

RELATION OF WATER QUALITY TO LITHOLOGY

Much of what has already been discussed in this book has to do with water-rock interaction, but the topic has been considered mainly from chemical or hydrologic viewpoints. The geologist and petrologist are perhaps more likely to approach this topic with the query, Given some knowledge of the type of rocks and their composition within a study area, what chemical properties and constituents should we expect to find in the surface and underground water? This approach to natural-water chemistry will be explored briefly in this section.

To begin with, not all the solutes in natural water come from dissolution of rock minerals. For example, the bicarbonate present in most water is derived in large

part from carbon dioxide that has been extracted from the air and liberated in the soil through biochemical activity. Some rocks serve as sources of chloride and sulfate through direct solution. The circulation of sulfur, however, may be greatly influenced by biologically mediated oxidation and reduction, and atmospheric circulation of chloride and other ions may be a significant factor influencing the anion content of many natural waters. The anions in rainfall are balanced by cations, partly H⁺ but also other cations. Consequently, a part of the cation content of natural water may be derived from nonlithologic sources. The importance of this effect on major-cation concentrations is usually rather small.

Many rock minerals may be viewed as hydrogen-ion acceptors, as indicated in the reactions shown previously. Hydrogen ions that participate in weathering

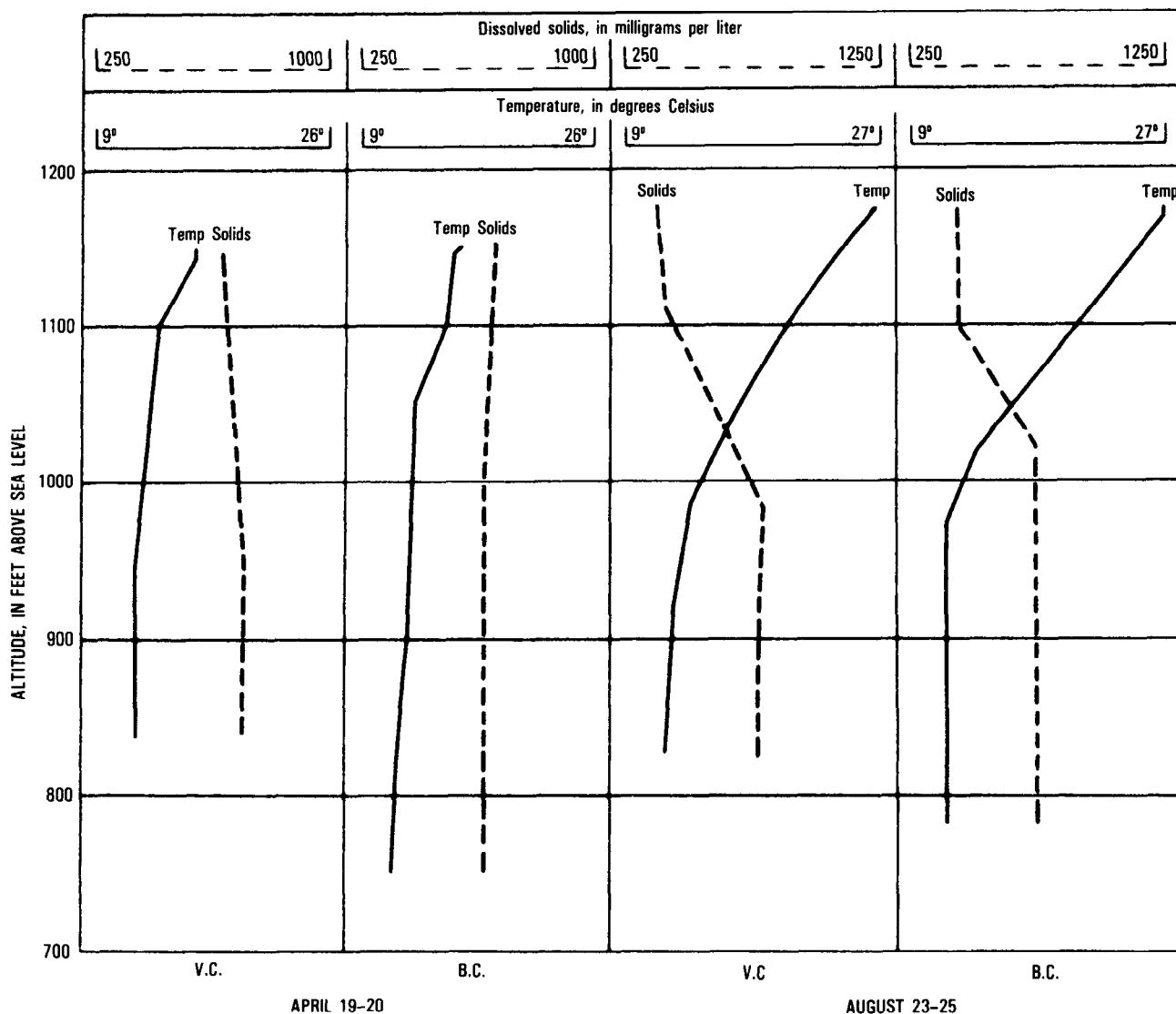


Figure 43. Temperature and dissolved solids of water in Lake Mead in Virgin and Boulder Canyons, 1948. Virgin Canyon=V.C.; Boulder Canyon=B.C. (Howard 1960)

reactions are produced in the respiration and decay of organic matter and in the oxidation of sulfides. Ideally, half the bicarbonate dissolved in water associated with carbonate rock came from the rock, and the remainder from soil air or from other similar carbon dioxide sources. In noncarbonate-rock environments, the hydrogen ions introduced through solution of carbon dioxide react with rock minerals but are mostly retained in solid residual species formed in the reaction, such as clay minerals. In a sense, the hydrogen ions release cations from the rock minerals, and the cations finally released into weathering solutions are balanced in solution by equivalent quantities of bicarbonate. Some of the H⁺ and OH⁻ in the reaction is also derived from hydrolysis. An excellent summary of weathering reactions by Keller (1957) pointed out the significance of hydrolysis in these reactions. More recently, Drever (1982, p. 138–199) reviewed the influence of weathering processes on natural-water chemistry and demonstrated the application of various techniques with examples from published literature.

A general relationship between the mineral composition of a natural water and that of the solid minerals with which the water has been in contact is certainly to be expected. This relationship may be comparatively simple and uncomplicated, as in the case of an aquifer that receives direct recharge by rainfall and from which water is discharged without contacting any other aquifer or other water. Or the situation may be rendered complex by the influence of one or more interconnected aquifers of different composition, the mixing of unlike waters, chemical reactions such as cation exchange, adsorption of dissolved ions, and biological influences. Processes involved in soil formation and the soil composition of the area may have considerable influence on composition of both surface and underground water.

Most rocks are complex mixtures of minerals that differ widely in their stability toward, or solubility in, water. Most rocks except the evaporites, however, are made up of minerals that are not readily soluble. The classification to which a particular rock is assigned is decided on the basis of its principal components. Such a classification may not adequately reflect the presence of the more soluble components that may exert an influence on the composition of water circulating through the rock. In some kinds of rock, minor components may control major features of the composition of circulating ground water. A carbonate-cemented sandstone composed largely of silica in the form of quartz, for example, might yield a water containing mostly calcium and bicarbonate ions. Resistate and hydrolyzate rocks may contain remnants of highly mineralized connate water, and this may strongly affect the quality of ground water or surface water associated with the rocks.

The complexity of rock-water-air systems obviously

imposes difficulties in applying a strict chemical-equilibrium model. Some rock species, the carbonates, for example, do lend themselves to this approach, but water associated with other rock types may be better considered as influenced by reaction rates and irreversible mechanisms. Garrels and MacKenzie (1967) described some of the effects that might be anticipated from the solution of igneous-rock minerals. If the dissolution of feldspars, for example, is viewed as an irreversible reaction, one might expect stoichiometric relationships among silica and cations in solution to resemble those in the original rock if water-rock contact time is short. Upper limits on most of the solute species would represent saturation with respect to some new solid phase, and the stoichiometry thus might be altered after long contact time of the solution with the rock minerals.

In spite of the acknowledged difficulties, many investigators have wished for a classification system for waters based on the chemical composition of the rocks from which the waters have dissolved their load of mineral matter. Regarding such a classification, Clarke (1924a, p. 8), in a paper on the composition of river and lake water, stated: "A classification of waters according to their origin is something quite different *** its purpose is geologic and although no complete scheme for it has yet been developed, the analyses as arranged in this memoir give some suggestions as to what may be possible." Clarke went on to mention limestone and dolomite waters and siliceous water, which "might be termed granitic or feldspathic, at least until a better name can be found."

In "The Data of Geochemistry," Clarke (1924b) cited a considerable number of studies, made mostly in central and western Europe, in which the writers had determined river-water composition and correlated it with drainage-basin geology. Some of these studies were made as early as the middle of the 19th century; hence, interest in this subject cannot be said to be a recent development.

It is certainly unrealistic to expect that any correlation system can succeed without considering the wide differences in weathering products and weathering rates that characterize similar rock terranes exposed in different climatic environments. If extreme conditions are left out, however, some systematic evaluation is possible. The analyses presented here show general trends and represent conditions occurring within the United States. The analyses were selected from tables given earlier in this report, and part of the basis for their selection was that their composition clearly showed the properties one might expect on a theoretical basis. More exacting studies, in which both the water and associated rock species are analyzed, have been made for granitic terranes in the California Sierra Nevada by Feth and others (1964) and for granitic and other terranes in a mountainous area

near Sante Fe, N. Mex., by Miller (1961) and in Wyoming by Miller and Drever (1977). Several such studies were reviewed by Drever (1982, p. 163–199). The general findings of these investigators and of Garrels (1967), who studied published data from several sources, are in accord with the statements about water from igneous terranes made in the first edition of this book, and the discussion is, therefore, repeated here with only minor changes. The analyses shown probably represent somewhat idealized situations, but they may aid the reader in cultivating an understanding of the composition of water that might be expected from different rock types.

Igneous Rocks

Rocks of igneous origin may be classified as extrusive or intrusive. The extrusive rocks include those ejected at the land surface as lava flows and the pyroclastic deposits resulting from explosive volcanic activity. The latter include such forms as volcanic ash and cinders, tuff, and breccia. Some of the extrusive deposits are permeable enough to permit rapid and extensive circulation of water and can be good aquifers. The intrusive rocks include batholiths, stocks, dikes, sills, and other forms that are intruded below the surface of the Earth and typically are dense and nearly impermeable to water except along fractures. Both the extrusive and intrusive rocks are further classified by geologists on the basis of chemical and mineral composition, texture, and other characteristics. The chemical and mineral composition is of principal importance in the relationships to be discussed here, and classifications based on other characteristics will not be considered. Extrusive rocks and intrusive rocks of the same chemical and mineral composition have different names but tend to yield similar weathering products to water. As a class, the extrusive rocks react more readily than the intrusive rocks for two reasons: (1) the extrusive rocks generally expose more surface area for reaction and (2) many are partly glassy—that is, not crystalline.

Igneous rocks consist predominantly of silicate minerals, although in glassy species the crystal organization may be poorly developed. The classification scheme for silicate minerals presented earlier aids somewhat in understanding the bases of the classification of igneous rocks. If oxygen is relatively abundant compared with silicon, minerals having neso- and inosilicate structures tend to be formed as the molten mass crystallizes. If oxygen is relatively depleted and silicon is abundant, the structures of minerals will more likely have the tectosilicate pattern. The intermediate classes of silicate structures will be formed in systems lying between the extremes. The crystallization process is complex, however, and products formed depend on availability of other elements and on temperature and pressure. The subject cannot be

considered here, but it is discussed more extensively in geochemical textbooks. (See Krauskopf, 1979, p. 287–367.)

Generally, rock analyses are expressed in terms of oxides. These can be recalculated to a statement that shows the proportions of the principal mineral species in the rock. Analyses in this form are the basis for the classification scheme used here.

Rocks of igneous origin exhibit a wide range of mineral compositions, for rock masses are generally mixtures of many different mineral species. Although it is not possible to design a simple classification scheme for these rocks, a general basis for the commonly used names for different rock types can be shown readily in terms of the major mineral components. Readers unfamiliar with petrology may thus gain some understanding of the meaning of such terms as granite or basalt and of the possible significance of the rock composition thus indicated in predicting the chemical composition of solutions of weathering products. The classification scheme used here is in general that of Peterson (1961), who considered it to represent a consensus of authorities on the subject. All rocks form a continuous series having a wide range of compositions and textures, and any assignment of classification and name must be entirely arbitrary.

The proportion of pure silica, generally in the form of quartz, that is present forms a convenient base from which to begin a rock-classification scheme: (1) rocks rich in quartz (>10 percent), (2) rocks impoverished in quartz and in feldspathoids (both <10 percent), and (3) rocks rich in feldspathoids and impoverished in quartz. Feldspathoids, a class of aluminosilicate minerals chemically similar to feldspar, form from melts enriched in sodium and potassium but containing too small an amount of silicon to produce tectosilicate feldspar structures. Rock masses belonging to the third class above are not common and will not be considered further in this book.

The second property used here in classifying igneous rocks is derived from the amount and type of feldspar present. The feldspar group is a very important class of igneous-rock minerals in which Al^{3+} ions substitute for some of the Si^{4+} ions in the tectosilicate structure. To compensate for the loss of positive charges, additional cations are bound in the structure, most commonly K^+ , Na^+ , or Ca^{2+} . The potassium feldspar KAlSi_3O_8 may occur in two different crystal forms, orthoclase or microcline. The plagioclase feldspars form an isomorphous series—a solid solution—whose composition ranges between the end members albite, $\text{NaAlSi}_3\text{O}_8$, and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$.

Rocks rich in quartz and having a large proportion of feldspar of which more than two-thirds is of the potassium or sodium type would be called granite if intrusive in origin and rhyolite if extrusive. A rock rich in

quartz and feldspar in which plagioclase predominates and the proportion of albite to anorthite is greater than 1:1 would be called quartz diorite if intrusive and dacite if extrusive. Both these two kinds of rock should contain less calcium than sodium and potassium.

Rocks impoverished in quartz but rich in feldspar, more than two-thirds of which is of the sodium or potassium type, are called syenite if intrusive and trachyte if extrusive. Rocks impoverished in quartz but rich in feldspar in which plagioclase predominates and the proportion of albite to anorthite is greater than 1:1 are called diorite if intrusive and andesite if extrusive. Rocks relatively impoverished in quartz and containing more than 10 percent feldspar, mostly plagioclase in which anorthite predominates, are called gabbro or diabase if intrusive and basalt if extrusive.

Rocks in the latter class generally contain considerable amounts of ferromagnesian inosilicate and nesosilicate minerals such as hornblende, amphibole, and olivine. In the peridotite rocks, quartz and feldspar are virtually absent and the ferromagnesian species of minerals predominate. Rocks of this type are commonly called ultrabasic.

Further information concerning the classification of rocks can be found in standard texts on petrology and geochemistry. In practice, the application of any system requires careful examination of the rocks, and the classification given to a particular rock based only on examination in the field may not always be as indicative of its composition as the foregoing scheme might suggest.

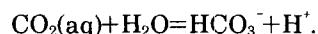
In considering igneous rocks in relation to water composition, the texture and structure of the rocks are significant because they determine the surface area of solid rock that may be exposed to attack. Ground water may be recovered in large amounts from some of the extrusive igneous rocks that contain shrinkage cracks and other joints, interflow zones, or other openings through which water may move. Most igneous rocks, however, are rather impermeable. Surface water originating in areas where igneous rocks are exposed is low in dissolved solids because, in general, the weathering attack on igneous rocks is slow. Concentrations are likely to be a function of contact time and area of solid surface exposed per unit volume of water. Where vigorous soil-forming processes and plant growth are occurring, an enhanced supply of carbon dioxide and, hence, hydrogen ions becomes available to circulating water. The amount of attack that occurs is related to the availability of H^+ , as well as the other factors cited.

Surface water in areas of igneous rocks may display the effects of rock solution less distinctly than underground waters that have better opportunity to participate in reactions with the rock minerals. A considerable and usually uncertain fraction of the solute load in a very dilute river or lake water may be related to solutes in

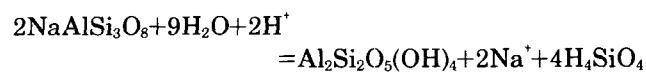
rainfall or to dust and other atmospheric fallout transported from other localities. The examples cited later in this section are mostly underground waters.

Detritus may be derived from igneous rocks by erosional processes that are largely mechanical, and subsequent circulation of water through detritus of this type can give rise to an assemblage of solutes closely similar to that to be expected from the unaltered rock. The detrital material, however, has greatly increased surface area where reactions with water can occur.

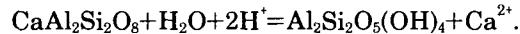
From the above generalizations, a much simplified view of the process of attack by water may be expressed in terms of chemical equations. The reaction of carbon dioxide and water supplies hydrogen ions:



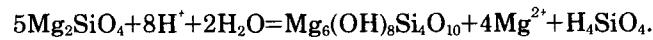
Hydrogen ions aid in the attack on feldspars that causes the feldspars to be changed to clay minerals, here represented by kaolinite, and silica and cations are released:



and



In tropical climates the clay minerals may break down or fail to form, leaving a residue of bauxite or of other metal oxides, if significant amounts of these metals were present in the original rock. Attack on ferromagnesian species may be represented by the decomposition of forsterite to form antigorite, silica, and magnesium ions:



The alteration of forsterite by this process requires much H^+ and, as shown by Barnes and O'Neil (1969), may result in water having a very high pH. A good many other similar reactions could be written for other mineral species, but for this discussion it is not necessary to go into further detail. The direct solution of quartz to give H_4SiO_4 is a possible source of silica in water also, but this is a slow reaction and is generally a less significant source than silicate decomposition.

The weathering solutions must maintain a cation-anion charge balance. Equations given above include HCO_3^- as the only anionic species, and it generally is the

principal one in these dilute solutions. Atmospheric sources of Cl^- and SO_4^{2-} are generally less important, but some accessory mineral species may provide larger quantities of these anions.

All these reactions involving dissolution of silicates probably are more complicated than the equations imply, but the equations can serve as a basis for some useful generalizations. The reactions as written are not reversible, but the rate at which the reaction proceeds will be speeded if H^+ activity increases and will tend to be retarded by the attainment of high activities of the dissolved products. The rate of reaction may also be a function of the area of surface of solids exposed per unit volume of solution and of the rates of ion transport away from the solid surfaces by water movement through the reaction sites. The reaction rate also is increased by increased temperature.

As the solutions move through the soil and the underlying rock, the composition of the water should be expected to change. At first the composition may reflect the stoichiometry of the initial weathering process. At later stages, saturation with respect to amorphous silica may be attained so that no further increase in dissolved-silica concentration can occur. Garrels and MacKenzie (1967) postulated that water from feldspathic terranes would, as it became more concentrated owing to evaporation, evolve to high-pH sodium carbonate solutions like some of the playa lakes on the east side of the Sierra Nevada of California.

Specific rates of reaction of feldspar have been studied in the laboratory rather extensively (Busenberg and Clemency, 1976; Petrović, 1976). Work also has been done on kinetics and mechanisms of reaction of other silicate rocks and minerals (Helgeson, 1971; White and Claassen, 1978; Clemency and Lin, 1981; Lin and Clemency, 1981). This research and work of others aids in understanding the mechanisms of silicate dissolution.

For the purpose of this discussion the stoichiometric relationships, and other considerations displayed in the simple equations, can be used to draw certain inferences. For example, it would appear that because sodium feldspar contains more silica than other rock minerals considered, water influenced by disintegration of this mineral to form solutes and kaolinite should have a high silica concentration. If the feldspar is a pure albite, the molarity of silica released to the water would be about double that of the sodium. If the clay mineral form is higher in silica content than kaolinite, the ratio would be lower.

In figure 44, analyses of several waters known to be associated with igneous rocks of different kinds are shown graphically. Analysis 12-2 (corresponding to analysis 2 in table 12) represents water from a spring issuing from rhyolitic terrane; the effect of dissolution of sodium-rich silicate minerals typical of this rock type is demonstrated both by the high silica content and by the high molar ratios of silica to sodium and silica to bicarbonate, although the theoretical maxima for albite dissolution are not reached. The water represented by this analysis issues

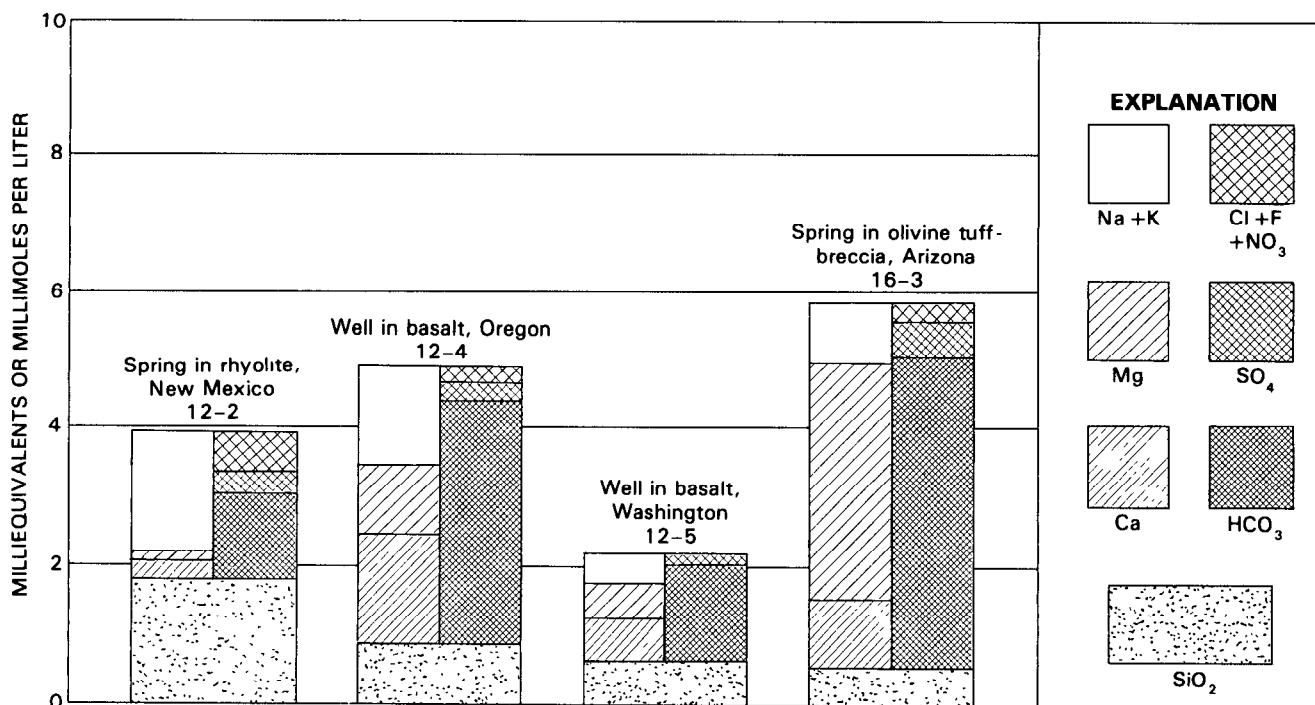


Figure 44. Composition of ground water obtained from igneous rocks. Numbers above bars indicate source of data in tables 12 and 16 (e.g., "12-2"=table 12, analysis 2).

from the ground at a temperature of 38°C. The elevated temperature increases the solubility of silica and also probably causes a more rapid attack on the rhyolitic glass and feldspars and a higher concentration of sodium than might otherwise be observed.

Analysis 16-3 represents water from a spring issuing from an ultrabasic rock. The molar ratio of magnesium to silica in this water is 3.3, which is a fairly close approach to the theoretical value of 4 suggested by the equation for dissolution of olivine. This water probably had a rather short contact time with the rock. A more unusual example is given in analysis 18-5 (fig. 50), which represents a water from an area where peridotite is being altered to serpentinite. Additional reactions related to this process that may control calcium and magnesium concentrations in the water were described by Barnes and others (1972).

In general, the amount of silica produced per hydrogen ion used up in water-rock interaction is higher for sodium-rich feldspar than for the other rock minerals considered. Thus, one might expect higher silica concentrations in relation to total ion content for water from granite or rhyolite than for water associated with basalt or ultrabasic rock in which sodium-rich feldspar would be rare or absent. Ideally, the ratio of calcium to sodium in water from feldspar-rich rocks should be related to the composition of the plagioclase feldspar present. Also, the proportion of magnesium to the other cations in the water could be an index to the relative abundance of ferromagnesian rock minerals in the rock environment.

Garrels (1967) made a number of generalizations, like the ones above, that he believed useful in considering broadly the geochemistry of natural water. It is evident, of course, that this is only a starting point in considering the highly complex systems commonly found in nature.

Analyses 12-4 and 12-5 represented in figure 44 are for water associated with a basalt transitional between the rhyolite of 12-2 and the ultrabasic rock of 16-3. The decreasing relative importance of sodium and the decrease in the $\text{SiO}_2:\text{HCO}_3$ ratio is evident in the change in the rock type to a form less likely to contain alkali feldspar; however, the relationship is obscured to some extent by the differences in total ion content among the different waters.

Sedimentary Rocks

The classification scheme for sedimentary rocks used in this section was introduced in an earlier chapter dealing with the composition of the Earth's crust. In a strict sense, most of the ground water and surface waters of the Earth are associated with sedimentary material for most or all of the time they spend in that part of the hydrologic cycle. Chemical characterization of these materials by any existing classification scheme can be only

approximate. As noted previously, resistates include sandstone and other species made up of relatively unaltered fragments of other rocks. Hydrolyzates are fine-grained species made up, in large part, of clay minerals. Precipitates are, for the most part, carbonate rocks. Evaporites consist of readily soluble minerals, such as gypsum and halite, that were deposited from water that became concentrated owing to evaporation.

Resistates

As the name implies, resistate sediments are composed principally of residual unaltered fragments of a precursor rock body. These fragments survived the weathering process because they were resistant to chemical attack; however, the intensity of weathering processes has a wide range, and the composition of mineral particles in this type of sediment reflects this fact. The particles also may range in size from boulders to submicrometer fragments, but generally these sediments have been reworked by moving water and the finest grain sizes are rare or absent.

An ideal resistate might be a sandstone composed of quartz grains and other highly resistant mineral fragments such as garnet, tourmaline, and zircon. In many resistate sediments, chemical attack may not have been strong enough to break down feldspars or even some of the less resistant minerals. Some sands and gravels are made up principally of comminuted fragments of the original rock that have undergone little chemical change. These fragments are subject to later attack and solution by water in the same way the original rock was, but perhaps at an accelerated rate owing to the increased surface area per unit weight of rock.

The consolidated resistate sedimentary rocks, such as sandstone, contain cementing material deposited on the grain surfaces and within the openings among grains. This cementing material normally is deposited from water that has moved through the rock at some past time and can be redissolved. The most common cementing materials include calcium carbonate, silica, and ferric oxyhydroxide or ferrous carbonate, with admixtures of other materials such as clay minerals.

Many resistate sedimentary rocks are permeable and may, therefore, easily receive and transmit solutes acquired by water from some other type of rock. In the course of moving through the sedimentary formations, several kinds of alteration processes may occur that may influence the composition of the transmitted water. One of these processes has already been mentioned—the precipitation of cementing material. This process is commonly a reversible one, but it may be more complicated than simple bulk precipitation and re-solution of a solid. For example, the electrostatic field in a solution near a mineral surface is different from the field farther away

from the surface. This influences solute ion behavior, and precipitation of solids may be catalyzed by this effect. The precipitation of a coating on the grain surfaces of a detrital rock may alter the composition of water that has reached the rock from some other formation. As this "foreign" water passes through its new environment, the coating of grain surfaces will progress slowly in the direction of water movement until all the active surfaces in the formation are covered, a process that may require a long time and a large volume of water. During the time this process is taking place, an advancing front of chemical change will occur. Many species of metal ions can be incorporated in the coatings by coprecipitation effects. The coprecipitation of certain metals with calcite has been studied by Alekin and Moricheva (1960). The possibility that coprecipitation might occur with some other kinds of cementing material, notably ferric oxyhydroxides, seems at least as great (Hem, 1977b).

Other factors that may control concentrations of major, as well as minor, constituents of water circulating through resistate sediments are adsorption and ion exchange. Most mineral surfaces exposed to water at near-neutral pH have a net negative electrostatic charge. Some sites on the surface have rather intense charges owing to imperfections in crystallinity and to broken chemical bonds of ions held in the lattice, and cations from solution will be attracted to and held at these sites. Less commonly, there may be sites with net positive charges, at which solute anions may be retained. Ions associated with the charge sites participate in equilibrium reactions with species in solution in the process of ion exchange. "Adsorption" is a more general term for retention of solutes at surfaces and sometimes is applied to all such effects, in contrast to "ion exchange," which is considered to occur at specific sites. The processes that are involved have been described earlier. Because some ion always is present at an exchange site, the reactions are replacements whereby ions from solution are adsorbed and sorbed ions are released, in a manner approximately predictable from equilibrium theory.

A sandstone that is deposited under marine conditions or that is later intruded by seawater would be expected to have sodium ions adsorbed on most exchange sites. Freshwater entering the sandstone at some later period can be expected to have its cation composition altered by ion-exchange reactions. Commonly, this takes the form of removal of most of the divalent cations from the entering water and their replacement by sodium present in exchange positions on the mineral surfaces. This natural softening effect has been observed in many aquifers. One would expect that an aquifer having this property would show general behavior like that of an ion-exchange column or of a water softener and would have a characteristic breakthrough point at which the exchange capacity became exhausted.

Adsorptive capacity for anions may well involve hydroxide groups that can occur at some charge sites. Hydroxide groups were shown by Halevy (1964) to be available at certain sites on kaolinite particles. These hydroxide ions could perhaps be replaced by fluoride ions because they have the same charge and the same approximate shape. Bower and Hatcher (1967) showed that such a process can occur in soils. Some ground waters high in pH show high concentrations of fluoride, possibly owing to the reversal of this effect (analysis 1, table 18). Other anions generally are larger than the fluoride ion and seem less likely to be involved in ion-exchange equilibria, although Yamabe (1958) believed the reaction could involve carbonate ions.

The participation of clay minerals in ion-exchange reactions has been indicated in some of the foregoing discussion. These minerals have high exchange capacity per unit weight and are present in considerable amounts in some resistate sediments, although the clay minerals are more characteristically found in hydrolyzates. Exchange reactions also are important, of course, in water in hydrolyzate sediments. Exchange processes are by no means confined to clay minerals. When exchange capacities of minerals are computed on the basis of sites per unit of effective surface area, the importance of clays as exchange substrates in ground-water systems can be viewed more realistically. Much of their effectiveness as cation exchangers in soils is due to the large surface area per unit weight that clay minerals have.

Neither the surface area encountered by a unit volume of ground water in an aquifer nor the exchange capacity per unit area is commonly determined. A realistic model for solute behavior may require attention to these factors, however (Hem, 1977b).

Many resistate sediments form in anaerobic environments and contain organic material or other solids that can maintain reducing conditions for long periods of time. The rock also may contain some reduced mineral species, such as pyrite. The solutions moving through the sedimentary rock at later periods in its history may bring in oxygen and may participate in oxidation or reduction reactions. Many such reactions may be biologically mediated—that is, they may be intimately involved with life processes of micro-organisms. Oxidation reactions can be expected in the part of the rock lying above the water table and to some extent at greater depth, depending on the availability of oxygen. Species stable in reduced environments, such as pyrite, will be altered by oxidation, with a release of energy. The sulfur of pyrite, for example, will be oxidized to sulfate, and ferrous iron will be released. Reduction processes that can occur where oxygen is depleted may convert sulfate to sulfur or sulfide, and both oxidation and reduction reactions involving nitrogen may be significant. Any of these reactions for which an outside source of energy is needed either require

some other material that bacteria can use for food or must occur where biota can obtain radiant energy from sunlight.

Figure 45 describes graphically the analyses of four waters from resistate sediments. Analysis 12-7 represents water from the Santa Fe Formation which underlies the Rio Grande valley at Albuquerque, N. Mex. The high silica concentrations and other properties suggest that the water has attacked particles of igneous rock included in this formation. The ground water associated with a pure quartz sand can be among the lowest in dissolved-solids content of any ground water. For example, water from wells in quartz sand aquifers on Long Island, N.Y., may contain less than 30 mg/L of dissolved solids (Kimmel and Braids, 1980).

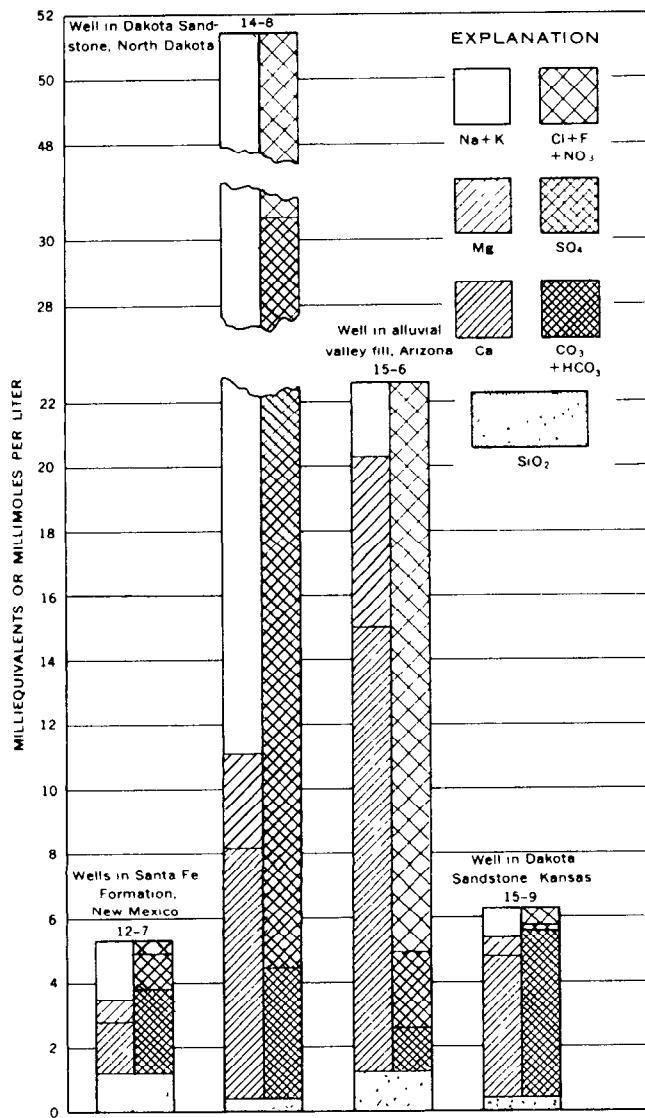


Figure 45. Composition of ground water obtained from resistate sedimentary rock types. Numbers above bars indicate source of data in tables 12, 14, and 15 (e.g., "12-7"=table 12, analysis 7).

Analysis 14-8 is for a much more highly mineralized water from the Dakota Sandstone in North Dakota, where the concentrations of sodium, chloride, and sulfate are high. These ions can best be explained as having migrated into the sandstone from other rock formations associated with the sandstone. The sluggish circulation of water in the sandstone retards flushing of solutes.

Analysis 15-6 represents water from valley fill at Phoenix, Ariz., that reflects the influence of irrigation-drainage water. The proportions of cations in this water probably have been altered by ion-exchange reactions in the overlying soil.

Some rock formations yield notable concentrations of unusual constituents to ground water and thus provide a natural tracer by which the lithologic source of the water can be recognized. One of the more outstanding examples of such an effect is the occurrence of strontium in water from certain sandstones and other rock formations in Wisconsin, as noted Nichols and McNall (1957).

Because of the many ways in which their composition may be affected, the water from resistate rocks has a wide range of chemical quality. Although water from a particular aquifer may have distinctive properties, these must generally be determined by actual sampling and analysis and can seldom be predicted solely from the knowledge that the water is associated with resistate sediments.

Hydrolyzates

Shale and other fine-grained sedimentary rocks are composed, in large part, of clay minerals and other fine-grained particulate matter that has been formed by chemical reactions between water and silicates. Almost all hydrolyzate rocks also contain finely divided quartz and other minerals characteristic of resistates, but such minerals are present as smaller particles. Shale and similar rocks are porous but do not transmit water readily because openings are very small and are poorly interconnected. Many such rocks were originally deposited in saltwater, and some of the solutes may remain in the pore spaces and attached to the particles for long periods after the rock has been formed. As a result, the water obtained from a hydrolyzate rock may contain rather high concentrations of dissolved solids. Because environmental conditions commonly change from time to time during deposition, many hydrolyzate sediments contain layers of coarser material, and water may be transmitted in those layers at a rate sufficient to supply a well or spring. Even where the material is too fine grained to transmit water to wells in useful amounts, the very wide lateral exposure of such formations to more porous overlying, and underlying, layers may result in a significant migration of water and solutes from the hydrolyzates into the aquifers with which they are interbedded. These effects can be noted in many places and can become important

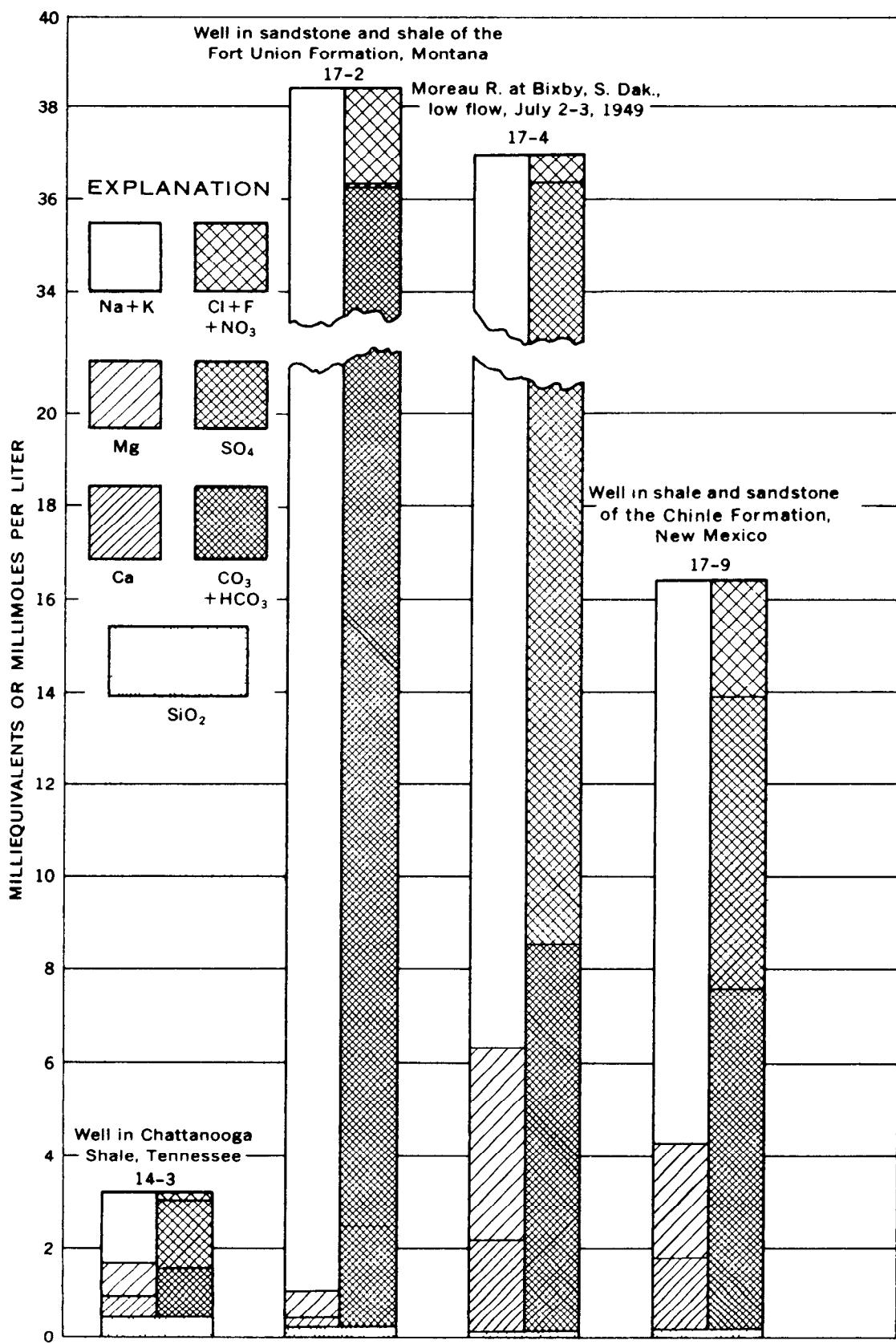


Figure 46. Composition of water obtained from hydrolyzate sedimentary rock types. Numbers above bars indicate source of data in tables 14 and 17 (e.g., "14-3"=table 14, analysis 3).

and damaging when hydrostatic pressures in the zone of saturation are changed extensively by withdrawals of ground water. Lofgren (1975) described extensive subsidence of irrigated land in San Joaquin Valley, Calif., following ground-water extraction. Similar effects have been observed in other areas. The effect of shale beds containing solutes on quality of surface runoff is worth noting, also.

Davis (1961), in a study of surface-water composition, noted that the runoff from areas underlain by certain geologic formations in California was characterized by low ratios of bicarbonate to sulfate. He correlated this fact with the presence of sulfide minerals in the sedimentary formations. These minerals formed when the sediments were laid down in reducing environments. Weathering caused the oxidation of the sulfide to sulfate. Reduced iron minerals, notably pyrite, are commonly associated with hydrolyzates.

Analyses in figure 46 represent four waters associated with hydrolyzate sediments. They share one dominant characteristic: sodium is their principal cation. This is not necessarily true of all water associated with hydrolyzates, however, as some contain large concentrations of calcium and magnesium. Clay minerals can have high cation-exchange capacities and may exert a considerable influence on the proportionate concentrations of the different cations in water associated with them. Direct solution of the hydrolyzate minerals themselves, however, is a less significant factor except in environments in which water circulation is rapid (in instances of high rainfall, for example) or in which a low pH is maintained in the circulating water.

Analysis 14-3 represents water from the Chattanooga Shale that has a low dissolved-solids concentration because of the abundant supply of water from rainfall. The rather high silica concentration in this water is somewhat unusual for water from hydrolyzates and may be the result of solution of unaltered silicate minerals. Analysis 17-2 represents water from sandstone and shale in the Fort Union Formation. This analysis shows the effect of both cation-exchange softening and sulfate reduction. The former process has increased the sodium concentration at the expense of the calcium and magnesium. The latter process has caused the bicarbonate to increase, partly at the expense of the sulfate.

The composition of water at very low flow in the Moreau River at Bixby, S. Dak., is shown by analysis 17-4. The drainage basin of this stream contains a high proportion of hydrolyzate rocks. Analysis 17-9 represents water from the Chinle Formation, which is sandy enough in some places to yield small amounts of water.

The effect of hydrolyzates containing readily soluble material can be observed in floodwaters of some streams, for example, in the basin of the Rio Puerco, which is a tributary to the Rio Grande above San Acacia, N. Mex.

Floodwaters from this tributary are heavily laden with suspended sediment and dissolved solids. Figure 47 shows the average analyses for normal flow and for summer-flood periods for the Rio Grande at San Acacia. The difference between the averages is in large part the effect of inflow from the Rio Puerco. Somewhat similar effects can be demonstrated for other streams draining hydrolyzate sediments, for example, the Powder River of Montana. The chemical relationships in that basin were described by Swenson (1953).

Precipitates

The sedimentary rocks termed "precipitates," for the purposes of this discussion, are composed of the common alkaline earth carbonates: limestone, which is mainly calcium carbonate, and dolomite, which is principally the compound $\text{CaMg}(\text{CO}_3)_2$. The magnesium limestones have a wide range of Ca:Mg ratios, up to equimolar.

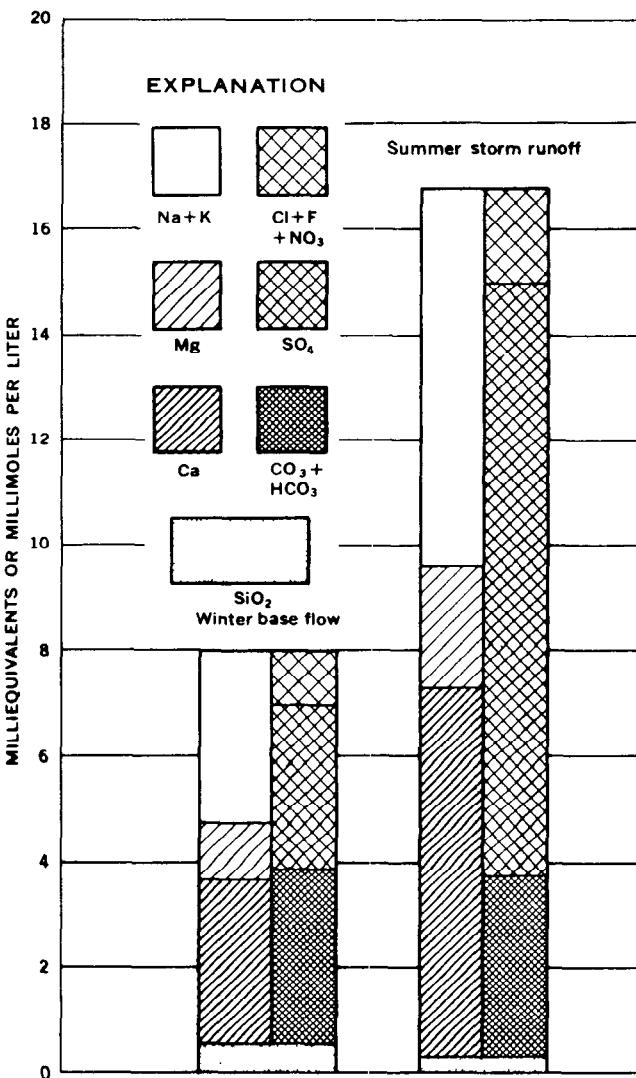


Figure 47. Average composition of water from Rio Grande during two periods in 1945 and 1946.

There are no massive carbonate-rock formations in which magnesium is more abundant than calcium, but several magnesium carbonate minerals with and without added hydroxide do exist. Carbonate minerals other than those of calcium and magnesium occur as impurities in many limestones and dolomites. As a class, the carbonate rocks can be viewed as fairly simple chemical substances compared with the silicate rocks.

The solution of limestone is principally the process of solution of calcium carbonate, which already has been discussed at length. The kinetics of dissolution and precipitation of calcite have been studied extensively. Both processes are fast enough to make it reasonable to evaluate limestone hydrochemistry by an equilibrium approach. However, the circulation systems in limestone are generally not entirely closed to the entry of outside reactants. Calcite equilibria are discussed more extensively in the section of this book dealing with calcium. The proportion of magnesium to calcium in water from limestone may reflect to some extent the composition of the limestone. This interpretation must be made cautiously, however, because there are many complications that can influence the calcium-to-magnesium ratio. Silica is normally a

minor constituent of water from limestone.

Analysis 15-1 in figure 48 represents water from a rather pure limestone. According to the calcite-solubility graph (p. 2), this water is a little below saturation with respect to calcite. The source is a spring of large discharge in a region where water is plentiful. The predominance of calcium and bicarbonate in the analysis, however, is obvious. This analysis also is shown graphically in figures 30-37.

Dolomite does not dissolve reversibly—that is, the conditions required for direct precipitation of dolomite are not generally reached, at least in the kind of environment in which ground water of potable quality occurs. As noted for limestone, however, the ratio of calcium to magnesium in water from dolomite tends to reflect the 1:1 composition of those ions in the rock, so long as the solution is not subjected to too many influences that might cause some calcium carbonate precipitation. Calcite precipitation from such a water can decrease the Ca:Mg ratio to values below 1. Analysis 16-1 in figure 48 represents water from the Knox Dolomite. It has Ca:Mg ratio near 1.0, and judging from its pH it seems to be virtually at saturation with respect to calcite. The influence

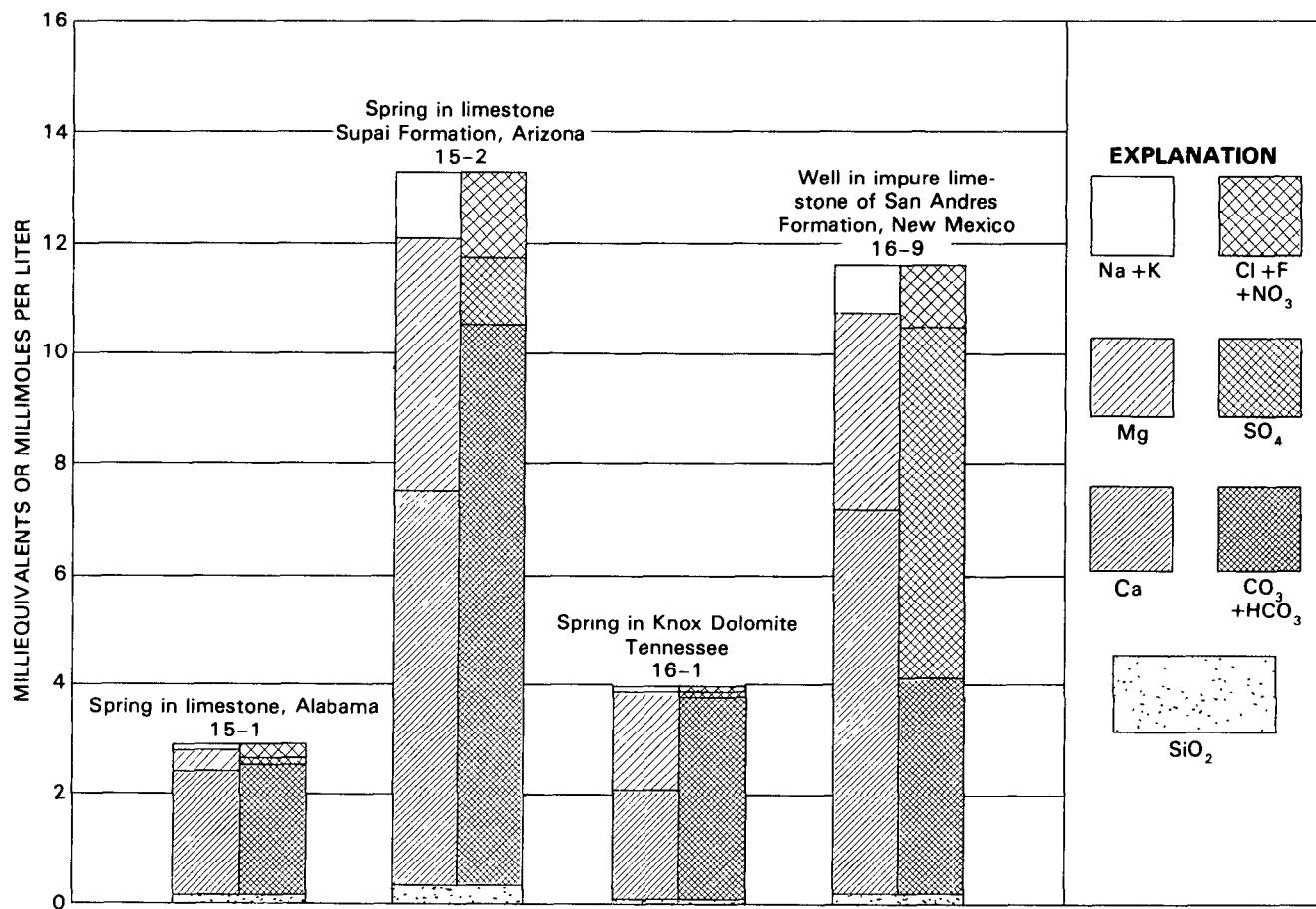


Figure 48. Composition of ground water obtained from precipitate sedimentary rock types. Numbers above bars indicate source of data in tables 15 and 16 (e.g., "15-1"=table 15, analysis 1).

of impurities in the rocks on these two analyses evidently is insignificant. The bicarbonate concentration is very nearly equal to the sum of calcium and magnesium in the two bar graphs, and sodium, chloride, and sulfate are all present in minor amounts.

Analysis 16-9 is for a water from impure limestone that contains both gypsum and dolomite; the water also has been influenced by solution of sodium chloride. The hydrology of the aquifer from which this water came, the San Andres Limestone of the Roswell basin, New Mexico, was first described by Fiedler and Nye (1933).

Water that moves for long distances through impure limestone and dolomite may participate in irreversible processes. Calcite saturation may be reached first, after which gypsum and dolomite continue to dissolve along the flow path while calcite is precipitated (Plummer and Back, 1980). The influence of gypsum is indicated by the large proportion of sulfate in solution in analysis 16-9, and the bicarbonate content is barely larger than that of analysis 16-1, although calcium and magnesium are much greater.

Analysis 15-2 represents a water from limestone in the deeply buried Supai Formation in the Grand Canyon region, Arizona. The constituents other than calcium, magnesium, and bicarbonate in this water may originate from other formations, as little is known of the circulation of the water in this aquifer. A point of interest, however, is the high degree of supersaturation with respect to calcite. The water deposits calcite on exposure to air. Obviously, at some point in its circulation path, this water achieved a considerably greater capacity than most waters for solution of limestone. Carbon dioxide released by metamorphic processes could supply additional solvent power. Orfanidi (1957) suggested that metamorphic alteration of carbonate rocks at depth could help explain the composition of some ground waters in the U.S.S.R. Barnes, Irwin, and White (1978) reviewed the metamorphic sources of CO₂ in other areas. In some terranes the bacterially mediated reduction of sulfate coupled to oxidation of organic matter also can produce substantial amounts of CO₂.

Readers interested in pursuing the subject of relationships between carbonate rocks and water composition will find more details in discussions in this book in the sections titled "Calcium," "Magnesium," "Alkalinity," and "Hydrogen-Ion Activity" and in the large literature on this subject that is available elsewhere (for example, Garrels and Christ, 1964, p. 74-92).

Evaporites

The highly soluble nature of evaporite sediments causes water associated with them to have high dissolved-solids concentrations. Gypsum and anhydrite are the least soluble of the rocks considered here as evaporites, and gypsum can transmit water through solution channels

as limestone does. A water moving through gypsum eventually becomes saturated with respect to that solid and has a composition like the one shown in analysis 15-3, figure 49. The distribution of solutes in two nearly saturated brines from southeastern New Mexico is shown graphically by two analyses in figure 49. One of these, analysis 17-8, is essentially a saturated Na⁺ + Cl⁻ solution. The other, analysis 16-6, has a high proportion of Mg²⁺

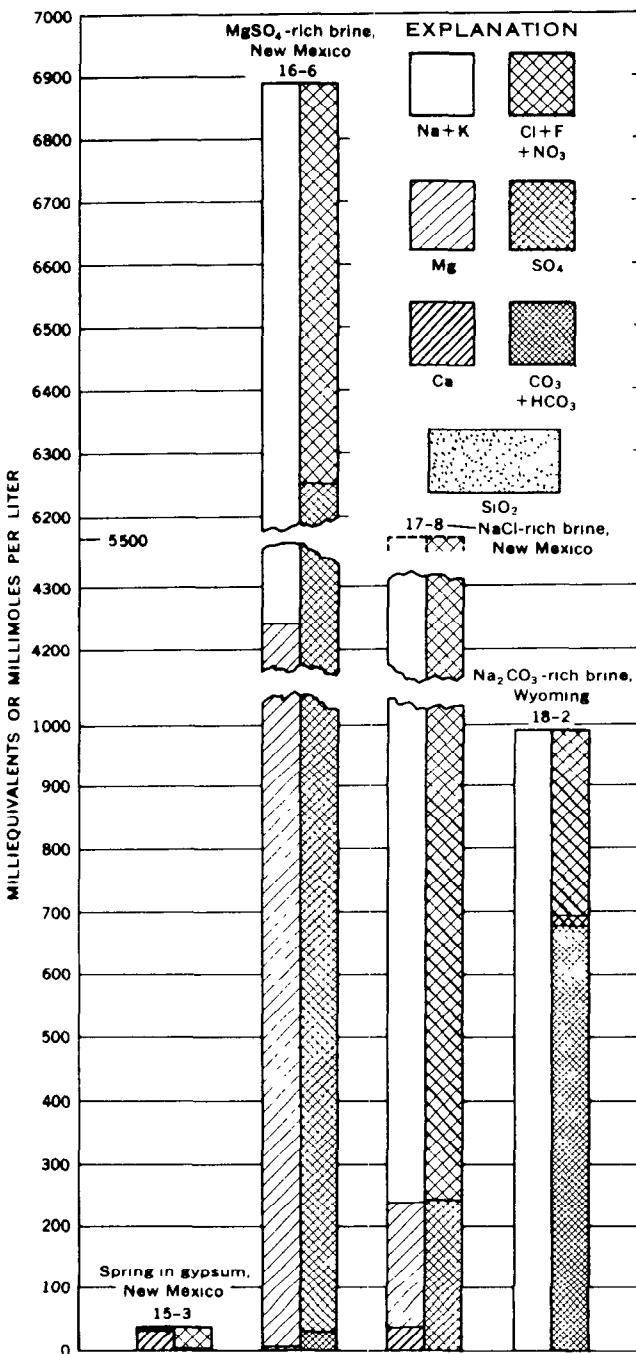


Figure 49. Composition of ground water obtained from evaporite sedimentary rock types. Numbers above bars indicate source of data in tables 15-18 (e.g., "15-3"=table 15, analysis 3).

and SO_4^{2-} . Analysis 18-2 is for a water associated with a Wyoming Na_2CO_3 deposit. The vertical scale in figure 49 is condensed by a factor of 50 as compared with figures 44-48; hence the graphs are not directly comparable. The scale used in figure 49 causes the graph for analysis 15-3, a water that has more than 30 meq/L of cations, to appear small even though the water is above the usual concentration limit for potability.

The composition of natural brines generally is closely related to the composition of the evaporite deposits from which they are derived and may include minerals of economic value. Some of the elements commercially recovered from such brines are magnesium, potassium, boron, lithium, and bromine. Many analyses of natural brines have been published by White and others (1963).

Metamorphic Rocks

Rocks of any kind may be metamorphosed. The process as considered here consists of the alteration of rock by heat and pressure to change the physical properties and, sometimes, the mineral composition. All degrees of alteration may occur, up to complete reassembly of rock components into new minerals. Considering the wide

possible variety of original rocks, it is evident that few simple generalizations about the composition of water to be expected in association with metamorphic rocks can be made.

If sedimentary rocks are subjected to sufficiently intense heat and pressure, they can be completely melted into a new igneous mass. Gneiss and schist result from heat and pressure that do not completely reorganize the initial rock. Although these rock types may be dense and non-water-bearing, there are places where ground water is recovered from them. Water from such formations generally can be expected to be low in solute concentrations and to resemble more closely the water from igneous terranes than the water from the sediments as they existed before being metamorphosed. Analysis 12-9, represented graphically in figure 50, is for water from schist. Analysis 13-5 represents water from a granitic gneiss. The rather high proportion of silica in both these waters shows the influence of silicate minerals.

The dense structures of slate, a metamorphosed form of shale, and of quartzite, a metamorphosed form of quartzose sandstone, tend to restrict water movement to fracture zones and thereby prevent contact of ground

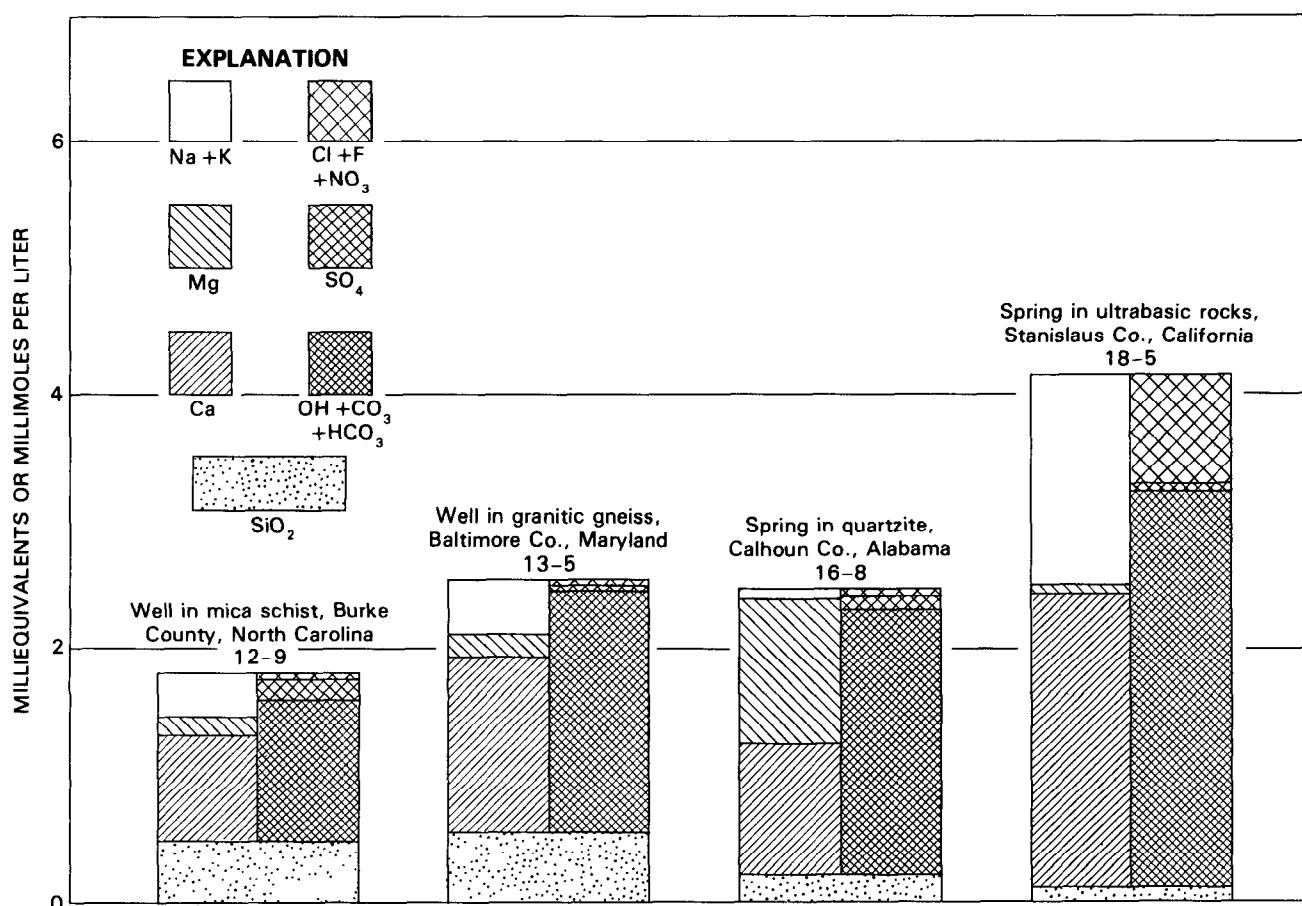


Figure 50. Composition of ground water obtained from metamorphic rocks. Numbers above bars indicate source of data in tables 12, 13, 16, and 18 (e.g., "12-9"=table 12, analysis 9).

water with surface areas of minerals as large as is normally expected in shale or in sandstone. The opportunity for water to pick up solutes from these metamorphosed rocks is, therefore, small, and water from slate or quartzite also is likely to contain low concentrations of solutes. Analysis 16-8, figure 50, represents water from a quartzite in Alabama. Limestone may be converted to marble without much chemical change, and the processes of solution in such a marble are much the same as those in limestone. If the original limestone was impure, however, it could yield a marble containing some minerals less soluble than calcite.

Processes of metamorphism generally involve aqueous solutions, and the alteration products that result may include hydrolyzate minerals. The release of water from some types of rocks during metamorphic processes can be expected. White (1957a) examined natural waters for possible features of their composition that could be attributed to metamorphism of rocks. Among the properties cited by White as possible indications of a metamorphic influence on water composition were high concentrations of sodium, bicarbonate, and boron and relatively low concentrations of chloride. Analysis 18-5 is for water described by Barnes and others (1967) to issue from a zone of alteration of ultrabasic rock to serpentinite.

The first three analyses in figure 50 represent waters that passed through metamorphosed rocks long after the processes of metamorphism were completed. In contrast, the water represented by analysis 18-5 is actively participating in the ongoing metamorphic process.

INFLUENCE OF ACTIVITIES OF HUMANS

All life forms interact with their environments in various ways. As a result of these interactions, complex ecologic structures have evolved, structures in which diverse life forms interact with one another in supportive as well as in predatory ways. One might view the present-day Earth-surface environment as having been shaped in many ways through these life processes interacting with their surroundings over the span of geologic time. Certainly this is true for the development of soils—and it has been thought by many geochemists that the atmosphere has attained much or all of its oxygen from activity of photosynthetic organisms. A more extreme view was expressed by Lovelock and Margulis (1974), who suggested that the life processes of organisms established and continue to maintain the composition of the atmosphere at an optimum for living species to thrive. It is perhaps less clear how natural waters might have been made more hospitable over a long time span by such processes, but one may readily observe ways in which organic processes currently maintain water bodies in a state favorable for life (oxygen and nutrient balances, for example).

Many human activities have adverse consequences for the environment. As human populations increase and civilizations become more and more technologically developed, the adverse effects become obvious, and they have been a matter of deep concern to thoughtful observers for more than a century. When human activities cause a decline in the quality of natural waters we use the term "pollution." This word has deep connotations and water pollution is difficult to define scientifically. For the purpose of this discussion it is defined as man-caused deterioration of water quality that is sufficiently severe to decrease substantially the usefulness of the resource, either by humans or by some other life form deemed to be beneficial.

In a broad general sense one can describe the interaction of life forms with their environment in the terms of thermodynamics. Life processes themselves, for example, involve an expenditure of energy to produce a form of internal order (decreased entropy). When the organisms die, the second law of thermodynamics predicts that this order will be largely destroyed and its stored energy partly released, with an increase in entropy in the products of decay. The energy loss is not total, however, and over geologic time large amounts of available energy have been stored, in coal and petroleum, for example.

The rise of modern civilization has brought with it a large and increasing use of energy, from fossil sources and more recently from nuclear fission. Much of this energy is employed in ways that influence the physical environment, as in agriculture, timber harvesting, and mining. These activities could be likened to increases in degree of order—at least humans generally consider the results beneficial. The side effects on natural water may sometimes be severe enough to constitute pollution as defined here. This general view of pollution problems has been discussed by Stumm and Morgan (1981, p. 724–725).

Some of the energy expended by an industrial civilization is used to produce entropy decreases that can be more exactly defined thermodynamically. The conversion of iron oxide ore to metallic iron, and the recovery of other metals from ores, give products that are thermodynamically unstable (that is, low in entropy). Their conversion to more stable forms can be a source of water pollution as the metals react with their environment. Production and use of synthetic organic chemical compounds also pose a pollution threat, one that may be difficult to evaluate because these substances would not be present in the environment under natural conditions.

From these considerations a generalization can be made: Industrial civilizations can be expected to have substantial intrinsic environmental effects, and some may bring about pollution of natural water as this has been defined here. Some parts of the definition are subjective. Specifically, the definition requires that judgments be