	132	3.8×10^{12}	1.1×10^{-4}
West Germany	156	1.6×10^{15}	4.9×10^{-4}
Hungary	156	7.9×10^{14}	6.3×10^{-4}
Italy	156	1.9×10^{15}	4.7×10^{-4}
United States	372	2.8×10^{14}	2.4×10^{-6}
Canada	372	2.5×10^{14}	2.0×10^{-6}

SOURCE: Anspaugh et al. (1988).

to be relocated. In addition, between 1988 and 1998 the risk of leukemia may double in the population living within 30 km of Chernobyl (Anspaugh et al., 1988). Although the cloud of radionuclides released by the accident contaminated most of the northern hemisphere inhabited by about 3 billion people, no cases of acute radiation sickness were reported outside of the former Soviet Union. Nevertheless, the lifetime expectation of fatal radiogenic cancer increased from 0 to 0.2% in Europe and from 0 to 0.003% in the northern hemisphere (Anspaugh et al., 1988).

The economic and social damage caused by this accident is very large. By extrapolating initial estimates by the former Soviet Union, the total damage may amount to \$15 billion, of which 90% occurred within the borders of the former Soviet Union. In addition, the accident has heightened concern about the safety of nuclear reactors and

has reinforced the conviction that *fossil fuels* are a *safer* source of energy than nuclear reactors. Unfortunately, the release of CO_2 , SO_2 , and oxides of N caused by the combustion of fossil fuel also has far-reaching environmental consequences that manifest themselves in the form of urban smog, acid rain, and climate change on a global scale.

A decade after the explosion of the nuclear reactor in Chernobyl, Ukraine, the damage to the health of the population and to the economy of the region continues to increase. Estimates now place the total amount of radioactive materials released by the explosion at about 90 million Curies.

The economic impact of this catastrophe is beyond reckoning because the expenses for remedial activities, such as the relocation of the inhabitants of the area around Chernobyl and their continuing medical care, as well as the stabilization of the explosion site, are still rising. The failure of

the Soviet government to act decisively to evacuate the population and to notify governments of neighboring countries ultimately contributed to the disintegration of the Soviet Union (Shcherbak, 1996).

The fire fighters who were called upon to extinguish the fire were exposed to high doses of gamma radiation ranging from about 100 to more than 100,000 rem. As a result of this exposure, 187 persons had to be hospitalized and 31 of them died. Subsequently, about 400,000 workers participated in the construction of a protective containment building (the "sarcophagus") and in the burial of contaminated materials. In this group about 30,000 persons became ill and 5,000 are too sick to work.

The symptoms of the so-called Chernobyl syndrome include fatigue, apathy, and a decrease in the number of white blood cells. As a result, there is an increase in the occurrence of malignant tumors, leukemia, and severe cardiac conditions, as well as a weakening of the immune system leading to an increase in common infections such as bronchitis, tonsillitis, and pneumonia.

Although ^{131}I has a relatively short half-life of 8 days, this isotope is especially dangerous because it is concentrated in the thyroid gland. According to Shcherbak (1996), about 4000 children received doses up to 2000 rems to their thyroid glands and a larger number received more than 200 rems. These exposures initially caused inflammation of their thyroids that in some cases has led to thyroid cancer. As a result, the incidence of thyroid cancers among children and adolescents in the Ukraine has increased from about five per year before the accident to an average of 43 cases per year in 1995. The only effective treatment is to surgically remove the thyroid gland, thereby making the patients dependent on supplemental thyroid hormones for the rest of their lives. The experience of Hiroshima and Nagasaki suggests that the population affected by the accident at Chernobyl will continue to experience an abnormally high rate of medical problems for many years to come.

The reactor building still contains several tens of thousands of tons of radioactive material with a decay rate of about 20 million curies. In addition, radioactive materials, including trees

that absorbed radionuclides from the atmosphere, have been buried in about 800 clay-lined pits within an area of about 190,000 square kilometers centered on Chernobyl. Nevertheless, sediment suspended in the Dnieper River and its tributary the Pripyat River has become contaminated with ^{90}Sr , ^{137}Cs , and Pu.

24.8 Summary

The consumption of natural resources and the disposal of the resulting waste generated by the world's growing population are threatening to alter the environment in ways that may be harmful. The need for increasing amounts of energy puts an added burden on the environment because both the combustion of fossil fuel and controlled fission of U generate waste products that can adversely affect the quality of life on the Earth in the future.

The waste products of nuclear reactors consist of radioactive fission products and of the unstable isotopes of the transuranium elements Np, Pu, Am, and Cm. The decay of these radionuclides, which is accompanied by the emission of α -particles, β -particles, and γ -rays, makes them lethal to all life forms for thousands of years. In fact, high-level waste (HLW) and spent unprocessed fuel (SURF) remain harmful to life for more than 100,000 years and must therefore be isolated in subsurface repositories.

The construction of such repositories is technically feasible but has been delayed by the need for thorough studies of the proposed sites and by the reluctance of people living near proposed repository sites to permit the storage of nuclear waste in their neighborhood. Nevertheless, countries that have a nuclear-power industry are proceeding toward the construction of nuclear-waste repositories involving different kinds of rocks. The evaluation of the long-term safety of these repositories depends partly on their ability to retain long-lived radioactive isotopes of the transuranium elements, including Np and Pu.

These two elements, as well as Am and Cm, have been dispersed over the surface of the Earth

as fallout from nuclear-weapons tests and by controlled discharge from fuel-reprocessing plants. Although the chemical properties of these elements can be predicted from Eh-pH diagrams, their behavior in the natural environment is strongly modified by the formation of complex ions and by the adsorption of their ions on organic and inorganic particles. For example, the distribution of Pu in the oceans and in lakes is controlled by the magnitude of the flux of suspended particles, by the composition and size distribution of the particles, and by their ability to adsorb Pu in the lower oxidation states (+3 and +4).

Because of the complex interaction of geochemical, hydrologic, thermal, and mechanical processes in the rocks surrounding aging nuclear-waste repositories, model calculations, intended to evaluate their future safety, must be tested by the study of natural analogs. One of the best opportunities to do so is provided by the high-grade U orebodies at Oklo, Gabon, in which chain reactions based on induced fission of ^{235}U occurred $\sim 2 \times 10^9$ yr ago. Careful studies of these natural reactors since their discovery in 1972 has indicated that Np and Pu, and many other elements having long-lived radioisotopes, did *not*

migrate out of the U ore in which they were formed, even though the properties of the rocks are far from ideal.

The energy released by nuclear fission is very large compared to combustion of fossil fuel. Therefore, nuclear reactors pose an inherent danger because accidents not only may liberate large amounts of energy but also can release radionuclides into the environment. The most recent reactor accident occurred on April 26, 1986, at Chernobyl, Ukraine. As a direct consequence of this accident, 31 persons were killed, 237 suffered acute radiation sickness, more than 100,000 people from the surrounding area had to be relocated, and the risk of leukemia and thyroid cancer in the affected population was increased significantly.

In addition, ^{137}Cs and other fission products were spread over the western region of the former Soviet Union and Europe, ultimately affecting 3 billion people in the entire northern hemisphere. Although no cases of acute radiation poisoning were reported outside the former Soviet Union, severe property loss and social damage did result, especially in Scandinavia, which was the first region to receive fallout from the plume emanating from Chernobyl.

Problems

1. Calculate the activity ratio (i.e., the ratio of the decay rates) of Pu having an atomic ratio $^{240}\text{Pu}/^{239}\text{Pu} = 0.18$. The half-lives are 6.54×10^3 yr for ^{240}Pu and 2.44×10^4 yr for ^{239}Pu .
2. Calculate the weight in grams of ^{238}Pu ($T_{1/2} = 8.78$ yr) that produces a decay rate of 17 kCi.
3. Calculate the disintegration rate of 1.0 g of ^{238}U ($T_{1/2} = 4.47 \times 10^9$ yr) and express the results in becquerels and in picocuries.
4. Between 1957 and 1978, 14 kCi of $^{239,240}\text{Pu}$ was released from the Windscale reprocessing plant. If the atomic $^{240}\text{Pu}/^{239}\text{Pu}$ ratio was 0.18, estimate the weight of the released Pu in grams. The masses of the isotopes are $^{239}\text{Pu} : 239.05218$ amu, $^{240}\text{Pu} : 240.05383$. The half-lives are given in Problem 1.
5. Convert 1.0 pCi (10^{-12} Ci) into the corresponding decay rate in disintegrations per minute (dpm).
6. Calculate the activity in picocuries of 1 kg of brine from Mono Lake, California, whose Pu concentration is 4.4 dpm/kg.
7. Calculate the concentration of Pu in seawater in parts per million by weight, given that the concentration of $^{239}\text{Pu} + ^{240}\text{Pu}$ is 0.4 fCi/L (1 femtocurie = 10^{-15} Ci). Assume that the density of seawater is 1.03 and that the atomic ratio $^{240}\text{Pu}/^{239}\text{Pu} = 0.18$.
8. Construct an Eh-pH diagram for Am in a system containing 10^{-3} mol/L of carbonate ions at 25°C. Include stability fields for the solids $\text{Am}_2(\text{CO}_3)_3$, AmO_2 , and $\text{Am}(\text{OH})_3$ and for the ions Am^{3+} and $\text{Am}(\text{OH})_5^-$. Draw the solubility boundaries at 10^{-8} mol/L.

9. Write a brief essay on the mobility of Am in natural environments and suggest a method of retarding the movement of Am ions out of a nuclear-waste repository.

10. Calculate the activity of $^{241}\text{Am}^{3+}$ in fCi/L of a solution that is in equilibrium with solid $\text{Am}_2(\text{CO}_3)_3$ at pH = 7.0. Assume that the activity coefficient (γ) of Am^{3+} in the solution is equal to 0.75.

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