Chapter 11

Groundwater and Geologic Processes
Groundwater plays an important role in many geologic processes. For example, the fluid pressures that build up on faults are now recognized to have a controlling influence on fault movement and the generation of earthquakes. On another front, subsurface flow systems are responsible for the transfer of heat and chemical constituents through geologic systems, and as a result, groundwater is important in such processes as the development of geothermal systems, the thermodynamics of pluton emplacement, and the genesis of economic mineral deposits. At depth, groundwater flow systems control the migration and accumulation of petroleum. Nearer the surface, they play a role in such geomorphologic processes as karst formation, natural slope development, and stream bed erosion.

In this chapter, we will discuss the role of groundwater in these and other geologic processes. The treatment is brief and the list of topics and references is far from exhaustive. Many of the developments we report are recent. The consequences of groundwater flow have not as yet been extensively evaluated in research on geologic processes.

11.1 Groundwater and Structural Geology

One of the most exciting recent developments in geologic thought concerns the influence of groundwater pressures on fault movement and the possible implications this has for the prediction and control of earthquakes. The concepts were first put forward by Hubbert and Rubey (1959) in their classic paper on the role of fluid pressure in the mechanics of overthrust faulting.

Hubbert-Rubey Theory of Overthrust Faulting

Hubbert and Rubey were addressing a geological mystery of long standing. It had been recognized since the early 1800's on the basis of field evidence that movements of immense thrust blocks over considerable distances had taken place along over-
thrust faults with extremely low dip angles. Many thrust faults had been mapped that involved stratigraphic thicknesses of thousands of meters and travel distances of tens of kilometers. What was not understood was the mechanism of movement. Many calculations had been carried out in which horizontal tectonic forces or gravitational sliding had been invoked as the mechanism of propulsion, but all had foundered on the need for unrealistically low frictional resistances on the fault plane. When more realistic coefficients of friction were used, the analyses showed that the horizontal forces necessary to cause thrusting would create stresses that greatly exceed the strength of any known rocks.

Hubbert and Rubey solved this mechanical paradox by invoking the Mohr-Coulomb failure theory, as developed in Section 10.1, in its effective stress formulation. Their analysis was the first to take into account the existence of fluid pressures on faults at depth. They utilized the relation presented in Eq. (10.8), but as seems reasonable for a smooth fault plane, they assumed the cohesive strength to be negligible and set $c' = 0$. The failure criterion then becomes

$$S_r = (\sigma - p) \tan \phi'$$  \hspace{1cm} (11.1)

where $S_r$ is the shear strength that must be overcome to allow movement, $\sigma$ the normal stress across the fault plane, $p$ the fluid pressure, and $\phi'$ the angle of internal friction for the rock-rock interface. They reasoned that large values of $p$ in Eq. (11.1) would serve to reduce the normal component of effective stress on the fault plane and hence reduce the critical value of the shear stress required to produce sliding. They showed that the horizontal forces of propulsion needed to produce these reduced shear stresses do not exceed the strength of rock. They referred to oil field measurements to support their contention that high fluid pressures are a common occurrence at depth. The more recent developments in our understanding of regional flow systems (as reported in Chapter 6) make it clear that these high fluid pressures are a natural outgrowth of the subsurface systems of fluid movement that exist in the heterogeneous geological environment in the upper few thousand meters of the earth's crust.

Figure 11.1 reproduces Hubbert and Rubey's free-body diagram for a thrust block of dimensions $x_1$ by $z_1$ being pushed from the rear down an inclined plane.
of slope \( \theta \). The block is propelled jointly by the total stress, \( \sigma_x + p \), applied to its rearward edge and the component of its weight parallel to the slope. A shear stress is created at the base of the block, and at the point of incipient slippage, \( \tau = S'_c \), where \( S'_c \) is the shear strength of the fault plane as given by Eq. (11.1). The equilibrium of forces acting on a section of unit thickness perpendicular to the diagram is given by

\[
\int_0^{x_1} (\sigma_x + p) \, dz + \rho_b g z_1 x_1 \sin \theta - \int_0^{x_1} (\sigma_x - p) \tan \phi' \, dx = 0 \tag{11.2}
\]

where \( \rho_b \) is the bulk density of the rock. Hubbert and Rubey solved Eq. (11.2) for \( x_1 \), the maximum length of block that can be moved by this mechanism. To make such a calculation, it is necessary to know the geometrical parameters, \( \theta \) and \( x_1 \), the mechanical properties, \( \phi' \) and \( \rho_b \), and the value of the fluid pressure, \( p \), on the fault plane. Hubbert and Rubey expressed this last parameter in terms of the ratio \( \lambda = p/\sigma_x \). They provide a table of calculated \( x_1 \) values for a rock slab 6000 m thick resting on a fault plane with representative \( \phi' \) and \( \rho_b \) values. For \( \theta \) values in the range 0–10° and \( \lambda \) values in the range 0–0.95, the maximum length of block that can be moved varies from 21 to 320 km. These lengths are in keeping with the observed travel distances of overthrust fault blocks. Hubbert and Rubey therefore concluded that consideration of the fluid pressures in the groundwater in the vicinity of fault planes removes the paradox surrounding the mechanism of overthrust faulting.

**Earthquake Prediction and Control**

Earthquakes are the physical manifestation of the movement of fault blocks. The Hubbert–Rubey theory is therefore pertinent to earthquake genesis. Dramatic confirmation of the influence of elevated fluid pressures on earthquake production came to light in the late 1960’s in a somewhat unexpected way in connection with the now-famous Rocky Mountain Arsenal disposal well near Denver, Colorado.

During the period April 1962 to September 1965 there were 710 small earthquakes recorded in the Denver area. This was a seismological mystery because prior to this time the only recorded earthquake had occurred in 1882. The solution to the mystery was provided by Evans (1966), who noted that the first earthquake occurred just 1 month after the first injection of liquid waste at a disposal well at the U.S. Army’s Rocky Mountain Arsenal. The injection well was designed for the disposal of contaminated wastewater from the chemical plant at the Arsenal. The well was drilled through sedimentary rocks, bottoming at a depth of 3671 m in fractured Precambrian schist and granite gneiss. Injection was carried out at rates of 12–25 \( \ell/s \) at injection pressures of 3–7 \( \times 10^6 \) N/m². Evans noted that the earthquake frequency in the period 1962–1965 was closely correlated with the volume of waste injected (Figure 11.2). Further investigations showed that the epicenters of almost all the shocks were located within a circular area 16 km in diameter centered at the Rocky Mountain Arsenal.
Each of the earthquakes that occurred in the Denver cluster presumably reflected movement on a preexisting fault at depth in the vicinity of the Arsenal well. Apparently, the increases in fluid pressures engendered by the injection had the effect of triggering the small fault movements. Evans’ observations thus provided convincing confirmation of the validity of the theoretical calculations of Hubbert and Rubey (1959). Healy et al. (1968) after an extensive review of the evidence conclude that the Hubbert-Rubey mechanism provides a complete and satisfactory explanation for the triggering of the Denver earthquakes.

If increased fluid pressures encourage fault movement, then decreased fluid pressures should retard fault movement, and the possibility of earthquake control is raised. Seismologists and groundwater hydrologists are now working together to examine the possibility of man-made intervention in the faulting process. The ultimate scheme would be to take a fault such as the San Andreas in California, tighten it along most of its length by dewatering the fault zone, and then encourage controlled movement in a small portion by injecting water into the fault zone at that point. In this way it might be possible to move sequentially along the fault, relieving the tectonic stresses that build up along its length with a series of small controlled fault movements rather than awaiting a large catastrophic earthquake.

The social and ethical conundrums that would result from the serious consideration of such a scheme, together with the momentous implications of a technical failure, will certainly delay, and may well prevent, implementation of earthquake control in heavily populated areas. However, large-scale field experiments have already been carried out in a less populated area at an oil field near Rangely,
Colorado. The Rangely site was chosen on the basis of seismic activity that was known to have occurred during the latter stages of exploitation of the oil reservoir when fluid injection was used as a part of a secondary recovery program utilizing the "waterflooding" approach. Healy (1975) reports that monitoring of the earthquakes associated with the oil field began in 1969 and continued through 1974. Purposeful modification of the fluid pressure in the active zone began in 1970 and continued through December 1973. In the first phase of the experiment, the pressure was reduced in the earthquake zone, and seismic activity was greatly decreased, particularly in the region within 1 km of the control wells. In November 1972, the pressure was raised and a new series of earthquakes was initiated. In March 1973, pumping was reversed, the fluid pressure in the earthquake-producing zone dropped, and earthquake activity decreased. After 6 months there were no further earthquakes within 1 km of the injection wells.

As a part of the same study, Raleigh et al. (1972) measured the frictional properties of the rocks in the laboratory on cores taken from the oil field. These data, together with some in situ stress measurements, allowed an independent calculation of the values of fluid pressure at which earthquakes would be expected to occur. The predicted critical level was \( p = 2.57 \times 10^7 \text{ N/m}^2 \). The values in the seismically active part of the reservoir at a time of frequent earthquakes were measured at \( 2.75 \times 10^7 \text{ N/m}^2 \). Healy (1975) concludes that the Rangely experiments establish beyond doubt the importance of fluid pressure as a critical parameter in the earthquake mechanism.

It has also been suggested that very detailed pressure measurements on faults may provide precursory evidence of impending earthquakes. Scholz et al. (1973) review the dilatancy model of earthquake prediction and describe the role played by the interaction between the stress field and the fluid-pressure field just prior to the actual triggering of movement on a fault.

### 11.2 Groundwater and Petroleum

It is now widely accepted (Weeks, 1961; Hedberg, 1964; Levorsen, 1967) that petroleum originates as organic matter that is incorporated into fine-textured sediments at the time of their deposition. However, while organic-rich clays and shales are found throughout the sedimentary basins of the world in great areal and volumetric abundance, present-day accumulations of petroleum are found only in localized concentrations of relatively small volume. Further, they do not occur in the clays and shales themselves, but rather in coarse-textured sandstones and in porous or fractured carbonate rocks. It is apparent that petroleum must undergo significant migration from its highly dispersed points of origin to its present positions of concentration and entrapment. During this migration petroleum is an immiscible and presumably minor constituent of the subsurface water-saturated environment. It is therefore reasonable to examine the processes of migration and accumulation of petroleum in light of our understanding of regional groundwater
flow systems. Such an examination has ramifications in the field of petroleum exploration.

**Migration and Accumulation of Petroleum**

Petroleum migration is often viewed as a two-step process. The term *primary migration* refers to the processes whereby water and entrained petroleum are expelled from the fine-grained source sediments into the more permeable aquifers of a sedimentary system. The term *secondary migration* is reserved for the movement of petroleum and water through the aquifer systems to the structural and stratigraphic traps, where oil and gas pools are formed.

Primary migration can be viewed as one result of the process of consolidation that takes place in newly deposited fine-grained sediments. Bredehoeft and Hanks (1968) have shown that the influence of the added load provided by the additional sediments that are continuously being emplaced at the top of a sedimentary sequence in a depositional environment is sufficient to produce significant consolidation. The mechanism is identical to that described in connection with land subsidence in Section 8.12. Once again, our understanding of the process hangs on the effective stress equation

\[ \sigma_T = \sigma_e + p \]  

(11.3)

In this case, it is the direct natural change in the total stress, \( \sigma_T \), that drives the consolidation process, rather than an artificial change induced in the fluid pressure, \( p \), as was the case where land subsidence is caused by overpumping. In either case, the result is an increase in effective stress, \( \sigma_e \), and a compaction of the highly compressible fine-grained sediments. During the consolidation process, water is driven out of the fine-grained sediments into any aquifers that may be present in the system. If the temperature and pressure environments in the consolidating sediments have been conducive to the maturation processes that transform organic matter into mobile petroleum, this entrained petroleum is driven into the aquifers with the water.

It has been recognized since early in the century (see Rich, 1921) that secondary migration of petroleum is brought about by the movement of groundwater in the reservoir rocks. It is the water that provides the transporting medium for the immiscible petroleum droplets that ultimately accumulate to form oil pools. Toth (1970) has noted that the accumulation of petroleum requires the favorable interaction of at least three processes: (1) continuous import of hydrocarbons, (2) separation and preferential retention of the dispersed hydrocarbons from the transporting water, and (3) a continuous removal of water discharged of its hydrocarbon content. The first and third processes require a suitable flow system. On the second point, it is usually assumed that the separation of petroleum from water takes place under the influence of pressure changes, temperature changes, or salinity changes. Any of these can lead to a flocculation of the entrained petroleum droplets into larger discrete oil accumulations until phase continuity is achieved and
buoyancy effects can come into play. Since oil and gas both have densities less than water, they become concentrated in the upper parts of the flowing aquifers. Oil pools arise where anticlinal structures or stratigraphic complexities create a trap for the low-density petroleum. Levorsen (1967) reviews the various geological conditions that give rise to traps. Hubbert (1954) discusses the capillary mechanism in a two-phase oil-water system that explains the efficiency of a low-permeability interface as a barrier to petroleum migration. In the following subsection, Hubbert's ideas will be traced further with respect to the interaction between petroleum entrapment and the subsurface hydraulic-potential field.

**Hydrodynamic Entrapment of Petroleum**

Movement of oil, gas, and water through a porous medium is an example of immiscible multiphase flow. As noted near the close of Section 2.6, the analysis of such systems is extremely complex. It is necessary to consider separate Darcy equations for each of the fluids flowing simultaneously through the system. It is also necessary to determine the effective permeabilities of the porous medium to each of the phases. Because the permeability of the medium is different with respect to each fluid, the magnitudes of the Darcy velocities for each phase will be different from one another.

Hubbert (1954) has shown that not only are the magnitudes of the three velocity vectors different, but so are the directions. In explanation of this point, consider first the diagram shown in Figure 11.3(a) for a single-phase fluid. The direction of movement of a unit mass of fluid at the point \( P \) is perpendicular to the

![Figure 11.3](a) Components of the impelling force \( E \) acting on a unit mass of water at a point \( P \) in a steady-state groundwater flow system; (b) Impelling forces on water, oil, and gas in a three-phase steady-state flow system (after Hubbert, 1954).
lines of equal hydraulic potential. The force acting on the unit mass in the direction of movements is denoted by $E$. Recall from Eq. (2.15) that the hydraulic potential $\Phi$ is defined as

$$\Phi = gz + \frac{p}{\rho}$$  \hspace{1cm} (11.4)$$

where $p$ is the fluid pressure and $\rho$ is the fluid density. In that the potential is defined in terms of energy per unit mass, the work required to move the unit mass from the potential $\Phi + d\Phi$ to the potential $\Phi$ is simply $-d\Phi$. With reference to Figure 11.3(a), it is also clear that the work is equal to $E \, ds$. Therefore, we have

$$E = -\frac{d\Phi}{ds}$$  \hspace{1cm} (11.5)$$

or, invoking Eq. (11.4),

$$E = g - \frac{\nabla p}{\rho}$$  \hspace{1cm} (11.6)$$

where $g$ is a vector with components $(0, 0, -g)$ and $\nabla p$ is a vector with components $(\partial p/\partial x, \partial p/\partial y, \partial p/\partial z)$. The vector $g$ acts vertically downward; the vector $\nabla p$ may act in any direction, and in general it will not be coincident with $g$. Figure 11.3(a) is a graphical presentation of Eq. (11.6).

In a three-phase system, the fluid densities are not equal. We have $\rho_w > \rho_o > \rho_g$, where the subscripts refer to water, oil, and gas, respectively. This fact leads to the vector diagram shown in Figure 11.3(b). This diagram provides a graphical explanation for the lack of coincidence of the directions and magnitudes of the impelling forces $E_w$, $E_o$, and $E_g$. The hydraulic gradients for each of the phases will be in the direction of their respective impelling forces.

The practical manifestation of this phenomenon is the hydrodynamic entrapment of petroleum as proposed by Hubbert (1954). In Figure 11.4 the oil and water equipotentials are shown superimposed on one another for a case where there is a buoyant upward movement of oil in an aquifer in which the flow of groundwater is from left to right. Hubbert (1954) shows that the slope of the tilted oil-water interface, $dZ/dl$, is given by

$$\frac{dZ}{dl} = -\frac{\rho_w}{\rho_w - \rho_o} \frac{dh}{dl}$$  \hspace{1cm} (11.7)$$

The interface will be horizontal only if there is no hydraulic gradient. In order for a structure or monocline to hold oil, the dip of the permeability boundary in the direction of fluid movement must be greater than the tilt of the oil-water interface. Otherwise, the oil will be free to migrate downdip along with the water. In areas where high hydraulic gradients lead to relatively fast groundwater flow, traps with steeper closing dips are required to hold oil than in areas with low hydraulic gradients and slow groundwater flow. Conversely, in areas where dips are relatively
uniform, those parts of the basin with low hydraulic gradients produce more locations for oil entrapment than hydrodynamically more active zones.

**Regional Flow Systems and Petroleum Accumulations**

It should be clear from the previous two subsections that there are two sets of conditions that lead to the entrapment of petroleum. The first is the set of geologic conditions that control the occurrence of structural and stratigraphic traps, and the second is the set of groundwater flow conditions that control the hydrodynamic aspects of entrapment. In considering these latter properties, Tóth (1970) noted that petroleum accumulation should be enhanced by (1) long flow systems that encompass a sufficient volume of possible source rock; (2) static or quasi-static hydraulic zones, where hydrodynamic entrapment can be expected to be most efficient; and (3) ascending groundwater movement, whereby a continuous removal of water from the traps is ensured. In the western Canada sedimentary basin, where many petroleum fields are known, Hitchon (1969a, 1969b) and van Everdingen (1968b) showed that, on the basis of both hydraulic and geochemical evidence, large flow systems extending from the Rockies to the Canadian shield exist in the deeper formations of the basin. Tóth (1970) found statistical confirmation of his own hypotheses in several areas of Alberta. In these areas, his results indicate that the relative probability of hydrocarbons being associated with each of the three conditions are as follows: ascending limbs, 78%; quasi-static zones, 72%; and large regional systems, 72%.
Hitchon and Hays (1971) applied a similar approach in the Surat basin of Australia. They found that hydrocarbon occurrences are concentrated in one of the discharge areas of the basin. However, they are not limited to this area, and there are large portions of the same discharge area that have not yet yielded petroleum. The deposits occur at depth in an area of upward-rising groundwater but not at points with particularly low gradients.

A basic fact that must be kept in mind (van Everdingen, 1968b) when dealing with the influence of major circulation systems on petroleum accumulation is the certainty that present-day hydrodynamic potential distributions are of recent geologic origin. The current topography in western Canada, for example, probably emerged in the late Tertiary. During pre-Tertiary times, potential distributions must have been different if for no other reason than the absence of the high relief recharge areas provided by the Rocky Mountains. It may be necessary to unravel paleohydrogeologic regimes to fully understand the interactions between groundwater flow and petroleum accumulations.

**Implications for Petroleum Exploration**

The results of Tóth (1970) and Hitchon and Hays (1971) are probably representative of the success thus far in relating present-day groundwater flow systems and petroleum accumulations. The relationships are discernible but far from universal. What should be clear from this discussion, however, is that in the search for oil an understanding of the existing three-dimensional subsurface flow system and its genesis is of an importance comparable to the knowledge of the stratigraphy and structure of a sedimentary basin. Hubbert (1954) notes that if hydrodynamic conditions prevail, as they almost always do, it is important that their nature be determined in detail, formation by formation over the entire basin in order that the positions of traps can be better determined and otherwise obscure accumulations of petroleum are not overlooked.

Hitchen (1971) makes the additional case that interpretations of geochemical exploration for petroleum should take the regional groundwater flow systems into account. He also notes that although surface prospecting for oil has been somewhat equivocal, the lack of success may not rest on any fundamental breakdown in the logical sequence of events between the occurrence of the indicator in the oil field and its appearance at the surface but rather on the usual absence of a careful examination of the possible subsurface flow routes by which hydrocarbons may be carried to the surface.

11.3 **Groundwater and Thermal Processes**

On a global scale the earth’s thermal regime involves the flow of heat from the deeper layers of the planet toward its surface. The *geothermal gradient* that gives evidence of this heat-flow regime has been widely measured by geophysicists involved in terrestrial heat-flow studies. On average, the temperature increases
approximately 1°C for each 40 m of depth. However, this gradient is far from uniform. In the upper 10 m or so, diurnal and seasonal variations in air temperature create a zone that is thermally transient. Beneath this zone the effects of air temperature are quickly damped out, but anomalous geothermal gradients can arise in at least three additional ways: (1) as a result of variations in thermal conductivity between geological formations, (2) as a response to geologically recent volcanic or intrusive sources of heat production at depth, and (3) due to the spatial redistribution of heat by flowing groundwater. In this section we will examine this third mechanism as it pertains to natural groundwater flow, geothermal systems, and the thermal regimes that accompany pluton emplacement.

Before examining these specific cases, some general comments are in order. The simultaneous flow of heat and groundwater is a coupled process of the type introduced in Section 2.2. The flow of water is controlled by the pattern of hydraulic gradients, but there may also be additional flow induced by the presence of a thermal gradient [as indicated by Eq. (2.22)]. Heat is transported through the system both by conduction and convection. Conductive transport occurs even in static groundwater. It is controlled by the thermal conductivity of the geological formations and the contained pore water. Convective transport occurs only in moving groundwater. It is the heat that is carried along with the flowing groundwater. In most systems convective transport exceeds conductive transport.

It is common to distinguish between two limiting types of convective heat transfer. Under forced convection, fluid inflows and outflows are present and fluid motion is due to the hydraulic forces acting on the boundaries of the system. Under free convection, fluid cannot enter or leave the system. The motion of the fluid is due to density variations caused by the temperature gradients. In the analysis of forced convection, density gradients are ignored and buoyancy effects are considered negligible; in free convection the fluid motion is controlled by buoyancy effects. The transport of heat by natural groundwater flow systems is an example of forced convection. Geothermal systems in which water-steam phase transitions occur are usually analyzed as free convection. Many geothermal systems include a combination of both phenomena. One refers to such conditions as mixed convection.

**Thermal Regimes in Natural Groundwater Flow Systems**

Consider a vertical two-dimensional cross section through a geological system that is thermally and hydraulically homogeneous and isotropic. Let us first examine a case, such as that shown in Figure 11.5(a), in which groundwater conditions are static. Hydraulic heads throughout such a system will be equal to \( z_0 \), the elevation of the horizontal water table that is the upper boundary of the system. Figure 11.5(b) displays the boundary-value problem that would represent the steady-state heat-flow regime for this case. The temperature, \( T_s \), on the upper surface is the mean annual air temperature. The vertical boundaries are insulated against horizontal heat flow. The vertical temperature gradient \( dT/dz \), on the base of the
system is equal to the geothermal gradient, $G$. The resulting isotherms are horizontal. Groundwater temperatures in the upper 100 m of the regime would be expected to be 1–2°C greater than the mean annual air temperature, in accordance with the uniform geothermal gradient.

Figure 11.5(c) and (d) is generalized from the results of Parsons (1970) and Domenico and Palciauskas (1973), each of whom studied the influence of regional groundwater flow systems on temperature distributions. Domenico and Palciauskas utilized analytical solutions to the coupled boundary-value problem; Parsons used numerical solutions and provided field evidence to support his findings. Figure 11.5(c) is the simple regional flow system first introduced in Chapter 6. Figure 11.5(d) shows how the thermal regime is altered by the convective heat transport. The geothermal gradient is greater near the surface in discharge areas than it is in recharge areas. It increases with increasing depth in recharge areas, and decreases with increasing depth in discharge areas. Domenico and Palciauskas (1973) show that the effects are more pronounced in flow regions in which the depth of the basin is of the same order of magnitude as the lateral extent, and less pronounced in shallow flow systems of large lateral extent. Parsons (1970) shows that the effects are greater in high-permeability deposits, where groundwater flow velocities are larger, than in low-permeability deposits, where velocities are small.
Cartwright (1968, 1974) has described methods whereby soil temperatures and shallow groundwater temperatures can be used in the field to distinguish recharge areas and discharge areas and to prospect for shallow aquifers. Schneider (1962) showed that local subsurface temperature anomalies can be used to detect infiltration from surface-water sources.

Stallman (1963), in presenting the equations of flow for the simultaneous flow of heat and groundwater, suggested that the measurement of vertical groundwater-temperature profiles might provide a useful method for estimating groundwater velocities. Bredehoeft and Papadopoulos (1965) provide a solution of Stallman's equations for one-dimensional, vertical, steady flow of groundwater and heat. They provide a set of type curves whereby groundwater velocities can be calculated from temperature data. If head measurements are also available, their method can be used to calculate vertical hydraulic conductivities.

Geothermal Systems

In recent years there has been considerable interest in the development of geothermal power, and this interest has led to increased research into the nature of geothermal systems. Elder (1965) and White (1973) provide excellent reviews of the characteristics of geothermal areas and the physical processes associated with them. Witherspoon et al. (1975) review the various mathematical models that have been proposed for simulating geothermal systems.

Geothermal energy is captured by removing the heat from hot waters that are pumped to the surface through wells. Geothermal reservoirs of practical interest must have temperatures in excess of 180°C, an adequate reservoir volume, and a sufficient reservoir permeability to ensure sustained delivery of fluids to wells at adequate rates. The shallower the geothermal reservoir, the more economically feasible is its exploitation. For this reason much interest has centered on an understanding of the mechanisms that can lead to high-temperature fluids at shallow depths. It is now clear that this situation is usually brought about by hydrothermal convection systems in which most of the heat is transported by circulating fluids. Two mechanisms can be envisaged. The first is the forced-convection system suggested by White (1973) and shown in Figure 11.6(a), whereby a local flow system is recharged and discharged vertically through high-permeability fracture zones and heated at depth during residence in more permeable strata. This configuration can give rise to geysers and hot springs at the surface in the discharge zone. Donaldson (1970) has described a simple quantitative model for the simulation of systems of this type.

The second mechanism is one of free convection in a confined aquifer at depth. As shown in Figure 11.6(b), a system in which the upper and lower boundaries of an aquifer are impermeable to fluid flow but conductive to heat flow will lead to the establishment of convective cells of fluid flow that distort the uniform geothermal gradient in the aquifer and create alternating hot spots and cool spots along the upper boundary. This type of convective flow has been known in pure
fluid mechanics since early in the century. Its importance to geothermal processes was brought to the attention of geophysicists by Donaldson (1962).

Regardless of the mechanism that brings hot fluid to shallow depths, geothermal systems can be further classified (White, 1973) into \textit{hot-water systems} and \textit{vapor-dominated systems}. In the hot-water type, water is the continuous phase throughout the system and thus provides the pressure control. In the vapor-dominated type, steam is the continuous pressure-controlling phase, although there is general agreement that liquid water is usually present as well. Because a few geothermal systems produce superheated steam with no associated liquid, vapor-dominated systems are sometimes called \textit{dry-steam systems}. The thermodynamics of steam-water geothermal systems under free and forced convection is an advanced topic of current interest to hydrogeological researchers.

Because the configuration of characteristics necessary to create an exploitable geothermal field occurs only rarely, the resource does not appear to offer any kind
of panacea to man's energy problems. White (1973) summarizes the geothermal-power-generating capacity of the world as of 1972.

In those areas where geothermal resources are economically significant, there is much ongoing research into the application of simulation models of heat flow/fluid flow systems. Mercer et al. (1975), for example, have developed a single-phase, two-dimensional, horizontal, finite-element model for the hot-water aquifer in the Wairakei geothermal system in New Zealand. The future hope is that models of this type will be able to increase the efficiency of exploitation of geothermal heat by aiding in the optimal design of well spacings and pumping rates in a similar manner to the conventional aquifer models discussed in Chapter 8. However, it is not yet clear whether the great expense and technical difficulty of obtaining the necessary data from great depth in hot systems can be overcome. Until its applicability is confirmed in the real world, geothermal simulation remains a potentially powerful but as yet unproven tool.

**Pluton Emplacement**

Norton and Knight (1977) have studied a heat flow/fluid flow system of considerable geological importance. They utilized a numerical mathematical model to simulate the thermal regime following pluton emplacement at depth. Figure 11.7 shows the boundary-value problem that they considered. The system is insulated against heat flow at the base and conductive on the other three sides. The system is one of free convection, in that the region is surrounded on all four sides by boundaries that are impermeable to fluid flow. Norton and Knight carried out transient simulations that show the time-dependent growth and decay of the anomalous thermal regime. The right-hand side of Figure 11.7 shows the temperature field 50,000 years after emplacement of a pluton at 920°C into a host rock with

![Figure 11.7](image-url)
an initial geothermal gradient of 20°C/km. The field is symmetric about the center line. The left-hand side of the diagram shows one of the two symmetric convective fluid-circulation cells at the same point in time. In the original paper the authors also showed some example pathlines (Section 2.8) that indicate the paths followed by individual particles of water during the transient event. They conclude that waters in natural pluton systems move away from their points of origin to positions several kilometers away in a few hundred thousand years. Such large-scale fluid circulation is of great importance in understanding the genesis of hydrothermal mineral deposits that are often associated with plutonic environments.

11.4 Groundwater and Geomorphology

*Karst and Caves*

A landscape that exhibits irregularities in surface form caused by rock dissolution is known as a *karst* landscape, after the characteristic Karst Region of Yugoslavia. Karst landscapes are usually formed on limestone and to a lesser extent on dolomite, but they can also develop in areas of gypsum or rock salt. Processes in carbonate rock will be the focus of this discussion.

The irregularities of the land surface in karst areas are caused by surface and subsurface removal of rock mass by dissolution of calcite or dolomite. Karst areas normally have caves developed as a result of dissolution along joints, bedding planes, or other openings. In major karst regions thousands of kilometers of caves exist, extending in places to depths of more than 1 km. In some parts of the world, networks of caves exist in areas where the original karst nature of the landscape has been obliterated by more recent geomorphic processes, such as glaciation or alluviation.

Thraikill (1968) states that investigations of limestone caves by various geologists have led to three generalizations with regard to cave origin: (1) most limestone caves are the result of solution by cold meteoric waters, (2) many of these solution caves were excavated when the rock was completely filled with water, and (3) some of these sub-water-table caves exhibit horizontal surfaces or horizontal distribution passages that are unrelated to bedding or other structures of the enclosing rocks.

It is evident that limestone at the start of the cave-forming process must have some open joints or bedding planes, or possibly well-connected pores. Of the innumerable open joints and bedding planes in karst areas, only a few are ultimately enlarged to form cavern passages. A combination of factors causes larger distances of penetration of calcite-undersaturated water in a small number of openings. This ultimately leads to preferential enlargement of these openings. This, in turn, causes more of the flow to be captured by the enlarged channels, and through the amalgamation of these channels the process of cavern development proceeds.

Figure 11.8 shows an example of a horizontal cave that cuts across joints and bedding planes. Such caves are believed to have formed in shallow sub-water-table
zones. This situation is intuitively reasonable when one considers the fact that channel or cavern enlargement must be accomplished by flowing groundwater that is undersaturated with respect to calcite. As the water flows in the rock, it will approach saturation and thus have less capability for enlarging the flow passage.

The most difficult problem in understanding the origin of caves is how to account for the occurrence of undersaturated water at considerable distances from ground surface. As indicated in Chapter 7, it is well known from laboratory experiments that water in contact with limestone attains saturation quickly relative to natural flow rates in karst limestone. The laboratory experiments by Howard and Howard (1967) are particularly illustrative of this process. Thraikill (1968) has concluded that the uptake of CO$_2$ in the soil bears little direct relation to cave excavation in the sub-water-table zone. Observations above the water table of the chemical character of water moving downward through secondary openings indicate that this water is typically saturated or supersaturated with respect to calcite, often as a result of the combined effects of calcite dissolution and off-gassing of CO$_2$. If this type of subsurface water is not aggressive with respect to the rock, we are faced with a dilemma with regard to channel enlargement in the sub-water-table zone. To produce the necessary undersaturated water in shallow sub-water-table zones, the following mechanisms have been suggested: (1) changes in groundwater temperature, (2) mixing of dissimilar waters, (3) floods in surface streams or rapid snowmelt causing large rapid recharge of undersaturated water, and (4) production of acid along the paths of flow.

It can be shown with the aid of geochemical reasoning that when some types of calcite-saturated waters mix, the mixed water is slightly undersaturated, providing that the original solutions have different CO$_2$ partial pressure (Wigley and Plummer, 1976) or temperatures (Thraikill, 1968). Since water in the shallow sub-water-table zone is commonly a mixture of waters from various inflow areas or fracture zones, and because only very slight undersaturation is necessary to excavate a cave over geologic time, this mechanism is often cited in discussions.
of cave genesis. It has proved difficult, however, to obtain corroborative data in the field.

Thraikill (1968) indicates that many of the processes thought to be important in cave excavation will operate most effectively during floods. He indicates that the shapes of some caverns suggest that the most active enlargement was localized between a low and a high water table.

Moore and Nicholas (1964) suggest that in some cases oxidation of small amounts of sulfide minerals, especially pyrite, may cause a decline in groundwater pH and, consequently, create cavern enlargement by calcite dissolution. Dissolved oxygen would be the most active oxidizing agent. If this process occurs, one would expect it to be limited to shallow zones, where dissolved oxygen in the groundwater is most abundant.

In summary, karst and caves are perhaps the most dramatic evidence of the ability of flowing groundwater to alter the form of the earth's surface and subsurface. It does not require special knowledge to recognize that limestone is sculptured and excavated by chemically aggressive water. On closer inspection, however, it is clear that a fuller understanding of cave genesis offers ample room for the application of hydrologic and geochemical concepts that involve complex interactions in time and space. Holland et al. (1964), Howard (1964a, 1964b), Thraikill (1968), and Ford and Cullingford (1976) provide more comprehensive discussions of the processes of fracture enlargement and cave genesis.

Natural Slope Development

The processes that lead to natural slope development have been described both qualitatively and quantitatively in great detail by Carson and Kirkby (1972). They note that any slope morphology can be viewed as the outgrowth of a two-step process whereby material must first be loosened from the bedrock by weathering before it can be moved downslope by a wide variety of possible transport processes. The saturated-unsaturated subsurface flow regime on the hillslope is an important element in both steps of the process.

Weathering of bedrock at the base of a soil is largely a chemical process. The principles and conceptual models outlined in Chapters 3 and 7 provide a suitable basis for understanding the mineral dissolution processes that lead to soil formation. Carson and Kirkby (1972) note further that in humid regions the chemical dissolution of material by groundwater and its downslope transport in solution can be a major form of hillslope erosion in its own right, in some cases of the same order of magnitude as all forms of mechanical erosion combined. The high dissolved loads of many rivers reflect the effectiveness of chemical removal as a transport agent. Carson and Kirkby (1972) provide a synthesis of data available from the United States that relates dissolved load concentrations in streams to mean rates of surface lowering by solution. For a watershed in the southern United States with mean annual runoff of 20 cm, an average solute concentration of 200 ppm in the gaged streams represents a rate of denudation of 0.003 cm/yr.
The downslope transport of material by mechanical means occurs both as discrete mass movements in the form of landslides, slumps, and earthflows, and as sediment transport in surface runoff. The influence of pore pressure distributions created by hillslope flow systems on the occurrence of slope instabilities was treated in Section 10.1. The concepts and failure mechanisms described there, in a geometrical context, are equally valid when examining the role of landslides as a process in landform evolution. We will not repeat that treatment here; rather, following Kirkby and Chorley (1967), we will examine the implications of the various mechanisms of streamflow generation, as outlined in Section 6.5, on the processes of surface-water erosion.

The classic analysis of hillslope erosion is a direct outgrowth of Horton’s (1933) concepts of streamflow generation. The Horton model presumes the widespread occurrence of overland flow. In that, the depth and velocity of overland flow on a hillslope will increase downslope, there should be some critical point at which the flow becomes sufficient to entrain soil particles from the slope. Below this boundary, stream channels will develop as a consequence of this erosion.

Kirkby and Chorley (1967) note that the Horton model is most appropriate on bare slopes in arid regions. However, on vegetated slopes in humid regions, the transfer of rainfall to runoff by means of subsurface stormflow or by the mechanisms proposed by Dunne and Black (1970a, 1970b), whereby overland flow is restricted to near-channel wetlands, are more likely to be encountered. Under these circumstances, surface erosion due to overland flow will be restricted to lowland areas adjacent to stream courses. Headward erosion of tributary streams will occur by piping (Section 10.2) at the exit points of subsurface seepage paths. The locations of these points of seepage are controlled in large part by the subsurface distribution of hydraulic conductivity. In this indirect way, subsurface stratigraphy exerts a strong influence on the density and pattern of the drainage network that develops in such a watershed. In summary, the relative positions of the saturated wetlands, variable source areas, and subsurface seepages that control the nature of the erosive processes on a hillslope in humid climates are a direct reflection of the subsurface saturated-unsaturated hydrogeologic regime.

**Fluvial Processes**

The classic approach to the analysis of bedload transport in streams completely neglects the effect of seepage forces in the bed. It is well established that river beds are either losing or gaining water in terms of subsurface flow, but it is not clear whether or not the seepage forces created by these flows play a significant role in streambed processes and the evolution of river morphology. This question has been addressed in a paper by Harrison and Clayton (1970), but their results are somewhat equivocal.

The inspiration for their study was a set of observations on an Alaskan stream in which the authors noticed striking contrasts between those portions of the stream accepting influent groundwater seepage and those portions losing water by effluent seepage. The gaining reach of the stream was transporting pebbles and cobbles
as large as a few inches, whereas the losing reach was transporting sediment no larger than silt or very fine sand. The competence of the gaining reach, defined as the maximum size of particle that will undergo incipient motion at a given stream velocity, was 500 times greater than that of the losing reach. In that this variation in competence could not be explained by differences in stream velocity, channel slope, or bank sediment, Harrison and Clayton concluded that differences in the seepage gradients in the streambed were responsible for the great increase in competence of the gaining reach. This conclusion seemed logical, in that upward seepage in the gaining reach should buoy up the grains in the streambed, reducing their effective density and allowing them to be transported at velocities much lower than normal.

To test this hypothesis, a laboratory study was initiated. Results of the experiments, contrary to expectation, showed that seepage gradients had little influence on competence. The only effect confirmed in the laboratory experiments concerned downward seepage in channels with a large suspended sediment load. Under these conditions, a mud seal tended to form on the streambed. This mud seal discouraged the entrainment of bed material in the sealed area. In retrospect, the authors concluded that the Alaskan field observations might well be explained by this mechanism.

Vaux (1968) carried out a study of the interactions between streamflow and groundwater flow in alluvial streambed deposits in a completely different context. His interest centered on the rate of interchange between stream water and groundwater as it affects the oxygen supply in salmon spawning grounds. He utilized an analog groundwater model to assess the controlling features of the system.

Glacial Processes
An understanding of glacial landforms is best achieved through an examination of the mechanisms of erosion and sedimentation that accompany the advance and retreat of glaciers and continental ice sheets. It is now widely recognized (Weertman, 1972; Boulton, 1975) that the occurrence of pore water in the soils and rocks that underlie an ice sheet exerts an important influence on its rate of movement and on its erosive power. The existence of water at the base of a glacier is a consequence of the thermal regime that exists there. Heat, sufficient to melt the basal ice, is produced by the upward geothermal gradient and by the frictional generation of heat due to sliding.

Let us consider the flow of glacier ice across saturated, permeable rock. The movement of glacier ice involves yet another application of Terzaghi's concept of effective stress as presented in Section 2.9. High pore pressures lead to reduced effective stress at the ice-rock boundary and rapid rates of advance. Low pore pressures lead to increased effective stress and slow rates of advance. Similar mechanisms have been considered in the application of Mohr-Coulomb failure theory to the analysis of landslides (Section 10.1) and in the Hubbert-Rubey theory of overthrust faulting (Section 11.1).

Glacial erosion occurs both by abrasion and by quarrying. Abrasion of surficial
bedrock by sliding ice is caused by the grinding action of glacial debris that becomes embedded in the sole of the glacier. Its presence there is evidence of the quarrying abilities of flowing ice to pluck material from jointed rock and unconsolidated sediments at other points along its travel path. In areas where permeable subglacial units exist, the fluid pressures in these layers can exert considerable influence on both of these erosive mechanisms. Boulton (1974, 1975) provides a quantitative analysis of the role of subglacial water in both abrasion and quarrying.

Clayton and Moran (1974) have presented a glacial-process model that places the glacial-erosion regime of a continental ice sheet in the context of the relationships between glacial flow, heat flow, and groundwater flow. Consider an ice sheet moving across a permeable geologic unit (Figure 11.9). Well back from the margins, where the flow of ice converges toward the glacier base, free water rather than permafrost should be present at the base, and pore-water pressures may be high. Because in this zone the glacier is not frozen to its base, sliding occurs and abrasion is the only mode of erosion. Near the margins of the glacier, on the other hand, ice flow diverges from the base, pore-water pressures are lower, the ice sheet is more likely to be frozen to its bed, and quarrying is the principal mode of erosion.

Moran (1971) and Christiansen and Whitaker (1976) provide a detailed description of the various glaciotectonic structures that can develop in glacial deposits due to large-scale block inclusion and thrust faulting at the glacier margins. Among the mechanisms suggested for the generation of the high porewater pressures that are a necessary condition for the development of these features are (1) the advance of the ice sheet over the pinchout of a buried aquifer, (2) the advance
of the ice sheet over debris containing buried ice blocks remaining from an earlier advance, (3) the consolidation of compressible sediments under the influence of the ice load, and (4) the rapid formation of a permafrost layer at the time of glaciation. These two latter concepts were first discussed by Mathews and MacKay (1960).

11.5 Groundwater and Economic Mineralization

The modern theories of groundwater hydrology have not as yet found widespread application in the field of mineral exploration. There is, however, great potential for their application on at least two fronts. In the first place, the genesis of many economic mineral deposits is closely bound to the physical and chemical processes that take place in the subsurface hydrologic environment. Much of the speculation into the modes of origin of various orebodies could benefit from hydrogeological analyses that utilize the flow-system approach of Chapter 6 and the hydrogeochemical concepts of Chapter 7. On a second front, it is clear that many anomalies uncovered during geochemical exploration could receive a more complete interpretation if groundwater flow theory were invoked in the search for the source. In the two subsections that follow, each of these questions will be briefly examined. There is a massive literature in the mineral exploration field and, apart from a few standard texts, our reference list is limited almost exclusively to those papers that invoke hydrogeological mechanisms or methodology.

**Genesis of Economic Mineral Deposits**

White (1968), Skinner and Barton (1973), and Park and MacDiarmid (1975) provide an excellent suite of recent references on economic mineral deposits and their genesis. Perusal of the ore-deposit classifications that they present makes it clear that there are very few types of deposits that do not in some way involve subsurface fluids. The direct influence of shallow groundwater is responsible for *supergene enrichment* in recharge areas, and for the deposition of *caliches* and *evaporites* in discharge areas. Residual weathering processes that lead to *laterites* also involve hydrologic processes.

By far the most important genetic mechanisms that involve subsurface flow are the ones that lead to *hydrothermal* deposits. White (1968) summarized the four-step process that leads to the generation of an ore deposit involving a hydrous fluid. First, there must be a source of ore constituents, usually dispersed in a magma or in sedimentary rocks; second, there must be solution of the ore minerals in the hydrous phase; third, a migration of the metal-bearing fluid; and fourth, selective precipitation of the ore constituents. White (1968) notes that very saline Na-Ca-Cl brines are potent solvents for such metals as copper and zinc. Proof that such brines exist lies in the fact that they are commonly encountered in deep petroleum exploration. There are three possible sources for these brines: magmatic, connate, and meteoric. *Connate* waters are those waters trapped in sediments at the time of their deposition. *Meteoric* waters are groundwaters that originated at the ground
surface. Deeply circulating meteoric waters can attain sufficient salinity only through such secondary processes as the solution of evaporites or membrane concentration (Section 7.7). The precipitation of ore minerals is brought about by thermodynamic changes induced in the carrier brine under the influence of cooling, pressure reduction, or chemical reactions with host rocks or host fluids. The processes are best understood by the use of mass-transfer calculations of the type pioneered by Helgeson (1970).

With these basic introductory concepts in hand, we will now limit our further discussion to consideration of a specific type of ore deposit that has been widely ascribed to mechanisms involving groundwater flow: lead-zinc-fluorite-barite deposits of the Mississippi Valley type.

The Mississippi Valley lead-zinc deposits (White, 1968; Park and MacDiarmid, 1975) are strata-bound in nearly horizontal carbonate rocks lacking congruent tectonic structures that might control their localization. They occur at shallow depths in areas remote from igneous intrusives. The mineralogy is usually simple and nondiagnostic, with sphalerite, galena, fluorite, and barite as the principal ore minerals. A wide variety of origins has been proposed for this type of deposit, but White (1968) concludes that deposition from deeply circulating, heated, connate brine is the mechanism most compatible with the available temperature, salinity, and isotopic data.

Noble (1963) suggested that the circulation of connate water may have been controlled by diagenetic compaction of the source beds. Brines expelled from the sediments in this way would then be transported through transmissive zones (Figure 11.10), which became the loci of major ore concentrations. The brines may have contained metals in solution prior to burial as well as metals acquired during the diagenesis of the enclosing sediments. Noble's theory is attractive in that it provides an integrated mechanism for the leaching of metals from a dispersed

![Figure 11.10](https://example.com/figure11.10.png)

**Figure 11.10** Idealized section showing aquifer transmitting mineralized brines of compaction from source beds (after Noble, 1963).
source, their migration through the geological system, and their concentration in high-permeability carbonate rocks.

McGinnis (1968) suggested a twist on Noble's theory whereby compaction of the source beds is accomplished by the loading provided by continental ice sheets. Under these circumstances, sedimentary brines would be forced to discharge near the margins of continental ice sheets in a manner similar to that described in the previous section in connection with Figure 11.9. The inspiration for McGinnis' explanation is the apparent clustering of Mississippi Valley type deposits along the southernmost extremity of continental glaciation and in the driftless area of Wisconsin.

Hitchon (1971, 1977) noted that oil pools and ore deposits in sedimentary rocks have several features in common. Both are aggregates of widely dispersed matter concentrated at specific sites where physical and chemical charges in aqueous carrier fluids caused unloading. He believes that the petroleum in the Zama-Rainbow oil field in northern Alberta and the Mississippi Valley type lead-zinc deposits of the nearby Pine Point ore body may have been sequentially unloaded from the same formation fluid. Both are located in the Middle Devonian Keg River Formation, and Pine Point is downstream from Zama-Rainbow in terms of the hydraulic head patterns that currently exist in the Keg River Formation. As an independent piece of evidence, Hitchon notes that petroleum is a common minor constituent in fluid inclusions from Mississippi Valley type lead-zinc deposits.

In closing this subsection it is worth noting, as has Hitchon (1976), that water is the fundamental fluid genetically relating all mineral deposits. It is the vehicle for the transportation of materials in solution and it takes part in the reactions that result in the original dissolution of the metals and their ultimate precipitation as ore. If the movement of subsurface water were to cease, chemical and physical equilibrium between the water and the rocks would eventually occur and there would be no further opportunities for the generation of mineral deposits. In this sense, the existence of subsurface flow is essential to the genesis of mineral deposits.

**Implications for Geochemical Exploration**

Hawkes and Webb (1962) define geochemical prospecting as any method of mineral exploration based on the systematic measurement of one or more chemical properties of any naturally occurring material. The material may be rock, soil, stream sediment, water, or vegetation. The objective of such a measurement program is the detection of abnormal chemical patterns, or geochemical anomalies, that might indicate the existence of an ore body.

Anomalous chemical patterns in groundwater or surface water are sometimes called hydrogeochemical anomalies. The most mobile metal elements, that is, the elements most easily dissolved and transported in water and therefore the most likely to produce hydrogeochemical anomalies, are copper, zinc, nickel, cobalt, and molybdenum (Bradshaw, 1975). Lead, silver, and tungsten are less mobile; gold and tin are virtually immobile. Because of the expense of drilling, groundwater
is seldom sampled directly, but springs and seepage areas are widely used in geochemical exploration. Figure 11.11 shows the various types of geochemical anomalies that might be expected to develop in the vicinity of an ore body. Groundwater plays an important role in delivering metal ions to the hydrogeochemical concentration zones in seepage areas and in lake and stream sediments.

Figure 11.11 Schematic diagram showing the development of geochemical anomalies in an area where bedrock is overlain by a residual soil (after Bradshaw, 1975).

Anomaly types: SL (R), residual soil anomaly; SP, seepage anomaly; SS, stream sediment anomaly; LS, lake sediment anomaly. The density of dots indicates anomaly strength.

Geology: 1, bedrock; 2, residual soil; 3, recent alluvium.

Other: OB, ore body; PPM, parts per million; % Cx, cold extractable concentration; →, groundwater flow direction.
One of the most successful applications of spring sampling techniques is that described by de Geoffroy et al. (1967) in the upper Mississippi Valley lead-zinc district. They sampled 3766 springs over an area of $1066 \text{ km}^2$. An interpretation of the measurements indicated 56 zinc anomalies. Of these, 26 coincided with known zinc deposits, and drill testing of a small number of the remaining anomalies confirmed the presence of zinc ore in their vicinity. In the carbonate terrain of this area, surface-water sampling is ineffective because the heavy metals are quickly precipitated from groundwater within a short distance of its emergence into the surface environment. De Geoffroy et al. (1967) conclude that spring sampling is the most satisfactory geochemical method in the search for ore bodies of moderate size in carbonate rocks.

There have been other instances of successful groundwater-oriented geochemical exploration programs. Among the most interesting conclusions are those of Graham et al. (1975), who found that fluorine in groundwater can act as a guide to Pb-Zn-Ba-F mineralization, and Clarke and Kugler (1973), who advocate dissolved helium in groundwater as an indicator for uranium ore. On a negative note, Gosling et al. (1971) report that hydrogeochemical prospecting for gold in the Colorado Front Range is unpromising.

Hoag and Webber (1976) suggest that sulfate concentrations in groundwater, because they are indicative of the oxidation environment of the sulfides that produce them, can be used to estimate the depth of mineralization of possible ore bodies. They note that this information might help determine what types of further exploration would be most helpful in locating possible sulfide deposits.

In all this, the recent developments in physical and chemical hydrogeology that have been reviewed in this book, are extremely pertinent. The rates at which metals are taken into solution from ore bodies by passing groundwater are controlled by the principles introduced in Chapter 3 and discussed in Chapter 7. The diffusion, dispersion, and retardation processes that accompany their transport by the groundwater system are identical to those described in Chapter 9 in connection with groundwater contamination. Perhaps the most direct suggestion for the application of groundwater flow theory in geochemical exploration has come from R. E. Williams (1970). He suggests that initial hydrochemical sampling be confined to discharge areas of regional flow systems. Once a geochemical anomaly has been located, the groundwater flow paths that lead to it would be determined by hydrogeological field mapping and the mathematical modeling methods introduced in Chapter 6.

**Suggested Readings**


