Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks

Part II
Sedimentary Carbonate Rocks

Donald L. Graf
GEOCHEMISTRY OF CARBONATE SEDIMENTS AND SEDIMENTARY CARBONATE ROCKS

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FOREWORD

Detailed knowledge of the chemical and mineralogical variations that exist in the carbonate rocks limestone and dolomite and of the processes responsible for this diversity is fundamental to the Illinois State Geological Survey's program of furthering the practical utilization of these natural resources of the state. Chemical composition is particularly important when the rocks are used as agricultural limestone and fluxing stone or in the manufacture of dolomite refractories, lime, calcium carbide, sodium carbonate, glass, and other products.

The invitation extended to Dr. Graf by the United States Geological Survey to prepare the chapter on sedimentary carbonates for their revision of F. W. Clarke's "Data of Geochemistry" has afforded a valuable opportunity for the state and federal geological surveys to cooperate in a basic review of selected topics in carbonate geochemistry. The resultant material is presented in five Illinois State Geological Survey Circulars and subsequently will serve as the basis for a condensed treatment in the revised "Data of Geochemistry."

Part I, published as Circular 297, includes an introduction and sections on carbonate mineralogy and carbonate sediments.

Part II, Circular 298, includes the section on sedimentary carbonate rocks.

Part III will deal with the distribution of minor elements.

Part IV will discuss isotopic composition, present chemical analyses, and also will contain the bibliography for the first four circulars.

Part V, concerned with aqueous carbonate systems, will be published at a later date.

John C. Frye, Chief
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ABSTRACT

The distribution of major and minor elements in sedimentary carbonate rocks and the mechanisms responsible for this distribution are considered on the basis of published information contained in geologic studies, and in studies of present-day environments of carbonate deposition, isotopic composition of carbonates, and experimental aqueous and nonaqueous carbonate systems. There are five parts in the series and an extensive bibliography for the first four parts appears in Part IV. Part V carries a separate bibliography.

DEPOSITS FORMED BY CARBONATE ENRICHMENT OF PRE-EXISTING MATERIALS

Caliche

More or less indurated, single or multiple carbonate-rich zones as much as 150 feet thick lie just under present-day soils in much of the semiarid western United States. On the northeastern Llano Estacado of Texas, this caliche consists of roughly equal parts by volume of CaCO$_3$ and SiO$_2$ in the form of calcite and opal or chalcedony (Brown, 1956). On the Southern High Plains of Texas, Sidwell (1943) reported as much as 90 percent CaCO$_3$, mixed with silica and clays. Rounded and frosted sand grains, volcanic ash, and glass fragments suggested to Sidwell that an appreciable part of the original material in these deposits is of eolian origin. Nine samples of lithified caliche caprock from southeastern New Mexico (Bretz and Horberg, 1949b) contained from 0 to 8.7 percent insoluble residue and "only a small percentage of magnesium oxide." Analysis 33 (Part IV) is of caliche from Mexico.

The caliche results from leaching of CaCO$_3$ and SiO$_2$ by downward percolation of rainwater and their subsequent deposition when the water evaporates long before it reaches the deeply buried water table (Brown, 1956). Sidwell (1943) noted that the deposits in his area seem to be especially carbonate-rich below surface drainage or shallow-water depressions that fill during rains. The distribution of CaCO$_3$-enriched zones in some of the thicker caliche sections is a function of both rate of leaching and rate of aggradation of eolian material on the surface, which together determined the amount of time available for leaching a given vertical portion of the deposit and the consequent degree of lithification of the CaCO$_3$- and SiO$_2$-enriched zone just below.

The operation of the process of calichification has been followed by Bretz and Horberg (1949b) and by Frankel (1957). Frankel found that loess from Nebraska had a variable content of snail shells. The relative rates of leaching and loess deposition at a given point in the section may be inferred by noting the extent to
which the shells are etched and the size and number of lime concretions formed by precipitation of CaCO$_3$ leached out higher in the section. Bretz and Horberg described a locality in southeastern New Mexico where downward-moving waters had by dissolution formed cup-like depressions in limestone pebbles in the upper part of a limestone conglomerate bed and deposited laminated CaCO$_3$ on the undersides of the pebbles. Pebbles in the lower part of the bed were unaffected.

The pisolitic, Tertiary capping-caliche of the Great Plains is apparently similar in origin to the older caliche described by Bretz and Horberg (Swineford et al., 1958). Superficial textural similarity to algal pisolites had earlier led to other explanations.

Loess in the Middle West often shows a weak development of caliche in the subsoil. In this relatively humid area with a well developed organic cover, it appears likely that the precipitating mechanism is not evaporation but a partial loss of the large amount of CO$_2$ picked up in passing through humus-rich soil.

Some underclays in the Pennsylvanian cyclothsms of Illinois contain, in their lower parts, concentrations of limestone nodules. Obviously concretionary in origin, these nodules have been attributed by some to superficial downward leaching of calcareous clay (see Grim and Allen, 1938; Wanless, 1957; Schultz, 1958). They are not to be confused with nodules and solid limestone benches that may occur in the same stratigraphic position but which contain fresh and brackish water fossils, and sometimes even marine fossils.

Surface Concentration

The carbonate concentrations described above are attributable to descending solutions. However, there are cases of carbonate cementation essentially at the surfaces of carbonate sediments and rocks, analogous to the surficial case-hardening of some carbonate rocks by silica.

Dapples (1941) believed that extensive cementation of Near East surficial desert sands by CaCO$_3$ results from evaporation of ground water charged with calcium carbonate from numerous local limestones and then carried to the surface by capillarity. Natural walls of dense limestone occur on Okinawa at places where there are nearly vertical exposures. On flat areas, organic acids from vegetation dissolve underlying limestone, but secondary cementation from the surface inward occurs at the steep exposures (Flint, 1949).

A surface limestone of Recent age from Natal, South Africa, the analysis of which is included in Hall's (1938) compilation of analyses, is probably typical of so-called calcrettes found in many arid regions. The rock contained 0.63 percent soluble silica, 1.14 percent alumina, 0.73 percent total iron as Fe$_2$O$_3$, 74.84 percent CaCO$_3$, 4.26 percent MgCO$_3$ and 16.56 percent insoluble material. Calcareous crusts such as those in the eastern and southeastern coastal area of Spain require for their formation a climate with periods of precipitation, the amount not being critical, followed by relatively longer, dry, hot periods during which the water can evaporate (Rutte, 1958). A number of attempts have been made to correlate crust formation with the warmer interglacial periods of the Pleistocene.

Crusts containing CaCO$_3$ and other materials have formed after periods of heavy rainfall in the semiarid Nebraska Sand Hills, when the water table has risen close to the surface (J. C. Frye, personal communication).
Post-depositional activity of ground water may markedly alter the CaCO₃/SiO₂ ratio of sedimentary rocks. It is evident in many places where the Dover Limestone of Pennsylvanian age in Lyon County, Kansas, is particularly high in silica (as sand) that it overlies massive beds of sandstone in the Langdon Shale, and that large sand-calcite crystals in the shale have been redeposited after ground-water leaching from the Dover Limestone (O'Connor, 1953). Sand-calcite crystals from Fontainebleau, France, contain as much as 50 percent calcite cement (Clarke, 1924). Calcite cement in calcareous sandstones of late Cretaceous age in the eastern Carpathians is preserved where the formation is contained by shales, but elsewhere the cement has been dissolved and reconcentrated in masses ten to twelve feet in diameter (Sujkowski, 1958).

Petrographic studies show that partial to complete calcite and dolomite replacement of detrital quartz and feldspar grains is not uncommon (Walker, 1957, 1960; Carozzi, 1960, p. 38-39; Alimen, 1944; Alimen and Deicha, 1958). The phenomenon has been observed even in Recent age calcarenite beachrock. Swineford et al. (1958) similarly explained the development of the late Tertiary capping-caliche of the Great Plains from calcareous feldspathic quartz sands and silts. The caliche contains only a few percent of acid-insoluble material. They believed that silica has been replaced by CaCO₃ and then redeposited to form the opal that occurs lower in the section.

Cayeaux (1935) mentioned a Pliocene age diatomite from Sendai, Japan, that has been completely calcified, with microstructures preserved. Radiolaria in the limestones of Barbados are preserved in some places and calcified remains are left in others. Lowenstam (1948) described an atypical case for the Racine Formation of Silurian age near Chicago in which beds consisting largely of remains of the siliceous sponge Astraeospongia meniscus Roemer have been replaced by carbonate.

CAVE DEPOSITS

No detailed chemical analyses of stalactites and other CaCO₃-rich cave deposits were found in the literature. The mechanisms and rates of solution and precipitation of CaCO₃ in such environments will be discussed in Part V.

Collophane has been described by Proudfoot (1956) as a component of stalagmites and as a cement in a cave stratum of Tornewton Cave, Devon, England. It was formed under normal weathering conditions by percolating solutions that had access to bat and hyena dung. Stalactites from 14 different cave deposits containing an average of 38.64 percent Ca (range, 25.24 to 42.42 percent) had an average of 4.88 percent P (range, 0.674 to 10.70 percent) (Neuberg and Grauer, 1957). An extensive discussion of cave guanos is given by Hutchinson (1950).

Gypsum excrescences of inorganic origin are not uncommonly found along with the calcareous deposits in caves (see Pohl and Born, 1936; McGill, 1933; Davies, 1949), and in two instances the growth rate during historical time, about 2 mm/100 years, is known from the thickness of overgrowth on dates scratched in cave walls. The sulfate at Crystal Cave, Kentucky, is believed to have been derived from abundant marcasite in a zone in the lower part of the Golconda Formation of Mississippian age that nearly everywhere caps the cavernous ridges in Kentucky. Merrill (1894) noted that gypsum incrustations were found in the old, dry chambers of Wyandotte and Mammoth Caves.
SPRING DEPOSITS

Dense, laminated travertine and the more spongy rock known as calcareous tufa are deposited from both cold and hot spring waters that lose CO\textsubscript{2} upon coming in contact with the air (analyses 15, 34-36, Part IV). The ferrous and manganous bicarbonates in solution in many of these waters are oxidized and precipitated as the accessory oxides commonly found in spring deposits. Dickey (1923) found only from 0.5 to 2 percent MgCO\textsubscript{3} in the material from spring-deposited terraces along the sides of valleys in Pennsylvania. Stout (1940) noted that travertine deposited to a depth of as much as 4 feet in the pond maintained by overflow from the Castalia spring in Ohio reaches a purity of 99.4 percent in places.

ALGAL LIMESTONES

The areally extensive Curley Limestone in central Utah is a fine-grained laminated bed with wave to domelike structures superimposed on the laminae, and contains-at some places, branching threads and leaf-like forms that Proctor and Clark (1956) believed to be algal in origin (analysis 40, Part IV). Wayland and Ham (1955) described a fine-grained limestone from the Baum Member of the Paluxy Formation of early Cretaceous age in Oklahoma that contains ostracodes, charophyte oogonia, and abundant remains of blue-green algae, and is believed to be a brackish water facies deposited in a protected bay (analysis 42, Part IV).

Eardley (1932) described a limestone bed as much as 300 feet thick with pisolitic texture and a freshwater fauna (*Goniobasis simpsoni*, *G. tenera*) that occurs interbedded in very coarse, poorly sorted alluvial fan deposits in the southern Wasatch Mountains of Utah. The matrix of the rock contains less than 0.03 percent insoluble material, mainly small well rounded quartz grains, but the limestone as a whole grades into conglomerate with increase in the number of quartzite and sandstone pebbles that form pisolite centers. The limestone is believed to be a lake deposit, and spongy structures within the pisolites, together with recurrent thin, dark bands therein, suggest algal origin.

Rezak (1957) attributed the stromatolites of the Belt Series in Montana to Cyanophyta and, possibly, unicellular Chlorophyta. Rutte (1953) described concretions, rhythmic incrustations, reefs, and detrital material, all attributable to blue-green algae, in the lacustrine limestones of Miocene age in the Engelwies region, Baden, Germany.

STREAM DEPOSITS

Conglomerates made up of stream-transported carbonate rock particles, although a relatively uncommon rock type, are known from a number of localities. Erosional remnants remain of a once continuous, indurated limestone conglomerate in the Ogallala Formation of New Mexico, a former river gravel supplied largely from the western uplands (Bretz and Horberg, 1949b). Ham (1954) described a limestone conglomerate from the late Pennsylvanian of Oklahoma, and Wayland (1954) one from the Lower Cretaceous of southern Oklahoma (see also Folk, 1959).

Streams receiving considerable volumes of calcium-bicarbonate-rich waters from springs and underground drainage through carbonate rocks may form extensive travertine deposits at falls and rapids where agitation accelerates equilibration of CO\textsubscript{2} between air and water. Masses as much as 100 feet thick and nearly half a mile in extent are described from creeks in the Arbuckle Mountains of Oklahoma (Emig, 1917); alternating periods of erosion and deposition are shown to have occurred (see Dickey, 1923).
TURBIDITES

Relatively few occurrences of calcareous turbidites are known (ten Haaf, 1959). They include the Teschen Limestone of the Polish Carpathians (Dzulynski et al., 1959), several coarsely clastic beds in nappes near Geneva (Carozzi, 1952; Kuenen and Carozzi, 1953), incidental intercalations in other noncalcareous formations (Kuenen and Migliorini, 1950), and a few graded calcarenitic turbidites in the Apennines regularly interbedded with homogeneous, fine-grained limestones (Kuenen and ten Haaf, 1956).

BEACHROCK AND DUNE LIMESTONE

Formation of beachrock and dune limestones by secondary CaCO₃ cementation of calcareous sediments has been reported throughout the tropic zone, in which sea water is apparently saturated with CaCO₃ and there is extensive organic and possibly chemical precipitation of CaCO₃. The bedrock exposed in cliffs and ledges of the Bermuda Islands is made up of lithified calcareous dune sands blown together during a low stand of sea level during Pleistocene time, and is now disaggregating and contributing to present-day beaches (Todd, 1939; Dunbar and Rodgers, 1957).

Calcareous beach sands along the Mediterranean coast of Egypt gradually change, away from the beach, to fairly well consolidated limestone ridges. Dune limestones in Victoria may contain up to 98.75 percent CaCO₃ (Coulson, 1940). Similar rocks have been described from Puerto Rico (Guillou and Glass, 1957), the northern Marshall Islands (Fosberg, 1954), and Kathiawar, some 30 miles inland from the present margin of the Arabian Sea (Chapman, 1900; Evans, 1900; Crickmay et al., 1941). The narrow zone of coquina along the east coast of Florida, formed on an old beach, shows at various points all gradations from pure shell rock to carbonate-cemented quartz sand grains (Mossom, 1925).

A similar phenomenon is observed at Mono Lake, California, and at Pyramid Lake, Nevada, where ordinary detrital minerals making up the beach sand are cemented by CaCO₃ (Emery and Stevenson, 1950).

CHALKS AND FORAMINIFERAL LIMESTONES

Chalks are poorly consolidated, relatively pure limestones consisting principally of fine-grained calcite and calcareous microfossils such as foraminifera, coccoliths, coccospheres, rhabdoliths, and rhabdospheres. Although some chalks are foraminiferal limestones, rocks such as the bed in the Comanchean of south central Texas that consists of abundant miliolid foraminifera embedded in clear calcite (Hanna, 1931) are certainly not chalks.

The foraminiferal assemblages of limestones may be quite indicative of depositional environments. Sediments in which planktonic foraminifera such as Globigerina sp. and Globorotalia sp. dominate probably were formed in at least moderately deep water for, although these foraminifera are more abundant in lagoonal waters, their contribution there is frequently masked by the high benthonic sedimentation rate (Forman and Schlanger, 1957).

Well sorted, foraminiferal-algal calcarenites, such as the limestones rich in benthonic foraminifera of the genus Heterostegina found at Guam and in southern Louisiana, may be associated with reefs but could have formed in a shoaling bank environment lacking a definite reef wall (Forman and Schlanger, 1957; Houbolt, 1957). Limestones containing abundant, thin-walled miliolid foraminifera in a fine-grained carbonate matrix, such as described by Henson (1950) from Iraq, are formed in back-reef and lagoonal environments.
Crickmay et al. (1941) discussed the probable depositional environments of various foraminiferal limestones, some of which (including the Upper Cretaceous chalks of England) were once thought to be the consolidated equivalents of deep-sea pelagic ooze. The siliceous tests of pelagic organisms and the finely divided terrigenous and volcanic detritus present universally in small amount in the Globigera limestones are missing from many of these rocks, some of which are interbedded with oolitic deposits. Most of the foraminifera in chalks (see Dunbar and Rodgers, 1957), such as those of Cretaceous age in Europe, are benthonic and the associations are not characteristic of the deep sea. Moderately shallow depths, perhaps 50 to a few hundred fathoms, are suggested. The Globigerina beds of the Oceanic Series of Barbados, which are interbedded with radiolarian ooze and red earths, may have been formed at somewhat greater depths. The thick, areally extensive Globigerina limestones of the La Luna Formation and equivalent beds of Cretaceous age in South America are highly bituminous and contain fish remains and phosphate pellets (Smith, 1951). Deposition may have taken place in the deeper parts of a seaway with impaired circulation.

Coccoliths occur in great variety and vast numbers in Cretaceous chalk formations, are even more abundant in Tertiary calcareous deep-sea deposits, and become successively less important in late Tertiary and Recent calcareous ooze (Bramlette, 1958). The dissolution and recrystallization that are apparent in Cretaceous chalks, especially in the more permeable nonclayey ones, may lead to low estimates of coccolith abundance.

Many of the minor but widespread carbonate beds interbedded in the siliceous rocks of the Monterey Formation of California (Bramlette, 1946) consist largely of foraminiferal remains. Current drifting of buoyant diatom and foraminiferal shells is believed by Bramlette to explain the uniformity of depth facies apparent in the foraminiferal zones over wide areas, as well as the remarkable thickness of diatomaceous rocks.

The Fort Hays Chalk of Kansas, the lower member of the Niobrara Formation of Cretaceous age, contains from 88.7 to 98.2 percent CaCO₃ (Runnels and Dubin, 1949) and consists of 60 to 80 percent very fine-grained material. There are also microfossils such as Gumbelina, Globorotalia, Globigerina, and Textularia. P₂O₅ in 30 samples ranges from a trace to 0.56 wt percent, mean 0.07 percent; S in 19 samples ranges from a trace to 0.23 wt percent, mean 0.05 percent.

**SHALLOW-WATER MARINE LIMESTONES**

Intraformational carbonate conglomerates are common in the geologic record, and at some places such reworking has produced unusual rock types. Thus, an intraformational conglomerate in the Upper Cretaceous of Haute Savoy, France, marking the transition from calcareous glauconitic sandstone to lithographic limestone, consists of wispy, streaked-out limestone pebbles, glauconitic micaceous sandstone, and occasional phosphatic nodules. Rather vigorous shallow-water wave action leading to mixing of glauconitic sand and still-plastic lime mud is indicated (Carozzi, 1956). Hobbs (1957) described intraformational limestone conglomerates from the Ordovician of Virginia, some of which contain limestone pebbles and quartz sand in a matrix of dolomite.

Lithified equivalents of the suite of rock types now forming in the Bahama-Florida area can be recognized. Bioherms in a number of areas were formed on broad carbonate platforms, such as the Cooking Lake Formation of central Alberta (Andrichuk, 1958). In this area sorted bioclastic and oolitic limestones formed in
agitated waters are associated with fine-grained, presumably precipitated limestones. Environments inferred from the lithofacies and biofacies paralleling the reef front correlate with those described by Ginsburg (1956) in the Florida area, allowing for the differences in available Devonian and Recent organisms.

Four laterally successive environments of carbonate deposition are shown by the Mission Canyon Formation and the lower part of the Charles Formation, both of Mississippian age, in Saskatchewan: (1) basinal, dark gray-brown, argillaceous limestones containing bituminous shale partings, and dark gray, dense, siliceous limestones, both containing finely disseminated organic matter and iron sulfides; (2) highly fossiliferous, open-shelf, marine limestones; (3) oolitic and lithographic limestones containing only the remains of algae and a few scattered brachiopods; (4) chalky, ostracodal, argillaceous limestones, anhydrite, and fine-grained dolomite (Edie, 1958). Plots of the ratios of bioclastics to fine-grained limestone and of true evaporites plus fine-grained dolomite to fine-grained limestone for these beds show abrupt lateral transitions. The massive Mission Canyon Limestone in the Little Rocky Mountains and at other Montana localities is a cross-laminated, calcareous sand whose grains are saccharoidal crystal aggregates or, more rarely, oolites (Sloss and Hamblin, 1942).

The granular cross-laminated "Bedford Oolite" of Mississippian age in Indiana (Spergen Formation, according to U. S. Geological Survey usage) is made up of small fossils and fossil fragments of similar particle size, apparently size-sorted by marine currents or waves (Patton, 1953). Calcite and dolomite cements, the latter microcrystalline, are noted (analysis 37, Part IV).

Frequently there is a close geographical association in lithified rocks between reefs, euxinic basin deposits, and evaporite deposits, with abrupt lateral facies changes (see Myers et al., 1956; Newell et al., 1953; Sloss, 1947; Ginsburg and Lowenstam, 1958). This association has not been reported from present-day environments. The basin margins between tectonically neutral platforms and tectonically negative basins, some of which were euxinic, are the loci for narrow but fairly persistent zones of such reef limestones (Sloss, 1947; Lowenstam and DuBois, 1946; Parkinson, 1957). The reefs themselves, by physically changing the amounts and directions of water flow, must have been to a considerable extent responsible for development of evaporite basins on the platforms.

The intracratonic Michigan and Williston evaporite basins of Silurian age owed their evaporite character at least in part to reefs (Krumbein, 1951). The rocks of Niagaran age in northeastern and northwestern Illinois consist of reef and interreef deposits that formed in the southwestern portion of the belt around the Michigan Basin. The interreef deposits consist of variable mixtures of locally derived reef detritus and regionally derived fine-grained terrigenous material deposited under a range of water turbulences and degrees of aeration (analyses 79, 80, Part IV) (Lowenstam, 1949). Normal shelf deposits including many coquinas are found in west-central Illinois, and the section in southwestern Illinois is made up mostly of quiet-water, muddy bottom deposits containing about 40 percent terrigenous clastics.

The Capitan Limestone in Texas is a great barrier reef 70 miles long and more than 2000 feet high in its exposed portion alone. It separated a normal marine sea to the south from a restricted sea to the north, which in later stages became highly saline and deposited salt and gypsum (Lloyd, 1929). A biothermal barrier in the Travis Group of Devonian age in western Michigan separates shallow-water facies to the east from evaporite-facies dolomites and anhydrites to the west (Jodry, 1957).
FINE-GRAINED LIMESTONES

Illing (1954) noted that recrystallization to microcrystalline limestone, obliterating fossils and ooliths, is already taking place in the Bahamas early in diagenesis. One broad type of source area that can produce microcrystalline limestone is thus defined.

The Upper Jurassic lithographic limestone of Solenhofen, Bavaria (analysis 49, Part IV) contains abundant marine fossils, dinosaur and Archaeopteryx remains, and many insects. It appears to have been formed from mud laid down on a shelf area within the lagoon of an atoll, into which remains of the land dwellers were blown or drifted out (Dunbar and Rodgers, 1957).

An eight-inch layer of fine-grained, argillaceous limestone with shrinkage cracks, found in the Upper Pennsylvanian nonmarine, coal-bearing Uniontown Formation of West Virginia, is probably a shallow marl-lake deposit (Dunbar and Rodgers, 1957). The thin, fine-grained Carmel Limestone of Utah, which occurs between nonmarine formations and contains some pellets, may represent recrystallized CaCO₃ that was originally a shallow-water precipitate or disintegrated algal debris (Bramlette, 1958).

Very fine-grained limestones in especially thin thin-sections are seen to consist of interlocking crystals, commonly only a few microns in size, that must have recrystallized from original particles of some sort (Bramlette, 1958). Bramlette suggested that the coincidence between the first appearance of coccoliths in abundance and the earliest occurrences of the relatively unlithified deposits known as chalk indicates that earlier fine-grained limestones may have been coccolith-rich and subsequently recrystallized. The fine-grained Upper Cretaceous chalk of central Tunisia consists of foraminifera, mostly pelagic, scattered among interlocking calcite crystals a few microns in size. In the less deformed stratigraphically equivalent formation to the south, these foraminifera are scattered among abundant coccoliths. Very fine-grained Tithonian (Upper Jurassic) and younger (Cretaceous) geosynclinal limestones of the sub-Alpine region of France consist of interlocking grains little larger than the coccoliths that occur in the somewhat older, though much less lithified, Oxfordian age marl of northern France.

Pre-Cretaceous fine-grained limestones in which comparatively robust microfossils are preserved also are known, indicating the original absence of planktonic foraminifera, but the finer matrix is recrystallized.

LIMESTONES AND DOLOMITES FROM EVAPORITE SEQUENCES

Briggs (1958) calculated the theoretical distribution of evaporite minerals in an ideal basin receiving an equilibrium influx of sea water and predicted that a carbonate-anhydrite-halite sequence should be found from the inlet and edges of the basin toward the center. This is a sequence recorded repeatedly in descriptions of evaporite deposits (Sloss, 1953).

Briggs' evaporite facies map for the Salina Formation of Upper Silurian age in the Michigan Basin and the Ohio — New York Basin, based on proportions of carbonate, halite, and anhydrite (or gypsum) in samples from 56 wells studied visually, is shown here as figure 1. The marginal position of the carbonate-rich zone agrees with that predicted by his model. His plot of limestone to total carbonate ratios, here reproduced as figure 2, shows dolomite to be the predominate carbonate rock within the area studied, except in the region of the inferred principal Salina connection to the open sea where the normal marine environment is believed to have projected into the basin.
The argillaceous dolomite facies of the Florena Shale of Permian age in Kansas (Imbrie, 1957; personal communication) is surrounded by limestone. Shallow-water fossils are present in the limestones but gradually disappear as the dolomite is approached, suggesting a salinity control over the formation of dolomite.

Folk (1958) cited a diminution in fauna as the dolomite facies is approached in the Beekmantown rocks of Pennsylvania, and believed that the presence of fresh, detrital K-feldspar indicates an arid coast to the west and a salinity control of dolomite formation. He pointed out (see also Strakhov, 1956) that the decrease in fossil content from limestone to dolomite is not solely due to destruction by dolomitization, inasmuch as large fossils are still recognizable in thin section because they differ from the matrix in organic content and the crystal size of the dolomite that has replaced them.

Ronov (1956) showed that the carbonate rocks of the Russian Platform have a similar distribution pattern throughout much of the Paleozoic: highly dolomitic rocks in a central area, which shifts about somewhat in different geologic periods,
surrounded by partly dolomitized rocks and then by limestones. This pattern would result from Briggs' model if the salinity of the water in the basin of deposition never became quite high enough for anhydrite precipitation. Strakhov (1956) and Ronov debated the relative effect of fresh water from streams and from rains on salinity and the resultant chemical precipitation in such a body of water. Briggs suggested that occasional rains would merely stop the deposition of evaporite minerals until the rainfall layer had evaporated, since the rainwater could not sink into the denser underlying layer and would add little or no mineral matter.

The extensive development of biostromal shoals on a relatively stable shelf area in the Stettler region of Alberta during late Devonian time resulted in the formation of dark bituminous limestones and then of interbedded anhydrite-dolomite and local halite (Andrichuk and Wonfor, 1954). Evaporite ratio maps show an area to the north in which there is only secondary dolomitization. Southward an evaporitic anhydrite-dolomite section in which halite locally becomes a significant component is followed by another area of secondary dolomitization. Reefs to the north are not dolomitized.
The St. Louis Limestone of Mississippian age in southwestern Indiana, normally a marine limestone, in places contains nonfossiliferous, saccharoidal, dolomitic limestone units that are succeeded by gypsum and anhydrite. The evaporite part of the formation contains a higher percentage of evaporite beds and is thickest in several intrasilled basins that have been outlined by isopach studies. There is a correlation between increasingly saline units and an increasing segregation into recognizable tectonic units (shelves, basins, and hinge lines) (McGregor, 1954).

Evaporite cycles in which dolomite, CaSO₄, NaCl, and KCl were successively deposited are described from the Permian rocks of northeast Yorkshire (Raymond, 1953). The basinal Zechstein beds of Permian age in north Germany include four evaporite cycles, each showing a clay-carbonate-anhydrite-halite-sylvite succession. Best shown by the second cycle, the facies in the carbonate horizon are massive dolomite (containing oolite and algal grains) along the basin rims and atop linear ridges near the rim, and, basinward, dark, fetid, better stratified dolomite; darker, thin-bedded, fetid limestone; and, finally, very dark, thinly bedded, fetid, clayey limestone (Füchtbauer, 1956; Andres et al., in press). The mineralogical composition of the last named bed as determined from optical and X-ray diffraction data is 77 percent calcite, 7.5 percent albite (authigenic), 6.5 percent quartz (detrital), 5.5 percent muscovite, 2.3 percent K-feldspar (detrital), 1.8 percent pyrite, and 0.2 percent anhydrite.

Limestones and dolomites occurring in evaporite sequences may contain considerable amounts of halite, gypsum, and anhydrite. Schwade (1947) described, from the upper Yeso Formation of Permian age in New Mexico, varve-like layers of salt-free dolomite alternating with layers of salt-dolomite intergrowths. Secondary salt occurs as fracture fillings, primary salt as discrete crystals. Martens (1943) studied cores from the Silurian of eastern Ohio that contained porous dolomite from which salt had been dissolved; one five-foot section of such material that was still intact contained 18 percent salt, well mixed with the less soluble ingredients. Secondary salt filling of porous Devonian limestones and dolomites underlying a salt bed at Dawson Bay, Saskatchewan, was described by Edie (1959).

Anhydrite commonly occurs as pore fillings and porphyroblasts in Mississippian age limestones underlain or overlain by evaporite units, described by Edie (1958) from Saskatchewan. Dense, nonfossiliferous, nonporous, thinly laminated dolomites contain intermixed salt casts and anhydrite. Edie noted that a complete gradation between cryptocrystalline anhydrite and cryptocrystalline dolomite exists in the Mission Canyon Formation. Breciated fragments of anhydrite layers are sometimes found in a dolomite matrix in the Salina Formation of Michigan (Dellwig and Briggs, 1953). The Middlebury Limestone of early Permian age shows a gypsum-crystal-bearing zone that grades into a gypsum bed in the Early Creek Shale (Kulstad et al., 1956). Mixed carbonate-anhydrite rocks occur in the Zechstein of Permian age of northern Germany (Füchtbauer, in press). There are, for example, anhydrite-filled oolites in dolomite, and algal pebbles in anhydrite beds.

Some dolomitic parts of the St. Louis Formation of Mississippian age in southwest Indiana contain porphyroblastic anhydrite in extensive lenticular beds, as well as later veins of anhydrite (Bundy, 1956). Saxby and Lamar (1957) made closely-spaced visual estimates, spotchecked by microscopic and X-ray analyses, of the mineralogy of cores through this formation in southern Illinois. Limestones containing as much as 40 percent gypsum and 15 percent anhydrite are noted, as are dolomites with up to 30 percent gypsum and 10 percent anhydrite.

Dolomite generally is subordinate in the compact dolomite-anhydrite layers of the halite-anhydrite zone in the Permian of northeast Yorkshire (Stewart, 1951a).
but locally may reach 70 percent. Mixed dolomite-anhydrite rocks of Permian age in South Cumberland and Furness consist of anhydrite crystals up to 0.5 mm long with interstitial fine-grained dolomite particles averaging 0.02 mm diameter. Anhydrite-calcite rocks also occur, including one in which spherical calcite aggregates about 0.04 mm in diameter are scattered throughout a matrix of anhydrite crystals 0.005 to 0.1 mm long (Dunham and Rose, 1949).

The replacement of dolomite by anhydrite in the Permian of Yorkshire can be demonstrated particularly well when carbonaceous impurities, originally present in the dolomite but not in the adjoining anhydrite, are present to serve as markers (see Stewart, 1951a). Scattered remnants of a single dolomite grain in optical continuity also occur (Carozzi, 1960, p. 436). Magnesite, anhydrite, and dolomite are sometimes found together, and Stewart (1949) concluded from petrographic evidence that the first two may have formed at the expense of the dolomite.

There is a considerable variety of thinly interlaminated carbonate rocks from evaporite sequences. Delicate laminae in the fine-grained dolomite of the Mission Canyon Formation of Mississippian age in Saskatchewan, associated with anhydrite, result from intermixing of small amounts of argillaceous, dark gray material in some layers, as well as interlayering of paper-thin shale partings (Edie, 1958). These laminae presumably resulted from fluctuations in the amount of detritus carried in by freshwater; most of the other known examples of interlaminated beds involve chemical precipitates and are believed by Briggs (1958) to indicate a nonconstant rate of sea-water influx. Yarzhemskij (1955) described almost sheet-like interlayering of dolomite and anhydrite, and noted that in the same small dolomite interlayers there are marked facies changes into anhydrite, NaCl, and even KCl.

In places in the Blaine Formation of Permian age in Oklahoma, dolomite beds 0.25 inch thick alternate with gypsum in beds 1.5 inches thick (Muir, 1934). Thin dolomite bands alternating with those of anhydrite in the Salina Formation of Michigan are believed by Dellwig (1955) to have resulted from water influxes from outside the evaporite basin. The bituminous material found in the dolomite laminae (but not in the anhydrite) is thought to have been formed from the remains of organisms that grew in the less saline surface layer of influx water, fell to the bottom on death, and were preserved there by reducing conditions. Von Hoyningen-Huene (1957) described a similar localization of organic matter in gray-black, thinly bedded, dolomite layers in the anhydrites of the Zechstein of Permian age of Germany. Fine interlaminations of anhydrite and bituminous calcite in the Castile Formation are attributed by Scruton (1953) to short-term fluctuations in water salinity (see also Stewart, 1954).

Hobbs (1957) described Ordovician carbonate rocks from Virginia containing millimeter-laminated alternations of limestone and dolomite (see also Sander, 1951), but an interpretation of variable salinity does not appear to have been attached to these alternations.

**OTHER DOLOMITES**

Some apparently lacustrine dolomites that formed in bodies of water of unknown salinity are described below. Sedimentary dolomites other than these and the evaporite dolomites described earlier are evidently replacive because individual dolomite rhombohedra cut pre-existing textures and fossil outlines. In completely dolomitized rocks of this type, the outlines of the larger fossils generally can still be identified. Inasmuch as no organism is known that forms its hard parts of dolomite, at least the dolomite of the large-fossil component of such rocks must be replacive.
Drill cores near Ipswich, Queensland, cut the Silkstone Series of Tertiary age, which includes four basalt layers and six beds of fine-grained dolomite with accessory chert, palygorskite (attapulgite), and montmorillonite (Rogers et al., 1954). There are also freshwater limestones containing Planorbis sp. The weathering of the basalts is believed to have produced Ca, Mg, and Si that were deposited in lakes as dolomite, chert, and sepiolite. The latter mineral can be seen as cores in the bands of palygorskite, which probably formed by subsequent addition of alumino.

**Dolomitized Shallow-Water Limestones**

The dolomite that replaces in mottled fashion certain very pure, shallow-water limestones of Devonian age from Alberta, which are made up of fine-grained fossil debris and well rounded lime sands, typically constitutes 10 to 40 percent of the rock, rarely almost 100 percent (Beales, 1953). The fossils are shallow-water, marine pelagic and benthonic forms, not present in great numbers. The dolomite distribution is controlled by bedding laminations and not by joints or faults. These rocks appear to be lithified equivalents of the material being deposited today in the central portion of the Bahama Banks, where fine-grained carbonate exceeds the skeletal carbonate contribution. Erosion to the west and dolomitization to the east made it impossible for Beales to locate the equivalents of the sediments rich in skeletal debris found on the edge of the Bahama Banks.

Dolomitization of shallow-water limestones in some instances is known to have occurred very early in the history of the rock. The Arbuckle Limestone of Upper Cambrian — Lower Ordovician age in Oklahoma contains detrital, sand-sized fragments of dolomite rock, dolomite crystals, and dolomitic limestone associated with limestone fragments derived from penecontemporaneous or slightly older beds, indicating the very early origin of the dolomite (Ham, 1951). Folk (1958) described cross-bedding and reworked dolomite pebbles in the dense Nittany Dolomite of the Beekmantown Group in Centre County, Pennsylvania. The Precambrian age Randville Dolomite of Dickinson and Iron Counties, Michigan, includes sandy dolomite and dolomitic sandstone lithologies (Greenman, 1951). Conglomeratic and oolitic facies suggest shallow, wave-agitated, near-shore waters. The conglomerates contain, in a sandy dolomite matrix, pure dolomite fragments that could have come only from reworked Randville Dolomite. This evidence is analogous to that cited by Greenman (1951) for the Shakopee Dolomite, in which sandy dolomites containing dolomite pebbles grade down into undisturbed dolomites that obviously gave rise to the pebbles.

A diagenetic origin appears likely for the zoned ferroan dolomite rhombohedra observed by Biggs (1957) only inside or within a one-inch distance from chert nodules in certain Paleozoic limestones from Illinois.

**Structurally-Controlled Dolomitization**

Where replacive dolomite has been localized by post-depositional structural elements, it generally has not been possible to define the nature of the replacing solution, which might have been low-temperature hydrothermal or merely ground water or connate water of a more or less saline nature. The Carboniferous age limestone of the Pennines has been invaded along planes of weakness — faults, joints, bedding planes, fractures — by secondary dolomite (Hatch et al., 1938).
Geikie (1903) described dolomitization of limestones of Carboniferous age in Ireland and northern England for a few feet or yards away from joints. Hobbs (1957) observed in the Ordovician carbonate rocks of Virginia that dolomitization may occur along stylolites and permeable zones in cross-bedded laminae and scour-and-fill structures, just as along joints and faults.

Dolomite masses which extend along faults in the Arbuckle Limestone of Oklahoma, through as much as 1200 feet of beds and for as much as three miles away from the faults, are in part ankeritic, containing up to 8 percent FeO. Ham (1951) believed they were introduced during one or more of the strong orogenic pulses that deformed the Arbuckle Mountains in Pennsylvanian time. Cayeux (1932) described several places in which the chalk of the Paris Basin contains dolomitic zones localized along anticlinal folds. Jodry (1955) showed a distinct grading-off of dolomite content in a normally fossiliferous limestone of the Michigan Basin, the Rogers City Formation of Middle Devonian age, away from apices of fold structures and from certain long, narrow dolomite zones not related to folding. He believed that tension fractures and faults localized the ascent of high-Mg brines from underlying evaporite beds. Tinklepaugh (1957) chemically analyzed 250 samples of this formation from 95 cores and found a highly significant difference, beyond the 1 percent level, for the Mg/Ca ratio of sets of cores from structural highs and those from troughs. The Fe content ranges from 0.01 percent to 8.50 percent, typically 1 or 2 percent, and is higher in the troughs, again giving a difference significant beyond the 1 percent level.

**Dolomitized Reefs**

Maximum dolomitization of reef cores, with lesser amounts farther away from the reefs, is noted for the Cooking Lake Formation of Alberta (Andrichuk, 1958). Illing (1956) noted that reefs form a zone of relatively high permeability through which connate water expressed by compaction or tectonic activity would tend to be funneled, and suggested that these fluids were the agents of secondary dolomitization. It should be emphasized that the reverse also occurs: Carozzi and Lundwall (1959) described a Middle Devonian bioherm in Indiana that is made of limestone and is both overlain and underlain by dolomite. Numerous bioherms in the northern Delaware Basin of New Mexico are limestone (Motts, 1960), with dolomite in areas between bioherms. Newell et al. (1953), noting that the Goat Seep reef mass of the Permian reef complex of New Mexico is completely dolomitized whereas the Capitan Reef is dolomitized only slightly, along sandstone dikes, suggested that the critical factor may have been availability of shelf brines enriched in Mg after deposition of anhydrite.

The dolomitized reefs in the Racine Formation of Silurian age in the Chicago area are exceptionally pure (Willman, 1943), often with less than 0.3 percent SiO₂, 0.1 to 0.4 percent iron oxides, less than 0.01 percent Na₂O + K₂O, no detectable P₂O₅ in a 5-gram sample, and 0.1 to 0.4 percent SO₃ (analysis 77, Part IV). The argillaceous interreef strata typically contain from 80 to 95 percent acid-soluble material, but may have as little as 60 percent (analysis 78, Part IV).

"Dolomite Sands"

Rocks consisting of a mixture of dolomite and calcite may be enriched in dolomite content by the preferential solution of calcite during weathering. The resulting material is frequently an unconsolidated sand made up of dolomite particles from the original rock. Bevan (see Murray, 1930) found cavities in dolomitic
Table 1. Calculated Contents, in Weight Percent, of \( \text{MgCO}_3 \) and \( \text{Ca}_3(\text{PO}_4)_2 \) in Marine Invertebrates
(Compiled from Clarke and Wheeler, 1922. Analyses by W. C. Wheeler, A. A. Chambers, R. M. Kamm, B. Salkover, and George Steiger of the U. S. Geological Survey.)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Number of analyses</th>
<th>Wt% ( \text{MgCO}_3 ) (range and av.) after elimination of organic matter and water from the analyses</th>
<th>Wt% ( \text{Ca}_3(\text{PO}_4)_2 ) (range and av.) similarly calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foraminifera</td>
<td>6</td>
<td>1.79-11.08(9.61)</td>
<td>Trace</td>
</tr>
<tr>
<td>Calcareous sponges</td>
<td>4</td>
<td>4.61-14.10(8.02)</td>
<td>Trace-9.96(3.38)</td>
</tr>
<tr>
<td>Madreporian corals</td>
<td>30</td>
<td>0.09-1.11(0.50)</td>
<td>Trace</td>
</tr>
<tr>
<td>Alcyonarian corals</td>
<td>22</td>
<td>*6.18-15.73(11.12)</td>
<td>Trace-8.57(2.34)</td>
</tr>
<tr>
<td>Coralline hydroids (\text{Millepora} and \text{Distichopora})</td>
<td>6</td>
<td>0.24-1.28(0.54)</td>
<td>Trace</td>
</tr>
<tr>
<td>Annelid tubes</td>
<td>3</td>
<td>0.00-9.72(3.35)</td>
<td>Trace-0.99(0.54)</td>
</tr>
<tr>
<td>Echinoderms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recent crinoids</td>
<td>24</td>
<td>7.86-13.74(10.86)</td>
<td>Trace-1.12(0.21)</td>
</tr>
<tr>
<td>Fossil crinoids (Eocene to Lower Ordovician)</td>
<td>10</td>
<td>0.80-20.23(3.43)</td>
<td>Trace(one had 0.20)</td>
</tr>
<tr>
<td>Sea urchins</td>
<td>12</td>
<td>5.41-13.79(8.51)</td>
<td>Trace-1.85(0.28)</td>
</tr>
<tr>
<td>Starfishes</td>
<td>29</td>
<td>7.79-14.35(10.94)</td>
<td>Trace-0.78(0.15)</td>
</tr>
<tr>
<td>Ophiuans</td>
<td>17</td>
<td>6.61-14.95(10.52)</td>
<td>Trace-1.14(0.17)</td>
</tr>
<tr>
<td>Holothurians</td>
<td>1</td>
<td>1.38</td>
<td>Trace</td>
</tr>
<tr>
<td>Bryozoa</td>
<td>13</td>
<td>0.17-11.08(5.41)</td>
<td>Trace-8.47(2.08)</td>
</tr>
<tr>
<td>Calcareous brachiopods</td>
<td>5</td>
<td>0.49-8.63(2.42)</td>
<td>Trace-0.57(0.19)</td>
</tr>
<tr>
<td>Phosphatic brachiopods</td>
<td>4</td>
<td>0.79-6.68(2.97)</td>
<td>74.73-91.74(82.91)</td>
</tr>
<tr>
<td>Mollusks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pelecypods</td>
<td>11</td>
<td>0.00-1.00(0.22)</td>
<td>Trace(two had 0.07, 0.40)</td>
</tr>
<tr>
<td>Scaphopods and amphineurans</td>
<td>2</td>
<td>0.20-0.45(0.32)</td>
<td>Trace</td>
</tr>
<tr>
<td>Gastropods</td>
<td>20</td>
<td>0.00-1.78(0.29)</td>
<td>Trace-0.85(0.10)</td>
</tr>
<tr>
<td>Cephalopods</td>
<td>3</td>
<td>0.16-6.02(2.60)</td>
<td>Trace</td>
</tr>
<tr>
<td>Crustaceans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barnacles</td>
<td>7</td>
<td>0.75-2.49(1.82)</td>
<td>Trace(one had 0.77)</td>
</tr>
<tr>
<td>Others</td>
<td>13</td>
<td>3.65-15.99(8.28)</td>
<td>6.57-49.56(17.12)</td>
</tr>
<tr>
<td>Calcareous algae</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\text{Lithothamnium}, \text{Lithophyllum}, \text{Goniolithon}, etc.</td>
<td>23</td>
<td>10.93-25.17(17.74)</td>
<td>Trace-0.43(0.05)</td>
</tr>
<tr>
<td>\text{Halimeda}</td>
<td>4</td>
<td>0.02-1.09(0.65)</td>
<td>Trace</td>
</tr>
</tbody>
</table>

* One value (\text{Heliopora cerulea}, Philippine Islands) of 0.35.

limestone of the Oregon Quadrangle, Illinois, that were partly filled by residual dolomite sand, and Stout (1940) described local areas of the Peebles Dolomite of Niagaran (Silurian) age in Pike, Adams, and Highland Counties, Ohio, that have been rendered soft and porous through leaching.
Table 2. - MgCO₃ in Calcareous Skeletal Materials
(Compiled from Chave (1954a). The analyses include 43 from Clarke and Wheeler (1922), for which water temperatures were known.)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Number of samples</th>
<th>Percent MgCO₃ in aragonite</th>
<th>Weight Percent MgCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foraminifera</td>
<td>23</td>
<td>0</td>
<td>&lt;4-15.9</td>
</tr>
<tr>
<td>Sponges</td>
<td>3</td>
<td>0</td>
<td>5.5-14.1</td>
</tr>
<tr>
<td>Madreporian corals</td>
<td>10</td>
<td>100</td>
<td>0.12-0.76</td>
</tr>
<tr>
<td>Alcyonarian corals</td>
<td>14</td>
<td>0</td>
<td>6.05-13.87</td>
</tr>
<tr>
<td>Echinoids</td>
<td>25</td>
<td>0</td>
<td>4.5-15.9</td>
</tr>
<tr>
<td>Echinoid spines</td>
<td>12</td>
<td>0</td>
<td>&lt;4-10.2</td>
</tr>
<tr>
<td>Asteroids</td>
<td>9</td>
<td>0</td>
<td>8.6-16.17</td>
</tr>
<tr>
<td>Ophiuroids</td>
<td>6</td>
<td>0</td>
<td>9.23-16.5</td>
</tr>
<tr>
<td>Crinoids</td>
<td>22</td>
<td>0</td>
<td>7.28-15.9</td>
</tr>
<tr>
<td>Annelid worms</td>
<td>12</td>
<td>0-99</td>
<td>6.4-16.5*</td>
</tr>
<tr>
<td>Pelecypods</td>
<td>11</td>
<td>0-100</td>
<td>0.09-2.80</td>
</tr>
<tr>
<td>Gastropods</td>
<td>7</td>
<td>5-100</td>
<td>0.08-2.40</td>
</tr>
<tr>
<td>Cephalopods</td>
<td>3</td>
<td>0-100</td>
<td>0.05-7.00</td>
</tr>
<tr>
<td>Decapod crustaceans</td>
<td>6</td>
<td>0</td>
<td>5.2-11.70</td>
</tr>
<tr>
<td>Ostracode crustaceans</td>
<td>6</td>
<td>0</td>
<td>&lt;4-10.2</td>
</tr>
<tr>
<td>Barnacles</td>
<td>9</td>
<td>0</td>
<td>1.35-4.60</td>
</tr>
<tr>
<td>Calcareous algae</td>
<td>15</td>
<td>0</td>
<td>7.7-28.75</td>
</tr>
</tbody>
</table>

* The highest values cited apply to small amounts of calcite found in the more aragonitic materials formed at higher temperatures.

MAGNESIUM DISTRIBUTION IN CARBONATE ROCKS AND SEDIMENTS

Magnesium in Skeletal Carbonates

Clarke and Wheeler (1922) presented an extensive series of original chemical analyses of invertebrate skeletal materials, summarized here as table 1, as well as an evaluation of earlier literature on the subject. Some of the materials contained more than 20 wt percent MgCO₃. Even though the available data on water temperatures at the points where the various organisms were collected were incomplete, Clarke and Wheeler were able to show quite clearly that the percentage of MgCO₃ in the skeletal material of alcyonarian corals and echinoderms increased with water temperature. Fossil crinoids contained distinctly less MgCO₃ than their present-day counterparts, the MgCO₃ content of sea urchin spines differed from that of shells and teeth, and the magnesia and phosphorus contents differed for lobsters of different ages.

Chave (1954a) showed by X-ray diffraction that the MgCO₃ in invertebrate skeletal materials is present in solid solution, and that the amount of solid solution in aragonitic materials (rarely more than 1 wt percent MgCO₃) is in general much less than that in calcitic materials (rarely less than 1 to as much as 20 or more wt percent MgCO₃) (see table 2).

In all groups of calcitic organisms for which sufficient data were available, a linear or nearly linear relation could be shown between Mg content of the skeleton and water temperature. An increase in phylogenetic level of the organism is in general accompanied by a decrease of MgCO₃ in the skeleton and by a decrease in the slope of the wt percent MgCO₃ vs. temperature plot. Chave, like Clarke and
Table 3. - Mineralogical Classification of Foraminifera by Families (after Blackmon and Todd, 1959)

<table>
<thead>
<tr>
<th>Imperforate</th>
<th>Perforate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Highly magnesian</strong> (&lt;10 mol % MgCO₃)</td>
<td><strong>Calcite low in magnesium</strong> (&lt;5 mol % MgCO₃)</td>
</tr>
<tr>
<td>Alveolinellidae</td>
<td>Single crystal</td>
</tr>
<tr>
<td>Spirilinidae</td>
<td>Calcarinidae</td>
</tr>
<tr>
<td>Fischerinidae</td>
<td>Camerinidae</td>
</tr>
<tr>
<td>Miliolidae</td>
<td>Discorbidae</td>
</tr>
<tr>
<td>Ophthalmidiidae</td>
<td>Heterohelicidae</td>
</tr>
<tr>
<td>Peneroplidae</td>
<td>Homotremaidae</td>
</tr>
<tr>
<td></td>
<td>Planorbulinidae</td>
</tr>
<tr>
<td></td>
<td>Buliminidae</td>
</tr>
<tr>
<td></td>
<td>Pegidiidae</td>
</tr>
<tr>
<td></td>
<td>Rotaliidae</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>* Indicates intermediate to low range</td>
<td></td>
</tr>
</tbody>
</table>

Wheeler, observed that the tests and spines of the same echinoid individuals frequently showed different MgCO₃ contents. Lowenstam (1954b) showed that the percentage of aragonite in serpulid worm tubes increases with increasing water temperature, and Chave pointed out that the total MgCO₃ content of such tubes should increase with temperature as more Mg is taken into the calcite, but decrease with further temperature rise because of the increasing percent of aragonite.

In a still more detailed X-ray diffraction study, Blackmon and Todd (1959) examined shells of 155 species of calcareous foraminifera, belonging to 29 Recent families, and found that the mineralogy with few exceptions fitted the pattern reproduced here as table 3. The calcite of some samples contains as much as 20 to 24 mol percent MgCO₃. The control of the carbonate mineralogy of these materials is believed to be mainly biologic, although a depression of MgCO₃ content, highly variable in amount among different species, is observed in colder waters for all foraminifera with shells of highly magnesian calcite.

Pilkey and Hower (1960) found that the percentage of MgCO₃ in specimens of Dendraster excentricus collected from the coast between British Columbia and Baja California ranges from 8.4 to 9.5 (215 analyses) and that the percentage of SrCO₃ ranges from 0.296 to 0.354 (117 analyses). These authors conclude that that Mg content is directly related to both water temperature and salinity, and that Sr content is inversely related to water temperature and independent of salinity.
Goldsmith et al. (1955) made additional spectrographic analyses and cell-size measurements on some 25 of Chave's samples, and described one Mg-rich algal calcite that contained several mol percent MgCO$_3$ in some form other than ideal solid solution, as shown by a measurable cell-size change when homogenization took place at high temperature.

In view of the several variables that affect the content of MgCO$_3$ in skeletal materials, summaries such as presented here in tables 1, 2, and 3 are of only general value in indicating skeletal MgCO$_3$ contributions to sediments. In apportioning the total MgCO$_3$ content of a sediment among the several skeletal contributors, so as to determine whether there has been a gain or loss of MgCO$_3$ to sea water, for example, it is necessary to identify the organisms as closely as possible and to refer to detailed information on the MgCO$_3$ contents of individual species or small taxonomic groups. Chave (1954b) obtained reasonable agreement between total and apportioned MgCO$_3$ in several sediments. He discussed earlier attempts by Vaughan (1918), Bramlette (1926), Goldman (1926), and Thorp (1935), suggesting that the use of average MgCO$_3$ contents from Clarke and Wheeler's data and the difficulty of distinguishing fine-grained fragments of aragonitic and calcitic algal calcites limited the accuracy of their results.

Chave (1954b) found that calcitic fossils in porous sandstones and oolites of Pleistocene age had lost Mg, that some of the fossils in silts and marls of intermediate porosity had lost Mg, but that fossils imbedded in relatively nonporous post-Paleozoic shales had retained their Mg. The Key Largo Reef and the Miami (back-reef) Oolite of Pleistocene age in south Florida have been above sea level most of the time since they were formed, and Mg has been leached by ground water. The Miami Oolite, which contains about 15 percent fossils originally high in Mg and mollusks and oolites that originally contained smaller amounts of Mg, now has only 0.37 percent MgCO$_3$.

Fig. 3 - The frequency of occurrence of various calcite-dolomite mixtures in the Middle and Upper Paleozoic carbonate rocks of the Russian Platform (Ronov, 1956): (a) computed from 23,101 individual analyses, and (b) based on measurements of areas on maps contoured for Mg content.
Relative Abundance of Various Calcite-Dolomite Mixtures

Plots of the frequency distribution of calcite-dolomite mixtures occurring in carbonate rocks, made for large numbers of samples (Steidtmann, 1917; Ronov, 1956; Nikolaev, 1956), show maxima near both ends of the range (figs. 3, 4, 5). If dolomitization in nature took place by some one process (for example, secondary replacement by Mg derived from an external source), this bimodal distribution would suggest that a threshold of some sort must be exceeded before dolomitization can proceed, but that once the threshold had been passed, dolomitization has a good chance of going essentially to completion. It appears more likely, however, that the two ends of the range are being reinforced statistically by carbonate rocks of special types, in the one case by fine-grained, virtually pure, supposedly chemically precipitated dolomite rocks from evaporite sequences, in the other by the weakly dolomitized rocks in which very local redistribution of the Mg originally in biogenic magnesian calcites is adequate to account for the dolomite present.

When Ronov’s analyses are used to plot maps of the Mg concentration in various parts of the Paleozoic sequence on the Russian Platform, and the areas of various Mg concentrations on the maps are made the basis of a frequency distribution, the picture shown in figure 3b is obtained and is quite different from that in figure 3a. Many of the intermediate mixtures in figure 3b must result from averaging of analyses for sub-layers, some of which are rich in dolomite, others in calcite. The frequency of intermediate mixtures in the plots of figures 3a, 4, and 5 probably is increased slightly by an analogous effect. Analyses of samples of finely interlaminated dolomite and calcite would necessarily be an average of a considerable number of such layers. Such an analysis may indeed be a perfectly valid statement of rock composition, but it does not correspond to either of the two depositional environments in which the successive laminations were formed.

Dolomitization Throughout Geologic Time

Daly (1909) compiled 900 chemical analyses of limestones and dolomites from Belgium, Canada, and the United States and found that the average Ca/Mg ratios were relatively constant for pre-Devonian rocks but rose steadily for Devonian and Carboniferous samples and reached an apparent maximum during Cretaceous time, although the number of samples of Tertiary and younger rocks was rather small. The increase of Ca/Mg ratios with geologic time for carbonate rocks of the Russian Platform (Vinogradov et al., 1952) is shown in figure 6. A number of explanations have been put forth to explain this distribution, including the increased time the
older rocks have had to undergo post-depositional replacement, the times at which particular groups of lime-secreting organisms appeared, and the possibility that the partial pressure of CO$_2$ in the atmosphere was greater in earlier geologic periods than more recently.

Strakhov (1956) pointed out that aridity and concomitant high evaporation rates seem to have played an important part in adjusting water composition for dolomite formation, both in present-day lacustrine deposits and in the Paleozoic rocks of the Russian Platform. Until comparisons of carbonate rocks of different geologic ages from similar climates can be made, the possibility remains that the compilations mentioned above are influenced by average past climates in the countries from which the samples came.

Some Empirical Generalizations

Fairbridge (1957) showed a correlation between dolomite content and the percentage of insoluble residue in the analyses of "Cambro-Ordovician" rocks from near Harrisburg, Pennsylvania, published by Lesley (1879). However, the Ellenburger
Fig. 6 - The change with geologic time of the Ca and Mg content of the carbonate rocks of the Russian Platform (after Vinogradov et al., 1952).
(I) Based on analyses of 97 composites of 3569 samples. (II) Based on 2826 published analyses for Ca, 2583 for Mg.

Limestones and dolomites analyzed by Goldich and Parmalee (1947), virtually all of which contain less than 7 percent insoluble residue, show no evident correlation between the calculated normative percentage of dolomite and weight percent insoluble residue.

Folk (1958) found an average of 12.56 percent insoluble residue in the nine dolomite beds of the Axemann Formation of the Beekmantown Group in Centre County, Pennsylvania, but an average of only 6.52 percent in nineteen limestones and dolomitic limestones in that formation. The difference lies in the kind and amount of authigenic silica; euhedral quartz crystals and overgrowths in limestones are outweighed by the large amount of disseminated chert in the dolomites, which also contain some quartz overgrowths and aggregates. It is possible that a similar explanation applies to Lesley's analyses.
When the Funafuti core was the only one available from the Pacific, the specific distribution of dolomite with depth in that core was made the basis for considerable speculation. It is now known that the distribution of dolomite with depth on Pacific islands is extremely variable (Ladd et al., 1948). On Kita Daito Jima there is strong dolomitization from the surface down to 103.5 meters, and then only a small MgO content except for a few intervals (Hanzawa, 1940); at Funafuti, dolomite is found below 637 feet (Cullis, 1904); at Bikini, there is no dolomitization down to the bottom of the hole at 2556 feet depth; two Great Barrier Reef bores to 600 feet and 732 feet showed no dolomite (Richards and Hill, 1942). Appreciable dolomite was found at Eniwetok in only four samples of Eocene age at depths below 4300 feet (Ladd et al., 1953). The MgCO₃ values do not appear to have been reported in detail for two holes drilled on Maratooa Atoll northeast of Borneo to depths of 856 and 1407 feet (Kuenen, 1947). The dolomite discussed above is inferred from chemical analyses; small percentages of MgO that, particularly in the upper parts of the cores, could be present in magnesian calcites have been ignored. In the Mg-rich horizon near the top of the Funafuti core, X-ray diffraction measurements (Schmalz, 1956; Graf and Goldsmith, in press) have shown that the Mg occurs in magnesian calcite and not in dolomite.

**IMPURE CARBONATE ROCKS**

Arenaceous and Cherty Carbonate Rocks

The silica in carbonate rocks occurs as detrital and authigenic quartz, chert, and the so-called amorphous silica. The last of these forms the shells of siliceous organisms such as diatoms, radiolaria, and siliceous sponges. It may be hydrated and consists of a disordered association of cristobalite crystallites very little larger than one unit cell and therefore not properly called crystalline cristobalite (Warren and Biscoe, 1938).

Although angular chert fragments have been described from the siliceous limestone portion of the Zesch Formation (Barnes et al., 1947), it is generally quartz that is encountered as a detrital contribution. The variation this contribution may show with change in depositional environment is well illustrated by the Ballyshannon Limestone of early Carboniferous age. In the Donegal Syncline this limestone shows rapid facies changes between deltaic sandstone members to the north and shallow-water oolites and fragmental bioclastic limestones with a gradually decreasing content of smaller and smaller quartz and feldspar grains to the south (George and Oswald, 1957). Unusual rock types in the Ballyshannon include an oolite made up of angular quartz grains with oolitic skins, and a fine-grained limestone containing an abundance of both fine silt and sponge spicules. Such fine-grained quartz-carbonate mixtures may be difficult to classify in the field. Two samples from the Paradox Member of the Hermosa Formation of Pennsylvanian age in southeast Utah which would routinely have been called calcareous shales were shown by X-ray diffraction analysis to consist of 50 percent calcite and dolomite, 40 to 45 percent quartz, and 5 to 10 percent illite, montmorillonite, and chlorite (Merrell, 1957).

The chert in carbonate rocks commonly occurs as beds and as nodules. The replacement origin of the latter is shown by, among other things, residual particles of organic matter outlining oolites and other replaced textural features (see Biggs, 1957; Folk, 1958). All gradations between pure limestone and pure chert occur. Ver Wiebe (1946), for example, described several wells in Sedgwick County, Kansas,
in which dolomitic layers in the Kinderhook Limestone of Mississippian age contain 40 to 50 percent chert; Dott (1958) found many limestone units in the Pennsylvanian rocks of northeastern Nevada that contain more than 30 percent chert. Porcelanite of the Lower Triassic Thaynes Formation of west-central Utah is seen in thin-section to contain about 50 percent disseminated quartz present in a fine mosaic in calcite and dolomite (Hose and Repenning, 1959). Chert generally does not, however, replace collophane (Carozzi, 1960, p. 323) or dolomite, which exists as euhedral crystals in chert nodules and passes through them as unreplaced laminae (Folk, 1958; Biggs, 1957; Hatch et al., 1938). The chert in most dolomites is a uniformly impalpable powder, which in the Beekmantown Group of Centre County, Pennsylvania, makes up 5 to 10 percent of the rock (Folk, 1958). Dolomites of the Ellenburger Group of early Ordovician age in central Texas at many places contain highly disseminated chert which seldom is visible on fresh rock surfaces but which on weathering yields spongy masses containing abundant holes of rhombic shape (Cloud et al., 1946).

Attempts have been made to distinguish the relative amounts of chert found in limestones of different types and origins. Vishnyakov (1953) claimed that chert is more common in fine- to medium-grained deeper water limestones and deep-water foraminiferal limestones than in shallower water brachiopod facies, and Teodorovich (1950) stated that oolitic limestones are poor in chert. Hattin (1957) noted that chert usually is not found in purely molluscan or purely algal limestones.

Reef cores and reef-like accumulations of skeletal remains are not entirely free of silica. There are, for example, small amounts of secondary chert and a little drusy quartz in the cores from the Horseshoe Atoll, of Pennsylvanian and early Permian age, in west Texas (Myers et al., 1956). However, there is typically a much greater amount of silica in the interreef limestones (see Pray, 1958). These estimates seem to indicate that limestones formed in waters agitated enough to winnow out the finer grained detrital silica and the invariably small and relatively buoyant siliceous shells, if indeed these materials enter the environment in significant amounts, are less likely to contain chert.

Nature and Origin of Chert in Carbonate Rocks

Jensen et al. (1957) made an X-ray diffraction study of 42 Danish "flints" and other siliceous rocks (all but one derived from chalk deposits of Cretaceous age) and found they contained from 4 to 95 percent fine-grained α-quartz, typically of 300 to 500 Å particle size. The remainder consisted principally of flaky, cryptocrystalline material having a two-dimensional cristobalite arrangement. These authors were able to correlate with fair to moderate accuracy estimates made by X-ray and petrographic methods of the amount of cristobalite-like material, which would be called opal by a petrographer. Chert in lacustrine dolomite beds of Tertiary age near Ipswich, Queensland, gives an X-ray diffraction pattern "similar but not identical to" that of β-cristobalite (Rogers et al., 1954). Significantly, Folk (1958) failed to detect by petrographic means any opal in the chert contained in the much older carbonate rocks of the Beekmantown Group of early Ordovician age, and Biggs (1957) detected no "amorphous silica" or opal, only microcrystalline quartz, on microscopic examination of chert from 18 Illinois limestone and dolomite formations ranging from Cambrian to Mississippian in age (see also Rubey, 1952, on the chert of the Burlington Limestone of Mississippian age in Illinois). Fibrous quartz ("chalcedony"; see Pelto, 1956) generally is restricted to places where a free surface is available as a starting point for its growth (Folk and Weaver, 1952; Biggs, 1957).
The "amorphous silica" in the siliceous tests of organisms is metastable, α-quartz being the stable form of SiO₂ at room temperature, and it is known from experimental studies of reactions in concrete to be highly reactive toward alkalis. Jensen et al. (1957) suggested that weakly alkaline waters saturated with CaCO₃ in the chalks apparently are sufficient to induce concentration and transformation of disseminated "amorphous silica" (see also Correns, 1950). CaCO₃-saturated water in chalk, not in contact with air, would have a pH of about 9.9; in contact with air, it would have a pH of about 8.3 (R. M. Garrels, personal communication). The first of these figures is significantly above the value of 9, which Krauskopf (1956) found to be the upper limit of the range in which silica solubility is essentially independent of pH. The water and residual CaCO₃ found in many chert nodules, as well as the very small particle size of the α-quartz therein, indicate the difficulty of obtaining the truly stable end product, macrocrystalline α-quartz.

There is additional support for the origin of at least some chert by reorganization of organic silica. Extensive solution of the silica of diatom shells in the Monterey Formation and its reprecipitation as a cement and as chert masses and beds are shown by lateral transitions within short distances between the cherty or porcelaneous beds and soft diatomites. Significantly, Bramlette (1946) suggested that the unaltered diatomites may be poorer in carbonate than the porcelaneous and cherty parts. Cayeux (in Newell et al., 1953) and others believed that the principal source of silica for chert in European chalks is the siliceous spicules of sponges. Nodular chert in the Helderberg Limestone of West Virginia contains sponge spicules and is clearly of replacement origin. All stages, from normally calcareous oolites and fossils to their completely silicified equivalents, can be observed. The sponge spicules in the limestone outside the nodules have been largely calcified, indicating at least a partial source for the silica of the nodules (Heald, 1952). Black, silica-rich concretions in a sponge-bearing Onondaga Limestone, found by Schwartz and Mathiasen (1934) to contain 0.38 percent finely subdivided free carbon, are believed by them to be recrystallized and calcite-enriched concentrations of siliceous sponge remains (analysis 55, Part IV). Limestone of the Rauracian Formation of Upper Jurassic age in southern Poland contains very abundant calcified sponge spicules, whereas many of the spicules in adjoining chert-rich beds seem to have served as nuclei for chert growth (Sujkowski, 1958).

A similar situation exists for the Turonian white chalk of Polish Volhynia. In the Phosphoria Formation of northwestern Wyoming there are all gradations between chert fairly rich in organic matter, which outlines relict sponge spicules, and chert recrystallized to spherulites that contain no carbonaceous matter and no relict sponge spicules (Sheildon, 1957).

At several localities chert is restricted to interreef facies rich in siliceous sponge remains, from which it apparently formed. For example, an unusually large amount of biogenic silica is contained in the sooty, black, thin-bedded limestone of the Marble Falls Formation of Pennsylvanian age, Lampasas County, Texas, which has from 20 to 45 percent siliceous residue consisting largely of sponge spicules (Damon, 1943; Barnes, 1952). It can be followed laterally into spiculite that contains some 88 percent siliceous residue, is hard, and appears under the microscope to have been partly cemented by silica. This altered spiculite in places passes into chert that is interbedded with the limestone. Nearby reef rock is of very high purity (analysis 44, Part IV) and the small amount of chert it contains is the porous, friable kind that replaces fossils.

In the post-Joliet formations of the Niagar Series in northeastern Illinois, chert is confined principally to the biostromes, composed mainly of siliceous sponges,
that occur in the dolomites of the interreef facies (Lowenstam, 1942, 1948). The nearby dolomitized reefs are extremely pure (analyses 79 and 80, Part IV). Chert in zones now devoid of sponge remains apparently also was sponge-derived, for a gradation exists between spiculeless chert in such zones and nearby chert containing completely preserved sponge skeletons, and the specialized fauna of the sponge biostromes also is found in the spiculeless chert zones but not in chert-free areas. Lowenstam found that well shaped chert nodules typically contained a complete siliceous sponge skeleton, whereas bedded cherts and incompletely chertified areas with poorly defined boundaries contained abundantly distributed flesh and tuft spicules that had served as centers for chertification. The relative rates of sedimentation, decomposition of soft parts, and reorganization of silica were presumably critical in determining whether recognizable sponge remains persisted or were disaggregated. Localized solution of isolated spicules and margins of already formed chert nodules has resulted in the silicification of fossils other than sponges. The remarkable preservation of morphologic details in chertified fossils and the poor detail in dolomitized and silicified fossils were taken by Lowenstam to indicate that chertification is pre-dolomitization in this area. Apparently assuming that the preservation of detail in silica replacements is relatively constant, he further concluded the silicified fossils must be replacements of already dolomitized ones.

Sponge spicules are absent in the core of the Wabash Reef, Wabash, Indiana (Carozzi and Zadnik, 1959), very scarce in the adjoining reef detritus, and abundant in the interreef area.

The relatively early formation of at least some chert is indicated by its occurrence as nodules in some of the desiccation polygons in the Hardy Creek Limestone of middle Ordovician age in southwest Virginia (Harris, 1958). The size and shape distribution of the polygons is distorted according to the size and shape of the contained nodules. An early age also is indicated by occurrences like those cited by Poor (1925) and Rubey (1952) in which chert pebbles of Mississippian age are found in the basal conglomerate of the Pennsylvanian in Illinois (see also Cayeux, 1941). Dolomite-free calcareous inclusions frequently found in cherts contained in dolomitized rocks indicate that chert formation usually precedes secondary dolomitization (Carozzi, 1960).

Silicification of exposed surfaces (Moore, 1955, Crystal River Formation of northwest Florida; Dott, 1958, Pennsylvanian limestones of northeast Nevada) and of the exposed portions of fossils (Howell, 1931; Lowenstam, 1948; Dott, 1958) generally is taken as evidence for continuing present-day redistribution of silica in carbonate rocks. However, Newell et al. (1953) noted that frequently only parts of fossils are silicified, whether they are collected from the surface or well within large blocks, and suggested that a portion of such a partly silicified fossil which stands in relief on the weathered surface of a carbonate rock would naturally be the silicified portion.

Available data on the solubility of "amorphous silica" and quartz and on the silica content of natural waters suggest that most natural waters are undersaturated with respect to "amorphous silica," but that solutions supersaturated with regard to quartz are not rare and may persist in that condition for years (Siever, 1957; Krauskopf, 1956). Synthetic crystalline quartz has not been formed directly from solution at anywhere near room temperature and pressure, and the mechanism of formation of authigenic quartz crystals in limestones and elsewhere is not yet understood.

The amount of silica dissolved in alkaline lakes with a pH above 9 increases markedly because of the formation of silicate ions, so that a subsequent pH drop
might be expected to result in inorganic precipitation of "amorphous silica" (Siever, 1957). The chert in the dolomite-rich, lacustrine Green River Formation of Eocene age in Wyoming, Colorado, and Utah might represent such a product. However, diatoms flourished in the Green River lake during at least part of its history, and they may have succeeded in keeping the silica concentration well below saturation.

Argillaceous and Glaucnconitic Limestones

Robbins and Keller (1952) examined the less than 2μ fraction of insoluble residues from 271 limestones and dolomites and found illite to be the dominant clay mineral in both marine and nonmarine carbonate rocks. However, they used 6N HCl, which could have deteriorated a good deal of chlorite. Weaver (1958) concluded from several thousand clay mineral determinations that illite is the predominant clay mineral in carbonate rocks, as Grim et al. (1937) and Millot (1953) had said earlier. However, he also found clay suites commonly composed entirely of montmorillonite and of mixed-layer materials. Occurrences of chlorite and kaolinite in carbonate rocks are not uncommon, but these minerals are seldom dominant in the clay mineral suite. Weaver found no particular clay mineral restricted to a particular environment. In another study, Degens et al. (1958) found that the illite/kaolinite ratio of 18 samples of marine and freshwater limestones of Pennsylvanian age did not reflect differences in depositional environment. The relative importance of the original character of detrital clay minerals and of diagenetic changes in depositional environments is at present under intensive study by many workers.

Myers et al. (1956) described a zone at the top of the reef limestone of the Pennsylvanian and early Permian Horsehoe Atoll of west Texas that lies under dark pyritiferous shale. The pores of the limestone have been filled with dark gray to black clay and, in a few places, with pyrite thought to have been precipitated from connate water originally contained in the shale.

Alternating laminae of relatively pure limestone and more argillaceous limestone were reported by Brill (1956) in the Berriedale Limestone of Tasmania. Hadding (1958, p. 37-40) described a similar alternation in which the individual layers are about 100 mm thick.

The small green pellets called glauconite are shown by X-ray examination to consist of a variety of layer-lattice materials (Burst, 1958a, b) in addition to the carefully defined glauconite of Gruner (1935) and Hendricks and Ross (1941). Burst believed that degraded layer-lattice silicates surrounded by local environments of reduction are nucleation centers to which Fe and K migrate, and he noted that glauconite formation in fecal pellets and inside foraminiferal shells fulfills these conditions. The argillaceous minerals of Recent age in Gulf Coast fecal and cavity-fill material are considerably degraded.

Hadding (1932) concluded from his study of Swedish glauconite rocks that glauconite formation is favored in agitated waters under conditions of limited deposition, an opinion strengthened by the glauconite deposition actually observed off southern California (Emery, 1960).

Some mica-booklet type of glauconite occurs in the Senonian age limestones of Sweden, in addition to that which impregnates sponges, porous fossil fragments, and gastropod shells (Hadding, 1932). Herzog et al. (1958) mentioned a richly fossiliferous, pyritic limestone of lowermost Ordovician age from a quarry at Stenbrottet, Sweden, from which chips containing more than 50 percent glauconite in 1 to 2 mm pellets can be selected. Many of the Eocene marls and chalks of the Gulf Coast are glauconitic and are likely to contain phosphatic concretions and internal molds of mollusks as well (Monroe, 1941; Burst, 1958a, b). The glauconitic chalks
of the Paris Basin all carry variable amounts of phosphate granules (Cayeux, 1935). A dense, nodular, black limestone described by Cayeux from the boundary zone between the Upper and Lower Cretaceous at Interlaken, Switzerland, contains abundant quartz, glauconite, and phosphate. The lower twenty feet of the Colon Limestone in Venezuela (Smith, 1951) is glauconitic, asphaltic, and highly pyritiferous. Pfefferkorn and Urban (1957) noted that the "Grunsandstein" of Westphalia is actually a limestone containing about 10 percent quartz and 10 percent glauconite.

**Tuffaceous Limestones**

The Tertiary limestones of Saipan include relatively pure reef and detrital bioclastic limestones, calcite-cemented conglomerates consisting of limestone pebbles and cobbles and material of volcanic origin, and rocks containing from 20 to 80 percent bioclastic carbonate fragments set in a matrix of tuffaceous material, quartz sand, and crystalline calcite (Cloud et al., 1956; Schmidt et al., 1957). Volcanic material typically makes up 3 to 5 percent of the Saipan limestones, but may reach 12 to 15 percent. When these rocks are exposed to weathering, recrystallization starts in the groundmass and the volcanic ash is altered to clay.

Ladd and Hoffmeister (1945) found at Lau, Fiji, all gradations between limestone, limestone containing water-worn grains of volcanic detritus and clay derived from weathering of volcanic material, and pyroclastic rocks.

**Pyritic Limestones**

Although many argillaceous and bituminous limestones contain some pyrite, in other less common limestones it is a substantial constituent. The Top Jet Dogger of the Upper Liassic succession in Yorkshire is a thin, platy, argillaceous limestone with coarsely crystalline lenses of calcite separated by irregular but laminated layers of pyritic shale. Hemingway (1951) considered the bed to be a diagenetically altered analog of the calcareous mud now forming in the western basin of the Black Sea (see Archangelsky, 1927).

The basal pyritic limestone bed of the Greenhorn Formation of Upper Cretaceous age in the Black Hills, South Dakota (Rubey, 1930; analysis 72, Part IV), contains, principally, *Inoceramus* shells and fine-grained calcite, pyrite (some 25 percent), and secondary gypsum and iron oxides probably derived from the pyrite. The pyrite is minutely crystalline, forms nodules and coatings, and is intimately associated with un replaced shell fragments and fine-grained CaCO₃. Rubey suggested that water escaping upward from immediately underlying black shale during compaction may have formed the pyrite. He noted that present-day oceanic black muds contain up to 35 percent CaCO₃ but are reducing in character and contain sulfides and H₂S below the sediment-water interface (Murray and Renard, 1891; see also Murray and Irvine, 1895, concerning the processes involved), so that the calcite-pyrite association is not inconsistent.

The Pumperston Shell Bed and the Pumperston Oil Shales of Lower Carboniferous age in Scotland contain large numbers (~1 x 10⁷/cm³) of pyrite grains 2 to 30 microns in size (Love, 1958). Microfossils, found only in pyrite grains, are obtained by treating a concentrate of the pyrite grains with nitric acid. The size distribution of pyrite grains virtually coincides with that of the microfossils, which are believed to be actinomycetes rather than bacteria. The even lamination of the oil shales indicates an anaerobic depositional environment free of bottom scavengers, and the carbonate cementation that has occurred suggests a late-diagenetic rise in pH.
Phosphatic Limestones

The small percentages of phosphate found in most limestones are contributed by detrital apatite, by either replaced or originally phosphatic fossils, and by detrital phosphate grains and pebbles. The weakly phosphatic limestones are compositionally quite distinct from phosphorites, for highly phosphatic limestones are rare. This rarity is believed to result from the fact that carbonate can precipitate in the ocean (with its present composition) only above a pH of 7.8, whereas apatite is stable above a pH of 7.0 (see discussion by Sheldon, 1959, p. 93). Carbonate-poor phosphorites thus presumably form at a lower pH than phosphatic carbonate rocks. Furthermore, the ratio of carbonate to apatite should be high when these two materials coprecipitate (Krumbein and Garrels, 1952).

Fish remains and the shells of certain inarticulate brachiopods (*Lințula* sp., *Discina* sp., *Glottidia* sp.) are the most important sources of organically deposited phosphate, with lesser contributions from vertebrate bones, alcyonarians, crustaceans, and conodonts (see also table 1). C. W. Collinson (personal communication) estimated that there is a 50 percent chance of recovering 15 or more conodonts in any 1000 grams of marine limestone of Ordovician through Pennsylvanian age in the midwestern United States. Fifteen conodonts would correspond to about 1 ppm Ca$_3$(PO$_4$)$_2$.

An original ecological control of phosphate content appears probable in some limestones. The number of conodonts is greater in sponge-crowded habitats of the interreef beds of Silurian age near Chicago than is in sponge-poor areas (Lowenstam, 1948), and *Lințula* are restricted to the sponge-crowded areas. Lowenstam suggested that putrification of inter-sponge passages by metabolism products of sponges may have kept the number of sessile benthos associates lower than the number of anchorage sites, allowing *Lințula* to move in. Willman (1943) stated that the P$_2$O$_5$ content of the nearby reefs is often so slight as to be undetectable in a 5-gram sample by conventional analytical methods.

Phosphate in the Cambrian and Ordovician limestones of Sweden occurs almost always in beds that contain glauconite (Hadding, 1958). Hadding contrasted these limestones with others rich in organic matter and clay that usually do not contain phosphate. He supposed that relatively agitated water in the depositional environment had removed bituminous muds from the phosphatic-glauconitic limestone sediment. This concept has been substantiated by the recent oceanographic work of Emery (1960) and others (see discussion of carbonate sediments).

Determinations of phosphorus (0.005 to 0.136 percent) and iron (0.15 to 3.22 percent) in some 380 argillaceous limestone samples from the Lower Malm of southern Germany (Seibold, 1955) show a pronounced negative correlation between P and CaCO$_3$ and between Fe and CaCO$_3$. There is a distinct positive correlation between P and Fe. The P/Fe ratio has a mean value of 0.046 but shifts progressively to higher values as CaCO$_3$ content increases. Part of the iron is present as sulfide, but an iron content in the clay minerals and the presence of iron carbonate, silicate, or oxide are suggested to account for the remainder.

Erosion remnants of the phosphatic, glauconitic chalk of Senonian age at Taplow, England, contain phosphate as bones, teeth, fish scales, and phosphatized coprolites and foraminiferal tests, and as a veneer coating nodules and rock bands (Willcox, 1952). The fossils are like those in normal chalk but much more abundant. Petrographic evidence argues against the deposit's being merely current-sorted phosphatic debris. A locally flourishing community of organisms is postulated in a nutrient-rich zone where the bottom currents were deflected upward by a submarine ridge, and where a trough provided tranquillity for phosphate accumulation.
Two thin, areally extensive beds in the limestone of the Delaware Formation of Middle Devonian age in central Ohio contain abundant crinoid fragments and fish teeth and plates, often worn and rounded (Westgate and Fischer, 1933). An analysis of one of the beds gave 16.80 percent Ca$_3$(PO$_4$)$_2$, 73.27 percent CaCO$_3$, 4.97 percent MgCO$_3$, 2.46 percent iron oxides, and 2.14 percent SiO$_2$, for a total of 99.61 percent (Orton, 1878).

Both bone beds and phosphate pebble concentrations often occur as basal conglomerates on old erosion surfaces, and are accompanied by pyrite and Mn-oxide stain (Pettijohn, 1926). Phosphate pebbles occur in carbonate rocks, above and below the phosphate zone, near the Quadrant-Phosphoria boundary in southern Montana. Many are found in the Noix Oolite Member of the Edgewood Formation of Silurian age in Illinois (Rubey, 1930). Phosphate pebbles and grains occur scattered throughout the Middle Miocene Hawthorn Formation of Alachua County, Florida (Pirkle, 1957), which is a variable mixture of sand, clay, and carbonate, any one of which may predominate locally. The phosphate particles include replaced fossils and fragments of impure limestone, aggregated masses and concretionary oolites, and phosphate filling organic cavities, such as bryozoan chambers.

A Cretaceous chalk near Mons and Liege in south Belgium contains numerous small phosphatic concretions "no larger than a mustard seed" that in many places form 10 percent of the rock (McCallie, 1896). The phosphatic limestone of the Bigby Formation of Tennessee contains worn and rounded fragments of small bryozoa and perhaps crinoid stems, in all stages of replacement by phosphate, set in fine-grained calcite (Whitlatch and Smith, 1940). Partial replacement of the fossils in a phosphate-rich environment before consolidation of the rock is indicated. In two areas the Bigby Limestone and part of the Leepers Limestone average 15 to 20 percent Ca$_3$(PO$_4$)$_2$; darker streaks have 40 percent or more. Thin beds of dark, greenish gray, silty dolomite in the Plympton Formation of Permian age in west-central Utah contain as much as 20 percent collophane as minute pellets and interstitial fillings (Hose and Repenning, 1959).

In cherty argillaceous limestone layers in the La Caja Formation of Jurassic age in Zacatecas, Mexico, containing 10 to 15 percent P$_2$O$_5$, the chert appears mainly to be replacing the phosphate (see also analysis 69, Part IV). This formation shows marked variation in thickness and contains terrestrial reptile remains, conglomerate units, and, in some units, cup-shaped gastropods and abundant ammonites; benthonic mollusks are rather scarce. A muddy environment and not too great a depth of water are suggested (Rogers et al., 1956).

Unconsolidated lime sands and gravels in the northern Marshall Islands are overlain locally by a consolidated 5 to 15 cm bed containing from 2.7 to 14 percent P (Fosberg, 1957). X-ray diagrams show the presence of an apatite that both fills interstices and replaces CaCO$_3$. The phosphatic limestone occurs only under humus-producing Pisonia grandis trees, which are a favorable nesting site for sea birds. Finely divided calcium phosphate in the guano is dissolved by rainwater enriched by humic acids and then precipitated when the solution is neutralized by the limestone below. McConnell (1943) described replacement of bioclastic limestone at Malpelo Island, Colombia, by phosphatic solutions derived from the leaching of superficial guano deposits.

Hutchinson (1950) concluded after a broad survey of guano deposits that rainfall must be less than 1500 mm a year to allow a consolidated phosphatic zone to form in underlying rock or soil, and less than 1000 mm a year to permit the formation of a major deposit.
Carbonate Rocks Containing Organic Material

The Avon Park Limestone of Eocene age in Citrus and Levy Counties, Florida, is a virtually unaltered sediment of unconsolidated calcareous mud with laminations of carbonaceous matter, much of which appears to be branches of land plants (Fischer, 1949). Sediments like this are found today in shallow, protected waters around mangrove islands in Florida Bay.

The rather common, dense, sparingly fossiliferous limestones rich in organic matter and often in pyrite are interpreted by Sloss (1947) as having formed at depth in areas where impeded circulation inhibited bacterial decay and was inhospitable to the existence of benthonic organisms. These rocks, according to Sloss, contain abundant chert but are rarely dolomitized. Pennsylvanian and Permain limestones of this type, such as the Bone Spring Limestone of the Permain age Leonard Series, occur interbedded with dark shales and silts in basinl off-reef areas in west Texas (King, 1942; Adams, 1951). The fauna in the Bone Spring Limestone is a characteristic pelagic one consisting mainly of ammonites, which could float at the surface and whose shells could float and drift after death. These basins were surrounded by epicontinental shelves furnishing but little sediment.

Newell et al. (1953) presented a monographic study of the Permain reef complex of Texas and New Mexico, with references to other fossil reefs in England, Greenland, and the Italian Tyrol that lie along the borders of euxinic basins. Some 95 percent of the black, pyritic, bituminous limestones of the Delaware Basin, such as the Bone Spring, are divided into light and dark laminae 0.1 to 3.0 mm thick. Some of the finer grained dark laminae contain up to 30 percent by volume of siliceous sponge spicules, many of which have been replaced by calcite. Spicule sorting is indicated by parallel alignment of spicules and by the fact that adjacent laminae show differences in mean spiculite size. Organic matter is tightly sealed in voids and is believed to have been emplaced before the matrix lost its connate water. The content of organic matter insoluble in organic solvents ranges from 0.10 to 1.76 percent.

Newell et al. believed that fluids driven out of the basin sediments by calcite cementation played a role in the several marginward diagenetic effects observed. Macroscopic fossils toward the basin margin, near the outer edge of the reef talus, are replaced by silica. Chert is very frequently associated with spiculites and is localized along noses of primary fold structures. The preferential replacement by silica of fossils rather than mud, and of certain types of fossils rather than others, does not appear to be a simple function of porosity or of the original content of aragonite. Dolomitization is significant only toward the basin margins, and in some horizons there is a marked replacement of foraminifera and bryozoae in preference to the matrix. A flood of secondary calcite cement also occurs toward the basin margin.

Another carefully studied suite of bituminous carbonate rocks is that contained in the Green River Formation, a series of lacustrine beds of Eocene age some 1500 to 2000 feet thick that today occupy several basins in Colorado, Wyoming, and Utah. Deltaic and fluvial sands and shales are followed basinward in turn (1) by a freshwater shore facies of reefs and algal limestones containing caddis fly larval cases, freshwater mollusks, and an abundance of ostracodes (Bradley, 1925); (2) by muddy limestones and limy mudstones; (3) by the so-called oil shale and its somewhat more saline facies. All of these rocks have high carbonate contents; Hunt et al. (1954) estimated that the limestones typically contain 82 percent carbonate as calcite, the saline "oil shales" and the marlstones of the "oil shales" have 52 to 55 percent as dolomite (analyses 73, 74, Part IV), and the platy and so-called Mahogany oil shales, 42 to 43 percent as dolomite.
The marlstones of the Green River Formation are varved and contain light colored layers rich in microgranular carbonate and dark colored layers with abundant organic matter. Studies of modern varved sediments from Lake Zurich (Nipkow, 1927) and other localities described in Circular 297, the first of this series, indicated that the Green River varves probably are annual, with carbonate precipitated at the surface by summer warming and photosynthesis. The presence of perfectly preserved fossil fish in the varved sediments, contrasted with the broken and chewed-up bones in the nonvarved sediments, indicates that the former were deposited in a stagnant bottom zone free of scavengers or bottom feeders. The remarkable suite of authigenic minerals in the "oil shale," described in Part III of this series, indicates that the lake waters at times must have been highly mineralized.

The organic matter in these beds, which at places is as much as 80 percent, is relatively rich in fatty and waxy matter, high in C and H and low in O. Bradley (1925) believed that it was derived almost entirely from plankton, for peat bogs are inconspicuous around the shore and there are no remains of large plants. The summer temperature maximum indicated by the larger land plants, insects, and animals would have been high enough to support a bloom.

"Oil shale" has been described from various other localities. That from Um Barek, Israel, is of Senonian age and contains 50 to 60 percent carbonates, mostly calcite, 15 to 20 percent silica and silicates, 1 to 4 percent P<sub>2</sub>O<sub>5</sub>, 2 to 7 percent R<sub>2</sub>O<sub>3</sub> (mainly Al<sub>2</sub>O<sub>3</sub>), 1 percent pyrite, 0.002 to 0.003 percent uranium, and from 4 to 25 percent total organic matter, mostly kerogen. The ultimate composition of the kerogen, estimated from total organic content and amount and elemental analysis of the assay products is C, 59.1; H, 8.6; N, 1.9; S, 11.0; O, 9.4 percent by difference. The more calcareous beds (Stinkseiberer) of the Posidonia bituminous shales of Liassic age in Swabia, Germany, consist of alternate light and dark units 1 mm thick, and contain 70 to 86 percent CaCO<sub>3</sub> and as much as 7 percent organic matter (Eisele and Mosebach, 1955; Wunnenberg, 1950).

The occurrence of free bitumens in carbonate rocks has been recorded from widely separated localities. Petrographic descriptions of chemically analyzed Scottish carbonate rocks (Geol. Survey Great Britain, 1956) include numerous cases in which there is observable bituminous matter interstitial to carbonate grains or mixed with accessory clay. Henson (1950) mentioned two fossil reefs of the Lower, Middle, and Upper Cretaceous in the Middle East that are highly bituminous at their outcrops. Reefs in this area pass through transition beds of reef detritus, which are bituminous if porous, into basinal anhydrites and Globigerina facies that are in part bituminous.

The organic material in Upper Jurassic bituminous limestones in the southern Jura region of eastern France consists principally of pseudoasphaltenes and resins and has high acidity and sulfur content (Gubler and Louis, 1956). The Seefelder marls of the Tyrol region are a sapropel facies with some layers containing up to 20 percent by weight of organic substances (Fischer, 1957). Swain (1958) gave detailed information about extracts, obtained by leaching of Middle Devonian limestones of the Mount Union area, Pennsylvania, with various solvents.

Viscous to solid organic matter has been observed coating cavities of various sorts in Mississippian and Pennsylvania limestones of western Missouri (Searight, 1957), Niagaran age limestone at Monon, Indiana, and the South Canyon Creek Dolomite Member of the Pennsylvanian and Permian (?) Maroon Formation at Glenwood Springs, Colorado (Bass, 1950). Schoch (1918) gave partial chemical analyses of a porous coquina, the Anacacho Limestone of Uvalde County, Texas, and of a Comanchean age limestone of Burnet County, Texas, which were impregnated
with 14.00 and 10.30 percent bitumens, respectively. Anthraxolite, a carbonaceous material similar to anthracite, occurs disseminated or in vugs, fractures, and within quartz crystals in the Upper Cambrian and Lower Ordovician dolomites of the Mohawk Valley, New York (Dunn and Fisher, 1954). A typical ultimate analysis is C, 90.42 percent; H, 3.94 percent; O, 3.42 percent; N, 1.30 percent; S, 0.57 percent; and ash, 0.35 percent. The occurrence of asphalt in porous areas of the reefs of the Chicago area is common (Willman et al., 1950).

<table>
<thead>
<tr>
<th>Stratigraphic unit</th>
<th>Hydrocarbons (ppm)</th>
<th>Asphalt (ppm)</th>
<th>Kerogen (ppm)</th>
<th>Age and location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amsden (limestone)</td>
<td>8.3</td>
<td>8.3</td>
<td>290</td>
<td>Mississippian-Pennsylvanian, Wyoming</td>
</tr>
<tr>
<td>Smackover (limestone)</td>
<td>87.</td>
<td>83.</td>
<td>460</td>
<td>Jurassic, Arkansas</td>
</tr>
<tr>
<td>Dundee (dolomitic limestone)</td>
<td>87.</td>
<td>100.</td>
<td>1900</td>
<td>Devonian, Michigan</td>
</tr>
<tr>
<td>Greenfield (argillaceous dolomite)</td>
<td>120.</td>
<td>150.</td>
<td>1200</td>
<td>Silurian, Michigan</td>
</tr>
<tr>
<td>Reed City (dolomite)</td>
<td>280.</td>
<td>170.</td>
<td>960</td>
<td>Devonian, Michigan</td>
</tr>
<tr>
<td>Phosphoria (carbonaceous dolomite)</td>
<td>290.</td>
<td>580.</td>
<td>2400</td>
<td>Permian, Wyoming</td>
</tr>
</tbody>
</table>

Table 4. - Organic Content of Some Carbonate Rocks  
(After Hunt and Jamieson, 1956. The values of barrels per acre foot originally reported have been converted to approximate values of parts per million by multiplying by the factor 41.7.)

More finely distributed organic matter, however, has been found in carbonate rocks. Hunt and Jamieson (1956) found that organic matter and, in most cases, elemental sulfur could be extracted from nonreservoir rocks showing no evidence of oil under close microscopic examination, by micronizing the samples to a particle size of 15 microns and refluxing with selected mixtures of solvents. The results for carbonate rocks are given here as table 4, in which hydrocarbons are defined as that part of the total refluxed extract eluted from an activated alumina column with heptane and benzene, minus free sulfur. The nonhydrocarbons (asphalt) are the total extract minus hydrocarbons, sulfur, and ash. The organic matter insoluble in the reflux mixtures (kerogen) is estimated as the organic carbon in the extracted rock times an empirical factor, 1.22. The hydrocarbons are similar in physical and chemical properties to natural crude oils, differing only in that their initial boiling point is 400° to 500°F. The kerogen from the Madison Dolomite has a H/C ratio of 0.68, within the range for coals. Age and depth of burial do not seem to have affected the distribution of types of organic matter present. Further work by Forsman and Hunt (1958) showed that there are two kinds of kerogen, one coal-like and the other more like the material from oil shale, as well as gradations between these types (see table 5). These kerogens are found in marine shales and limestones of various ages. The kerogen type appears to be controlled by depositional environment and by subsequent metamorphism.

Philippi (1957) found small amounts of hydrocarbons, generally ranging from 5 to 5000 ppm, in dense sediments, including marls and argillaceous limestones. He stated that the indigenous hydrocarbon content can be recognized by the proportionality between it and the total organic content and that apparently only a small part of the oil generated by the source beds is released to reservoirs.
Table 5. - Kerogen in Some Carbonate Rocks

<table>
<thead>
<tr>
<th>Analysis of rock after extraction of soluble organic matter by solvents</th>
<th>Elemental analysis of kerogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org. C (%)</td>
<td>Kjeldahl N (%)</td>
</tr>
<tr>
<td>Lower argillaceous beds of the Duvernay Limestone, Alberta</td>
<td>7.63</td>
</tr>
<tr>
<td>Green River marl, Eocene, Wyoming</td>
<td>12.40</td>
</tr>
<tr>
<td>&quot;Mahogany shale&quot; unit Green River marl; Eocene, Wyoming</td>
<td>18.33</td>
</tr>
<tr>
<td>&quot;Papery shale,&quot; Traverse Limestone; Devonian, Michigan</td>
<td>0.53</td>
</tr>
<tr>
<td>Ste. Genevieve Limestone; Mississippian, Kentucky</td>
<td>0.036</td>
</tr>
<tr>
<td>Stylolite filling in Ste. Genevieve Limestone; Mississippian, Kentucky</td>
<td>40.97</td>
</tr>
<tr>
<td>Madison Dolomite (pink); Mississippian, Wyoming</td>
<td>0.04</td>
</tr>
<tr>
<td>Collier Limestone (black); Cambrian, Mt. Ida, Arkansas</td>
<td>0.16</td>
</tr>
<tr>
<td>La Luna Limestone (black, argillaceous); Cretaceous, Colombia</td>
<td>3.73</td>
</tr>
</tbody>
</table>

* Total S includes sulfide S.
† Percent total organic matter Percent organic carbon
†† If the total is greater than 100 percent, inorganic S as pyrite is contributing both to ash and total S. If the total is less than 100 percent, fluorides have volatilized during ashing with HF.
Lucas (1952) isolated from fetid limestones a volatile, water-soluble substance containing phosphate and ammonia, but no sulfur, which he believed to be similar to the phosphenates.

The principal carbohydrate that has been isolated from fossils is cellulose (Abelson, 1959b). Abderhalden and Heyns (1933) also identified chitin in a fossil coleopteron from the Middle Eocene. It appears that relatively impermeable biogenic carbonate rocks that have had a sufficiently mild thermal history may still contain measurable amounts of the amino acids originally present in skeletal materials. The various amino acids, following breakdown of the protein structure, undergo thermal degradation even at earth-surface temperatures. The process is accelerated by exposure to bacterial action, water, oxygen, and the aragonite-to-calcite transformation or other recrystallization.

Conway and Libby (1958) measured the half-life for decarboxylation of alanine, one of the thermally most stable amino acids, at temperatures down to 373 K, using radioactive labeling and low-level counting techniques. The indicated half-life at room temperature is about 10^{10} years. Abelson (1954) obtained a value of about 2 \times 10^9 years by extrapolation of the decomposition rate of alanine in aqueous solutions at a series of higher temperatures. If oxygen is present, carboxyl carbon is released at a rate corresponding to a half-life of about 2 \times 10^4 years at the same temperature.

The thermally more stable amino acids have been found in suitably preserved fossils as old as Ordovician. An Ordovician brachiopod, Plaeostomus subquadrata, from Waynesville, Ohio, had 0.005 percent amino acids, and a plate from the armor of the Devonian fish Dinichthys terelli had 0.03 percent (Abelson, 1957). Although there are amino acids in ground water and it has been shown by Abelson that aspartic and glutamic acids in particular are adsorbed by CaCO_3, differences in amino acid content of different fossils from the same locality indicate that adsorption is probably only a minor contributing factor.

The organic matter, found in some stylolites mixed with clay (analysis 75, Part IV) has been considered a concentrate of material originally disseminated in the limestone, in view of the difficulty of introducing it later into such an impervable host (Myers et al., 1956).

Intimately distributed organic matter is expelled into intercrystalline spaces during calcium carbonate recrystallization and during dolomitization. Contacts between dolomitic rock and embedded algal nodules in the Lockport Dolomite of Silurian age in Orleans County, New York, are marked by a zone of dolomite grains two or three times the normal size, as well as by a band of organic matter expelled during crystallization of the large grains (Cannon, 1955). Organic matter in dolomitic rocks of the Phosphoria Formation in northwestern Wyoming is concentrated into inclusions in the dolomite grains and crusts around these grains (Sheldon, 1957). Folk (1958) observed 0.002-inch rims of organic matter around dolomite crystals from rocks of Ordovician age in Pennsylvania. During the dolomitization of the Metaline Limestone in northeastern Washington, the organic coloring matter was expelled and, in places, it accumulated in vugs as rounded globules of anthracite composition less than half an inch in diameter (Park, 1938). Some dolomites have light and dark bands, generally less than half an inch thick. Analyses by R. C. Wells of fine-grained black dolomites versus relatively coarser grained, lighter colored dolomites are almost identical except for a small amount of organic matter in the darker bands. Rejection of bituminous and argillaceous material during the secondary growth of macroscopic calcite crystals in the Swedish antraconites (bituminous argillaceous limestones) has resulted in the interstitial concentration of these materials (Hadding, 1958).
Oolites enclosed in a layer of dolomitic calcilutite described by Wherry (1916) have light upper portions and dark lower portions rich in organic matter, with nuclei occurring toward the bottom. Post-lithification solution of the aragonite of the oolites apparently left a solution residue at the bottom of the voids, which were subsequently filled by fine-grained secondary dolomite.

Chemical analyses show that the organic matter in siliceous Cretaceous limestones from two localities in the French Pyrenees was not expelled or destroyed during metamorphism of the limestones to hornstones. Small granules of organic matter are enclosed in wernerite and diopside crystals. Louis and Ravier (1952) found 1.43 percent organic carbon and 0.036 percent total nitrogen in a hornstone, compared with 0.98 percent organic matter and 0.065 percent total nitrogen in the unmetamorphosed equivalent.

Hunt (1953) attempted to correlate differences in crude oil types in Wyoming with differences in depositional environment and thus of organisms contributing organic compounds to the sediment, but the problem in that area may be complicated by migration, by differences in depth of burial, and by other post-depositional changes. More positive results were obtained for the lacustrine carbonate rocks of Eocene age in the Uinta Basin. The change in mineralogy of the basinward facies in the Uinta Basin from calcite through dolomite to the sodium carbonates, proceeding through the increasingly younger Wasatch, Green River, and Uinta Groups, was taken by Hunt et al. (1954) to indicate a progressive change in salinity. The progressive change in hydrocarbons in these beds, from ozocerite to albertite to gilsonite to wurtzilite, represents an increase in N and S and in condensed ring structures as opposed to chains. The parallel changes in the composition of organic and inorganic materials indicate that the hydrocarbons have not migrated appreciably and that progressive changes in the composition of the lake, and perhaps of the kinds of organisms inhabiting it, are reflected in the hydrocarbon compositions now observed, in spite of whatever post-depositional alteration may have occurred.

The median organic carbon content of 461 limestones from the United States examined by Trask and Patnode (1942) was 0.49 percent, compared with 0.75 percent for 2245 clastic rocks. The median C/N value for 492 limestones was 19.3, and for 2105 clastic rocks was 15.5.

Readily observable changes take place in the amount of organic matter and FeO in limestones during weathering. In eastern South Dakota, black unweathered chalk of the Niobrara Formation analyzed 10 to 11 1/2 percent volatile matter, excluding CO₂, and about 3 percent FeO. For the weathered white equivalent, the comparable figures are about 1.5 percent and about 1 percent (Rothrock, 1931). Partial analyses by W. A. Noyes (in Loughlin, 1930) of several samples of the well-known oolitic limestone at different quarries near Bedford, Indiana, gave for the unweathered gray material 0.24, 0.21, and 0.22 percent organic matter; 0.067, 0.063, and 0.055 percent FeO; and 0.196, 0.044, and 0.089 percent Fe₂O₃. For buff weathered equivalents at the same localities, the comparable values were 0.12, 0.11, and 0.13 percent organic matter; 0.050, 0.055, and 0.050 percent FeO; and 0.126, 0.150, and 0.119 percent Fe₂O₃.

**Feldspathic Carbonate Rocks**

Tester and Atwater (1934) found authigenic feldspar throughout all of the Paleozoic, in shell-rich limestones as well as in recrystallized and dolomitized rocks. Adularia, albite, and microcline were observed in various combinations, either completely authigenic without cores, or overgrown upon detrital feldspar.
cores of the same or different minerals. Tiny secondary crystals of both albite and potash feldspar were described by Trumpy (1916) from even younger rocks, the Tertiary (Flysch) limestones of the western Rhatikon, Switzerland.

Authigenic feldspars from 40 localities, ranging in age from Precambrian to Triassic, were studied by Baskin (1956), who found that these feldspars were randomly distributed irrespective of fractures (see also Honess and Jeffries, 1940) and rarely exceeded 2 percent of the rock. All carbonate rocks containing them had been partially or completely recrystallized or dolomitized. Authigenic Na-feldspars were found only in carbonate rocks (see also Füchtbauer, 1950), rarely had detrital cores, unlike the K-feldspars, and were all low-temperature albite except for crystals structurally intermediate between albite and analbite, which were found at one locality. The majority of the potash feldspars were monoclinic.

Authigenic feldspars have idiomorphic crystal shapes, are nonperthitic, and show fourfolding twinning never observed in nonauthigenic microcline or in albite crystals formed at higher temperatures than those at which authigenic feldspars crystallize. They are remarkably pure, as would be expectable from the K-feldspar — Na-feldspar immiscibility gap at low temperatures. Authigenic potash feldspars rarely contain more than 0.3 percent Na₂O (2 mol percent albite), and the K₂O and CaO contents of Na-feldspars rarely exceed 0.4 percent (3 mol percent K-feldspar) (see also Honess and Jeffries, 1940) and 0.2 percent (1 mol percent anorthite), respectively. These feldspar crystals cut single crystal outlines of the carbonates and contain carbonate inclusions, usually rounded.

At least two localities have been reported where authigenic potash feldspar is a major constituent of carbonate rocks. The so-called Kristallituff of Monte San Giorgio (Tessin) contains about 40 percent feldspar and 60 percent limestone (Füchtbauer, 1950). Daly (1917) described an apparently unmetamorphosed Precambrian dolomite from the Waterton Formation of Alberta that contained about 40 percent by volume of disseminated, glassy, clear crystals (analysis 85, Part IV).

Füchtbauer (1956) noted a correlation between the amount of authigenic K-feldspar in the Muschelkalk of Göttingen and the amount of illite that is available to furnish K₂O for the reaction. There is no correlation between amount of clay minerals and amount of authigenic albite, which Füchtbauer (1950) believed formed before complete lithification at a time when sea water was still available to furnish sodium. Carozzi (1953) and Topkaya (1950) described similar relations.

Arkosic limestone of the Baum Member of the Paluxy Formation of early Cretaceous age in southern Oklahoma consists of soft, fine-grained limestone cementing the quartz and feldspar that overlie Precambrian granite (Wayland, 1954).

SEDIMENTARY SIDERITES AND FERROAN DOLOMITES

A number of relatively thin but laterally extensive Pennsylvanian limestones have been observed to contain ferroan dolomite in samples taken over large areas. Siever and Glass (1957) observed this phenomenon in the Cutler (Plasa), Galum, and Bankston Fork Limestones of the Illinois Basin in Illinois, using a differential thermal analysis technique by which the ferrous iron substitution in the dolomite could be determined as less than or greater than about 2½ mol percent. No correlation with depositional facies could be established.

Miles (1958) made some 350 X-ray diffraction runs to study further the carbonate composition of the Bankston Fork, which is a thin, argillaceous, relatively discontinuous, marine limestone of Pennsylvanian age in southern Illinois. The ferroan dolomite in most cases makes up from 20 to 60 percent of the rock, calcite is responsible for 50 to 70 percent, and siderite is relatively uncommon, constituting
only 10 to 20 percent of portions of the cores examined. The siderite is present as disseminated crystals, spherulitic masses 10 to 20 microns in diameter, and patches of very fine mosaic.

Thin beds and thin nodular zones rich in siderite are in general not uncommon in Carboniferous rocks (Lowe, 1914; Edwards and Stubblefield, 1948; Crane, 1912; Singewald, 1909, 1911; Scheere, 1955). Hunt et al. (1954) found minor amounts of siderite in the bituminous lacustrine beds of the Green River Formation in the Uinta Basin, and commented that the dolomites of this formation are ferroan. Rubey (1930) found abundant iron-stained concretions and thin beds of siderite in the Pierre Shale of late Cretaceous age in the Black Hills region. He also described (1952) nodular sideritic beds a few inches thick interlaminated with calcareous shales in the lower and middle portions of the Maquoketa Formation of Ordovician age in Illinois. Refractive index determinations show that the dolomite in a number of analyzed Scottish carbonate rocks is ferroan (Geol. Survey Great Britain, 1956). Spherules of kaolinite about 0.5 mm in diameter and containing small lenticular apatite crystals occur in a microgranular siderite rock described by van Tassel (1955).

Lenticular and interbedded masses of siderite in irregularly shaped bodies of bauxite in the Eocene age Ackerman Formation are thought (Burchard, 1924) to have formed in a peat swamp environment (see also Mead, 1915). The iron carbonate ore described by Burchard (1915) in northeast Texas, apparently derived from glaucinite in Eocene rocks, is one of a number of Tertiary glauconite-siderite ores on the Gulf Coast.

Mansfield (1922) described a 6-foot bed of hardpan, composed largely of iron carbonate and containing scattered grains of glauconite, from the Hornerstown Formation of Upper Cretaceous age in New Jersey. Rolshausen (1934) encountered a zone of siderite with minor impurities in the caprock at Carlos Dome, Grimes County, Texas (analysis 93, Part IV), associated with quartz, sphalerite, and galena.

The Mesozoic sedimentary iron ores of England and Western Europe include a number of unusual rock types made up of varying proportions of chamosite, calcite, siderite, and iron oxides formed by oxidation of the chamosite and siderite (analyses 94-96, Part IV). Well defined beds in which oolites and shell fragments are heavily pyritized also occur there. The existence of current bedding, pebble beds, oolites, and a normal shallow-water marine fauna, together with lateral transitions to sandstone, indicate marine deposition (the Yorkshire Lias, for example) in a basin or lagoon of limited extent (Rastall and Hemingway, 1940; Hemingway, 1951; Rastall and Hemingway, 1941; see, more generally, Hallimond, 1925; Cayeux, 1909, 1922). The chamosite in such sedimentary ironstones has been shown to be a member of the kaolin group having a virtually trioctahedral structure, typically with 2.9 octahedral sites out of 3 occupied by Fe, Mg, or Al (see references in Youell, 1958).

The siderite widely distributed in Devonian rocks in the Bashkirian A.S.S.R. (Florenskij and Bal'shina, 1948) also is mixed with chamosite oolites, in addition to detrital minerals and lesser amounts of pyrite, marcasite, and sphalerite. Rocks containing from 50 to as much as 70 percent siderite have been described (analysis 92, Part IV).

The preservation of fine bedding and slump structures, constancy of chemical composition, and presence of fragments of each rock type in intraformational breccias and clastic dikes argues for a primary rather than a replacement origin for the interlaminated chert, siderite, and other rock types in the Precambrian of the Iron River District, Michigan (James, 1951). The rocks have been intensely deformed structurally but only slightly metamorphosed.
SEDIMENTARY MAGNESIUM CARBONATE DEPOSITS

Longwell (1928) and Rubey and Callaghan (1936) described magnesium carbonate beds of limited lateral extent in the almost fossil-free Horse Springs Formation of Miocene age in the Muddy Mountains of Nevada. The 1- to 2-micron particles of magnesium carbonate make up a dense, white rock that is interbedded with almost indistinguishable dense, clayey dolomite, and is associated in the formation with beds of gypsum and other salines, volcanic ash, colemanite-bearing clays, and argillaceous sandstones. The exceedingly fine grain size of the carbonates, excellent preservation of all details of depositional bedding, concordance and diverse composition of successive beds, and uniform composition of individual beds traced laterally argue for a sedimentary origin in an inland lake enriched in Mg.

Similar magnesium carbonate beds from Bissel, California (Gale, 1914; Rubey and Callaghan, 1936) are limited to certain basinal areas and associated with thin, hard beds of dolomite and dark, silty clay. Small surface deposits up to 18 acres in extent at Atlin, British Columbia (Gwillim, 1899; Young, 1916; Bain, 1924), and Bannock County, Idaho (Yale and Stone, 1923), are made up of white, powdery magnesium carbonate. Bedded magnesium carbonate at Needles, California, makes up a thin lens enclosed in Tertiary volcanic and sedimentary rocks. These Tertiary rocks include beds of dolomite, some of which contain uniform, continuous, cherty layers up to a tenth of an inch thick (Vitaliano, 1950).

These several materials are surely sedimentary magnesium carbonates (analyses 22, 23, 85, Part IV), although the possible effect of associated volcanic activity on the composition of the waters in some of the lakes involved is not known and the mineralogy remains to be worked out. The general failure of (MgO + CaO) to balance CO₂ in some of these analyses has led, depending upon the amount of water present, to two assumptions: the magnesium carbonate is hydromagnesite, or hydrous magnesium silicate is present.

Magnesite, identified by partial chemical analyses, indices of refraction, and a positive reaction to the diphenylcarbazide test reaction, occurs as micro-layers and isolated well defined masses in a number of Lower Permian anhydrites of the Volga region (Frolova, 1955). The highest concentrations of magnesite are restricted to anhydrite rocks containing chlorides. A thin-bedded, anhydrite-bearing magnesite horizon having regional distribution contains up to 75 wt percent magnesite, as computed by Frolova from the analytical data shown as analysis 88 in Part IV. The rock described by Hartwig (1955) from the Rhön region of West Germany (analysis 91, Part IV) is, on the basis of chemical analysis and X-ray diffraction data, about one-third halite and two-thirds magnesite, the latter apparently containing as much as 15 mol percent FeCO₃ in solid solution.

Brown layers a few millimeters thick and consisting largely of magnesite are frequent in the Upper Evaporite Bed, Eksdale No. 2 boring, east Yorkshire (Stewart, 1951b). A carbonate, identified as magnesite by its refractive indices and difficult solubility in acid, occurs in anhydrite and polyhalite of the Permian potash field of New Mexico and Texas (Schaller and Henderson, 1932) as disseminated crystals and layers up to an inch thick. All gradations between almost pure magnesite and almost pure clay are present. Clear, glassy, authigenic crystals of magnesite several millimeters long have been described from a dolomitic outcrop sample of the Eocene age Green River Formation in Utah (Milton and Pahey, 1960). Magnesite crystals 1 by 5 mm in size, often stained with petroleum or asphalt, were described by Lonsdale (1930) from a cherty dolomitic limestone of Permian age encountered in drill cores. An analysis of the crystals by P. J. A. Zeller gave MgO, 47.24; CaO, 1.47; FeO, 1.67; CO₂, 49.49; total, 99.87 percent.
 Beds of magnesite several feet thick, interbedded with dolomitic shale, chert, and tillite in the Lower Adelaide System of Precambrian age, are consistent in thickness and composition over many miles of lateral distance in South Australia (King, 1956). Aside from variable amounts of chert and minor quartz veins, impurities in a typical case might be MnO, 0.06 percent; Fe₂O₃, 0.8 percent; Al₂O₃, 0.9 percent; CaO, less than 1 percent. There is disseminated talc in some samples.

Well crystallized magnesite from the Pyrenees (Gomez de Llarena, 1950) is now interbedded with limestone, dolomite, schist, and graywacke, but ripple-marked surfaces are preserved and an original lacustrine precipitation of magnesium carbonate is postulated. Donath (1957) described bitumen-containing magnesite of the Bela Stena deposit, Serbia, which is interbedded with sandstones, marls, and clays in a faulted basin. The magnesite at Ajani is associated with impure dolomite in an essentially undisturbed young Tertiary sedimentary succession. There is serpentine in both regions from which Mg-rich solutions in the depositional basins could have been derived.

SEDIMENTARY MANGANESE CARBONATE DEPOSITS

The examples of sedimentary manganese carbonate that can be cited all occur in beds that are now somewhat metamorphosed, but the authors who have described the deposits do not believe that the metamorphism was severe enough to mask the fundamentally sedimentary nature of the MnCO₃ formation.

The MnCO₃-rich beds in the nonfossiliferous Lower Cambrian of North Wales (Mohr, 1956) are intercalated in blue-gray shales and have been subjected to low-grade metamorphism. They typically contain subordinate quartz and 50 to 55 percent spessartite, believed to have formed by reaction of clay and siliceous material with fine-grained MnCO₃ (analysis 97, Part IV).

On the Avalon Peninsula of southeast Newfoundland, interbeds of manganiferous carbonate, manganese oxide, and associated barite, hematite, and calcium phosphate are found in Cambrian shales (analysis 98, Part IV) (Dale, 1915; Hanson, 1956). Similar thin layers are found in southeast New Brunswick, near Woodstock, interbanded with sharply folded slate, clastic sedimentary rocks, and hematite of Silurian age (Anderson, 1954).

Thinly laminated beds of Silurian (?) age including argillite, slate, hematitic ironstone, and siliceous carbonate rocks containing ferrous chlorite, ferroan rhodochrosite, and some calcic manganiferous carbonate are found in a belt some 65 miles long in Aroostook County, Maine (Crittenden, 1956; White, 1943). Radugin (1940) described a bed in the Cambrian section on the Usa River in the Kuznetsk Alatau (Siberia) that is a white to gray, fine-grained, rhodochrosite marble containing 32 to 34 percent Mn. Crushed diabase dikes and massive porphyryite are present in the section.