Polygonal mudcracks with large salt crystals growing between them in the Devil's Golf Course, Death Valley, California. (Photo © Tom Bean.)

14

Chemical and Nonepiclastic Sedimentary Rocks

This chapter discusses two unrelated groups of rocks: (1) chemical sedimentary rocks that are precipitated from solution inorganically (for the most part); and (2) a mixed group of miscellaneous sedimentary rocks generated (at least in part) by processes other than the weathering of pre-existing rocks.

The first group, chemical sedimentary rocks, includes (1) iron-rich sedimentary rocks such as banded iron formations and ironstones, and (2) evaporites. The dissolved components that precipitate to form these rocks are decomposed from pre-existing rocks and minerals. Iron-rich rocks and evaporites make up less than 2% of the total sedimentary rocks on Earth, but they are major sources of iron, many salts, and other chemicals.

The second group includes rocks that are nonepiclastic in origin. Unlike the epiclastic (mainly siliciclastic) sedimentary rocks discussed so far (all of which are produced by the mechanical disintegration of pre-existing materials), nonepiclastic rocks are generated by processes other than mechanical weathering. For example, while some **volcaniclastic** (literally, rich in fragments of volcanic rock and glass) sedimentary rocks are simply weathered and reworked from volcanic rocks, many are generated by processes other than weathering, such as explosive volcanism (which produces **pyroclastic** material). The term **volcanogenic** is used for all sedimentary deposits generated by volcanic processes. The impact of extraterrestrial objects (bolides) with the surface of the Earth produces **meteoritic** clastic sediment; folding and faulting generate **cataclastic** deposits; and the dissolution and collapse of cavern ceilings and walls produce **solution breccias.**

SOLUTION GEOCHEMISTRY

To understand chemical sedimentary rocks, we must begin with a general review of chemical solutions. Most chemical and biogenic sedimentary rocks form from seawater. The dissolved constituents in seawater are weathered from the continental blocks and carried to the oceans as runoff. Table 14.1 compares the chemistry of mean river water with that of seawater. **Salinity** is the total amount of dissolved con-

Table 14.1 Relative Abundance of Dissolved Ions in Mean River Water and Seawater

	Mean River Water[a] Total Dissolved Solids (%) (Salinity = 121 ppm or 0.0121%)	Seawater[b] Total Dissolved Solids (%) (Salinity = 35,000 ppm or 3.5%)
Bicarbonate $(HCO_3)^-$ and carbonate $(CO_3)^{2-}$	48.6	0.4
Calcium (Ca^{2+})	12.4	1.2
Amorphous silica (H_4SiO_4)	10.8	<0.01
Sulfate $(SO_4)^{2-}$	9.3	7.7
Chlorine (Cl^-)	6.5	55.0
Sodium (Na^+)	5.2	30.6
Magnesium (Mg^{2+})	3.4	3.7
Potassium (K^+)	1.9	1.1
Iron (Fe^{2+} and Fe^{3+})	0.6	<0.01
Aluminum $Al(OH)_4^-$	0.2	<0.01
Nitrate $(NO_3)^-$	0.8	<0.01
Total	99.7	99.7

[a] Livingston, 1963.

[b] Mason, 1966.

stituents in water. It is expressed either as parts per million (ppm) or as weight percent. The salinity of mean river water is 121 ppm, or 0.00121%. The salinity of seawater is much higher—35,000 ppm, or 3.5%. The major ions dissolved in river water and seawater are also quite different. Modern rivers contain mainly dissolved HCO_3 and CO_3, with minor amounts of Ca, H_4SiO_4, SO_4, Cl, Na, Mg, and K. Seawater contains principally SO_4, Cl, Na, and K. These differences in overall salinity and in the specific proportion of components dissolved in river water and seawater result from modern processes of chemical and biochemical sedimentation. They reflect the degree to which components are extracted from seawater (with or without the assistance of organisms) and incorporated into sediment and sedimentary rock.

The high overall salinity of seawater is due primarily to the buildup of two major constituents over time, sodium and chlorine. These occur in dilute solution in river water and are predominant in seawater because they are removed from solution and incorporated into sedimentary rocks very slowly. In fact, evaporite precipitation is the only way sodium and chlorine leave seawater, and they are the most important constituents of evaporite rocks. Calcium, silica, carbonate, and bicarbonate are abundant in river water but scarce in seawater. They are removed from seawater more rapidly than are sodium and chlorine and are incorporated into siliceous and calcareous sediments—chert and limestone (see Chapters 11 and 13).

The tendency of a component to remain in solution or to be selectively removed is expressed by the **residence time.** Residence time is measured in years and can be calculated easily by dividing the total mass of an ion in seawater by its annual mean flux (the amount of ion that enters and leaves the sea yearly). Table 14.2 lists residence times for major ions dissolved in seawater and the sedimentary rock types in which those components are eventually concentrated.

Ions with extremely long residence times, such as sodium and chlorine, are removed from solution very slowly. Such substances are not metabolized by organisms. The conditions that favor the inorganic precipitation of these ions require special circumstances; principally, the isolation of seawater in settings where the rate of evaporation exceeds the rate of precipitation and runoff.

Ions such as calcium, carbonate, bicarbonate, silica, and iron have extremely brief residence times because they are removed from seawater rapidly. The short residence time reflects the ease with which these ions are either metabolized by organisms and incorporated into shells (silica, bicarbonate, carbonate, and calcium) or extracted inorganically (iron and aluminum). Ions with intermediate residence times, such as potassium and magnesium, must be extracted by slower, more complex processes.

What are the sources of the various constituents? How are they removed from solution and incorporated into sediment? Most of the calcium and some bicarbonate (HCO_3), and carbonate (CO_3) dissolved in river water are derived from the dissolution of limestone and dolomite. Additional bicarbonate and carbonate come from the dissociation of carbonic acid (H_2CO_3). Carbonic acid is produced as falling rain absorbs atmospheric carbon dioxide. Almost all this dissolved bicarbonate, carbonate, and calcium is rapidly removed from seawater by organisms, forming limestone. Shallow marine organisms such as corals form reef complexes; algae produce lime mud and promote the accretion of ooids. Calcareous oozes are produced when the shells of floating, carbonate-secreting organisms such as foraminifera, coccoliths, and pteropods sink to the seafloor and, with burial and compaction, recrystallize as pelagic limestone.

Most of the silica dissolved in river water as H_4SiO_4 is a by-product of the weathering of feldspars to clay minerals. Like bicarbonate, carbonate, and calcium, the silica is rapidly removed from seawater by organisms. Pelagic radiolaria and diatoms form their shells (tests) of silica. These shells sink to the ocean floor and accumulate as siliceous oozes. Burial and compaction of these oozes cause their recrystallization as bedded chert.

Other important ions dissolved in river water do not show a dramatic dropoff in abundance in seawater and have residence times of intermediate length. For example, the relative proportion of magnesium dissolved in river water is almost identical to the proportion dissolved in seawater. Dissolved magnesium is derived largely from the weathering of such Mg-bearing minerals as dolomite, pyroxene, and amphibole. The relative proportion of potassium in seawater is about half that dissolved in river water. Most of this potassium is released during the hydrolysis of feldspar and muscovite to clay minerals. The longer residence times for both magnesium and potassium reflect the processes that systematically withdraw them from seawater. Dolomitization eventually consumes magnesium; some potassium is removed through absorption by clay minerals. Absorption converts gibbsite and kaolinite to illite.

The relative abundances of dissolved sulfate (SO_4) in river water and seawater are similar. Sulfate has a long residence time because no sedimentation process in the open ocean removes large amounts of it rapidly. Sulfate is eventually extracted from seawater and incorporated into such evaporite minerals as gypsum and anhydrite. Much dissolved sulfate is produced by volcanism and the weathering of sulfide minerals. Some is the undesirable by-product of the burning of sulfur-bearing coal. Burning coal injects sulfur gases into the atmosphere as SO_2 (which oxidizes to SO_3), where it is absorbed by rain and eventually ends up in seawater.

Table 14.2 Selected Ions Dissolved in Seawater: Their Residence Time and Ultimate Fate

Ion	Residence Time (years)[a]	Principal Sediment and Sedimentary Rock Sites
Chlorine	Infinity	Bedded evaporite
Sodium	260,000,000	Bedded evaporite
Magnesium	12,000,000	Dolomite, bedded evaporite
Potassium	11,000,000	Clay mineral diagenesis, bedded evaporite
Sulfate	11,000,000	Bedded evaporite
Calcium	1,000,000	Calcareous ooze, carbonate
Carbonate, bicarbonate	110,000	Calcareous ooze, carbonate
Silica	8000	Siliceous oozes, chert
Manganese	7000	Manganese nodules
Iron	140	Iron-rich sediment
Aluminum	100	Clay minerals, mudrocks

[a] Based on Ross, 1982, and Stowe, 1979.

Tiny amounts of iron are dissolved in river water; only a trace is found in seawater. Iron is typically found as a fine colloid rather than in true solution because ferric iron (Fe^{3+}) is extremely insoluble. Colloidal iron is usually flocculated along the coast as rivers enter the sea and is disseminated as a minor constituent in conventional siliciclastic sedimentary rocks. During certain times in the geologic past, however, conditions permitted the formation of unusual iron-rich sedimentary rocks.

IRON-RICH SEDIMENTARY ROCKS

Most iron dissolved in river water is derived from the chemical decomposition of iron-bearing minerals such as biotite and pyroxene. Ionic iron occurs in two forms. Ferrous iron (Fe^{2+}) is relatively soluble; ferric iron (Fe^{3+}) is essentially insoluble. In the presence of oxygen, ferrous ion almost immediately oxidizes (rusts) to ferric iron. Because oxygen is abundant in the modern terrestrial atmosphere, the predominant form of iron in most settings is the extremely insoluble ferric iron. As Table 14.1 shows, the already low abundance of iron in river water drops to nearly zero in seawater. The residence time of iron is very brief because it is removed rapidly and concentrated in modern sediment by inorganic flocculation (see Table 14.2).

Flocculation of iron has been important throughout the Phanerozoic. It occurs as soon as dissolved ferric iron (Fe^{3+}) enters the sea. The increased salinity of seawater and the presence of organic matter cause small particles of iron-rich material to crystallize. These particles adhere to one another, accrete, and settle to the seafloor. Ordinarily, only a small amount of iron is generated by flocculation. Flocculated iron particles are incorporated into ordinary sedimentary rocks, mainly as components of silicate minerals. Almost all sedimentary rocks contain some iron. A typical sandstone contains 2%–4% iron (weight percent FeO plus Fe_2O_3), mudrock contains 5%–6%, and limestone contains less than 1%.

Iron-rich sedimentary rocks are a special category defined by a total iron content that exceeds 15%. The two principal iron-rich sedimentary rock types, **Precambrian banded iron formations** and **Phanerozoic ironstones,** make up less than 1% of the sedimentary rocks in the geologic record but are of enormous importance. Virtually all the world's iron and steel comes from these rocks, particularly the Precambrian banded iron formations. The presence of abundant iron in the "iron ranges" of northern Minnesota and the Upper Peninsula of Michigan was critical to the industrial growth of the United States in the late 1800s. This iron was shipped in great iron boats through the Great Lakes to steel plants along the waterways of Pennsylvania, Ohio, and Michigan. The other essential ingredient, coal, came from the anthracite mines of the Appalachian belt in Pennsylvania and West Virginia. This is why the steel industry in the United States has long been concentrated in cities such as Pittsburgh and many

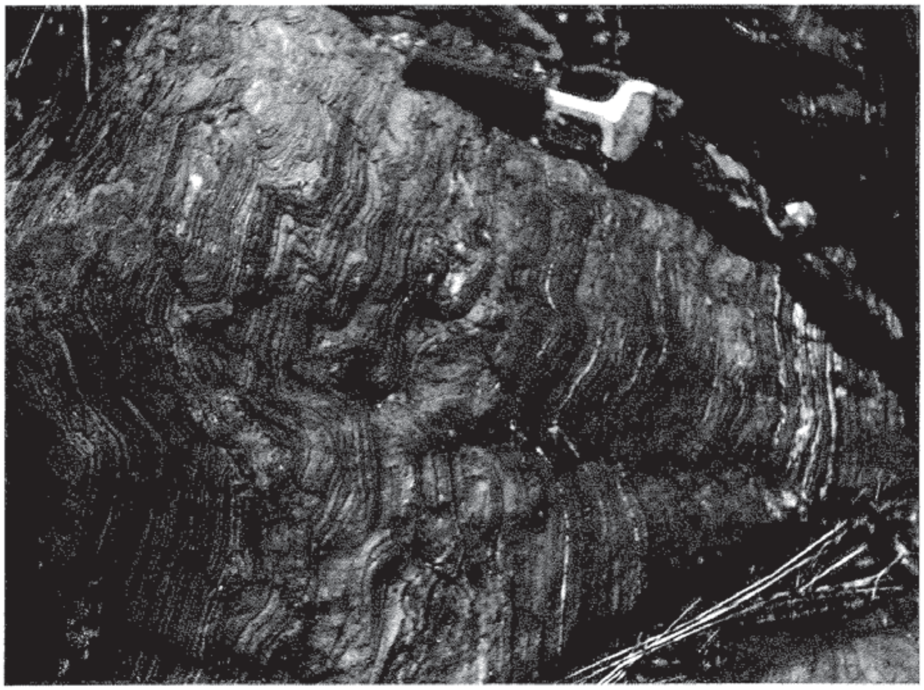


Figure 14.1

Contorted banded iron formation near Jasper Nob, Ishpeming, Upper Peninsula of Michigan. Note the characteristic alternating bands of chert (dark red) and iron (gray). (Photo courtesy of R. H. Dott, Jr.)

towns in eastern Ohio and why the auto industry grew up in Detroit.

Precambrian banded iron formations (**BIF** for short) consist of centimeter-thick interlayered alternating bands of chert and iron-rich minerals (Fig. 14.1). These formations are thought to be direct chemical precipitates, although organisms may have played some role in their genesis. Their restriction to the earlier Precambrian indicates that iron behaved differently in the first 1800 million years of Earth's history, possibly because of lower levels of free oxygen in the early terrestrial atmosphere. In the presence of the modern aerobic (containing abundant free oxygen) atmosphere, soluble ferrous (Fe^{2+}) iron is rapidly oxizided to extremely insoluble ferric iron (Fe^{3+}). As a result, iron can only be transported and deposited as clastic sediment. The texture and mineralogy of banded iron formations clearly indicate that iron was transported in solution and concentrated by precipitation. This means that iron survived over a long interval of time in its ferrous state. Such a condition would only occur in an anaerobic (or at least locally oxygen-poor) Precambrian atmosphere.

The other major iron-rich sedimentary rock, **Phanerozoic ironstone,** is actually a conventional siliciclastic sedimentary rock (mainly mudrock) in which a high percentage of iron is concentrated. The origin of ironstones is better understood than that of banded iron formations, but their unusual temporal and spatial distribution warrants some sort of special explanation.

Banded Iron Formations

No model to explain the origin of banded iron formations has won unanimous acceptance (Trendall and Morris, 1983). The banded appearance is caused by the intimate interbedding of millimeter- to centimeter-thick beds of gray to black chert and red to maroon iron-rich mudrock. Most banded iron formations are early Proterozoic in age (between 1800 and 2400 million years old). Some are Archean, and there are deposits as young as Cambrian. Deposits in the Canadian Shield have been studied the most extensively. Two major categories are recognized, Algoma type and Superior type.

Algoma-type Banded Iron Formations.

This variety is almost entirely of Archean age. Individual units are interbedded with deep-water graywackes, mudrocks, and submarine volcanic rocks in greenstone belts. These linear synformal belts of metasedimentary and metavolcanic rocks "float" in the "sea" of granite and high-grade metamorphic rocks that make up most Archean shields. BIF sequences range from a few millimeters to a few meters thick. They are lenticular in shape and of limited areal extent. Belts are a few kilometers wide and long. The principal iron minerals in these bands of delicately laminated ferruginous mudrock are the oxides hematite and magnetite. Small proportions of iron sulfide, iron carbonate, and iron silicate minerals also occur. Algoma-type deposits are interbedded with deep abyssal plain floor deposits. Their concentration along narrow zones that might coincide with ancient ocean crustal fractures has led to the suggestion that iron-bearing hydrothermal fluids served as the source of iron.

Superior-type Banded Iron Formations.

These lower Proterozoic rocks are striking in outcrop because of their spectacular banding (see Fig.14.1). Millimeter- to centimeter-thick layers of reddish iron-rich material alternate with gray to black layers of bedded chert. Sequences of this type are thicker and more extensively developed than Algoma-type deposits. Individual units range from fifty to several hundred meters thick and occupy broad belts a hundred or more kilometers wide and several hundred to more than a thousand kilometers long. BIFs of the Superior-type are intimately associated with stable shallow-water shelf sediments such as quartz arenite, limestone, dolomite, and mudrock. Channels, desiccation cracks, cross-bedding, and ripple marks are common. Oolites and intraclasts of iron-rich minerals are abundant.

Origin.

There is considerable difference of opinion about how these deposits form, but most speculation centers on the properties of the early terrestrial atmosphere. Some geochemists argue that initially low levels of atmospheric oxygen (which imply higher partial pressure of atmospheric carbon dioxide) led to more acidic rainfall and lower pH levels in Archean and Proterozoic ocean waters (Garrels et al., 1973; Clemmey and Badham, 1982). These factors would increase the amount of iron leached during weathering. Lower levels of atmospheric oxygen would also slow the oxidation of soluble ferrous iron to insoluble ferric iron, permitting large volumes of leached iron to be transported to the oceans in solution.

One of the most popular models (Holland, 1973; Klein and Beukes, 1989) suggests that Proterozoic oceans were stratified into deeper masses of anoxic bottom waters containing large amounts of iron, and

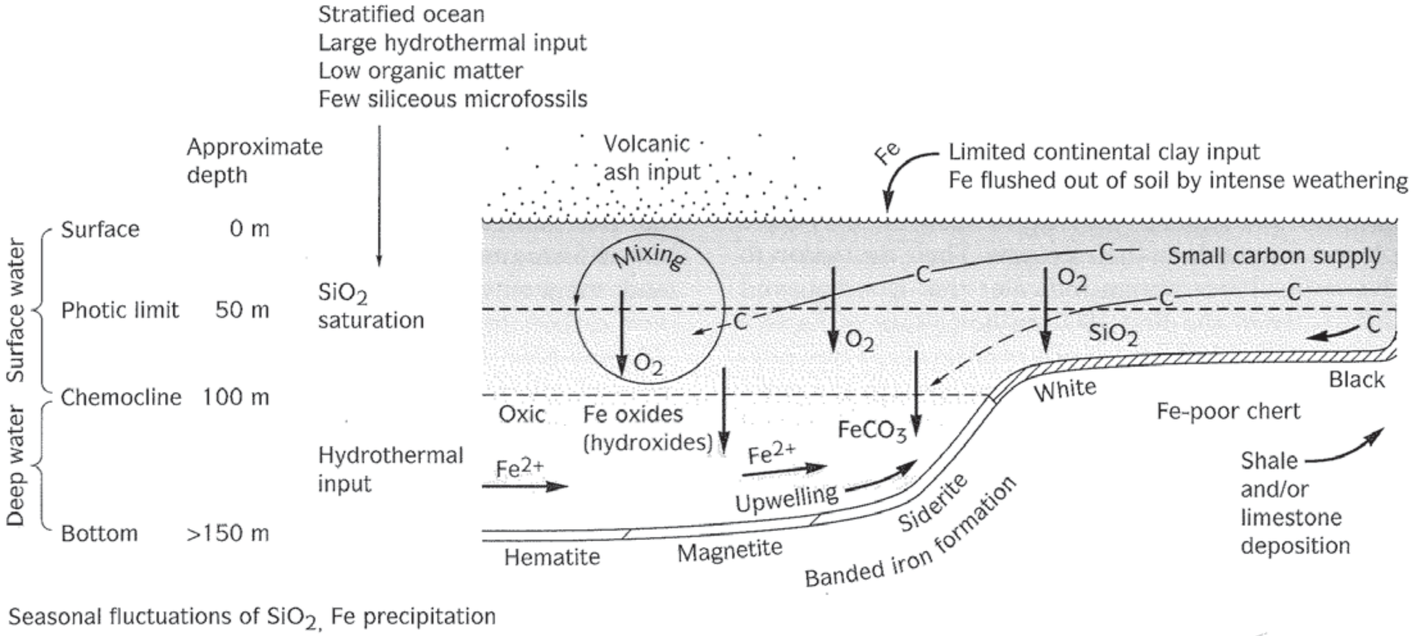


Figure 14.2

Depositional model for banded iron formations. (Modified from Beukes and Klein, 1993.)

less dense, more oxic surface waters (Fig. 14.2). This model postulates that periodic overturning of these ocean waters and upwelling onto subjacent shelf areas generated alternating episodes of chert precipitation and deposition of iron-rich mudrock. Although some of this iron may have been weathered from the continental blocks, the lack of clays in the cherty BIFs suggests that most of the iron was released from submarine vents. Studies of modern hydrothermal vents in mid-ocean ridges show that they contain 10^5 times more iron than typical seawater.

Primitive plants and animals probably played an important role in forming both the iron bands and the interbedded chert, so perhaps these are not perhaps purely chemical sedimentary rocks after all (Cloud, 1973; Nealson and Meyers, 1990). Garrels (1987) hypothesized that seasonal changes in water temperature and geochemistry controlled organic activity.

Whatever the origin(s) of the BIFs, the conditions crucial for their formation were vanishing by about 1800 million years ago. The oldest oxidized hematite-rich soil horizons first appear at the same time, and detrital pyrite and uraninite (unstable in an oxidized atmosphere) disappear. These coincidences further suggest that the Earth's low atmospheric oxygen content was a major factor in controlling the deposition of BIFs; as oxygen levels began to rise, BIFs rapidly became rare.

Phanerozoic Ironstones

There are fewer Phanerozoic ironstones than banded iron formations, but their origin is better understood. They have a strikingly uneven distribution over time with a few peaks of development. Well-known units that mark these peaks include the Ordovician Wabana Formation of Newfoundland; the Silurian Clinton Formation in the Appalachians; and various Jurassic ironstones of Western Europe, such as the Minette deposits of Luxembourg and Alsace-Lorraine.

The iron in most ironstone deposits is concentrated in ooids (Fig. 14.3). Detrital nuclei are grains of quartz, feldspar, mica, and carbonate. The iron occurs as crystalline iron oxide (especially hematite and goethite) and iron silicate (chamosite) in the mineral layers coating the nuclei. Shells of shallow marine littoral and neritic fossils found within these deposits are partly or completely replaced by iron minerals.

Ironstone beds are a few meters to a few tens of meters thick. Body fossils, cross-bedding, ripple marks, bioturbation, and scour-and-fill structures are common, and ironstones are associated with shallow marine shelf deposits such as limestone, dolomite, mudrock, and sandstone. These features indicate that ironstones accumulated on nearshore shelves. Flocculation of iron-rich clays occurs when detritus

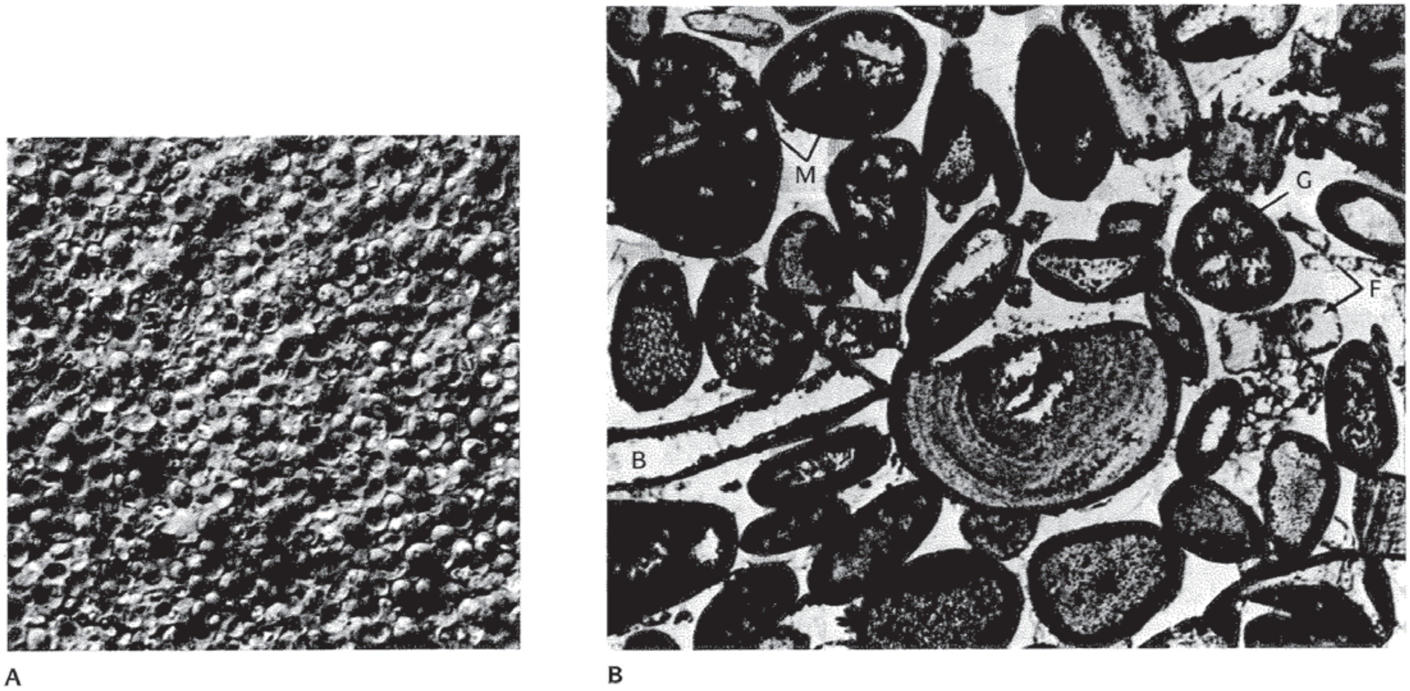


Figure 14.3

Phanerozoic ironstones and banded iron formations have very different textures. (A) Fractured surface of fresh oolitic ironstone from the Cretaceous of Nigeria. Ooids and matrix consist of siderite, magnetite, and chlorite, with iron hydroxides and clay minerals. Width of photo is 30 mm. (From Jones, 1965, *J. Sed. Petrology* 35:840; by permission of the SEPM.) (B) Oolitic hematite, Silurian Keefer Sandstone, Pennsylvania. Most ooid nuclei are crinoid fragments, but others have nucleated on fragments of brachiopods (B), gastropods (G), and intraclasts made of fossil fragments in a hematite matrix (M), presumably reworked from another part of the ironstone. Hematite permeates the fossil nuclei and their pores, but some of the fossils (F) are only slightly replaced and lack oolitic coatings. The rock has been cemented with clear, nonferruginous calcite. The crinoid in the center is 1 mm in diameter. (Photo courtesy of R. E. Hunter.)

comes into contact with seawater, promoting the snowball-like growth of ferruginous oolites. Van Houten (1982) was able to define a series of facies belts using iron minerals. Nearshore shallow-water deposits rich in hematitic oolites grade into an offshore belt of chamosite oolites and eventually into inner and outer shelf deposits characterized by glauconite, an iron-rich clay.

Although the uneven distribution of ironstones is puzzling, their origin has been linked to the erosion and redeposition of lateritic soils. Lateritic soils are typically produced when low-lying, iron-rich source rocks such as granite and other crystalline rocks weather in a warm, humid climate (see Chapter 6). This weathering promotes extensive leaching of iron and the buildup of a thick, near-surface soil layer of ferruginous laterite or ferricrete. Well-developed laterites containing more than 50% ferric oxide and hydroxide occur today in the tropical Amazon River Basin of South America where Precambrian shield rocks rapidly decompose to well-leached, ferruginous clayey soils.

The erosion of lateritic soils does not typically generate a coastal belt of ironstone sediment, however. Other special circumstances must be required. When conventional siliciclastic detritus is deposited at a rate equal to or exceeding the rate at which transported lateritic soil debris accumulates, ironstone is prevented from forming by sedimentary masking. The normal background sedimentation overshadows any accumulating lateritic material. Ironstone forms when the depositional site receives only iron-rich muddy detritus; that is, only when there is no supply of normal terrigenous debris.

The restricted distribution of ironstones in time and space confirms that conditions necessary for their formation seldom occurred during the Phanerozoic. Ironstone sedimentation requires the erosion of broad, low-lying source regions mantled with lateritic soil. The eroded material must be transported onto coastal plains that receive little additional siliciclastic detritus. Coincidentally, most of the Phanerozoic ironstones formed during the Ordovician through Devonian and during the Jurassic and Cretaceous. These were periods of greenhouse conditions, when the global climate was warm, ice caps vanished, and sea levels were unusually high (Van Houten and Arthur, 1989). These were also times of black shale deposition, as discussed in Chapter 6. Clearly, warm climates during greenhouse conditions would stimulate the type of deep weathering needed to release so much iron to the sea. Kimberly (1981) points out that minor regressive episodes within the globally high sea level are also needed, so that continental iron-rich muddy sediments can spread over the former seafloor. In this way, iron oxide–rich solutions can percolate down through the marine limestones and replace calcareous ooids.

Other Iron-Rich Sedimentary Rocks

Carbonaceous black shale and limestone containing 10- to 40 cm-thick layers in which crystals of pyrite (iron sulfide) are distributed are another type of iron-rich sedimentary rock. Pyrite forms only in locally reducing (anoxic) environments. The lack of oxygen results from several factors. In the modern Black Sea, for example, the absence of convective overturn prevents the replenishment of oxygen in organic-rich muds accumulating on the bottom. As a result, organic material ceases to decay and any iron present is reduced and recrystallized as pyrite. Ancient pyrite-bearing black shales may have formed in a similar setting.

Modern bog iron deposits represent another iron-rich sedimentary rock type. They consist mainly of the iron minerals goethite and siderite and various manganese minerals such as psilomelane and pyrolusite. They are well developed only in a few high-latitude swamps and lakes in the northern hemisphere. The slow influx of iron- and manganese-bearing acidic groundwater into oxygenated bodies of water seems to promote their formation. Dissolved ferrous iron crystallizes when pH rises.

Finally, irregularly shaped nodules of manganese and iron are scattered across lake bottoms and some portions of the modern deep seafloor. These nodules are rarely larger than a few centimeters in any dimension and are especially prominent in abyssal plain areas where little other sediment accumulates, especially on the flanks of mid-ocean ridges. Iron and manganese nodules result from exceedingly slow concentric accretionary growth. The ultimate source of the manganese and iron (submarine hydrothermal activity?) and the mechanism by which precipitation proceeds, whether organic (bacterial action?) or inorganic, are uncertain (Glasby, 1977).

EVAPORITES

Evaporites are bedded sedimentary rocks that crystallize from hypersaline solutions known as brines. Brines develop where the amount of water lost through the evaporation of seawater or terrestrial water exceeds freshwater influx from precipitation, surface flow, and groundwater inflow. High temperatures and the lack of precipitation found in arid climates promote brine formation.

More than 100 different minerals occur in bedded evaporite deposits, but few are abundant (Table 14.3). Most consist of highly soluble ions such as sodium and chlorine that have lengthy residence times. This fact underscores the scarcity of brines that are sufficiently saturated to permit minerals composed of these ions to precipitate. The most common evaporite minerals are carbonates (calcite, aragonite, magnesite, and dolomite); sulfates (gypsum and anhydrite); halides (halite, sylvite, and carnallite); and a few borates, silicates, nitrates, and sulfocarbonates.

The few regions of the world that are current sites of evaporite deposition are characterized by both very high mean temperatures and an annual rainfall that totals only a few centimeters. Such localities include the semiarid playa lakes scattered across the Great Basin in California and Nevada and the various hypersaline supratidal flats (sabkhas), salt pans, estuaries, and lagoons of the Persian Gulf region in the Middle East. These settings serve as natural laboratories for observing the processes by which evaporites form. But they may not be good analogs of the settings in which many ancient evaporites were deposited.

The few ancient evaporite deposits thought to be nonmarine consist of areally restricted, thin crusts of evaporite minerals. Most ancient sequences extend across broad regions and are hundreds or even thousands of meters thick. They must have been deposited on the floor of broad basins thousands of square kilometers in area.

In 1849, the Italian chemist Usiglio first evaporated a bucket of seawater and analyzed its contents.

Table 14.3 The Common Marine and Nonmarine Evaporite Minerals

Common Marine Evaporite Minerals		Nonmarine Evaporite Minerals	
Halite	NaCl	Halite, gypsum, anhydrite	
Sylvite	KCl	Epsomite	$MgSO_4 \cdot 7H_2O$
Carnallite	$KMgCl_3 \cdot 6H_2O$	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Kainite	$KMgClSO_4 \cdot 3H_2O$	Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Anhydrite	$CaSO_4$	Thenardite	$NaSO_4$
Gypsum	$CaSO_4 \cdot 2H_2O$	Bloedite	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
Polyhalite	$K_2MgCa_2(SO_4)_4 \cdot 2H_2O$	Gaylussite	$Na_2CO_3 \cdot CaCO_3 \cdot 5H_2$
Kieserite	$MgSO_4 \cdot H_2O$	Glauberite	$CaSO_4 \cdot Na_2SO_4$

Since then, geochemists have used laboratory experiments to trace the steps by which seawater of normal salinity evolves into the hypersaline brines from which the evaporite minerals grow. In some circumstances, evaporitic calcite or aragonite can precipitate when the water volume has been reduced by 50%. Crystallization of evaporite minerals begins only after seawater of normal salinity (35,000 ppm) has been reduced to about 20% of its original volume. The least soluble constituents crystallize first. Calcium and sulfate ions form gypsum and anhydrite. When the volume of seawater is reduced to 10% of the original volume, more soluble components such as potassium, sodium, and chlorine solidify as the minerals halite and sylvite. Finally, the remaining seawater evaporates almost entirely. This allows the most soluble components to solidify from the last remaining droplets of briny fluid. These last minerals are bitter borates and nitrates.

This orderly process of crystallization as a function of solubility is not always apparent when naturally occurring evaporite mineral sequences are studied. Only some ancient evaporites show a systematic vertical cyclicity in mineralogy that mimics that seen in the laboratory, a pattern that is compatible with progressive crystallization of an increasingly saline brine. Most of these deposits show repetition. Vertical sequences of evaporite minerals are stacked successively on top of one another, suggesting alternating episodes in which brines were repeatedly evaporated and then replenished. In many of these ancient sequences, mineral species appear at random. No apparent relationship exists between a mineral's physical position in the sequence and the solubility of the ions it contains. The natural world of evaporites is far more complex than models based on laboratory experiments.

Evaporite deposits range in age from the Precambrian to the present, but very few are older than Cambrian. Their distribution is uneven. Peaks of development occur during the Cambrian, Permian, and Triassic periods. Presumably, regionally extensive evaporites occur infrequently because the conditions necessary to form them are rare. Widespread aridity must be coupled with a tectonic setting that produces broad, shallow basins or marine estuaries only intermittently connected with the open sea. For this reason, evaporite deposits are typically confined to the high-pressure belts between 10° and 30° latitude, where most of the world's deserts occur. Ancient evaporites also seem to be concentrated in this paleolatitudinal belt, so evaporite deposits have long been used to reconstruct ancient continental positions and test other hypotheses of climate and paleogeography.

Other types of sedimentation must be minimal so that evaporite deposition is not masked. Because evaporites form in such restricted conditions and tightly constrain ancient paleogeography and climate, it is appropriate to describe the characteristics of the three principal ancient types: nonmarine, shallow marine, and deep marine evaporites.

Nonmarine Evaporites

Nonmarine evaporites accumulate in closed lakes with interior drainage and no external outlets that develop in arid and semiarid regions (Hardie et al., 1978). When rainfall is high, large amounts of dissolved substances enter the lakes. With no outlets and with a hot and dry climate, evaporation reduces the water volume and increases salinity to the point where evaporite minerals begin to crystallize. Con-

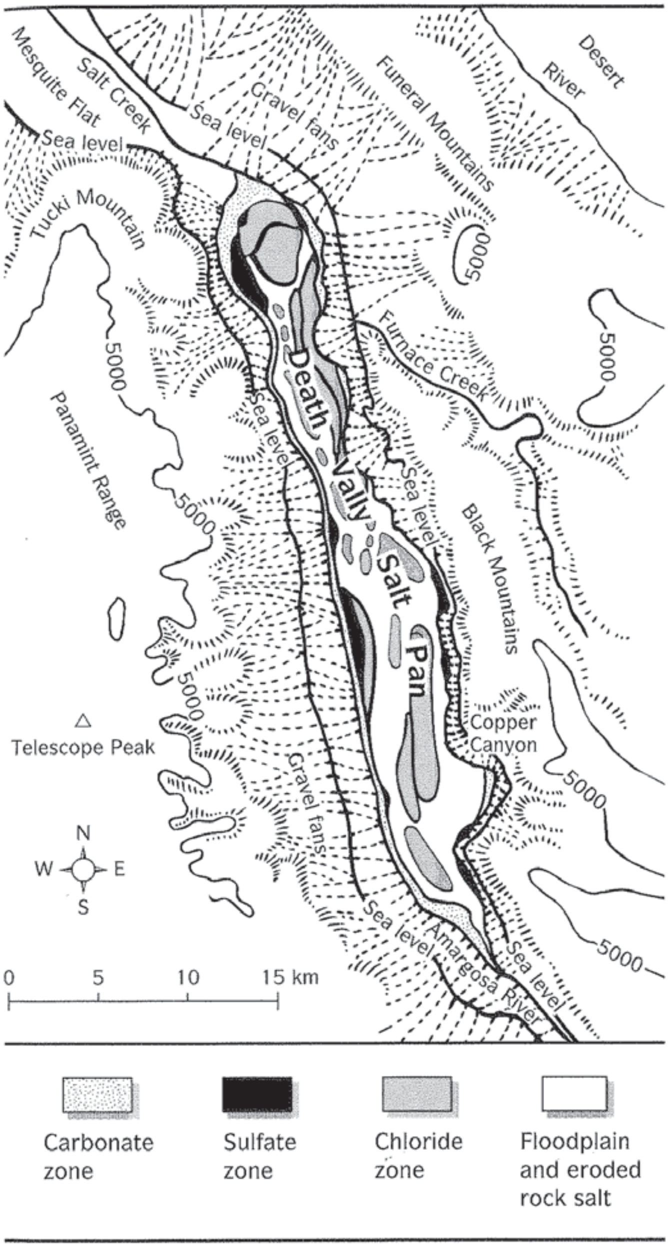
Figure 14.4

Death Valley, California, is a classic example of a lake basin with concentrically zoned evaporites. (A) Overview of Death Valley from Dante's View (on the southeast rim looking northwest.) The center of the dry lake is halite from the chloride zone, but the arcuate white area in the bottom center of the picture is composed of gypsum. Carbonates and borates are found on the periphery of the gypsum zone at the northern end of the dry lake. (Photo by C. B. Hunt, courtesy of U.S. Geological Survey.) (B) Map of Death Valley evaporite zones *(on the facing page)* showing the concentric arrangement of chlorides in the center of the bull's-eye, surrounded by a ring of gypsum and, on the outer fringe, by carbonates or borates. (Modified from Hunt, 1966, *U.S. Geol. Survey Prof. Paper* 494-A; courtesy of U.S. Geological Survey.)

tinued evaporation shrinks the volume and area of closed lakes. They eventually disappear, leaving a residue of nonmarine evaporites.

Ephemeral dry lakes (playas) occur today in many desert areas. Examples include the Great Salt Lake of Utah, Mono Lake in the Owens Valley of California, and the Dead Sea. Ancient analogs can be identified in a number of ways. Bands of lacustrine evaporites define a bull's-eye pattern (Fig. 14.4). The most soluble minerals, such as halite, are concentrated near the lake center and occur at the top of the evaporite sequence. The least soluble minerals, such as carbonates and sulfates, are concentrated around the rim of the ancient lake and are found at the bottom of the evaporite sequence. A bull's-eye pattern defined on a local scale, together with the association of such evaporites with other demonstrably nonmarine sedimentary rocks, allows this type of evaporite to be identified. Specific mineralogy also helps. Only nonmarine evaporites contain large quantities of borax, epsomite, trona, gaylussite, and glauberite.

Ancient nonmarine evaporites are not particularly common in the stratigraphic record, but some are truly spectacular. One of the most famous is in the Eocene Green River Formation in Wyoming (see Box 8.4). In ancient Lake Goshiute (the Wyoming portion of the Green River system), the Wilkins Peak Member contains many beds of trona (hydrous sodium bicarbonate) and halite totaling more than



B

50 m in thickness and covering several thousand square kilometers. In some places, the large trona crystals interlock and penetrate upward (see Fig. 8.4.2E). These trona and halite deposits also show the classic bull's-eye pattern, with the most concentrated deposits near the original center of the lake bed in southwesternmost Wyoming.

Shallow Marine Evaporites

Shallow marine evaporites include (1) supratidal and intertidal (coastal sabkha) deposits like those forming today around the perimeter of the Persian Gulf, and (2) truly shallow marine ancient evaporites that formed in what were marine shelf areas with water depths seldom in excess of 5 m. Few if any modern analogs of these latter deposits are known.

Sabkha Deposits. As discussed in Chapter 12, sabkhas are broad coastal supratidal and intertidal flats developed along the margins of arid landmasses. Sediments that accumulate on sabkhas include: (1) siliciclastic detritus eroded from adjacent land washed onto the sabkha; (2) offshore deposits of sand and mud that periodic storms wash up and onto the sabkha; and (3) the indigenous sediments of the sabkha itself. Much of the evaporite sediment produced in sabkhas precipitates as saline groundwater seeps into, through, and up and out of the sabkha (Fig. 14.5). Much of this groundwater is seawater that is continually replenished (recharged) beneath the sabkha, but groundwater from the adjacent landmass can also feed the system. Groundwater circulation is driven by capillary action and evaporative pumping. Intermittent flooding by the sea also occurs, and beach ridges can trap a reservoir of additional seawater.

Typical sabkha evaporite minerals are anhydrite, gypsum, and dolomite. Much of the anhydrite occurs as irregularly shaped lumps or nodules. These nodules replace altered gypsum crystals originally formed within layers of interbedded carbonate mud or shale. The term **chickenwire structure** is used to refer to this mixture of elongate, irregular clumps of anhydrite separating thin stringers of carbonate and/or siliciclastic mud (Fig. 14.6A, B). This structure is particularly common in sabkha evaporites but is not confined to them.

Cyclicity is common in sabkha evaporite sequences. As deposition proceeds, sabkha deposits naturally prograde oceanward and eventually lie upon intertidal sediments (stromatolites, gypsum, fenestrated birdseye pelleted carbonate mud; see Chapter 12). These in turn rest on oolitic and bioclastic subtidal carbonate rocks of the subtidal zone (Fig. 14.6C). Ancient sabkha evaporites of Permian age have been recognized in the Delaware Basin of Texas and New Mexico (Warren and Kendall, 1985).

Shallow Marine Shelf and Basin Deposits. The classic ancient evaporite deposits of the world appear to be of shallow marine origin. Examples include the Permian Zechstein deposits of northern Europe, much of the Permian Delaware Basin deposits of west Texas (Fig. 14.7), Silurian-Devonian deposits of the Elk Point Basin in western Canada and the Salina Basin of Michigan and upstate New York, and Devonian-Jurassic evaporites of the Willis-

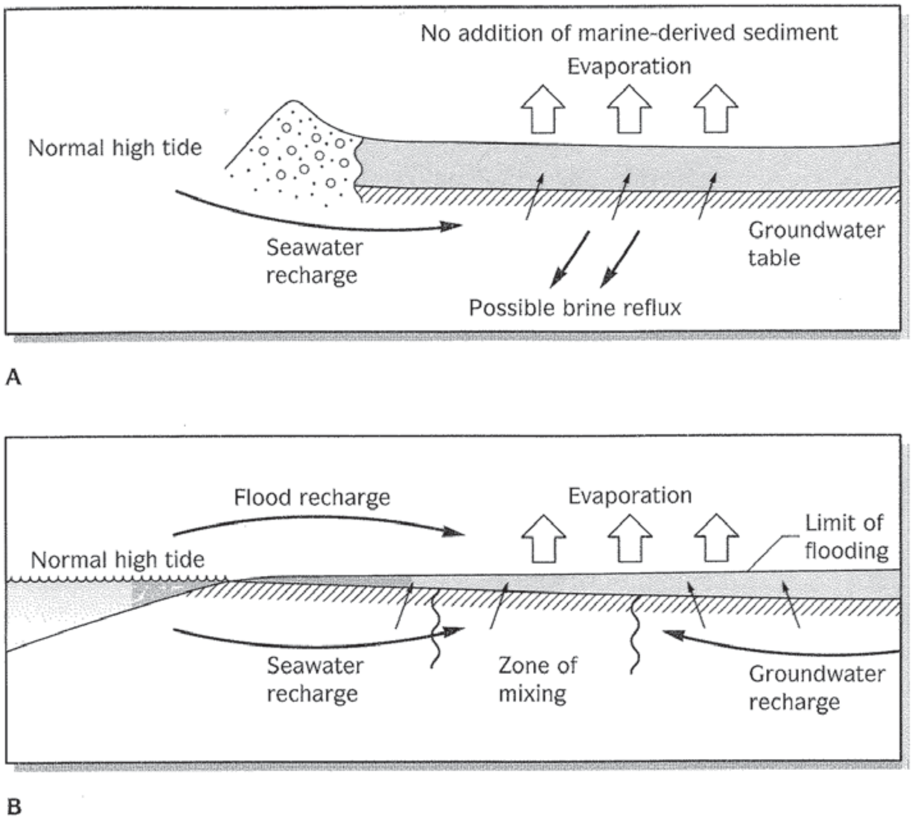
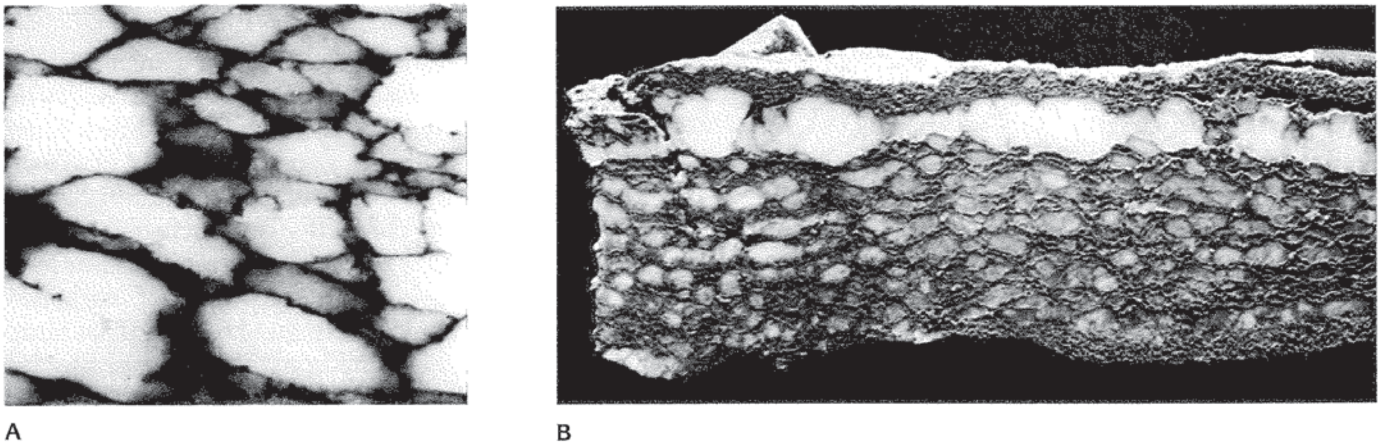


Figure 14.5

Sabkhas receive water from a variety of sources. (A) Sabkha with seawater recharged through the subsurface and with relatively little groundwater influx. (B) Sabkha groundwaters are recharged by a mixture of seawater and groundwater, plus seawater flooding from major storms. (From R. G. Walker, ed., 1984, *Facies Models,* p. 271; courtesy of Geoscience Canada.)



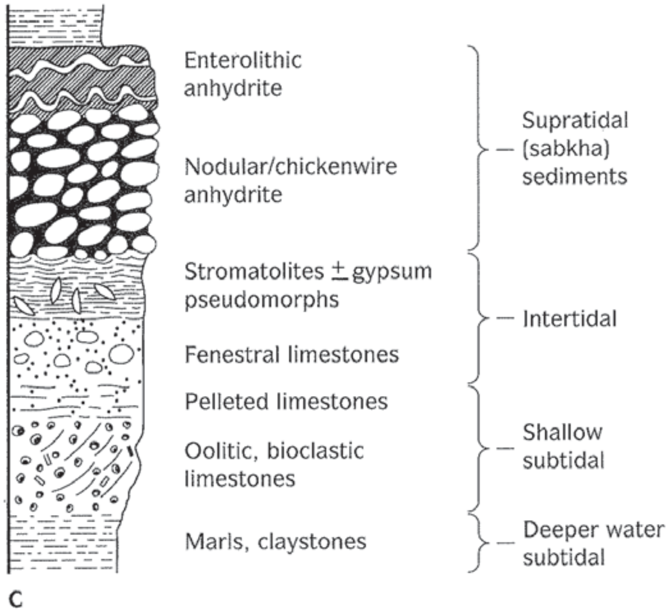


Figure 14.6

Sabkhas produce a number of distinctive structures. (A) Mosaic anhydrite (chickenwire structure) commonly formed when anhydrite nodules coalesce, shown at actual size. (Photo courtesy of R. P. Glaister.) (B) Nodular gypsum is common just below the surface of the sabkha. (Photo courtesy of L. A. Hardie.) (C) Typical vertical cycle of sabkha sediments. Such cycles range from several meters to several tens of meters in thickness. (After Tucker, 1981, *Sedimentary Petrology: An Introduction,* p. 171; by permission of Blackwell Scientific Publications, Oxford.)

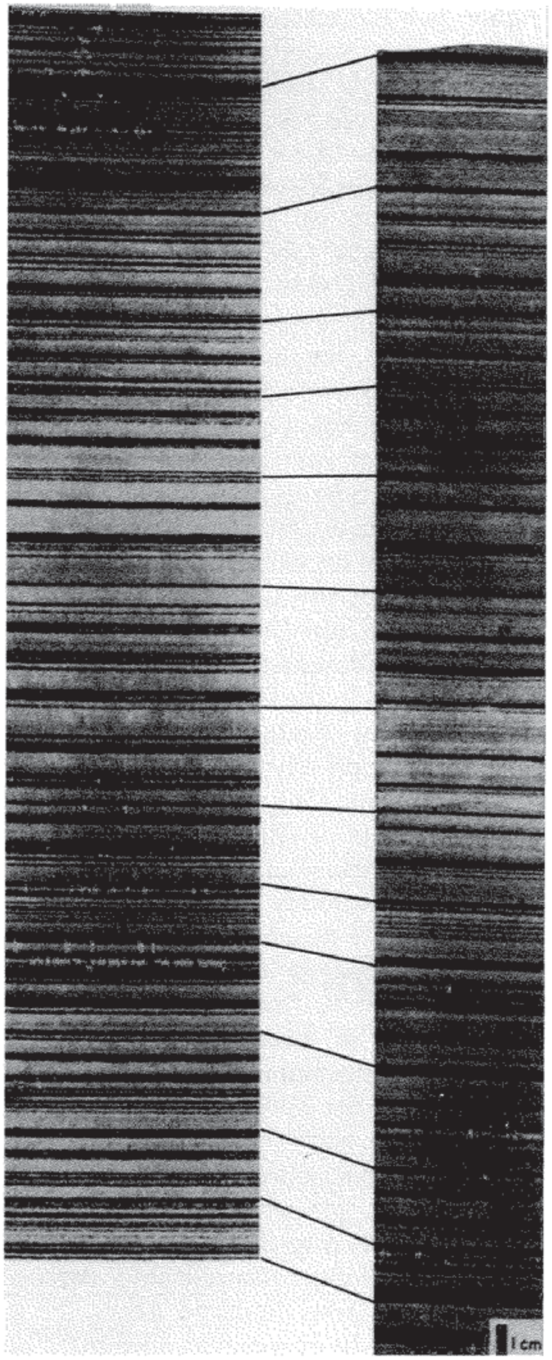


Figure 14.7

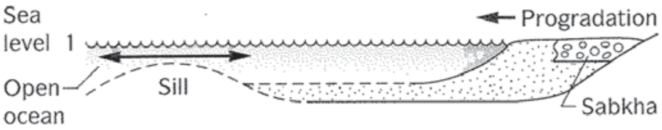
The Permian Castile Formation evaporites of the Delaware Basin of west Texas show spectacular fine-scale lamination, presumably from fluctuating climatic cycles. These subsurface cores from areas 95 km apart show the possible correlation between laminae of calcite (dark) and anhydrite (light.) (From Dean and Anderson, 1982, in C. R. Handford et al., *Depositional and Diagenetic Spectra of Evaporites: A Core Workshop*, p. 340.)

ton Basin of Montana. The great volume of these deposits is particularly striking and puzzling. Each consists of hundreds of meters of bedded evaporite minerals, especially halite and gypsum, that extend across thousands of square kilometers. This is surprising because evaporation of a single column of seawater 1 km thick yields only a 15-m sequence of evaporite. Of this 15 m, 3 m would be gypsum and another 1.5 m would be halite.

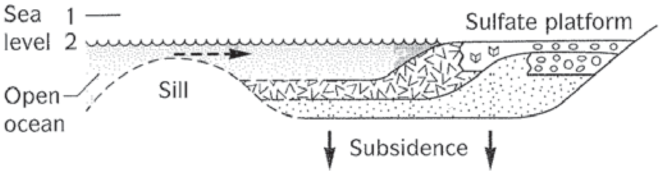
How can we explain the classic ancient sequences consisting of meters and even several tens of meters of gypsum and anhydrite and overlying beds of halite several meters thick? Does their existence imply evaporation of an enormous volume of seawater? Precipitation of thick sequences consisting only of gypsum dictates a level of salinity produced by evaporating at least 70% but less than 90% of the original volume of seawater, or else halite and other salts would also be found. Such brines must have been replenished continually with additional seawater so that salinity stayed in an equilibrium between these narrow limits for long periods of time. The repeated vertical cycles (see Fig. 14.7) of evaporite minerals (for example, calcite and anhydrite) must also be explained.

Obviously, these sequences do not form in a single episode during which tremendous volumes of seawater are evaporated. To produce a thick, regionally extensive evaporite sequence, a basin must somehow be periodically isolated from the open ocean (Clark and Tallbacka, 1980; Hardie and Eugster, 1970). A physical barrier, perhaps a structural ridge or growing reef strategically positioned at the basin mouth, can function as a screen or filter, making such a **barred basin** an evaporating "pan." At times of high tide or during storm surges, seawater of normal salinity enters the basin and replenishes its stock of normal seawater. During episodes of low tide, especially those that coincide with daily temperature highs, rapid evaporation of seawater can raise salinity to the saturation point. Crystallization thus proceeds in a quasi-orderly cyclical fashion (Fig. 14.8). Barred basins permit partial or incomplete sequences of evaporite minerals to develop. For example, layers of halite and potash salts that would normally overlie basal carbonate and gypsum-anhydrite beds would not form if denser, late-developing hypersaline brines escaped by reflux. And the timing of episodes of high tide, low tide, and peaks of evaporation might be out of sync.

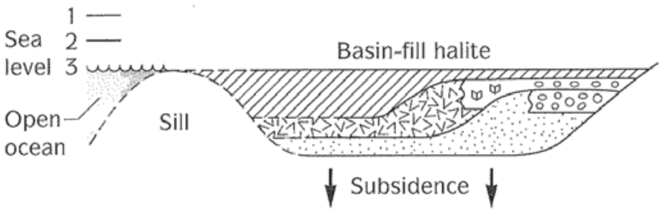
This is a delicate system, requiring both the barrier and the basin to persist over a long time. Most North American shallow marine evaporites probably accumulated in this kind of broad, barred cratonic or intracratonic basin, with the evaporite minerals forming in several environments: on the floor of shallow brine pools, on salt flats, and in estuaries and lagoons. Depths must have been very shallow (rarely more than a few meters, routinely perhaps only a few centimeters), so that high salinities in seawater could be reached repeatedly within hours. Cu-



High sea level: normal marine, carbonate deposition



Intermediate sea level: restricted marine, gypsum deposition



Low sea level: salt lake – saline pan, halite precipitation

Figure 14.8

Model depicting the filling of a barred evaporite basin. Repeated refilling of the basin with normal seawater, followed by repeated evaporation, generates enormously thick evaporite sequences. (After Clark and Tabacka, 1980; modified from R. G. Walker, ed., 1984, *Facies Models,* p. 271; courtesy of Geoscience Canada.)

riously, delicate internal laminations extending for tens of kilometers in these sequences imply that this extremely shallow sediment surface remained remarkably undisturbed.

Deep Marine Evaporites

Ancient evaporite deposits that lack the delicate, regionally extensive laminations are interpreted as deep-water deposits. They contain transported size-graded clasts of gypsum and anhydrite (slope-driven turbidites?) and broken and contorted masses of slumped evaporite (Schmaltz, 1969). The exact depth at which they formed is uncertain. Estimates based on slope requirements and paleotopography range from as little as 40 m (Davies and Ludlum, 1973) in the Devonian Elk Point Basin of Montana up to 600 m for the Pleistocene Dead Sea (Katz et al., 1977).

Figure 14.9 illustrates general basin models for deep-water evaporite deposits as well as models that combine shallow- and deep-water origins. The major problem with deep-water deep-basin models is that it's hard to *keep* the water deep if evaporation is occurring fast enough to precipitate minerals. To circumvent this problem, it is suggested that most evaporites originally form along the shallow margins of the basin but then are transported by gravity sliding to the center of the basin.

Most authors suggest that deep basins with evaporite deposits were filled with shallow water. Under these circumstances, a large sill would allow repeated inflow of seawater down into the basin where it would then evaporate. The famous late Miocene (Messinian Stage) evaporites of the Mediterranean are an example of this process (Fig. 14.10). Throughout the Cenozoic, the great Tethys seaway that once ran from the Mediterranean to Australia became fragmented and destroyed. India collided with Asia in the Eocene, and Africa collided with the Arabian Peninsula during the middle Miocene, shutting off what is now the eastern end of the Mediterranean. Only the western connection through the Straits of Gibraltar remained open, as they do today. Because of high mean temperatures, the Mediterranean today (and in the past) evaporates at a very fast rate, and the few rivers that drain into it are insufficient to maintain it. Thus, the huge one-way flow of water from the Atlantic through the Gibraltar Straits is essential to maintaining the Mediterranean at normal marine salinity.

At the end of the Miocene, however, Africa also began to collide with Spain, forming the Atlas Mountains and restricting the Gibraltar Strait. A pulse of Antarctic glaciation in the latest Miocene triggered a global drop in sea level, and suddenly the Atlantic no longer flowed into the Mediterranean. Within a few thousand years, 2.5 million km^3 of water slowly evaporated, forming a gigantic version of Death Valley or the Dead Sea, complete with a bull's-eye pattern of evaporites in several of the sub-basins of the Mediterranean. Unlike Death Valley or the Dead Sea, however, this basin was 4000 m (13,000 feet) deep!

This staggering discovery was made in 1970, when the Deep Sea Drilling Project drilled core after core in the Mediterranean and found thick deposits of upper Miocene evaporites in the basin center and thick alluvial fan conglomerates and sands around the margins. The entire basin had evidently become one huge, deep salt pan with 3000 m of relief on its flanks. Seismic imaging of the Nile Delta region showed that the Nile is underlain by an ancient canyon almost 2500 m deep, now filled by river sediments. This could occur only if

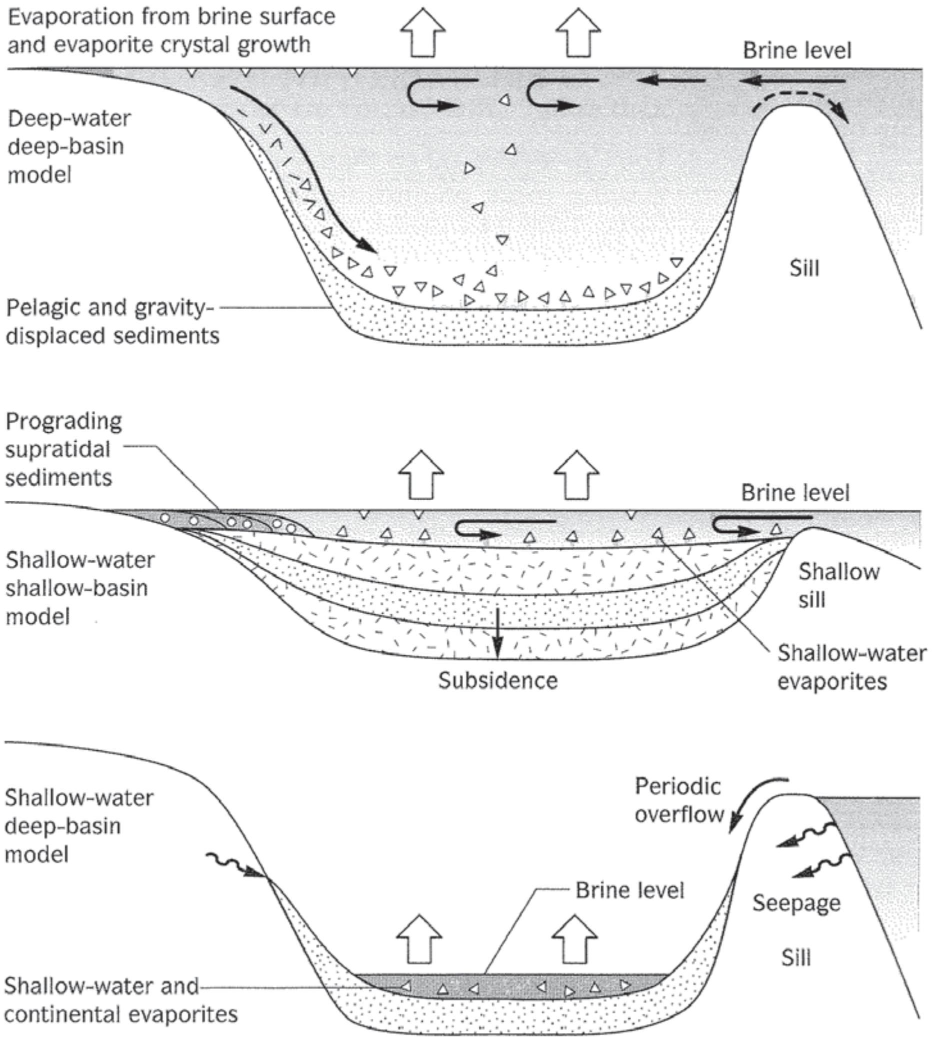


Figure 14.9

Three different barred basin models for the production of evaporite sequences in deep waters and deep basins, shallow waters and shallow basins, and shallow waters and deep basins. (From R. G. Walker, ed., 1984, *Facies Models,* p. 290; courtesy of Geoscience Canada.)

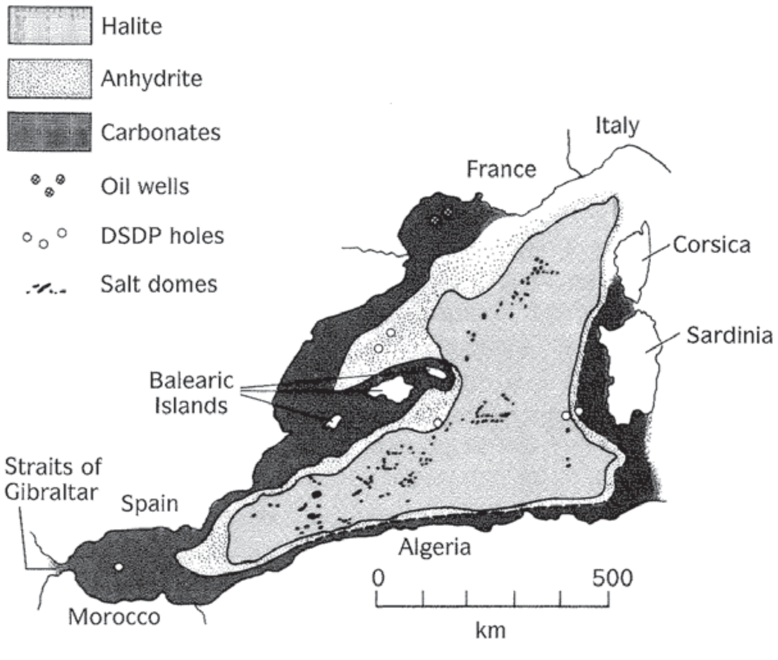


Figure 14.10

Concentrically zoned marine evaporites occur in the Balaeric Basin of the western Mediterranean Sea, immediately east of the Straits of Gibraltar. Apparently, this basin was completely dried up and 4000 m below sea level during the peak of the Messinian event. Carbonates and sulfates (anhydrite) form concentric rings around the coastal region. The center of the basin is occupied by halite, and potash salts, such as sylvite, occur in the very center of the bull's-eye. (After Hsü, 1972, *Earth-Science Reviews,* 8:390; by permission of Elsevier Science Publishers.)

the Mediterranean had dried up completely, incising the river valleys as much as 3000 m lower than their present level. Since the best known outcrops of these late Miocene evaporites occur on the island of Sicily near the Straits of Messina, this great evaporation event is known as the **Messinian event,** after the name for the final stage of the Miocene.

Multiple cycles of evaporites in these Messinian deposits imply that the Mediterranean refilled and dried up many times. Some halite and gypsum deposits reach a staggering 2000 m in thickness. Since a single episode of complete evaporation would produce only 100 m of halite and gypsum, at least 40 separate drying events in less than a million years would be required to produce all these evaporites.

NONEPICLASTIC SEDIMENTARY ROCKS

Four processes other than the weathering of preexisting rocks produce sediment and sedimentary rocks. Table 14.4 shows how nonepiclastic sedimentary rocks are classified. The most important of these classes are the **volcanogenic sedimentary rocks.** These rocks are formed directly by volcanic processes and are closely linked temporally and spatially with active volcanism. **Pyroclastic sedimentary rocks** are produced by explosive activity; other kinds of volcanogenic rocks are produced by less spectacular processes related to the cooling of lava. As previously noted, any sedimentary rock containing a large number of volcanic fragments, without

Table 14.4 Classification of Nonepiclastic Sedimentary Rocks

Type	Mechanism of Origin	Subcategories
I. VOLCANOGENIC	Directly produced by processes associated with the extrusion and cooling of igneous magmas	A. Pyroclastic: Composed of tephra—fragments of rock, mineral, and glass generated by volcanic explosions. Pyroclastic sedimentary rocks are subdivided on the basis of tephra size into *agglomerate* and *breccia* (>64 mm), *lapilli stone* (2–64 mm), and coarse ($\frac{1}{16}$–2 mm) and fine (<$\frac{1}{16}$ mm) *tuff.* Pyroclastic deposits are subdivided on the basis of origin into 1. Air-fall deposits 2. Volcaniclastic flow deposits a. Ignimbrites b. Pyroclastic surge deposits c. Lahars (mudflows) B. Autoclastic: Produced by the uneven cooling and brecciation of hot lavas in contact with the atmosphere C. Hyaloclastite: Produced by the uneven cooling and brecciation of hot lavas in contact with water
II. CATACLASTIC	Directly related to the crushing, grinding, and brecciation associated with intense folding and faulting	A. Fault breccia and mylonite B. Fold breccia and mylonite C. Crush conglomerate
III. COLLAPSE OR FOUNDER BRECCIA	Produced by the collapse or foundering of rocks into open spaces generated when underlying material is removed	A. Collapse breccia: The mechanism responsible for removal of underlying material is indeterminate B. Solution breccia: Selective dissolution of carbonate or evaporite causes collapse
IV. METEORITIC OR IMPACT OR FALLBACK BRECCIA	Produced by the impact of high-velocity extraterrestrial bodies (bolides) of indeterminate origin (from the asteroid belt or Oort's cometary cloud?)	

regard to its origin or environment, is called **volcaniclastic.** Thus, sedimentary rocks weathered from volcanic source rocks are volcaniclastic, rather than volcanogenic.

Three other kinds of nonepiclastic, nonvolcanogenic sedimentary rocks are recognized. They are generally coarse-grained and much less common than volcanogenic rocks. **Cataclastic rocks** form as the result of tectonic activity, mainly fragmentation and brecciation associated with folding and faulting. **Collapse** or **solution breccias** develop where solution or stress cause overlying rock units to collapse into open spaces below. **Impact** or **fallback breccias** are produced by the impact of extraterrestrial bodies with Earth's surface.

Volcanogenic Sedimentary Rocks

Most sedimentary geology courses and textbooks focus on sandstones and carbonates, and rarely discuss volcanogenic sedimentary rocks in any detail. Yet in some parts of the world, sedimentary rocks of volcanic origin are far more abundant than epiclastic sandstones or other types of sedimentary rock. In the geologic past, volcanogenic and volcaniclastic sedimentary rocks have made up a significant percentage of the total rock record (typically about 25% of the sedimentary record). In some areas, volcanogenic and volcaniclastic sediments are at least twice as abundant as epiclastic sandstones (which rarely make up more than 10% of the sedimentary record, according to Ronov, 1968) or carbonates (which make up less than 15%, on the average).

Volcanogenics are especially important for understanding the stratigraphy of active mountain belts. They were common in the Archean, when most sediments were composed of fresh or reworked volcanic material, ranging from lithic graywackes to pillow lava breccias. Volcanogenics also have economic importance; many of them are associated with hydrothermal mineralization, which makes them major sources of gold, uranium, and sulfide minerals. Finally, volcanogenics have a disproportionate effect on human affairs, as demonstrated by the fatal eruptions at Mount Vesuvius in Italy, Krakatoa and Tambora in Indonesia, Mount St. Helens in Washington State, Nevado del Ruiz in Colombia, Mount Unzen in Japan, and Mount Pinatubo in the Philippines.

Given the great geologic and economic importance of volcanogenic sediments and the fact that volcanoes have always inspired awe, fear, and fascination, it is surprising that these sediments have been so neglected. Although sedimentary petrologists concede that volcanogenic sedimentary rocks are voluminous, few have studied them. There are many reasons for this neglect. Distinguishing the various volcanogenic components in hand specimen or in thin section is difficult. Volcanic constituents are quite susceptible to chemical decomposition and textural diagenesis. For example, shards of volcanic glass older than Tertiary are almost unknown because they devitrify into clay minerals and zeolites.

Much of the neglect for volcanogenic rocks by sedimentary petrologists stems from deliberate bias, however. Traditionally, volcanogenics are the domain of igneous petrologists, and sedimentary geologists are reluctant to trespass in unfamiliar territory. Because volcanogenic rocks are hybrids of igneous and sedimentary processes, sedimentary geologists have long avoided them.

By historical accident, stratigraphy was first studied and thus much better understood in the stable continental interior (the domain of quartz arenites and carbonates), rather than in mountain belts, with their structural complexity and abundant volcanogenic sediments. Consequently, sedimentary petrologists have hesitated to work in geologic terrains where large volumes of volcanogenic sedimentary rocks occur, preferring instead to study sedimentary rock sequences that lack volcanogenic components. Plate tectonics and terrane tectonics now demonstrate that ancient mobile belts incorporate volcanic arcs and subjacent forearc and back-arc basins (see Chapter 19). Because immense volumes of volcanogenic rocks occur in these domains, the renewed interest of sedimentary petrologists in these areas is producing great strides in our understanding and interpretation of these fascinating deposits. The short section that follows cannot begin to do justice to the subject. We strongly recommend the excellent texts by Fisher and Schmincke (1984) and Cas and Wright (1987), or the chapter by Lajoie and Stix (1992), for a detailed discussion of the subject.

Pyroclastic Rocks

are produced when tephra lithifies. **Tephra** is material of any size or composition ejected by volcanic explosions. Several size classes of tephra similar to the major size classes of siliciclastic sedimentary rocks are used to categorize pyroclastic sedimentary rock types without regard to composition (Table 14.5). Coarse tuff consists predominantly of sand-sized tephra (lithified coarse ash); fine tuff is silt-sized tephra (lithified fine ash) (Fig. 14.11A). **Lapilli** (2–64 mm) stone contains mainly pebble-sized tephra (Fig. 14.11B). Very coarse-grained pyroclastic deposits are either volcanic **agglomerates** (mainly bombs) (Fig. 14.11C) or volcanic **breccias** (mainly blocks) (Fig. 14.11D). **Blocks** and **bombs** are very coarse (>64 mm)

Table 14.5 Size Classification of Tephra and Pyroclastic Sedimentary Rocks

Size Class Range	Siliclastic Sediment Size Class	Tephra Name	Pyroclastic Sedimentary Rock Type
>64 mm	Cobbles and boulders	Blocks[a] (angular) Bombs[a] (rounded)	Volcanic breccia[b] Agglomerate[b]
2–64 mm	Granules and pebbles	Lapilli	Lapilli stone
$\frac{1}{16}$ – 1 mm	Sand	Coarse ash	Coarse tuff
$<\frac{1}{16}$ mm	Silt and clay	Fine ash	Fine tuff

[a] Blocks are angular to subangular clasts of pre-existing congealed lava; bombs are rounded blobs of lava that congealed in flight.

[b] If very coarse clasts that are bombs dominate, the pyroclastic rock is agglomerate. If very coarse clasts that are blocks dominate, the pyroclastic rock is volcanic breccia.

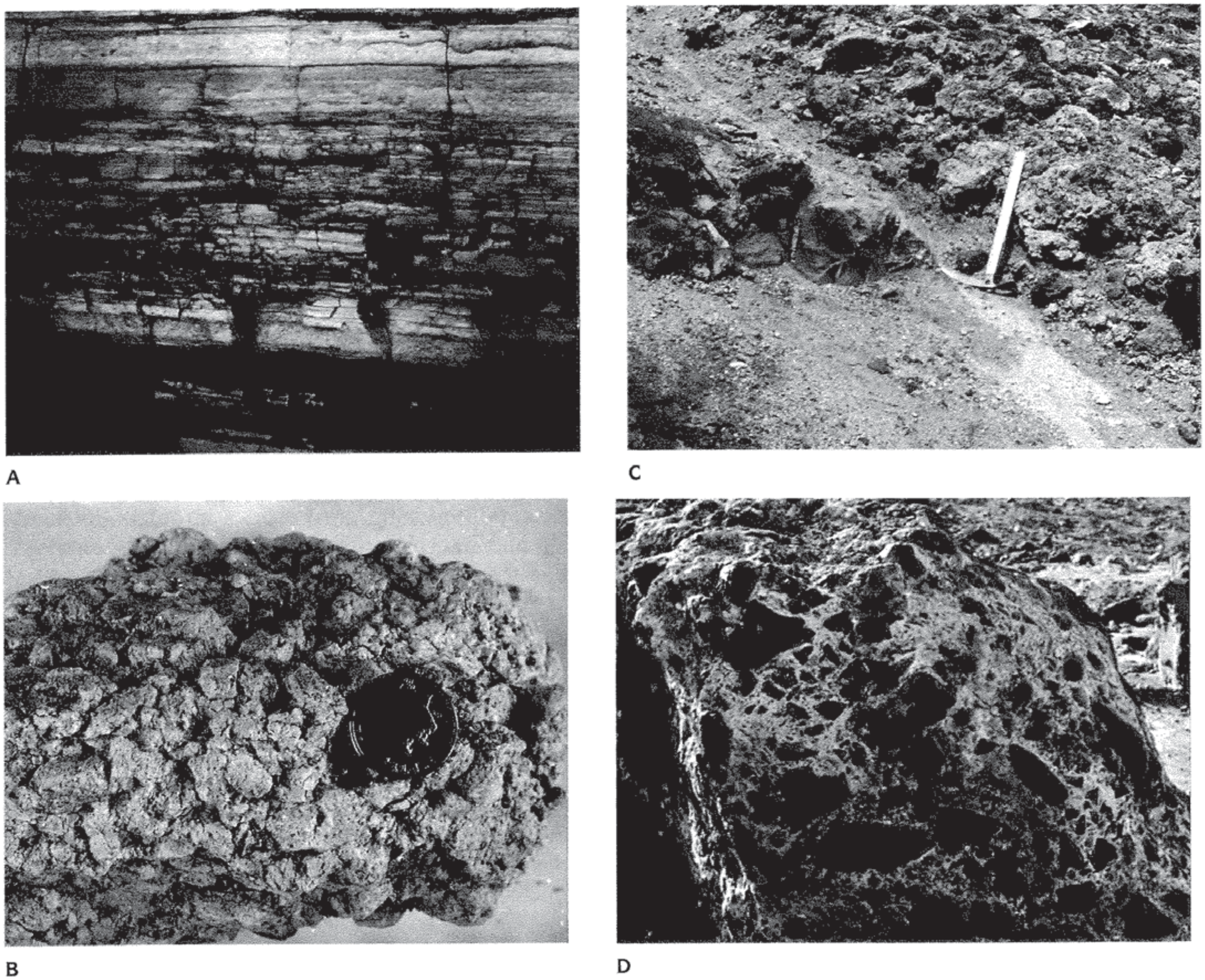


Figure 14.11

Pyroclastic tephra deposits are classified by size and shape. (A) Thick sequence of sand- and dust-sized volcanic ash deposits. (Photo by D. R. Prothero.) (B) Popcorn-sized lapilli made of pumice, from the Jemez volcanic field, New Mexico. (Photo by D. R. Prothero.) (C) Agglomerate is composed of volcanic bombs. This example is from Karymsky volcano, Kamchatka Peninsula, Russia. (Photo courtesy of R. Hazlett.) (D) Volcanic breccia, Augustine volcano, Alaska. (Photo courtesy of H.-U. Schmincke.)

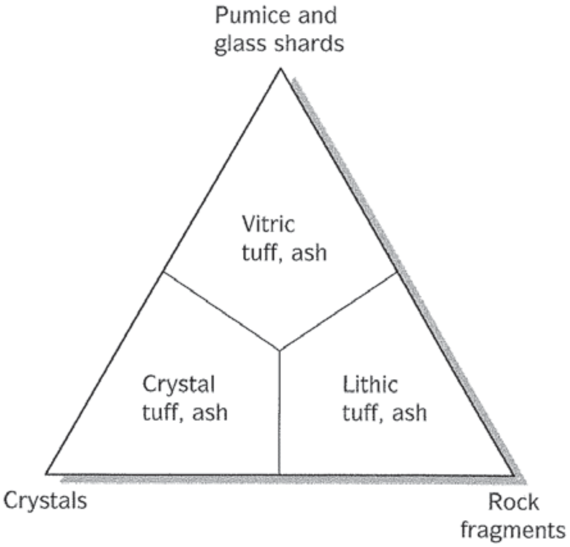


Figure 14.12

Triangular diagram for classifying tephra of various sizes using three end members: ash (<2 mm), lapilli (2–64 mm), and blocks and bombs (>64 mm.) (Modified from Friedman et al., 1992, p. 41; by permission of Merrill, New York.)

tephra. Blocks are large, angular, sharp-edged fragments of lava that congealed prior to explosive volcanism. Bombs are the same size as blocks but are rounded, bloblike masses of lava that congealed during flight after being erupted. Different size classes of tephra are typically intermixed.

Some classification schemes use differences in the mineralogy and petrology of tephra to categorize pyroclastic sedimentary rocks. (In fact, agglomerates and volcanic breccias are separated using compositional distinctions that are related to the contrasting origin of blocks and bombs.) Figure 14.12 illustrates a classification scheme for subdividing tuff based on the proportion of three principal components: (1) pumice and shards of glass, (2) crystals, and (3) rock fragments.

The physical characteristics used to distinguish these three components are shown in Figure 14.13. Tephra in tuff derived directly from magma is composed of volcanic glass. Volcanic glass forms mainly from the disaggregation of highly vesicular pumice or scoria. It appears as sickle-shaped or lunate glass

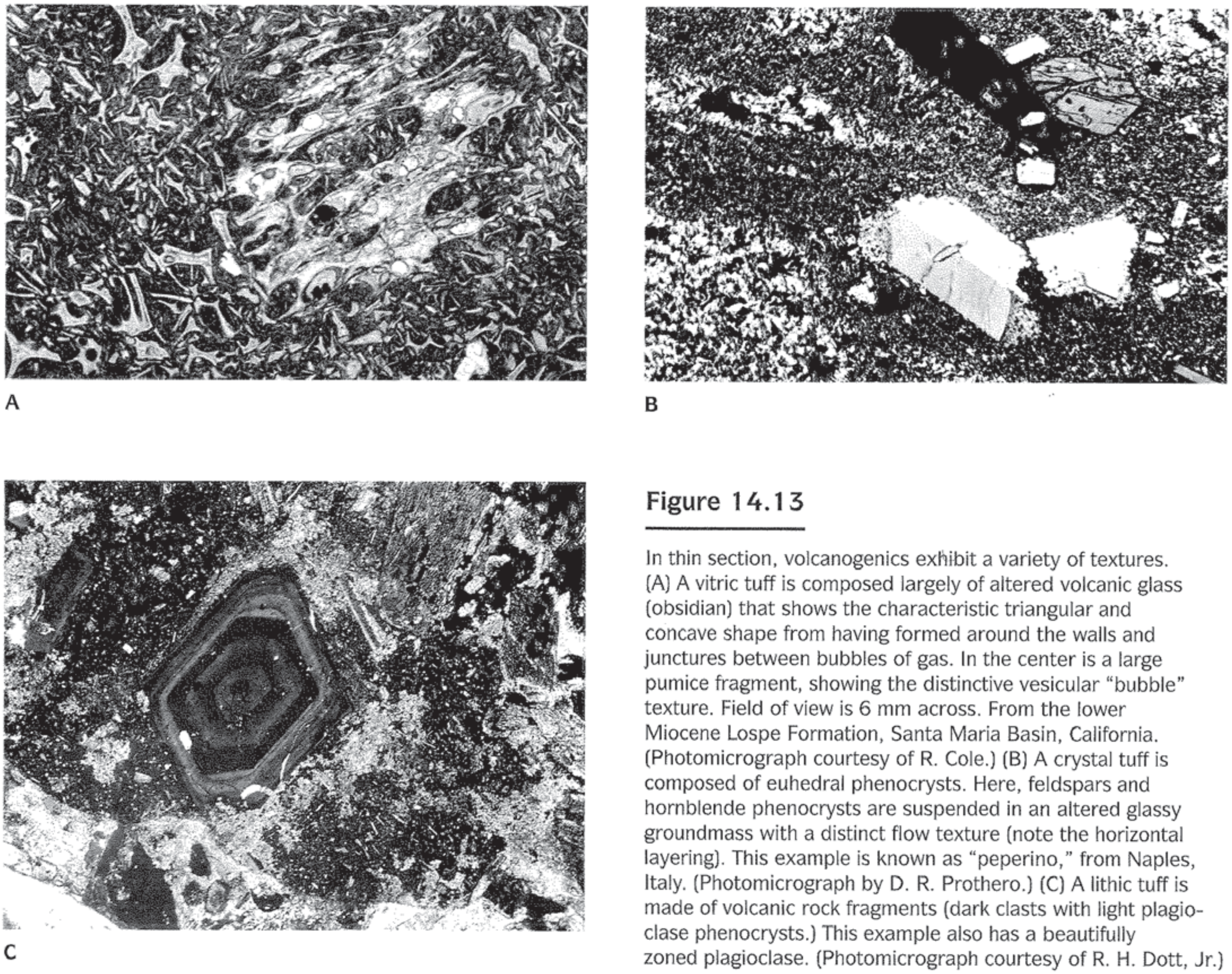


Figure 14.13

In thin section, volcanogenics exhibit a variety of textures. (A) A vitric tuff is composed largely of altered volcanic glass (obsidian) that shows the characteristic triangular and concave shape from having formed around the walls and junctures between bubbles of gas. In the center is a large pumice fragment, showing the distinctive vesicular "bubble" texture. Field of view is 6 mm across. From the lower Miocene Lospe Formation, Santa Maria Basin, California. (Photomicrograph courtesy of R. Cole.) (B) A crystal tuff is composed of euhedral phenocrysts. Here, feldspars and hornblende phenocrysts are suspended in an altered glassy groundmass with a distinct flow texture (note the horizontal layering). This example is known as "peperino," from Naples, Italy. (Photomicrograph by D. R. Prothero.) (C) A lithic tuff is made of volcanic rock fragments (dark clasts with light plagioclase phenocrysts.) This example also has a beautifully zoned plagioclase. (Photomicrograph courtesy of R. H. Dott, Jr.)

shards that are pale white to yellow and isotropic in thin section (Fig. 14.13A). If crystallization occurred before the eruption, most tephra is composed of mineral crystals (Fig. 14.13B). Components identified as crystals are fragments of quartz and feldspar or, less commonly, pyroxene and amphibole. Because these crystals grow in a fluid medium before they are ejected, they tend to be euhedral. Zoning is common. Tephra can also consist of any rocks present in the immediate vicinity of the volcanic eruption (Fig. 14.13C). Country rocks quite often include large volumes of pre-existing congealed lava, but no igneous, metamorphic, or sedimentary rock type is excluded.

The name assigned to a pyroclastic deposit incorporates both tephra size and the relative percentages of volcanic glass, mineral crystals, and rock fragments. These are measured in the field with pebble counts (if overall grain size is sufficiently coarse) or by point-counting thin sections. The following categories are distinguished: (1) glass-rich vitric tuff or lapilli vitric tuff, (2) crystal-rich crystal tuff or lapilli crystal tuff, and (3) lithic tuff or lapilli lithic tuff. An alternative nomenclatural scheme designates the rock as either tuff or lapilli stone. A prefix added to this term lists end-member components in order of increasing abundance. A rock fragment, crystal lapilli stone would be a pyroclastic sedimentary rock in which granule- and pebble-sized tephra are composed mainly of mineral crystals with some rock fragments.

Pyroclastic sedimentary rocks originate in several ways. Most are pyroclastic air-fall deposits or various kinds of volcaniclastic flow deposits.

Pyroclastic air-fall deposits form when ejecta thrown into the air by a volcanic eruption fall back to the surface, mainly in the immediate vicinity of the volcanic vent or fissure. Not surprisingly, these deposits rapidly coarsen and thicken towards the source, with large, poorly sorted, angular blocks and bombs immediately circumscribing the explosive center. A widespread thin blanket of better sorted, better rounded ash can be spread downwind (see Fig. 15.26). The extent of a pyroclastic fall deposit largely reflects the volume of the eruption, the strength and frequency of prevailing winds, and the volume and texture of the tephra produced. Individual falls may exhibit primitive size grading. Clasts can be welded together, depending on the temperature of the material as it falls and the rate at which the falling material accumulates. Individual falls accumulate as uniformly thick blankets of tephra that mantle topographic highs and lows (Fig. 14.14). Air-fall deposits that land in bodies of water are more complex.

Volcaniclastic-flow deposits form when tephra is remobilized and moves downslope as a pyroclastic flow (producing ignimbrites), a pyroclastic surge, or a lahar.

Ignimbrites are produced by *nuée ardente* (literally "glowing cloud") eruptions (Fig. 14.15A). These are gravity-propelled clouds of ground-hugging hot tephra and gas that move downslope at velocities of up to 200 km/hr (125 mph). They are basically hot, subaerial density currents. Ignimbrite deposits are not well organized internally, but coarser clasts may show upward size grading (Fig. 14.15B). In this respect, they are similar to the inverse grading seen in

Figure 14.14

Ashfalls often cover pre-existing topography and can accumulate on relatively steep slopes. This example of mantle bedding from O-shima Island, Japan, shows multiple ashfall layers that have covered an irregular topographic surface like a blanket. (Photo by S. Aramaki.)

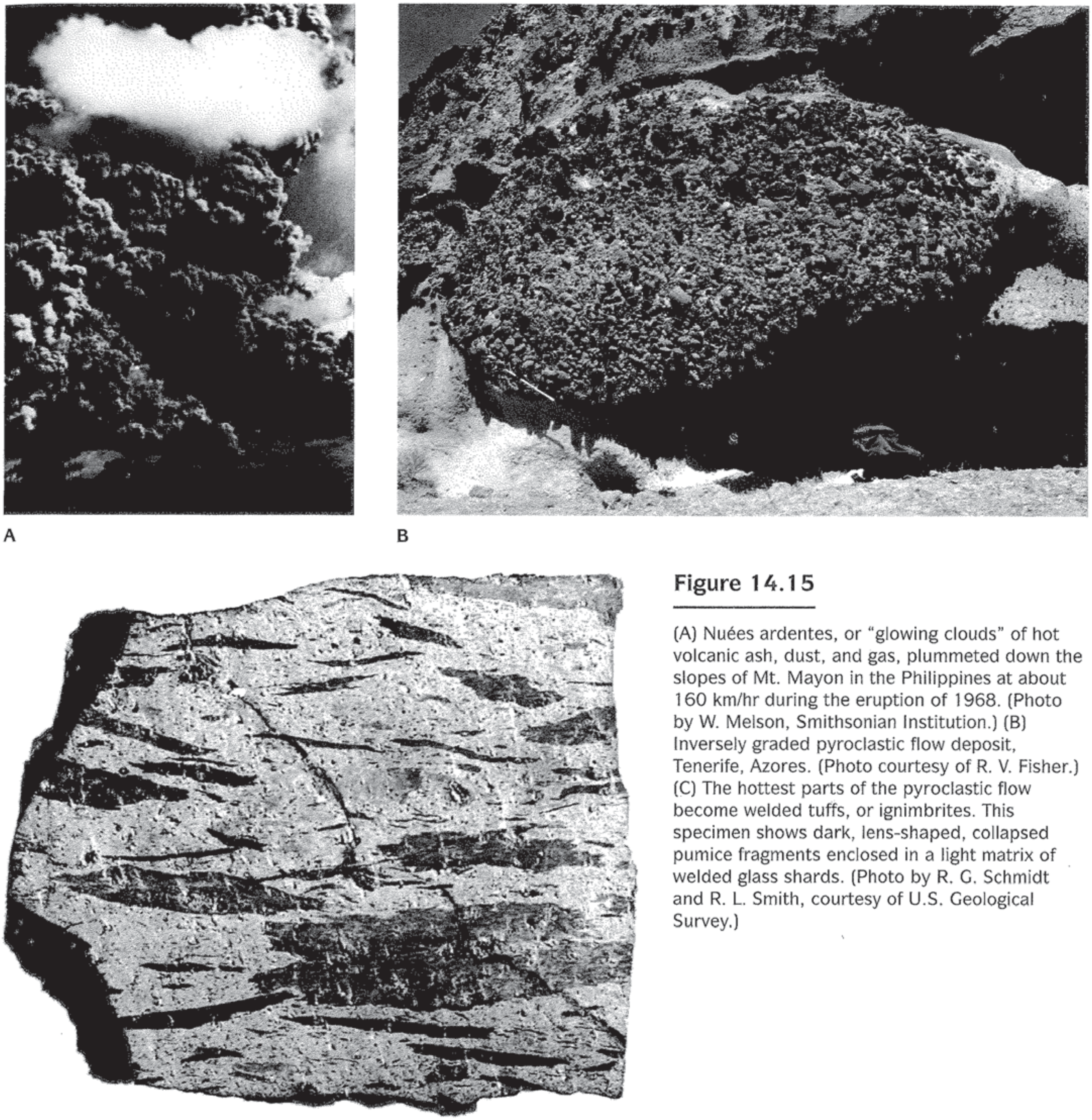


Figure 14.15

(A) Nuées ardentes, or "glowing clouds" of hot volcanic ash, dust, and gas, plummeted down the slopes of Mt. Mayon in the Philippines at about 160 km/hr during the eruption of 1968. (Photo by W. Melson, Smithsonian Institution.) (B) Inversely graded pyroclastic flow deposit, Tenerife, Azores. (Photo courtesy of R. V. Fisher.) (C) The hottest parts of the pyroclastic flow become welded tuffs, or ignimbrites. This specimen shows dark, lens-shaped, collapsed pumice fragments enclosed in a light matrix of welded glass shards. (Photo by R. G. Schmidt and R. L. Smith, courtesy of U.S. Geological Survey.)

debris flows (see Fig. 3.10). Like debris flows, pyroclastic flows are nonturbulent fluidized sediment gravity flows that carry a great range of particle sizes. Particles are suspended by upward-escaping gases and by grain-to-grain contacts. The concentration of particles is high and there is little pore space, so dilation must occur for the particles to move past one another and flow. Because the shear effects are greatest at the base of the flow, the smaller ash and lapilli are found there; larger lapilli, blocks, and bombs are driven toward the top of the flow, where there is less shear (as in aqueous debris flows).

The interior portions of ignimbrite deposits are insulated because they lie between cooler basal and surface layers. Consequently, they retain heat and often alter to welded tuff (Fig. 14.15C). Ignimbrites have a distribution quite unlike that of air-fall deposits. They follow and fill pre-existing drainage corridors (Fig. 14.15B) but do not mantle intervening topographic divides.

Nuée ardentes and their ignimbrites can be truly catastrophic in nature. The most famous and deadly of these was the May 8, 1902, eruption of Mt. Pelée on the Caribbean island of Martinique. Although the volcano had been rumbling and producing ash clouds for weeks, the island's inhabitants did not evacuate. Scientists and photographers recorded the growth of a huge spine of rock plugging the vent as it gradually rose out of the summit. Suddenly, the mountain exploded and blew off its volcanic plug, and a nuée ardente rushed down the flanks at speeds up to 160 km/hr (100 mph). In a few minutes and with no sound, the searing emulsion of gas, ash, and dust enveloped the city of St. Pierre and killed 29,000 people almost instantly. The only survivor of the eruption was a prisoner in a deep dungeon, who was protected from the blast by his cell. He later became a side-show celebrity in the Barnum & Bailey Circus.

Pyroclastic surge deposits are produced by rapid, episodic, or discontinuous downslope movements of pyroclastic material, gas, and, in some cases, water. Individual deposits are thinner and finer grained than ignimbrite units and are often richer in crystals and lithic fragments than pyroclastic flows. Surge deposits differ from ignimbrites because they have well-defined internal organization expressed by planar lamination, trough cross-bedding, and planar cross-bedding (Fig. 14.16). Like ignimbrites, pyroclastic surge deposits mantle both topographic highs and lows, but these deposits systematically thicken in valleys and thin in drapelike fashion over topographic divides.

Pyroclastic surges are low-concentration density currents with the particles supported mainly by turbulence (rather than gas fluidization, as in ignimbrites). The surge is driven by the momentum of the expanding gas, by the momentum of the particles, and by gravity (depending on the slope). Particle concentration occurs at the base of the surge, so sedimentation takes place in the density-stratified bedload region. As in aqueous flows, many of the particles are moving by saltation and traction.

Lahars are mudflows formed of saturated volcanic material. They can occur when large amounts of precipitation fall onto slopes that are mantled

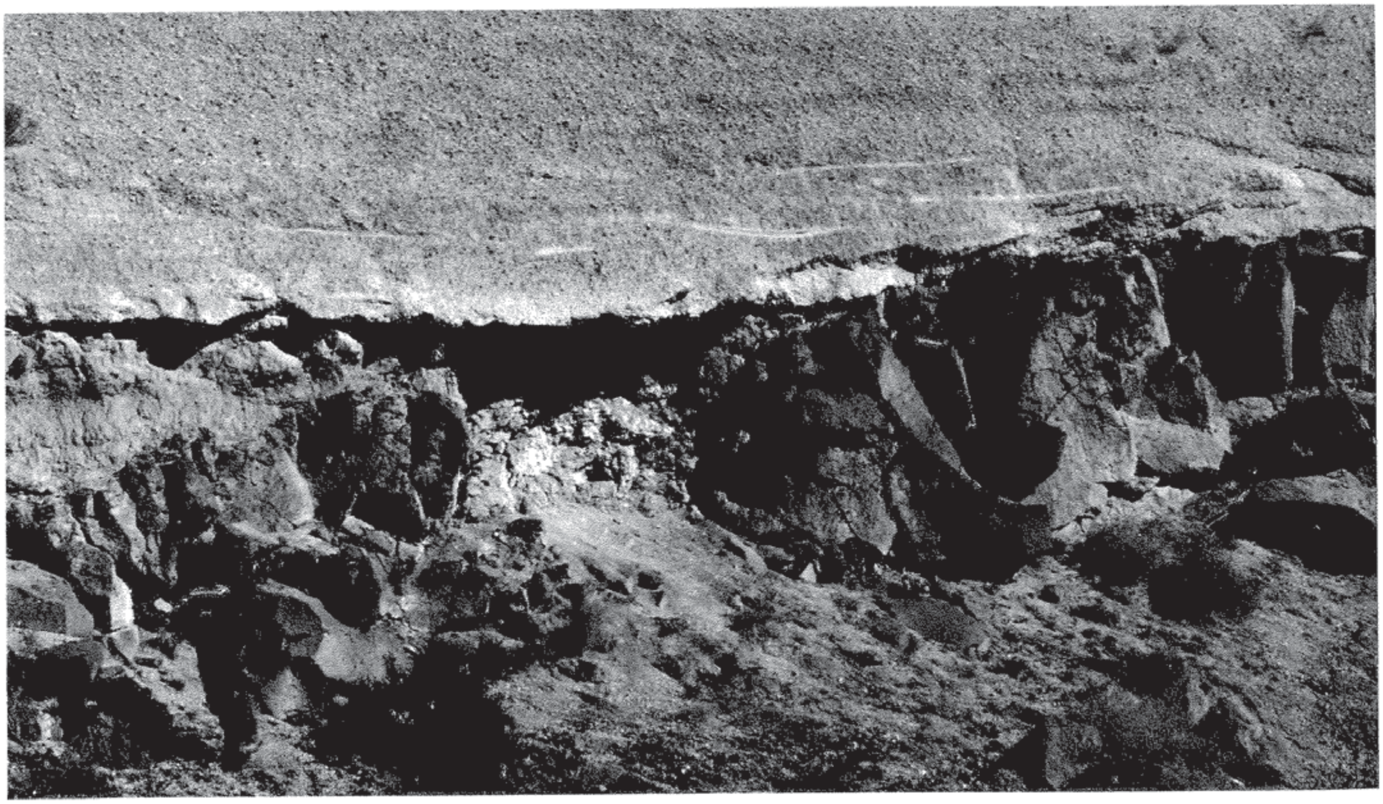


Figure 14.16

Pyroclastic surge deposits show well-developed internal bedding features, unlike most pyroclastic flows. In this example from the Bandelier Tuff, Jemez Mountains, New Mexico, a pumice lapilli tuff (see Fig. 14.11B) exhibits faint cross-bedding and scouring into the underlying columnar-jointed ignimbrite flow. (Photo by D. R. Prothero.)

Figure 14.17

Lahars are debris flows composed of volcanic material. They usually form when a volcano melts its snowcap or heavy rains mobilize loose volcanic ash and debris. (A) The valleys emanating from Mount St. Helens were filled with thick lahar deposits, characteristically covered by trees and boulders that were carried along. (Photo courtesy of R. Hazlett.) (B) Outcrop of inversely graded lahar deposits, from the 1929 eruption of Mount Pelée, Martinique. (Photo courtesy of R. V. Fisher.)

with unconsolidated ash or when a volcanic eruption mixes with water from a river or melting snowcap (Fig. 14.17A). Except for the abundance of volcanic materials, lahars resemble conventional mudflows. They are very poorly sorted with a matrix-supported fabric and little or no internal bedding. Like conventional mudflows and debris flows, they often exhibit reverse graded bedding (Fig. 14.17B) or reverse grading at the base of the flow changing to normal grading at the top (called reverse-to-normal grading).

Although lahars superficially resemble reverse-graded pyroclastic surges, lahars can be distinguished by evidence (such as abundant wood fragments) that they were water-saturated, not composed of superheated gases. Indeed, lahars can be full of tree trunks and branches (Fig. 14.17A), which are oriented subparallel to the bedding surface and may point downstream.

Although wet, muddy lahars may not seem as terrifying as hot nuées ardentes roaring down the sides of a volcano, they can be just as destructive. The eruption of Mount St. Helens on May 18, 1980, produced many destructive lahars formed when the snowcap melted during the eruption. They swept down the flanks of the volcano and flooded the river valleys, causing more damage and loss of life than the actual blast or ash cloud. Lahars can be very voluminous and extensive, and make up more total material than all other products of a volcano combined. One formation in the Sierra Nevada of California contains 8000 km^3 of lahar material, enough to cover Delaware with a deposit more than 1 km thick.

The most famous of recent lahars struck the towns below Nevado del Ruiz in Colombia after its November 5, 1985, eruption. Formed from the melted snowcap and from rivers swollen by recent rains, lahars rushed down 11 flank valleys of the volcano at speeds of 35 km/hr. A number of smaller villages were inundated, and thousands of people were killed. The greatest loss of life occurred when a wall of mud 5 m high swept through the city of Armero at 11 P.M., while most people were asleep. Of the 25,000 residents of the city, 20,000 died in minutes. Survivors reported that the initial wall of mud was cold but became increasingly hot, eventually "smoking" or "scalding." Most of the victims were buried under 5 m of hot mud and could not be located unless a pool of blood seeped to the surface. The majority were never found.

Base surges are sediment gravity flows that form when steam-saturated eruption columns col-

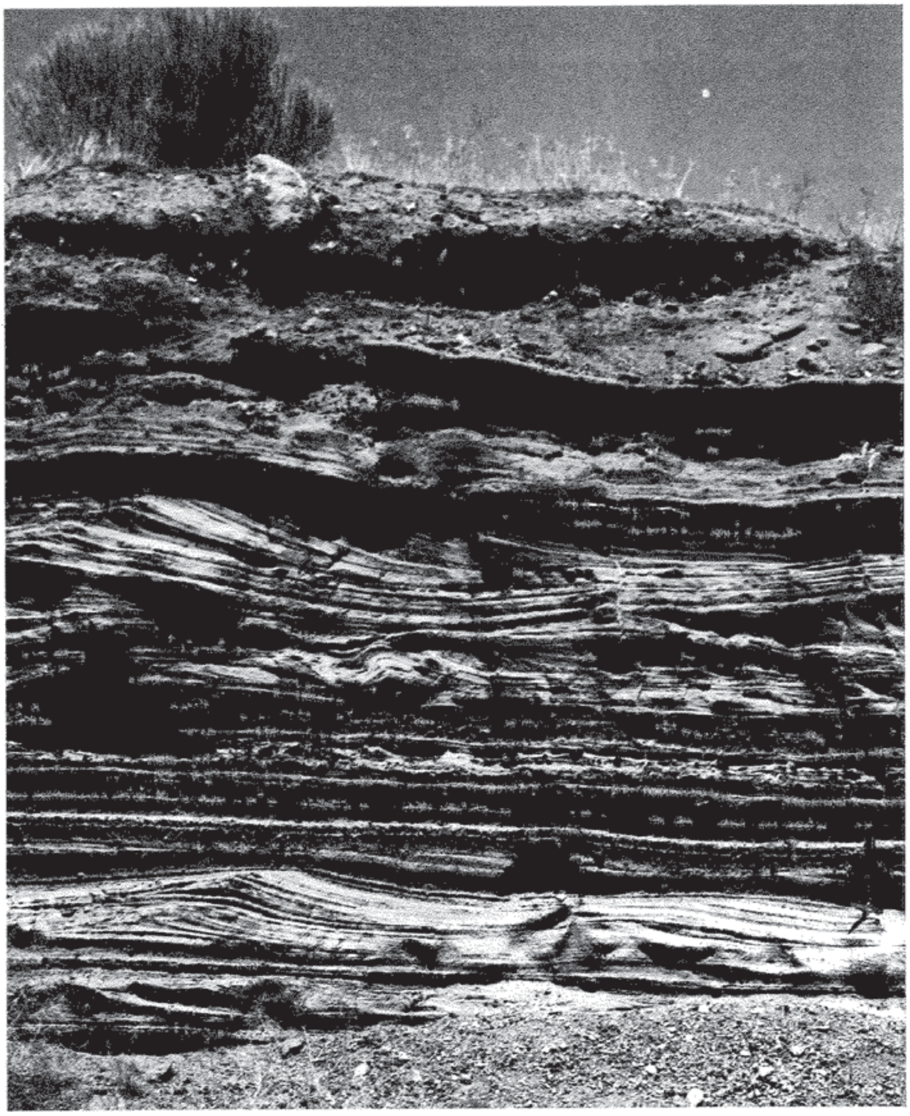


Figure 14.18

Base surge deposits are much better sorted than pyroclastic flows and may exhibit sedimentary structures. This example from the Tule Lake area, northern California, shows both well-developed cross-bedding and parallel lamination. Note hammer at lower right for scale. (Photo courtesy of R. V. Fisher.)

Figure 14.19

Hyaloclastites are produced when submarine pillow lavas break up. This pillow breccia from the Oregon coast shows a few remnant pillows but is mostly made of loose angular fragments. (Photo courtesy of R. V. Fisher.)

lapse and travel outward across the ground surface. They were originally described from a surge developed from the base of the mushroom cloud over the underwater nuclear explosion at Bikini Atoll in 1947, and they have since been seen emanating from explosive volcanic plumes. Base surges are composed of a turbulent mixture of water vapor or condensed droplets and solid particles. The surge may start out dry if the water is vaporized, but if water condenses during transport, the wet mixture will behave as a fluid. The surface tension of the water on the particles binds them together and causes the mass to exhibit plastic flow.

Base surges are moderately to poorly sorted, with a rapid decrease in grain size and thickness away from the source. They commonly exhibit sedimentary structures, such as cross-bedding and fine lamination, that resemble nonvolcanic flows (Fig. 14.18).

Other Volcanogenic Sedimentary Rocks. Other volcanogenic sedimentary rock types owe their origin to igneous activity other than volcanic eruption. For example, lava flows typically cool in an orderly fashion. The basal portion of a flow is chilled against underlying bedrock. Simultaneously, the upper portion cools as thermal energy is radiated into the atmosphere. A delicate and brittle crust is generated by cooling of the upper lava surface. Because it rests on underlying material that is moving, this crust easily breaks into angular, pancake-like blocks. The rock that results is **autoclastic breccia.** Continued flow of lava further fragments these brecciated slabs; the slabs slide off the nose of the flow and become incorporated into its base. As a result, upper and lower zones of autoclastic breccia enclose a massive or flow-banded central portion.

Hot lava flows also come into direct contact with water, causing rapid and dramatic cooling that produces thin, brittle, easily brecciated chilled rinds enveloping still-moving masses of magma. These breccias are known as **hyaloclastites.** Many pillow lavas show these well-developed rinds of breccia (Figure 14.19).

Nonepiclastic, Nonvolcanogenic Sedimentary Rocks

Cataclastic Rocks. These rocks are produced by the mechanical fragmentation of pre-existing rocks due to intense folding and faulting. The movement of one crustal block relative to another grinds and pulverizes narrow zones of the rocks into fine-grained, banded, powdery **cataclastic breccia** or **microbreccia (mylonite)** that is extremely granulated and sheared. There are three principal varieties. **Fault breccias** consist of blocks of country rocks floating in finer-grained powdery fault gouge. When mapped, brecciated zones are largely confined to the belt of faulting. **Fold breccias** form where layers of brittle sedimentary rock such as sandstone lie within less competent, plastic lithologies such as mudrock. As the sequence bends, brittle rock layers are brecciated and jostled together within the surrounding carapace of plastic material, especially where folding creates sharp anticlinal crests and synclinal troughs. **Crush breccias** develop where brittle rocks are cut by a series of close joints. The intersection of joints produces cubic blocks of material that, with further deformation, rotate against one another and generate breccia.

Collapse (Founder) and Solution Breccias.

These rocks are formed when material underlying a rock unit is selectively removed. The unsupported rock ceiling collapses, and large angular blocks tumble down or free-fall into the underlying space. Solution breccias are a specific type of collapse breccia. They form when the underlying material is excavated by solution. Solution breccias are associated with readily soluble subterranean bedded evaporite and limestone units.

Meteoritic, Impact, or Fallback Breccias.

These breccias are produced when bodies of extraterrestrial origin **(bolides)** impact the Earth's surface at high velocity. The tremendous kinetic energy produced by the impact fragments the solid material at the target. Ma-terial excavated from craters is injected into the atmosphere and stratosphere. The bulk of the material produced falls back to the Earth near the point of impact.

Few impact or fallback breccias are well preserved. The material produced is notoriously susceptible to the ravages of weathering and erosion. Also, breccias produced by impact events are largely confined to the local region surrounding the target point. Finally, the Earth rarely collides with bolides massive enough to generate sizable amounts of fallback material. These bolides are of uncertain origin, but they are probably derived from the asteroid belt or from clouds of cometary material far out in space.

Identifying a deposit as an impact breccia requires careful examination of a number of features. Defining characteristics include close association of the deposit with **tektites** ("splash droplets"; see Fig. 15.27), the presence within the deposit of such high-pressure polymorphs of SiO_2 minerals as coesite and stishovite, and the presence of a widespread contemporary layer of fine-grained ejecta that is enriched in platinum group metals such as iridium.

Bolide impacts may be an important process that has initiated significant global change over the course of geologic time. Some geologists and astronomers believe that impacts have caused mass extinctions periodically throughout Earth's history.

CONCLUSIONS

Iron-rich sediments are our primary sources of iron and steel and yield important clues about the Precambrian atmosphere and oceans. Evaporites are literally the "salt of the earth," essential in all cultures not only for diet but for a wide range of industrial uses. Evaporites also reveal fascinating aspects of the geologic past, such as the great salt basins associated with the Silurian-Devonian reefs, the amazing evaporite episodes in the great Permian basins, and the staggering implications of the Mediterranean as a desert. Volcanogenic deposits are becoming increasingly important as stratigraphers begin to decipher mountain belts. Impact deposits not only capture the imagination, but some geologists think they hold the key to understanding great mass extinctions, such as the one that wiped out the dinosaurs.

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