Water-Quality Principles
QW1022–TEL

Lesson 2—Environmental Systems and the Hydrologic Cycle

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COMPOSITION OF THE EARTH'S CRUST

The relative abundance of elements in the crustal material of the Earth has been a subject of much interest to geochemists for many years. Although the subject of natural-water chemistry is only indirectly concerned with these averages, a knowledge of rock composition is essential to understanding the chemical composition of natural water, and it is therefore desirable to discuss the subject briefly.

The Earth is generally considered to be made up of an iron-rich core surrounded by a thick mantle made up of magnesium- and iron-rich silicates and a thin outer crust made up of rather extensively reworked silicates and other minerals. The outer crust, where it is exposed above the level of the oceans, exerts a direct influence on the composition of natural terrestrial water. Although it has been studied more extensively than less accessible parts, the composition of most of the outer crust still must be estimated by extrapolation. The bottom of the crust is considered to be at the Mohorovičić discontinuity, which occurs at a depth of 30-50 km beneath most of the continental areas. The influence of material more than a few kilometers below the surface on the composition of water circulating in the hydrologic cycle is slight.

Estimates of average composition of the Earth's crust by Clarke (1924b) and by Clarke and Washington (1924) are still extensively quoted, although more recent estimates for minor constituents have the advantage of many more analyses and better values. Among the better known more recent estimates and compilations are those of Fleischer (1953, 1954), Turekian and Wedepohl (1961), Taylor (1964), Parker (1967), and Wedepohl (1969). Data on concentrations of some of the rarer elements still are incomplete, however, and some further revisions of the abundance estimates can be expected as better analytical values become available. The amount of extrapolation and inference required to extend the analyses to large volumes of rock that cannot be sampled is obvious.

Combinations of data from earlier compilations and averages for individual elements published in current research papers commonly are used by authors of general reference works. In this vein, data assembled in table 1 were taken principally from a compilation by Horn and Adams (1966), which in turn is a synthesis, by electronic computer, of estimates published by others from Clarke's time to the date of their study. Table 1 gives values for the 65 elements covered by Horn and Adams and for two others omitted by them that are of particular interest in natural-water chemistry—nitrogen and carbon. Data on which these two values are based were taken from tabulations by Parker (1967). Oxygen is the most abundant of all the elements in the crustal rocks; according to Goldschmidt (1954, p. 512), it constitutes 466,000 parts per million, or 46.6 percent of the weight of the lithosphere. Oxygen is not included in table 1. Other omissions include the elements produced in the radioactive decay of uranium and thorium, the elements produced artificially in nuclear reactions, the noble gases, hydrogen, and a few elements for which data are inadequate to make any estimates of abundance. The values of Horn and Adams were arbitrarily carried to three significant figures by the computer program from which they were produced. In preparing table 1, all concentrations reported below 100 parts per million were rounded to two significant figures. Because of the uncertainties in the estimates, they can hardly be expected to be accurate enough for many elements to justify two significant figures, and the reader should not accept the accuracy the values seem to imply; for many of the less common elements, especially when located in sedimentary rocks, the estimates may well be inaccurate by more than an order of magnitude.

Table 1 is intended simply to provide a general indication of the amounts of the various elements available in rocks for possible solution by water and, in an even more general sense, to show how some elements are typically concentrated or depleted in processes of conversion from igneous to sedimentary rocks.

According to Clarke and Washington (1924), 95 percent of the Earth's crust to a depth of 16 km (10 miles) is igneous rock. Therefore, the average composition of the 16 km crust closely approaches the average for igneous rocks. In the consideration of natural water and its relation to rock composition, however, this predominance of igneous rock is not of overriding importance. Most recoverable ground water occurs at depths of less than 2 km below the land surface, and in the part of the crust near the surface, sedimentary rocks are more prevalent than igneous rocks. As a rule, igneous rocks are poor aquifers, so they transmit little water; also, they do not present large areas of active mineral surface to be contacted by relatively small volumes of water, as do more porous rock types. In the headwater areas of many mountain streams, igneous rocks are at the surface, and they may contribute solutes to surface runoff both directly and through leaching of partly decomposed minerals in overlying soils. The areas where igneous rocks are exposed to attack by surface streams are not a predominant part of the Earth's surface. Therefore, the sedimentary rocks and the soil assume major importance as the immediate sources of soluble matter to be taken up by circulating underground and surface water. Reactions between water and the minerals of igneous rocks, however, are of fundamental importance in studies of geochemical processes, and they will be considered in some detail later in this book.

Table 1. Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks

[After Horn and Adams (1966)]

Element	Igneous rocks	Sedimentary rocks		
		Resistates (sandstone)	Hydrolyzates (shale)	Precipitates (carbonates)
Si	285,000	359,000	260,000	34
Al	79,500	32,100	80,100	8,970
Fe	42,200	18,600	38,800	8,190
Ca	36,200	22,400	22,500	272,000
Na	28,100	3,870	4,850	393
K	25,700	13,200	24,900	2,390
Mg	17,600	8,100	16,400	45,300
Ti	4,830	1,950	4,440	377
P	1,100	539	733	281
Mn	937	392	575	842
F	715	220	560	112
Ba	595	193	250	30
S	410	945	1,850	4,550
Sr	368	28	290	617
C	320	13,800	15,300	113,500
Cl	305	15	170	305
Cr	198	120	423	7.1
Rb	166	197	243	46
Zr	160	204	142	18
V	149	20	101	13
Ce	130	55	45	11
Cu	97	15	45	4.4
Ni	94	2.6	29	13
Zn	80	16	130	16
Nd	56	24	18	8.0
La	48	19	28	9.4
N	46	.....	600	.....
Y	41	16	20	15
Li	32	15	46	5.2
Co	23	.33	8.1	.12
Nb	20	.096	20	.44
Ga	18	5.9	23	2.7
Pr	17	7.0	5.5	1.3
Pb	16	14	80	16
Sm	16	6.6	5.0	1.1
Sc	15	.73	10	.68
Th	11	3.9	13	.20
Gd	9.9	4.4	4.1	.77
Dy	9.8	3.1	4.2	.53
B	7.5	90	194	16
Yb	4.8	1.6	1.6	.20
Cs	4.3	2.2	6.2	.77
Hf	3.9	3.0	3.1	.23
Be	3.6	.26	2.1	.18
Er	3.6	.88	1.8	.45
U	2.8	1.0	4.5	2.2
Sn	2.5	.12	4.1	.17
Ho	2.4	1.1	.82	.18
Br	2.4	1.0	4.3	6.6
Eu	2.3	.94	1.1	.19

Table 1. Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks—Continued

Element	Igneous rocks	Sedimentary rocks		
		Resistates (sandstone)	Hydrolyzates (shale)	Precipitates (carbonates)
Ta	2.0	.10	3.5	.10
Tb	1.8	.74	.54	.14
As	1.8	1.0	9.0	1.8
W	1.4	1.6	1.9	.56
Ge	1.4	.88	1.3	.036
Mo	1.2	.50	4.2	.75
Lu	1.1	.30	.28	.11
Tl	1.1	1.5	1.6	.065
Tm	.94	.30	.29	.075
Sb	.51	.014	.81	.20
I	.45	4.4	3.8	1.6
Hg	.33	.057	.27	.046
Cd	.19	.020	.18	.048
In	.19	.13	.22	.068
Ag	.15	.12	.27	.19
Se	.050	.52	.60	.32
Au	.0036	.0046	.0034	.0018

The three classes into which sedimentary rocks are divided in table 1 are adapted from Goldschmidt (1933) and from Rankama and Sahama (1950, p. 198). This classification is based on the chemical composition and the degree of alteration of the minerals making up the rocks. It is probably better suited to studies related to chemical composition than are the usual geologic classifications of sedimentary rocks by means of mineral character, texture, and stratigraphic sequence.

For the purpose of this book, the following definitions are applicable:

Resistate—A rock composed principally of residual minerals not chemically altered by the weathering of the parent rock.

Hydrolyzate—A rock composed principally of relatively insoluble minerals produced during the weathering of the parent rock.

Precipitate—A rock produced by chemical precipitation of mineral matter from aqueous solution.

A fourth rock type, evaporites, consists of soluble minerals deposited as a result of evaporation of the water in which they were dissolved. Quantitative data on composition of evaporite rocks have been given by Stewart (1963). The evaporites influence the composition of some natural water, but their average content of most of the minor elements is still not accurately known; data for this class of rocks are not included in table 1.

The severity of chemical attack in weathering ranges widely. Under severe attack, the residue from a given igneous rock might consist almost wholly of quartz sand. Under less severe attack, an arkose containing unaltered feldspar along with the quartz might be produced from the same rock. Some types of weathering could leave less stable minerals of the original rock in the residue.

Another important factor in determining the composition of sedimentary rocks is the process of comminution and mechanical sorting accompanying weathering and transport of weathering products. Resistates, as the term is usually interpreted, are rather coarse grained. Some of the resistant mineral particles, however, may be converted to a very fine powder and deposited with the naturally fine grained hydrolyzates.

Chemical precipitation may occur in a saline environment, and the differentation between precipitate and evaporite rock is somewhat arbitrary; thus, precipitate and evaporite components may be interbedded.

Geochemists often add other classifications such as oxidates, typified by iron ore, and reduzates, for material of largely biological origin such as black shale or coal. However, the dividing lines between these and the classes already considered are inexact.

Because so many of the sedimentary rocks contain mixtures of weathering products, any division into classes must be somewhat arbitrary. Thus, although one might think of a pure quartz sand as the ideal representative of the resistates, for the purpose of this book the class also includes sandstone, conglomerate, arkose, graywacke, and even unconsolidated alluvium. Likewise, although clay is the ideal representative of the hydrolyzates, the class also includes shale, which commonly contains high percentages of quartz and other nonclay minerals. Both classes of rock commonly contain chemically precipitated

minerals as coatings, cement, or discrete particles. The precipitate rocks, such as limestone and dolomite, generally are aggregates of calcitic or dolomitic particles, with many impurities, and may be aggregates of detrital material rather than massive crystalline precipitates. More extensive discussions of classification and identification are contained in texts on sedimentary rocks.

THE HYDROSPHERE

The hydrosphere is generally defined by geochemists as the vapor, liquid, and solid water present at and near the land surface, and its dissolved constituents. Water vapor and condensed water of the atmosphere are usually included, but water that is immobilized by incorporation into mineral structures in rocks is usually not thought of as part of the hydrosphere.

The oceans constitute about 98 percent of the hydrosphere, and thus the average composition of the hydrosphere is, for all practical purposes, that of seawater. The water of the ocean basins is generally fairly well mixed with regard to major constituents, although concentrations of most minor elements are not uniform with depth or areally. The average concentrations of the major dissolved elements or ions, and of some of the minor ones, are given in table 2, which is based on a compilation by Goldberg and others (1971). These authors also suggested, on the basis of stabilities of complex species, the predominant forms in which the dissolved constituents occur.

Substantial differences in concentration between water near the surface and water at depth, as well as areally, are characteristic of solutes that are used as nutrients by marine life. Some of the minor elements have distributions that resemble those of the nutrients. Quinby-Hunt and Turekian (1983) used this and other types of correlations to estimate mean oceanic concentrations of most of the elements. Their estimates, and results of extensive continuing research since 1971 on the behavior of minor elements in seawater, suggest that previously accepted mean values for many of these elements were too large. Average concentrations for minor constituents given in table 2 are useful in a broadly descriptive sense, but they may not be of much value in defining individual elemental behavior.

For various reasons, many geochemists have compiled estimates of the average composition of river water. Obviously, the chemical composition of surface runoff waters of the Earth is highly variable through both time and space, and this book discusses the variations and reasons for them at some length. For our purposes a global average has little significance except, perhaps, as a baseline for comparison. A widely quoted average computed by Livingstone (1963) is given in table 3. The value given in his published average for dissolved iron

Table 2. Composition of seawater

[After Goldberg and others (1971)]

Constituent	Concentration (mg/L)	Principal form(s) in which constituent occurs
Cl	19,000	Cl^-
Na	10,500	Na^+
SO_4	2,700	SO_4^{2-}
Mg	1,350	Mg^{2+}
Ca	410	Ca^{2+}
K	390	K^+
HCO_3	142	HCO_3^-, $H_2CO_3(aq)$, CO_3^{2-}
Br	67	Br^-
Sr	8	Sr^{2+}
SiO_2	6.4	$H_4SiO_4(aq)$, $H_3SiO_4^-$
B	4.5	$H_3BO_3(aq)$, $H_2BO_3^-$
F	1.3	F^-
N	.67	[a]NO_3^-
Li	.17	Li^+
Rb	.12	Rb^+
C (organic)	.10	.....
P	.09	HPO_4^{2-}, $H_2PO_4^-$, PO_4^{3-}
I	.06	IO_3^-, I^-
Ba	.02	Ba^{2+}
Mo	.01	MoO_4^{2-}
Zn	.01	Zn^{2+}
Ni	.007	Ni^{2+}

Table 2. Composition of seawater—Continued

Constituent	Concentration (mg/L)	Principal form(s) in which constituent occurs
As	.003	$HAsO_4^{2-}$, $H_2AsO_4^-$
Cu	.003	Cu^{2+}
Fe	.003	.....
U	.003	$UO_2(CO_3)_3^{4-}$
Mn	.002	Mn^{2+}
V	.002	$VO_2(OH)_3^{2-}$
Al	.001	.....
Ti	.001	.....
Sn	.0008	.....
Co	.0004	Co^{2+}
Cs	.0003	Cs^+
Sb	.0003	.....
Ag	.0003	$AgCl_2^-$
Hg	.0002	$HgCl_2(aq)$
Cd	.00011	Cd^{2+}
W	.0001	WO_4^{2-}
Se	.00009	SeO_4^{2-}
Ge	.00007	$Ge(OH)_4(aq)$
Cr	.00005	.....
Ga	.00003	.....
Pb	.00003	Pb^{2+}, $PbCl_3^-$, $PbCl^+$
Bi	.00002	.....
Au	.00001	$AuCl_4^-$
Nb	.00001	.....
Ce	.000001	.....
Sc	<.000004	.....
La	.000003	$La(OH)_3(aq)$
Y	.000003	$Y(OH)_3(aq)$
Be	.0000006	.....
Th	<.0000005	.....
Pa	2×10^{-9}	.....
Ra	1×10^{-10}	Ra^{2+}

[a] Does not include dissolved N_2.

appears to be much too high and is omitted here. Meybeck (1979) has compiled more recent data on river water composition and has computed an average total concentration slightly lower than that of Livingstone. This average is also given in table 3. With coworkers (for example, Martin and Meybeck, 1979), Meybeck has also studied composition of particulate matter carried to the ocean by rivers and many of the factors that influence river-water quality.

Averages like those of Livingstone and Meybeck are strongly influenced by the composition of the world's large rivers. An average analysis for the Mississippi is given in table 3, along with a single analysis for the Amazon, the world's largest river. The major-ion composition of the Mississippi is well known, through many years of intensive sampling. That of the Amazon, however, was poorly known until studies by Brazilian and other scientific agencies were intensified in the 1960's and 1970's. The average discharge for the Mississippi into the Gulf of Mexico is given by Iseri and Langbein (1974) as 18,100 m^3/sec (640,000 ft^3/sec). For the Amazon, a total mean discharge to the ocean of 175,000 m^3/sec (6,100,000 ft^3/sec) was estimated by Oltman (1968). The analysis for the Amazon is of a sample taken at a time of high discharge, and the water has a lower than average concentration of dissolved ions. The period represented by the Mississippi River analysis had an average discharge nearly equal to the long-term mean and is probably more nearly representative of average conditions than the analysis given in the second edition of this book.

THE ATMOSPHERE

The composition of the atmosphere in terms of volume percentage and partial pressures of the gaseous

Table 3. Composition of river water

[Date under sample number is date of collection. Sources of data: 1, Oltman (1968, p. 13); 2, U.S. Geological Survey Water-Supply Paper 1964; 3, Livingstone (1963, p. G41); 4, Maybeck (1979)]

Constituent	1		2		3		4	
	July 16, 1963		Oct. 1, 1964 – Sept. 30, 1965					
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	7.0	...	7.9	...	13	...	10.4	...
Aluminum (Al)	.07	...	...	...	...	...	...	...
Iron (Fe)	.06	...	.02	...	...	...	...	...
Calcium (Ca)	4.3	.215	38	1.896	15	.749	13.4	.669
Magnesium (Mg)	1.1	.091	10	.823	4.1	.337	3.35	.276
Sodium (Na)	1.8	.078	20	.870	6.3	.274	5.15	.224
Potassium (K)	...	...	2.9	.074	2.3	.059	1.3	.033
Bicarbonate (HCO_3)	19	.311	113	1.852	58	.951	52	.852
Sulfate (SO_4)	3.0	.062	51	1.062	11	.239	8.25	.172
Chloride (Cl)	1.9	.054	24	.677	7.8	.220	5.75	.162
Fluoride (F)	.2	.011	.3	.016	...	...	...	...
Nitrate (NO_3)	.1	.002	2.4	.039	1	.017	...	...
Dissolved solids	28.	...	232	...	89	...	73.2	...
Hardness as $CaCO_3$	15	...	138	...	54	...	47	...
Noncarbonate	0	...	45	...	7	...	5	...
Specific conductance (micromhos at 25°C).	40	...	371	...	...	...	...	...
pH	6.5	...	7.4	...	...	...	...	...
Color	...	...	10	...	...	...	...	...
Dissolved oxygen	5.8	...	...	...	...	...	...	...
Temperature (°C)	28.4	...	...	...	...	...	...	...

1. Amazon at Obidos, Brazil. Discharge, 216,000 m^3/s (7,640,000 cfs) (high stage).
2. Mississippi at Luling Ferry, La. (17 mi west of New Orleans). Time-weighted mean of daily samples.
3, 4. Mean composition of river water of the world (estimated). Dissolved-solids computed as sum of solute concentrations, with HCO_3 converted to equivalent amount of CO_3.

components is given in table 4. Local variations in atmospheric composition are produced by the activities of humans, plant and animal metabolism and decay, and gases from volcanoes and other geothermal areas. Particulate matter carried into the air by wind, discharged from smokestacks, or entering the atmosphere from outer space provides a number of atmospheric components that may influence the composition of water but that cannot be readily evaluated in terms of average contents. Minor constituents such as CO, SO_2, O_3, and NO_2 or other nitrogen-containing gases may play important roles in air pollution and may influence the composition of rainwater; they may be present locally in concentrations greater than those given in table 4.

Among the minor constituents of air are certain nuclides produced in the outer reaches of the atmosphere by cosmic-ray bombardment and by other processes. Some of these nuclides are radioactive, notably tritium and carbon-14. Naturally produced radioactive materials are present in the atmosphere in very small concentrations, however, and can be detected only by highly sensitive techniques.

Ultraviolet radiation from the Sun is depleted by photochemical reactions with atmospheric gases, and most of the radiation with wavelengths less than 300 nanometers (nm) does not reach the Earth's surface. These reactions produce traces of highly reactive intermediates such as peroxy and hydroxyl radicals that oxidize

Table 4. Mean composition of the atmosphere

[After Mirtov (1961)]

Gas	Percentage by volume	Partial pressure (atm)
N_2	78.1	0.781
O_2	20.9	.209
Ar	.93	.0093
H_2O	.1–2.8	.001–0.028
CO_2	.03	.0003
Ne	1.8×10^{-3}	1.8×10^{-5}
He	5.2×10^{-4}	5.2×10^{-6}
CH_4	1.5×10^{-4}	1.5×10^{-6}
Kr	1.1×10^{-4}	1.1×10^{-6}
CO	$(0.06–1)\times10^{-4}$	$(0.06–1)\times10^{-6}$
SO_2	1×10^{-4}	1×10^{-6}
N_2O	5×10^{-5}	5×10^{-7}
H_2	$\sim5\times10^{-5}$	$\sim5\times10^{-7}$
O_3	$(0.1–1.0)\times10^{-5}$	$(0.1–1.0)\times10^{-7}$
Xe	8.7×10^{-6}	8.7×10^{-8}
NO_2	$(0.05–2)\times10^{-6}$	$(0.05–2)\times10^{-8}$
Rn	6×10^{-18}	6×10^{-20}

Relationships Among Environmental Factors and Natural-Water Composition

The chemical processes and the relevant thermodynamic principles that have been summarized briefly represent mechanisms for transfer of solid or gaseous components of the Earth and atmosphere into the liquid water of the hydrosphere. For these processes to operate, there must be a means of supplying water and the other reaction components, and the effectiveness of the chemical processes is influenced by numerous environmental factors.

The supply of liquid water is replenished by precipitation. Obviously, amount and rate of rainfall, runoff, and evaporation are important factors in the control of natural-water composition. The temperature of the systems also is of obvious importance. These are all components of regional climate.

The supply of naturally occurring solid reactants is ultimately controlled by geologic processes. Elements not available in the rock minerals contacted by the water cannot be expected to be present in the final solution. Nonavailability can be related to the structure of the rocks as well as to their composition.

Besides factors influencing reactant supplies, the ways in which the chemical reactions occur and their results are influenced by and may be controlled by biologic and biochemical processes.

Climate

The processes of rock weathering are strongly influenced by temperature and by amount and distribution of precipitation. The influence of climate on water quality goes beyond these direct effects, however. Climatic patterns tend to produce characteristic plant communities and soil types, and the composition of water of streams draining such areas could be thought of as a product of the ecologic balance. A somewhat similar concept seems to have been used in the study and classification of water composition in some areas of the U.S.S.R., but has not been widely applied in water-quality studies by investigators in the United States.

Certain of the major ionic constituents of natural water are influenced more strongly than others by climatic effects. Bicarbonate, for example, tends to predominate in water in areas where vegetation grows profusely. Some metals are accumulated by vegetation and may reach peak concentrations when plant-decay cycles cause

extra amounts of these metals to enter the circulating water. These effects are most readily observed in river water, because most of the runoff that enters the streams has spent some time within soils of the drainage basin and also may contact fallen leaves and other plant debris.

Humid temperate climates and warm, wet climates generally are the most favorable for growth of vegetation. Runoff from tropical rain forest areas commonly is low in dissolved-solids concentration. An example is the water of the Amazon, for which an analysis is given in table 3. An arid climate is unfavorable for rapid rates of solvent erosion, but concentration of dissolved weathering products in the soil by evaporation can give rise to water high in dissolved-solids content. On the other hand, the occasional flood runoff in such regions can be very low in dissolved material if soluble weathering products are not available in major quantity.

Climates characterized by alternating wet and dry seasons may favor weathering reactions that produce considerably larger amounts of soluble inorganic matter at some seasons of the year than at other seasons. Streams in regions having this kind of climate may fluctuate greatly in volume of flow, and the water may have a wide range of chemical composition. The influence of climate on water quality may thus be displayed not only in amounts and kinds of solute ions, but also in the annual regime of water-quality fluctuation. Kennedy (1971) made an intensive study of some of these effects in a stream in north-coastal California.

Effects of very cold climates on water composition are at least twofold: the low temperature inhibits weathering reaction rates, including any processes mediated by biota, and most of the precipitation in cold regions generally is in the form of snow, so that water is in the solid state much of the time. Thus, most surface runoff in cold regions is likely to be low in solute concentration. The Greenland and Antarctic icecaps are, in fact, mostly fossil snow, and they offer a record going back thousands of years of the chemical composition of precipitation in those regions. Studies of trace metal compositions in ancient ice have been made by various investigators, including Murozumi and others (1969) and Herron and others (1977).

Analyses of water from Arctic rivers in the U.S.S.R. have been published by Alekin and Brazhnikova (1964). Analyses of rivers and lakes in the Mackenzie River basin in northwestern Canada were published by Reeder and others (1972). The Mackenzie data show effects of different rock types on water composition.

Rates of solvent erosion by streams that are fed by glaciers in the temperate climate of the northern Cascade Range of Washington are among the highest reported in the literature (Reynolds and Johnson, 1972). The mechanical action of the moving ice presumably aids the breakdown of rock minerals in such environments.

Geologic Effects

The ultimate source of most dissolved ions is the mineral assemblage in rocks near the land surface. This topic will be discussed in more detail later in this book, with the aim of developing some indications of the rock type that might have been associated with a given water. The importance of rock composition, however, is only part of the story. The purity and crystal size of minerals, the rock texture and porosity, the regional structure, the degree of fissuring, the length of previous exposure time, and a good number of other factors might influence the composition of water passing over and through the rock.

Rock temperatures increase with depth below the land surface. Where water circulates to a considerable depth, it attains a substantially higher temperature than water near the land surface. Increased temperature raises both the solubility and the rate of dissolution of most rock minerals. With the recent interest in geothermal energy sources, renewed attention has been given to these effects. The chemical composition of water of thermal springs may give indications of the temperature of the rocks at depth.

Most thermal ground waters (hot springs) are found in areas where the temperature gradient with depth is abnormally steep. The solute content of such water is commonly higher than that of nonthermal water. Some thermal water may be notably high in dissolved-solids concentration and may contain unusual amounts of metal ions. The brines from deep wells in Imperial Valley, Calif. (White, 1968), and from deep basins at the bottom of the Red Sea (Miller and others, 1966) are interesting examples. The Imperial Valley brine contained 155,000 mg/kg (milligrams per kilogram) of chloride, and also contained about 2,000 mg/kg of iron, 1,400 mg/kg of manganese, 500 mg/kg of zinc, 90 mg/kg of lead, and 1.4 mg/kg of silver, as well as considerable concentrations of other unusual constituents. The compositions of some of these waters may be the result of metamorphic alteration of associated rocks. More recently, oceanographers have discovered water discharging at high temperatures on the ocean bottom near the Galapagos Islands in the eastern Pacific Ocean. This water appears to be high in sulfur and metal ion concentrations (East Pacific Rise Study Group, 1981).

The term "metamorphic water" was first defined by White (1957a). In recent years, many examples of metamorphic water having unusual composition have been cited by other workers and have been correlated with rock alteration processes occurring below the surface (Barnes, 1970; Barnes and others, 1972; Barnes and O'Neil, 1976).

White (1957b) also defined "magmatic water" as water released when rocks deep within the crust or mantle are converted to a molten state. An older term

used by some geochemists is "juvenile water," meaning water that has not previously been involved in the circulating system of the hydrologic cycle. The water that is, or has recently been, in circulation is termed "meteoric." The difficulty in ascertaining whether any fraction of a natural water is juvenile makes this classification virtually useless. Some water of meteoric origin may remain in storage in aquifers for very long periods of time.

Magmatic water may perhaps be associated with volcanism. The amount of water that might be released by fusion of rocks has been thought by some geochemists to be substantial. For example, Clarke and Washington (1924) estimated that a little over 1 percent of the weight of average igneous rock is water. Others have doubted the validity of this estimate (Goldschmidt, 1954, p. 126).

The data reported by White and Waring (1963) on the composition of volcanic gases show that water vapor is generally predominant. However, the degree to which the water associated with volcanic activity is of magmatic origin rather than meteoric origin is difficult to determine. White (1957a, b) studied the composition of water from many thermal-spring areas and concluded that in such areas there are few, if any, conclusive indications that any of the water is juvenile.

Another classification term sometimes applied to water having high solute concentrations is "connate," which implies that the solute source is fossil seawater trapped in sedimentary formations when they were laid down. The high dissolved-solids concentrations of oilfield waters commonly are thought to be of connate origin. Collins (1975) discussed many aspects of the geochemistry of water associated with petroleum. Analyses for many oilfield waters are tabulated in White and others (1963).

Biochemical Factors

Life forms and the chemical processes associated with them are intimately related to water and to the solutes contained in water. Extensive discussions of this relationship can be found in the literature of various branches of the life sciences. Although the principal concern of this book is inorganic aspects of water chemistry, the biological aspects cannot be avoided. In fact, the water chemist will find that biological factors are important in almost all aspects of natural-water composition. Much of the support for a water chemist's work derives from the importance of water to humans and the standards required for safe drinking water. Water pollution control programs commonly aim to benefit desirable forms of aquatic life as well as to provide water safe for domestic use. The following brief discussion points out some biochemical processes and shows how they fit into and complement other factors that control natural-water composition.

Ecology Applied to Natural Water

Ecology is the study of relationships between organisms and their environment. It thus implies what might be considered a study of biological systems and the way in which the various parts of such systems influence each other. For example, the development of a particular set of plant and animal species, soil type, and general land form can be thought of as the end result of a particular set of climatic and geologic factors that have reached an optimal, steady-state condition. Input of energy from outside the system must equal output plus storage changes. Living species in the system can be considered as locally decreasing the net entropy of the system, a process that requires a continuing energy input—from the Sun and from incoming reactants. Or the entropy decreases in one part of the system may be balanced by increases in another part.

Obviously, this kind of system is not readily treated by a thermodynamic equilibrium model, because, on the scale implied, the processes that go on are irreversible. Attainment of a steady state in such a system, at least as viewed in a broad sense, is possible if the inputs remain relatively constant. But biological systems in any regional sense are subject to such an enormous number of feedbacks and variations, some cyclic and some random or one-time-only, that conditions are in a continual state of dynamic flux. Studies in ecology, therefore, probably should be directed toward understanding and evaluating mechanisms and rates.

In a sense, the study of natural-water composition involves concepts of ecology, because a large number of factors and processes are interrelated in bringing about the composition of the water. As in ecologic systems, changes in one factor may bring about a considerable number of other changes that can influence the particular variable being observed. Also as in ecologic systems, the separation of cause from effect can become difficult.

Whether biochemical processes like the ones described here are best viewed as independent factors or as integral parts of the chemical thermodynamic system governing water composition is partly a matter of opinion, but their importance is unquestionable. The life processes of principal interest in water chemistry can be classified in a general way on the basis of energy relationships, to include the following:

1. Processes that use energy captured from the Sun or some other source for promotion of chemical reactions that require a net energy input.
2. Processes that redistribute chemically stored energy.
3. Processes that convert chemically stored energy to other forms of energy.
4. Processes without significant energy transfer.

The first type of process is represented by photosynthesis, in which carbon dioxide, water, and radiant energy are used to manufacture carbohydrates and gaseous oxygen is liberated. This process in turn provides the fuel for most of the processes of the second and third type.

Processes of metabolism and decay are included in types 2 and 3. These chemical reactions may involve a net release of energy from the original materials, but not all the reactions can be made to proceed at observable rates in the absence of life forms. For such reactions, the biological processes seem to offer pathways for reactions that do not have the high stepwise energy barriers that prevent the reaction from occurring spontaneously or that cause it to be slow in the absence of biota.

Reactions that promote chemical reduction or oxidation might be thought of as type 3, although no actual electrical energy may be produced. It is possible, however, to make a cell that is capable of producing a current as a result of biochemical processes. The production of heat, chemiluminescence, and motion are biological manifestations of the third type of reaction.

Effects that come within type 4 can be represented by indirect influences such as stabilization of inorganic colloids in water by soluble organic matter or the release of various waste products to water.

The processes that sustain life are particularly strongly developed in water bodies exposed to air and sunlight. In environments in which neither is present, as in ground-water aquifers, biological activity normally is much less important. At some stage in its movement through the hydrologic cycle, however, all water is influenced by biochemical processes, and the residual effects of these processes are widely discernible, even in ground water.

Influence of Soil and Soil-Forming Processes

The systems of classification of soils in common use emphasize strongly the effect of climate and vegetation and do not place as much emphasis on the nature of the original rock from which the soil came. Soils of high productivity generally contain a considerable amount of organic debris, and in most the mineral-species distribution inherited from the parent rock has been altered extensively. The minerals themselves also commonly have been changed. Discussions of rock-weathering processes that lead to soil formation are plentiful. Examples are papers by Keller (1957) and Reiche (1950), who discussed the processes with some attention to soluble products and from a geologically oriented viewpoint. Drever (1982, p. 162–199) discussed these relationships for several areas having differing climatic and geologic conditions.

The major features of the chemical composition of many natural waters are the result of soil-forming processes or reactions that occur within the soil zone. Consequently, a considerable area of common interest exists between water chemistry and soil chemistry. This fact, however, has not been recognized very extensively by workers in the two fields. A large part of the atmospheric precipitation that reaches the land surface falls on soil surfaces; generally, the fraction that ultimately appears as runoff or ground water has had some contact with the soil, and much of it has spent a considerable period of time as soil moisture. The chemical composition of soil moisture and the processes that go on in soil to dissolve or precipitate minerals or otherwise to alter the composition of soil moisture probably have not received adequate attention from workers in the field of natural-water chemistry.

Among the factors influencing the chemical composition of soil moisture are dissolution or alteration of silicate and other minerals, precipitation of sparingly soluble salts (notable calcium carbonate), selective removal and circulation of nutrient elements by plants, biochemical reactions producing carbon dioxide, sorption and desorption of ions by mineral and organic surfaces, concentration of solutes by evapotranspiration, and conversion of gaseous nitrogen to forms available for plant nutrition. Of these, one of the most important is the production of carbon dioxide. The air in soil interstices is commonly 10–100 times richer in CO_2 than ordinary air (Bolt and Bruggenwert, 1978, p. 11). Water moving through soil dissolves some of this CO_2, and the H^+, HCO_3^-, and CO_3^{2-} ions are potent forces in controlling the pH of the water and in attacking rock minerals.

Aquatic Biota

Those life forms that occur in water bodies or in close association with them form an ecologic system that has been studied widely. The science of limnology is concerned to a high degree with freshwater ecology. Hutchinson's (1957) well-known text covers this subject in considerable detail. The ecology of river systems has been discussed in detail by Hynes (1970).

Many of the chemical processes occurring in soil also occur in freshwater bodies. Photosynthesis by plant species rooted in the pond or stream bottom, as well as by floating species, produces oxygen and consumes carbon dioxide, and respiration and decay consume oxygen and produce carbon dioxide. A well-defined diurnal cyclic fluctuation of pH often can be observed in near-surface water of lakes and streams (Livingstone, 1963, p. 9). Aquatic plants also require nutrient elements, especially nitrogen and phosphorus, which they may take up through roots in the bottom sediment or may assimilate directly from the water. The photosynthesizing biota help provide food and oxygen for other life forms in the water where they grow. Cycles of growth and decay produce organic

debris that is partly precipitated to the bottom of the water body, where it may serve as food for other kinds of organisms. Diatoms extract silica from water in which they grow. Other solutes, including some trace constituents, are essential nutrients for certain species of biota. As a result, the concentrations of some trace elements may be controlled by biological processes. Biological effects on iron concentrations were noted by Oborn and Hem (1962).

Respiration, in which oxygen is consumed and carbon dioxide is formed, is a basic process of all aerobic life forms. Oxygen is supplied to surface water bodies by direct assimilation from the atmosphere as well as from photosynthesis. Under normal conditions, an ecologic balance is (or should be) attained in most rivers and lakes, with the various species of biota living together in harmony. A measure of the amount of biologic activity in a water body is its productivity. This is generally expressed in terms of the amount of organic carbon that is produced within a specified area or a volume of water per unit time.

Water bodies in environments in which water is plentiful and soluble nutrients are scarce will support very little living material. Such waters are sometimes called "oligotrophic." This term was coined from Greek words equivalent to "nutrient-poor." Its opposite, "eutrophic," strictly means "nutrient-rich" but is often used as the equivalent of "polluted." During warm weather, nutrient-enriched lakes may exhibit surges of algal growth that can interfere with the ecologic balance.

Lakes in environments in which growing conditions are favorable and nonaquatic vegetation is abundant generally are highly productive and may have short careers in the geologic sense. Such water bodies tend to evolve into marshland or peat bog, owing to accumulation of organic debris. Lakes in environments less favorable to vegetative growth may fill with inorganic sediment or may be drained by stream erosion at their outlets. Obviously, the career of a lake involves factors in addition to organic productivity, but pollution by organic wastes can bring about extensive changes in properties of the water and in a rather short time may convert a clear, oligotrophic lake to a turbid, eutrophic one. The rates at which such changes might occur and the feasibility of reversing them are areas that are being studied by limnologists.

The Hydrologic Cycle

A characteristic property of the free water of the Earth is its continual motion, imparted primarily by the input of radiant energy from the Sun. This energy input causes some liquid water, wherever a water surface is exposed to the atmosphere, to be converted to the vapor state and carried off by wind. When atmospheric conditions become favorable, the vapor returns to the liquid state with a release of energy, first forming the very small droplets of clouds and then, if temperatures are low enough, tiny ice crystals. Rain or snow may be produced if the condensation proceeds under favorable conditions. The amounts of energy involved in water circulation in the atmosphere are very large in total and when concentrated, as in tropical storms, may have spectacular consequences. The water reaching the land surface by precipitation moves downgradient in the general direction of the ocean or a point of minimum gravitational energy.

A wide variety of representations of the hydrologic cycle exist in the literature (for example, U.S. Department of Agriculture, 1955, p. 42), and the hydrologist interested in detail can find many different paths through which continuous circulation can occur or places where water can be stored for very long periods. The cycle itself, however, deals only with pure H_2O. In those parts of the cycle when water is in the liquid state, solutes are always present, and amounts and rates of solute transport are of substantial interest in many ways in hydrology and geochemistry. Livingstone (1963, p. 38) calculated that rivers of North America carry an average load of 85 metric tons (tonnes) per year in solution from each square mile of drainage basins. This is equivalent to 32.8 tonnes per square kilometer.

Sources of Solutes in the Atmosphere

Table 4 shows the principal gaseous constituents of the atmosphere. Any liquid water in the atmosphere naturally would be expected to be saturated with respect to these gases, the amount in solution being proportional to the solubility and the partial pressure of each and to the temperature. Gases that enter into reactions with water in general are more soluble than those that do not. For this reason, the effect of carbon dioxide is relatively great, even though it makes up only 0.03 precent by volume of normal air.

The composition data in table 4 are supposed to represent clean air that is not affected significantly by local environmental factors. Gases such as H_2O, SO_2, NH_3, N_2O, NO_2, HCl, CO, and CO_2 are produced in substantial amounts by burning of fuels, by metallurgical processes, and by other anthropogenic activities, and also by biochemical processes in soil and water and by volcanic or geothermal activity. This can result in local enrichment of these gases. The chemical properties of rainwater can be substantially affected by these substances.

Some elements form solids or liquids with a significant vapor pressure at ordinary temperatures. Certain boron compounds, for example (Gast and Thompson, 1959), tend to evaporate from the ocean to a significant extent for this reason. The elements iodine and mercury

have appreciable vapor pressures at low temperature, but those elements are comparatively rare and do not influence air or rainfall composition appreciably.

Radionuclides such as tritium and carbon-14 are produced in the atmosphere by cosmic-ray bombardment. The atmosphere also contains particles of extraterrestrial material introduced from outer space. On the basis of the nickel content of snow in Antarctica, Brocas and Picciotto (1967) estimated that 3 to 10 million tons of such material fall on the Earth's surface each year.

Naturally occurring atmospheric particulate matter consists of terrestrial dust carried aloft by wind or propelled upward by volcanic eruptions and of sodium chloride or other salts picked up as a result of wind agitation of the ocean surface. This material is augmented by manmade discharges from industrial plants, vehicle exhausts, and many other sources. The particulate matter is important in forming nuclei for condensation of water and as a source of solutes in precipitation; it also influences surface-mediated chemical processes.

The subject of atmospheric chemistry has a large literature of its own. Well-known textbooks are those of Junge (1963) and Holland (1978). Chameides and Davis (1982) summarized more recent developments. Efforts to understand and control air pollution have increased greatly in recent years, especially in areas affected by "acid rain."

Composition of Atmospheric Precipitation

Studies of the composition of rainfall have been carried on for many years. In summarizing this subject, Clarke (1924b) quoted some 30 early investigators who published data between 1880 and 1920. In more recent times, interest in this field has increased, especially in northern Europe and the U.S.S.R. and in the United States and Canada. Continuing studies in Scandinavian countries have produced many data, beginning about 1950 (Egner and Eriksson, 1955). A major emphasis in much of this early work was determining quantities of plant nutrients and of sea salts that were transported to the land in rainfall. Ericksson (1955, 1960) was particularly interested in evaluating the influence of airborne salts on river-water composition. He estimated that, on the average, rainfall deposits 10 kg of chloride per hectare per year on the land surface, and about the same amount of sulfur computed as S. In terms of SO_4^{2-} ions, the weight would be about three times as great. Not all this sulfur can be attributed to marine sources.

Gorham (1955) made extensive observations of rainfall composition in the English Lake District, an area about 50 km east of the Irish Sea. These data showed a resemblance to seawater in the ratios of sodium to chloride and magnesium to chloride. Gorham (1961) discussed the general influence of atmospheric factors on water quality in a later paper. Some of the rather voluminous data from work done in the U.S.S.R. were summarized by Drozdova and Makhon'ko (1970). The occurrence of minor constituents, for example fluoride (Mikey, 1963), in rainfall was studied in some of this work.

The first nationwide study of rainfall composition in the United States was conducted by Junge and his associates. These investigators operated about 60 rainfall-sampling stations distributed over the entire country (except Alaska and Hawaii) for a year, from July 1955 to July 1956. The results, described by Junge and Gustafson (1957) and by Junge and Werby (1958), showed that the average chloride concentration in rainfall decreases rapidly from several milligrams per liter near the oceans to a few tenths of a milligram per liter inland, whereas sulfate increases inland to values between 1 and 3 mg/L on the average. Nitrate and ammonia concentrations also were determined.

Feth, Rogers, and Roberson (1964) reported data for snow in the Western United States, especially in the northern part of the Sierra Nevada, and Gambell and Fisher (1966) reported on composition of rain in North Carolina and Virginia. A study of rainfall composition in New England and New York was made by Pearson and Fisher (1971). In other studies of rainfall chemistry, the content of minor and trace constituents was emphasized (Chow and Earl, 1970; Lazrus and others, 1970; Dethier, 1979). A compilation of rainfall-composition data for North America for the period 1971 to 1981 was prepared by Munger and Eisenreich (1983).

Concern about evident trends toward lower pH of rainfall and surface water in Scandinavian countries and England began to be expressed in the 1950's and 1960's, and this aspect of the chemistry of precipitation has been studied extensively in the United States and Canada in subsequent years. Likens and Bormann (1974) stated that annual average pH's of rainfall in parts of the northeastern United States were near 4.0 in 1970–71. "Acid rain" has become a matter of substantial national and international concern. Cowling (1982) has reviewed the history of scientific efforts in this field and has assembled an extensive bibliography. Reliable measurements of pH and concentrations of other ions in rainfall do not extend far enough back in time to permit a close estimate of the date of the onset of acidification. Peters and others (1982) observed no general downward trend in pH of rain in New York State during the period 1965–78; some sites showed increases, and others showed decreases. A review of chemical models and evaluation techniques that might be used for comparing historical and recent data for poorly buffered waters has been published by Kramer and Tessier (1982).

The reported composition of rainfall is influenced by the methods used to obtain samples for analysis. The samples collected for some investigations represent only

material present in rain or in snow; particulate matter was filtered out before analysis and the sampling container was kept closed when rain was not falling. Other investigators wanted to obtain total fallout and kept their sampling containers open at all times; generally, however, the insoluble material was filtered out of these samples also. For meteorologic purposes, the composition of rainfally without any influence from antecedent or subsequent dry fallout is perhaps of primary interest. The geochemist, however, and most other users of such data may well need total values, including dry fallout; this is the "bulk precipitation" defined by Whitehead and Feth (1964). The extent to which data of the two kinds may differ is uncertain. Whitehead and Feth ascribed considerable importance to the dry fallout factor, but Gambell and Fisher (1966) did not. It has also been pointed out by some investigators that aerosols may deposit particulate matter on vertical surfaces on which the wind impinges. Thus, the foliage of trees near the seacoast may pick up salt particles from landward-blowing winds. The importance of this effect is not known.

The values given in table 6 show that rainfall composition is highly variable, not only from place to place, but also from storm to storm in a single area—and within individual storm systems as well. A very large volume of air passes through a storm system. The very nature of the conditions that often produce rain, a mingling of air masses of different properties and origins, ensures a high degree of vertical and horizontal nonhomogeneity. Analyses 3 and 4 in table 6 represent samples of rain collected successively during a rainy period at Menlo Park, Calif. The later sample shows a considerably higher concentration of solutes than the earlier. Analyses 2 and 6 in table 6 represent bulk precipitation, and analysis 1 probably can be assumed to have been influenced by dry fallout. The other data in the table represent composition of rainfall unaffected by dry fallout. The variability of solute concentrations in rain at Menlo Park and at a site about 550 km further north was studied intensively by Kennedy and others (1979) during parts of 1971 and 1972.

Reactions of sulfur and nitrogen species in the atmosphere tend to generate H^+ and are commonly thought to be the main causes of decreased pH of rainfall.

Table 6. Composition, in milligrams per liter, of rain and snow

Constituent	1	2	3	4	5	6
SiO_2	0.0	.....	1.2	0.3	.....	0.1
Al	.01	.....	.....	.....	.....	.....
Fe	.00	.....	.....	.....	.....	.015
Ca	.0	.65	1.2	.8	1.41	.075
Mg	.2	.14	.7	1.2	.....	.027
Na	.6	.56	.0	9.4	.42	.220
K	.6	.11	.0	.0	.....	.072
NH_4	.0	.....	.....	.....	.....	.....
HCO_3	3	.....	7	4	.....	.....
SO_4	1.6	2.18	.7	7.6	2.14	1.1
Cl	.2	.57	.8	17	.22	.....
NO_2	.02	.....	.00	.02	.....	.....
NO_3	.1	.62	.2	.0	.....	.....
Total dissolved solids	4.8	.....	8.2	38	.....	.....
pH	5.6	.....	6.4	5.5	.....	4.9

1. Snow, Spooner Summit, U.S. Highway 50, Nevada (east of Lake Tahoe) (Feth, Rogers, and Roberson, 1964).
2. Average composition of rain, August 1962 to July 1963, at 27 points in North Carolina and Virginia (Gambell and Fisher, 1966).
3. Rain, Menlo Park, Calif., 7:00 p.m. Jan. 9 to 8:00 a.m. Jan. 10, 1958 (Whitehead and Feth, 1964).
4. Rain, Menlo Park, Calif., 8:00 a.m. to 2:00 p.m. Jan. 10, 1958 (Whitehead and Feth, 1964).
5. Average for inland sampling stations in the United States for 1 year. Data from Junge and Werby (1958), as reported by Whitehead and Feth (1964).
6. Average composition of precipitation, Williamson Creek, Snohomish County, Wash., 1973–75. Also reported: As, 0.00045 mg/L; Cu, 0.0025 mg/L; Pb, 0.0033 mg/L; Zn, 0.0036 mg/L (Deithier, D.P., 1977, Ph.D. thesis, University of Washington, Seattle).

Influence of Humans

A major impact on the environmental factors influencing the composition of water results from the activities of humans. The power of humans to alter the environment is great and is widely evident in the changes they can bring about in water composition. Solutes may be directly added to water by disposal of wastes, or may be directly removed in water treatment or recovery of minerals. The ecology of whole drainage basins may be profoundly altered by bringing forested land into cultivated agriculture. Water-movement rates and solute-circulation rates may be altered by water diversions and by structures and paved surfaces that replace open land as cities expand in population and area. After the addition of nutrients, especially phosphorus and nitrogen, to lakes and rivers as a result of the increasing density of human population and intensified agriculture in much of the United States, many water bodies have undergone substantial changes in ecologic balance. Increased crops of algae that result from nutrient enrichment are plainly visible to any observer, and changes of this type may take place in rather short periods of time. Most inorganic composition changes are more subtle and attract less attention, but they may be more difficult to reverse.