CALCITIC LIMESTONES

THEIR PROPERTIES, ORIGIN, AND CLASSIFICATION.

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CALCITIC LIMESTONES: THEIR PROPERTIES, ORIGIN, AND CLASSIFICATION

—A Comprehensive Study of Calcitic Limestone and Its Variety—

By

Chee Sun Mok

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ABSTRACT

A short survey of the chemical properties of calcium carbonate is given, followed by an extended discussion of its solubility and the conditions under which it is precipitated. The importance of the physicochemical and biochemical processes on the precipitation of calcium carbonate from solutions of bicarbonate is emphasized. Whether the calcium carbonate is precipitated as calcite or aragonite depends on the temperature, other ions present in the solutions, and organisms. The physicochemical processes involved in the formation of calcitic limestones are (a) decrease of CO_2 content, (b) evaporation of water, (c) increase in salinity, and (d) mingling of solutions; organisms act through (a) photosynthesis of aquatic plants, (b) activities of bacteria, and (c) deposition in calcareous tissues and shells. The classification of calcitic limestones is discussed according to the origin and texture, in which 15 types are distinguished. These are related to the geological conditions under which the deposition of each takes place. A second classification according to chemical composition, in which 10 types are mentioned, is similarly treated.

ACKNOWLEDGMENTS

In preparing this paper, the writer is much indebted to Professor C. B. Slawson of the Department of Mineralogy and Petrography, University of Michigan, not only for his kind directions but also for his many valuable suggestions and corrections. He also wishes to express his appreciation to Professor M. W. Senstius of the Department of Geology in the same university for his kind informations and discussions.

INTRODUCTION

Limestone is one of the commonest sedimentary rocks. By commonest we mean both its universal use as a raw material in the long history of mankind and its wide distribution over the earth's surface. Limestone has since prehistoric times been used in making mortar. As early as the year of 75 A. D., Dioscorides described the preparation of caustic lime—unslaked as he called it—by calcining mussel-shells, limestone, or marble at a white heat. His contemporary, the elder Pliny, in the book titled HISTORIA NATURALI, described the process of burning and slaking lime(16). Today limestone is very well known for its use as a raw material in chemical industry, cement manufacture, blast furnace operation, and as a constructional stone. Although limestone constitutes only five per cent of the total sedimentary rocks, yet nearly all geological formations contain one or more limestone members. In fact, the occurrence of limestone is quite common and the distribution of limestone over the earth's surface is widespread.

As a rock, limestone possesses a distinct mineralogical and chemical composition. It has also definite chemical and physical properties. Topographically, limestone, under favorable climatic conditions, always develops into characteristic landforms as the Karst topography. This constitutes a very interesting phase of geomorphology. Geologically, the occurrence and distribution of limestone bears some important significance to the ancient changes of lands and seas, and to the environments of organic evolution. Furthermore, under different climatic conditions limestone develops into different kinds of soils, and therefore serves as an indicator of climates. This is particularly true in the development of the so-called endodynamomorphic soils.

The study of limestone is, therefore, very important in the understanding of some fundamental problems of geology and its related sciences.

Limestone consists largely of two types, calcitic limestone and dolomitic limestone which have distinctly different properties as well as origins. The present paper is restricted to calcitic limestone.

PART I. THE PROPERTIES OF CALCITIC LIMESTONES

I. THE MINERAL COMPOSITION OF CALCITIC LIMESTONES

Calcitic limestone consists of two essential minerals, calcite and aragonite, the former being by far the most common. Aragonite is much less stable than calcite under normal conditions, and is thus relatively rare in limestone. They have, however, the same chemical composition, $CaCO_3$, but different crystalline structures.

Calcite under normal condition crystallizes in the hexagonal system. Its crystals as a rule are well developed and perfect. As a rock-making mineral, however, calcite is massive, and shows different shapes in different varieties of limestone. It is coarse to finely granular in marble, or loose and powdery in chalk. It has an open-work or spongelike structure in travertine and a rounded, stalactitic structure in the dripstone of cave deposits and in concretions. It is not uncommonly fibrous. In the ordinary dense limestone, the calcite grains can be observed only in thin section under the microscope.

Aragonite is the orthorhombic form which calcium carbonate normally adopts when organically precipitated from sea water. This crystalline modification is unstable in the presence of pure or nearly pure water, and is liable to be converted into the more stable calcite. The older limestones normally contain no aragonite, and the shells which originally consisted of this mineral are found to be represented by open moulds or by coarsely crystalline calcite. Calcite and aragonite are the two essential minerals of calcitic limestone and the factors that control their occurrence will be discussed in a later chapter.

Limestone, however, is a more or less impure form of calcium carbonate. Besides calcite and aragonite, it may contain a number of accessory minerals, which, in the order of frequent occurrence, may be described as follows:

Dolomite, the double carbonate mineral ($MgCO_3 \cdot CaCO_3$), is often an important constituent of calcareous rocks, generally formed as a result of chemical alteration after deposition. If a limestone contains 45.65 per cent or more of $MgCO_3$, it is then classified as the rock, dolomite.

Magnesite ($MgCO_3$), although hardly ever found as separate crystals, is present in many organic limestones in solid solution with calcite.

Phosphorite (calcium triphosphate) when present in limestones, sometimes occurs as an original part of organic skeletons, such as those of horny brachiopods or crustacea, but not uncommonly it takes the form of secondary concretions or replacements.

Glauconite is present in many limestones, sometimes in considerable abundance, and occurs in both concretionary aggregates or replacements.

Detrital sediments are frequently mixed with limestones in almost all proportions. The common detrital minerals of shales and sandstones such as quartz, feldspar, and muscovite are usually found in the insoluble residues of most limestones. Grains of garnet, kyanite, staurolite, tourmaline, topaz, zircon, titanite, monazite, rutile, apatite, magnetite, ilmenite, pyrite, corundum, anatase, brookite, chloritoids, spinels, as well as amphiboles and pyroxenes have also been reported as occurring in limestones.

Non-calcareous organic remains are common, of which the siliceous sponge spicules and tests of radiolaria are the two most important constituents.

Many of the impurities in limestones are liable to be redistributed or altered in composition during the diagenesis of the rock. Iron compounds may combine with sulphur derived from organic debris, to form the disulphides, pyrite and marcasite. Colloidal silica tends to be dissolved and reprecipitated as chert and flint.

II. THE CHEMICAL COMPOSITION OF CALCITIC LIMESTONES

Theoretically, limestone, if it is absolutely pure, is composed entirely of calcium carbonate, which has 56 per cent CaO and 44 per cent CO_2. In nature, as stated above, it is hard to find a single piece of limestone which does not contain more or less impurities. Actually, nearly all kinds of limestones contain, besides the essential constituent of calcium carbonate, other chemical elements in varying quantity. The tables listed below give analyses of limestones, chalks, calcareous sinters, and oozes, from which one can obtain a good idea of the average chemical composition of limestone and its varieties.

TABLE I: ANALYSES OF LIMESTONES(3)

	A	B	C	D	E	F	G	H
SiO_2 . .	0.95	5.27	1.15	[a]4.03	0.25	0.23	5.19	14.09
TiO_2 . .	. .	. .	. .	. .	. .	. .	0.06	0.08
Al_2O_3 .	0.09	1.07	0.45	0.20	0.56	trace	0.81	1.75
Fe_2O_3 .	none	0.71	. .				0.54	0.77
FeO . .	0.10	0.32	0.26	. .	. .	. .	. .	. .
MnO . .	. .	. .	. .	. .	. .	. .	0.05	0.03
CaO . .	54.75	50.36	53.80	51.33	51.52	55.16	42.61	40.60
MgO . .	0.56	0.56	0.56	0.72	2.08	0.20	7.90	4.49
K_2O . .	0.15	0.10	0.07	0.63	. .	. .	0.33	0.58
Na_2O .	0.02	0.20			. .	. .	0.05	0.62
Li_2O .	. .	. .	. .	. .	. .	. .	trace	trace
H_2O . .	0.08	0.78	0.23	0.83	3.19	0.54	0.21	0.30
H_2O^- . .			0.69				[b]0.56	0.88
PO_4 . .	0.03	0.06	. .	trace	. .	. .	o.o4	0.42
CO_2 . .	43.38	40.34	42.69	41.07	41.58	43.74	41.58	35.58
S . . .	. .	. .	. .	. .	. .	. .	0.09	0.07
SO_3 . .	0.05	0.07	none	0.89	. .	. .	0.05	0.07
Cl . .	. .	. .	. .	. .	. .	. .	0.02	0.01
Organic	. .	. .	. .	0.27	. .	. .	. .	. .
Total	100.16	99.84	99.90	99.97	99.18	99.87	100.09	100.34

a, Insoluble in hydrochloric acid.
b, Includes organic matter.

A. Limestone, Lee, Massachusetts. Analysis by G. Steiger.
B. Limestone, Silverdale, Kansas. Analysis by C. Catlett.
C. Lithographic stone, Solenhofen, Bavaria. Analysis by G. Steiger.
D. Oolitic sand, Great Salt Lake, Utah. Analysis by T. M. Chatard.
E. Coquina, Key West, Florida. Analysis by F. M. Clarke.
F. Recent coral (SIDEROSTRIA), Bermuda. Analysis by L. G. Eakins.
G. Composite analysis, by H. N. Stokes, of 345 limestones.
H. Composite analysis by Stokes of 498 limestones used for building purposes. Does the high proportion of silica determine the availability of these rocks to structural ends?

TABLE II: ANALYSES OF CHALKS(18)

	A	B	C
$CaCO_3$	94.20	96.40	98.40
$MgCO_3$	1.40	1.40	0.10
SiO_2	3.50	1.60	1.10
$(Fe,Al)_2O_3$ . .	1.40	0.40	0.40
H_2O	0.50	0.20	. .
Total	101.00	100.00	100.00

A. White chalk, White Cliffs, Little River, Arkansas.
B. Lower Cretaceous chalk, Burnet Co., Texas.
C. White Chalk, Shoreham, England.

TABLE III: ANALYSES OF CALCAREOUS SINTERS(3)

	A	B	C	D
Insoluble	......	......	1.70	......
SiO_2	0.09	0.05	. .	8.40
Al_2O_3	. . .	. . .	. .	1.31
Fe_2O_3	. . .	. . .	. .	trace
CaO	55.37	52.46	50.48	46.38
MgO	0.35	0.90	2.88	3.54
K_2O	0.04	0.71	. .	0.22
Na_2O	. . .	0.33	. .	0.48
Li_2O	. . .	. . .	. .	trace
NaCl	0.10	1.45	. .	. .
Cl	. . .	. . .	trace	. .
SO_3	0.44	1.82	trace	. .
CO_2	43.11	40.88	41.85	38.20
PO_4	. . .	. . .	0.30	trace
H_2O	0.32	1.02	2.07	1.71
C,organic	0.17	0.30	. .	. .
Total	100.10	100.03	99.53	100.24

A. Travertine, Terrace Mountain, Mammoth Hot Springs, Yellowstone National Park. Analysis by F. A. Gooch.
B. Travertine, near Pulsating Geyser, Mammoth Hot Springs. Analysis by J. E. Whitfield.
C. Lithoid tufa, Lahontan basin, Nevada. Analysis by O. D. Allen.
D. Calcareous tufa, main terrace, Redding Spring, Great Salt Lake Desert. Analysis by R. W. Woodward.

TABLE IV: ANALYSES OF OOZES(17)

	Globigerina oozes		Pteropod ooze
	1450 fathoms	2200 fathoms	450 fathoms
SiO_2	1.83	10.37	4.14
Al_2O_3	1.00	3.75	1.80
Fe_2O_3	1.72	1.51	3.00
MnO	. .	trace	. .
$CaSO_4$	0.73	0.58	1.00
$CaCO_3$	91.32	65.67	84.27
Ca_3PO_4	0.28	1.74	trace
$MgCO_3$	0.30	1.33	1.28
Insoluble	1.82	12.23	2.05
Loss on ignition	. .	. .	2.60
Loss, ignition	1.00	2.82	. .

III. THE CHEMICAL PROPERTIES OF CALCITIC LIMESTONES

A. SOLUBILITY Calcitic limestone or calcium carbonate is only slightly soluble in pure water. Its solubility in different solvents, however, has attracted much attention on account of its influence on geological processes, and on the nature of soil solutions.

In pure water, approximately 75,000 parts of water are required to take into solution one part of calcium carbonate. According to J. Kendall (16), the results, in grams per litre, are as follows:

	25°	50°	100°
Calcite . . .	0.0143	0.0150	0.0178
Aragonite . .	0.0154	0.0162	0.0190

It may be diagrammatically represented by the Fig. 1, in which the solid curves are for the solubility of calcite and aragonite in a litre of water freed from CO_2 and in an atmosphere freed from the same gas.

The solubility of calcium carbonate is much affected by the presence of CO_2, and by the changes of temperature and pressure. For instance, the dotted curve in Fig. 1 gives the solubility of calcite in water exposed to atmospheric air, and it shows also how the solubility of calcite, in a water in equilibrium with air, increases as the temperature decreases.

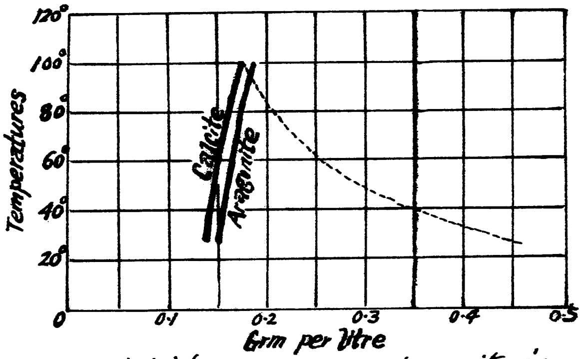


Fig. 1, Solubility of Calcite and Aragonite in Water.

According to the experiment made by R. C. Wells (16), the solubility of calcite and aragonite are rather higher than those obtained by J. Kendall. This is possibly because of the greater concentration of the atmospheric CO_2, and when the atmosphere contained between 3.02 and 3.27 parts of CO_2 in 10,000, Wells found the solubility of calcium carbonate in grams per litre to be:

	0°	10°	20°	25°	30°	40°	50°
$CaCO_3$	0.081	0.070	0.065	0.050	0.052	0.044	0.038

H. L. J. Backstrom found the solubilities in the presence of CO_2 at a pressure of 742-777 mm. to be for calcite 1.30, 0.943, and 0.765 grams per litre respectively at the temperatures of 9°, 25°, and 35°, and likewise for aragonite 1.46, 1.066, and 0.876 grams per litre.

The solubility of aragonite in water is a little greater than that of calcite, which is in harmony with the generalization: of two different forms of a compound, the less stable modification is usually the more soluble.

T. Schlosing (16) measured the solubility of calcium carbonate in water with CO_2 in solution. J. Johnston calculated the solubility of calcium carbonate in water, at 16°, from measurements by T. Schlosing, and R. Engel, and expressing the results in gram-atoms of Ca and in mols of $Ca(HCO_3)_2$ per litre, when the partial pressure of the CO_2 is p atmosphere, found:

p . . .	0.000504	0.000808	0.003330	0.028200	0.050100	0.142200	0.553300
Ca . .	0.000746	0.000850	0.001372	0.002965	0.003600	0.005330	0.008855
$Ca(HCO_3)_2$	0.000731	0.000837	0.001364	0.002961	0.003597	0.005328	0.008854

H. N. McCoy and H. J. Smith (16) obtained the following solubility for calcium carbonate at 25°, in contact with air containing CO_2 at partial pressure p atmosphere, when the results are expressed in grams per litre of saturated solution:

p	0.1	1.1	9.9	13.2	16.3	25.4
H_2CO_3	0.22	2.3	20.6	27.5	34.1	53.2
$Ca(HCO_3)_2$	0.67	1.58	3.62	4.04	4.21	4.22
Solid phase	$CaCO_3$				$Ca(HCO_3)_2$	

These results show that the solution is saturated with calcium bicarbonate when the CO_2 exerts about 15 atmospheric pressures, and that it should be theoreticaally possible to convert all the normal carbonate into bicarbonate by introducing sufficient CO_2 at 15 atmospheres.

B. FORMATION OF CALCIUM BICARBONATE It is very well known that when calcium carbonate is in contact with the carbonated water or water containing CO_2, the latter acts upon it readily and calcium bicarbonate is thus produced as the following formula:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

The resulting bicarbonate is thirty times as soluble as the calcium carbonate, even in the pure water. Since this chemical change is fundamental to the explanation of a great many other changes of limestone, a more detailed discussion on the process of formation of calcium bicarbonate is necessary.

F. W. Kuster (16) has shown that in aqueous solution calcium carbonate is not only ionized, but is also hydrolyzed. G. Bodlander calculated that between 80 and 83.4 per cent of calcium carbonate is hydrolyzed in aqueous solution. Consequently, assuming that the reaction is typified by the equation: $CaCO_3 + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2CO_3$, the dissociation of the carbonic acid is determined by the partial pressure of CO_2 of the atmosphere in contact with the solution. It follows from the balanced reaction that the greater the concentration of the CO_2 in the solution, the less the solubility of the calcium carbonate. The direct converse actually obtains, for calcium carbonate readily dissolves in aqueous solution of carbonic acid because of the formatiom of the bicarbonate. Saturated lime-water is rendered turbid by CO_2 as $CaCO_3$ is precipitated, but as the passage of the gas is continued, the opacity nearly disappears, and if a little more water is added, a clear solution is obtained. When the aqueous solution is exposed to air, or boiled, normal calcium carbonate is precipitated. It is therefore inferred, by analogy with other cases, that soluble calcium bicarbonate, $Ca(HCO_3)_2$, is formed:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$
$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

J. Johnston and E. D. Williamson (16) have shown that the concentration of the calcium carbonate in solution at equilibrium in the system CaO—H_2O—CO_2 can be represented by three curves along which the stable solid phase is hydr~~o~~oxide, carbonate, and bicarbonate respectively. In Fig. 2, the stable solid phase along AP_1 is hydr~~o~~oxide; between P_1 and P_2 it is carbonate; and along P_2B it is bicarbonate. These curves were plotted from the data given in Table V.

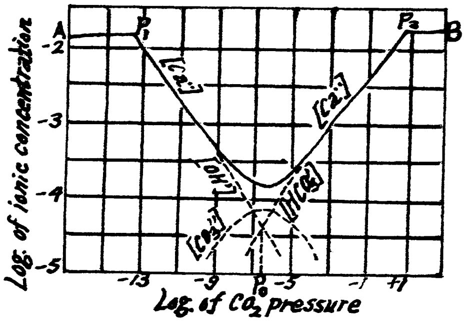


Fig. 2. Relation between the Partial Pressure of CO_2 and the Concentration of the several Ions in the System, $CaO-H_2O-CO_2$, at 16° C.

As to what extent the product of the respective concentrations of calcium-ion and carbonate-ion would be resulted, Johnston and Williamson gave the following conclusions (13):

1. In a solution at a fixed temperature saturated with pure calcite, the solubility-product—i. e. $[Ca^{++}]$ $[CO^{--}]$, the product of the respective concentrations of calcium-ion and carbonate-ion—is constant, independent of the proportion of free CO_2 in the solution and of the presence of other salts. This characteristic solubility-product constant is to be carefully distinguished from the solubility which,

TABLE V: IONIC CONCENTRATIONS OF SOLUTIONS OF CALCITE IN CONTACT WITH AIR HOLDING CO_2 AT A PARTIAL PRESSURE P, AT 16°C.

P	$[HCO_3^-] \times 10^4$	$[OH^-] \times 10^4$	$[CO_3^{--}] \times 10^4$	$[Ca^{++}] \times 10^4$	Parts $CaCO_3$ per million
2.15×10^{-4}	10.0	0.0174	1.188	5.197	56
7.63×10^{-5}	7.0	0.034	0.26	3.777	40
7.62×10^{-6}	3.0	0.147	0.478	2.051	22
6.07×10^{-7}	1.0	0.614	0.666	1.473	16
3.85×10^{-7}	0.8	0.774	0.672	1.459	15.9
3.73×10^{-7}	0.787	0.787	0.672	1.459	15.9
2.19×10^{-7}	0.600	1.02	0.665	1.476	16
6.14×10^{-8}	0.300	1.82	0.593	1.654	18
9.78×10^{-9}	0.100	3.82	0.414	2.377	26
2.80×10^{-10}	0.01	13.30	0.144	6.810	74
3.16×10^{-14}	0.0000235	277.00	0.0071	138.500	2000

as ordinarily measured, is the concentation of total calcium in a solution in equilibrium with solid calcite; and this calcium is associated with bicarbonate and hydroxide (and with any other anion present, e. g., chloride or sulphate) as well as with carbonate—indeed, under ordinarily atmospheric conditions but a small fraction of the total calcium is ever associated with carbonate.

2. The concentration of H_2CO_3 ("free" CO_2) in solution is regulated by the partial pressure or proportion of CO_2 in the layer of atmosphere in contact with the solution, and conversely; and for a given value of partial pressure, it diminishes with rising temperature, since the absorption coefficient (solubility) of CO_2 diminishes.

3. At a given temperature the total solubility as usually measured —i. e., the total concentration of calcium in solution—varies with the concentration of H_2CO_3 (hence with partial pressure), owing to the fact that the latter determines the proportion of carbonate-ion CO_3^{--}, bicarbonate-ion HCO_3^-, and hydroxide-ion OH^- in accordance with

definite mathematical expressions; and since the product $[Ca^{++}]\ [CO_3^{--}]$ remains constant $[Ca^{++}]$ must vary inversely as $[CO_3^{--}]$. The presence of other salts also affects this total solubility; so long as pure calcite is the stable solid phase in equilibrium with the solution, the magnitude of this effect is readily calculable, since the several concentrations always adjust themselves until the solubility-product $[Ca^{++}]\ [CO_3^{--}]$ attains its characteristic value.

4. The solubility-product constant diminishes with rising temperature; it is **not** affected to an appreciable extent by change of hydrostatic pressure. The mathematical expressions are as follows:

$$[H_2CO_3] = cP$$
$$[Ca^{++}][CO_3^{--}] = Kc \text{ (in presence of solid calcite)}$$
$$[HCO_3^{-}]\ /\ [CO_3^{--}] = l[H_2CO_3] = lcP$$
$$[OH^{-}]\ /\ [CO_3^{--}] = m/[H_2CO_3] = m/cP$$

Where c, Kc, l, and m are constants at any given temperature. It may be noted, moreover, that the free CO_2 and the total CO_2 (i. e., $[H_2CO_3] + [CO_3^{--}] + [HCO_3^{-}]$) determine $[OH^{-}]$, the alkalinity (or acidity) of the solution; and that no changes can be made in any one of these quantities without affecting each of the others.

Recent investigations (19) of the relationships between the various forms of carbonic acids in sea water have made it possible to delimit experimentally the solubility of calcium carbonate in the sea and to estimate quantitatively the relative affects on the solubility of variations in salinity, temperature, hydrostatic pressure, and CO_2 content. Although the experimental results obtained by various workers for the solubility-product are not in agreement, it is at least certain that surface sea water at a temperature of 30°C is saturated with calcium carbonate. It is shown that except for water in equilibrium with the atmosphere the most important factor controlling the solubility of calcium carbonate in sea water is the CO_2 content of the water, which in turn, is chiefly dependent upon the nature and amount of biological activity. The order of importance of the other factors is temperature, salinity, and hydrostatic pressure. For water in equilibrium with the atmosphere, a condition probably only rarely attained, changes in temperature have the greatest effect on the solubility.

C. EFFECT OF OTHER IONS ON SOLUBILITY 1. In Boiling Water: The aqueous solution of calcium carbonate was found by M. Pettenkofer (16) to be neutral towards turmeric, but if the solution has lost some CO_2 the indicator is browned. As shown by A. Laugier and others, if water is boiled with powdered marble or chalk, it colors red-litmus blue. Powdered marble, chalk, calcite, or aragonite were found by C. A. Kenngott and others to be alkaline towards litmus or extract of violets.

H. le Chatelier (16) showed that calcium carbonate dissociates in boiling water and loses CO_2, and A. Cavazzi found that in consequence it is not possible to get a solution of calcium carbonate alone in boiling water, for calcium hydroxide also passes into solution. This quantity depends on the duration of boiling, and on the concentration and volume of the solution. The limit of the dissociation is attained when 15 c. c. of a solution of calcium hydroxide, saturated at ordinary temperature, is present per litre.

2. In Hydrochloric Acid: Calcitic limestone is readily soluble in hydrochloric acid. As soon as limestone is in contact with hydrochloric acid, it effervesces briskly and the CO_2 escapes from it. The chemical reaction takes place as shown in the following equation:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

The speed of the reaction between them may be illustrated by W. Spring's diagram as Fig. 3. In his diagram, Spring observed (16) that there is a marked period of induction, OB, and this is followed by a period, BC, during which the speed of the reaction is proportional to the concentration of the acid. There is then a period, CD, during which the speed of the reaction is greater than what would occur if the rate of the reaction were proportional to the concentration of the acid. Spring represents the effect of the temperature θ on the velocity V by the exponential equation: $V = K^{20.05\theta}$, where K is a constant. He also found all cleavage surfaces of calcite are dissolved at the same rate; and at 15° a surface cut parallel to the chief axis is dissolved by 10 per cent hydrochloric acid at the same rate as cleavage surface, but at 35° the former surface is attacked 1.23 times as fast, and at 55°, 1.28 times as fast as the cleavage surface. The speed of dissolution of a surface cut normal to the chief axis is 1.14 times as great as one cut parallel to that axis. The hydrochloric acids attack aragonite rather more slowly than calcite, for, at 15°, the speed of dissolution of aragonite in 10 per cent hydrochloric acid is 0.476. L. Lavizzari found that the rate of attack of aragonite on the basal and prismatic surfaces are as 3 : 1.

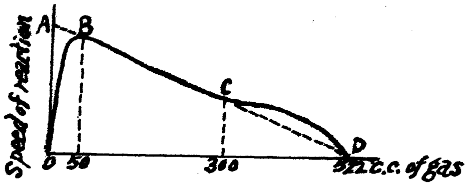


Fig. 3. W. Spring's Diagram showing the Speed of the Reaction between Calcium Carbonate and Hydrochloric Acid

3. In Contact With Sodium Compounds: F. K. Cameron (16) and others measured the solubility of calcium carbonate in aqueous solution of sodium chloride. Expressing the solubilities in grams per 100 c.c. of solution, at 25°, they found with solution in equilibrium with ordinary air:

NaCl . .	1	4	8	10	15	20	25
$CaCO_3$ . .	0.0112	0.014	0.0137	0.0134	0.0119	0.0106	0.0085

for solution in contact with air freed from CO_2, at 25°:

NaCl . .	1.60	5.18	9.25	11.48	16.66	22.04	30.50
$CaCO_3$ . .	0.0079	0.0086	0.0094	0.0104	0.0106	0.0115	0.0119

These figures show clearly that the solubility of calcium carbonate in CO_2 free water increases as the salinity increases. In addition T. Warynsky and Kouropatwinska (16) found a litre of an aqueous solution containing 175.5 grams of sodium chloride dissolved 0.062 gram of calcite, or 0.071 gram of aragonite at 60°.

F. K. Cameron and A. Seidell (16) measured the solubility of calcium carbonate in solution of sodium sulphate in contact with air at 24°. Expressing the results in grams per litre:

$NaSO_4$ . .	5	10	20	40	80	150	250
$CaCO_3$ . .	0.175	0.232	0.277	0.332	0.400	0.510	0.725

and for solution in contact with air freed from CO_2, at 25°:

$NaSO_4$ . .	0.97	1.65	4.90	12.69	14.55	19.38	23.90
$CaCO_3$ . .	0.151	0.180	0.262	0.313	0.322	0.346	0.360

These results indicate that the higher the concentration of sodium sulphate in solution, the greater the solubility of calcium carbonate, regardless of the presence or absence of CO_2 in the air.

J. Spiller noted that the presence of sodium citrate raises the solubility of calcium carbonate in water (16).

4. In Contact With Ammonium Compounds: S. Kouropatwinska (16) found for the solubility of calcite and aragonite in aqueous solution of ammonium chloride, when the results are expressed in grams per litre, at 60°:

NH_4Cl . . .	0	1.07	5.035	10.70	26.76	53.52	160.56
Calcite . .	0.028	0.164	0.333	0.453	0.664	0.934	1.21
Aragonite .	0.041	0.184	0.371	0.505	0.728	1.015	1.36

5. In Contact With Other Compounds: R. Irvine and W. S. Anderson (16) treated corals with solutions of manganese, zinc, chromium, mercury, and tin chlorides, iron sulphates, nickel, cobalt, copper, lead, and silver nitrates, and ammonium phosphate. The reaction of salts of

nickel and cobalt was very slow, while that with salts of copper and manganese was rapid. In most cases there is a direct interchange, the oxide of the metal taking the place of the lime. Silver and mercury salts are deposited as oxides.

According to W. Meigen (14), aragonite immersed in a dilute solution of cobalt nitrate slowly become lilac and the color develops rapidly on boiling; calcite in a similar solution remains uncolored in the cold but slowly becomes blue on heating. In a solution of ferrous sulphate calcite causes a yellow precipitate, aragonite a dark green one.

F. Gothe (16) thus summarizes his results: The solubility of calcium carbonate is increased by the presence of alkali chlorides, nitrates, and sulphates in the water, but decreased by alkali carbonates, and by alkali earth chlorides, nitrates, and sulphates; ammonium salts decompose the carbonate. The solubility is increased when the water contains organic (humus) substances, especially when alkali salts are also present, but is decreased in the presence of alkaline-earth salts.

IV. THE PHYSICAL PROPERTIES OF CALCITIC LIMESTONES

A. COLOR Limestone has a great variety of color. It may be white, gray, dove color, bluish gray, dark gray, or black; red is less common. Yellows and browns result from iron oxide; grays and black from organic matter.

B. SPECIFIC GRAVITY The specific gravity of limestone ranges from less than 2.00 to 2.70, depending on the amount of impurities present and on the porosity of the rock.

C. HARDNES Limestone has a hardness of less than 4, and of 3 if pure calcite; hence it can be readily scratched or cut by the knife.

The deposition of colloidal silica may increase this nature considerably.

D. FRACTURE Fine-grained limestone has an even fracture, and the most minutely grained has a conchoidal fracture. On exposed surfaces limestone, because of its solubility, tends to show the effects of solvent action: edges and corners are rounded off, and fissures and joints have been widened.

E. TEXTURE There are many opinions regarding the classification of textures of limestones. The following one is used in this paper and will be discussed in detail in Part III.

1. Shelly Limestone
2. Reef Limestone
3. Fossiliferous Limestone
4. Chalky Limestone
5. Calcareous Oozes
6. Ordinary dense Limestone
7. Non-metamorphosed Crystalline Limestone
8. Oolitic and Pisolitic Limestones
9. Travertine and Tufa
10. Stalactitic and Stalagmitic Limestones
11. Onyx
12. Aragonite Mud and Calcite Mudstone
13. Marly Limestone
14. Conglomeratic and Brecciatic Limestones
15. Miscellaneous

F. STRENGTH The strength of limestone differs according to their textures. Firm, compact varieties are strong, and loose, porous ones are weak. Thus a fine-grained variety has a crushing strength of over 40,000 pounds per square inch, whereas others scarcely exceed 3,000 pounds per square inch. The torsion modulus for limestone is 1,900-3,000 kilograms per square mm., and the elastic modulus of it is 1,900 kilograms per square mm.

G. POROSITY In limestones, the ratio of pore space to rock volume —the porosity—ranges from 25 per cent to practically nothing. The ratio between the weight of water a rock can absorb and its total porosity—the effective porosity—is in general much less than the total porosity, generally not more than one-half as much. The effective porosity is so much less because many of the pores are sealed off by cement and do not form part of a freely intercommunicating system. Some types of limestone such as travertine and reef limestone, however, have high efective porosity. The reef limestone, because of its high porosity, is particularly prized as one of the best reservoir rocks for oil.

H. STRUCTURE Some structural features are characteristically developed in limestones. The most important structure feature is stratification. Others are cone-in-cone structure, stylolite, concretion, geode, and ripple mark.

Limestone as a whole is always very well stratified. It is either thin-bedded or thick-bedded. The stratification may arise from variations in color, texture, dimensions of particles, and composition, or to temporary cessation of deposition that permits already deposited layers to undergo some changes before renewal of deposition.

Cone-in-cone structure consists of parallel nests of cones fitting into each other. It frequently occurs in the limestone containing impurities. It is formed by the solution of calcite under the pressure derived from the load of the overlying sediments. Solution began after establishment of shear planes, calcite was removed, and an insoluble residue of clay was left with the resulting cone-in-cone shapes.

Stylolite is largely confined to limestones and dolomites. It is vertically striated column, pyramid, and cone of various heights, widths, and shapes on bedding planes and less commonly on planes of other origin. It is developed along the parting planes through solution controlled by differences in the application of pressure and differences in the solubility of the rock.

Concretions of different size are quite commonly observed in limestones. They are composed mostly of cherts and flints, and iron compounds. Of the latter the iron sulphides are more common. Some limestones contain such large amounts of cherty nodules that they are named cherty limestones.

Geode is a crystal-lined cavity in a rock. It is commonly formed by deposition of mineral matter from solution, chiefly quartz and calcite, along structural and fracture surfaces of shells and thus frequently occurs in limestones. The shells that form the geodes of this origin are commonly enclosed in calcareous shales or marly limestones, and every stage in the formation of geodes from crinoids, brachiopods, gastropods, and other shells has been observed. There are also geodes in cavities formed by solution which may be regarded as small caves.

Ripple mark, in general, is rarely developed in limestones. There are, however, many limestones that have large ripple-like structures which vary from very symmetrical to very asymmetrical. These have been designated para-ripples by W. H. Bucher (25).

V. THE TOPOGRAPHIC CHARACTERISTICS OF CALCITIC LIMESTONES

As already stated before, limestone is soluble in water containing CO_2 . Since the water on surface contains always greater or lesser amounts of CO_2, the limestones through which water passes or penetrates become inevitably dissolved. Under favorable climatic conditions, such as in a hot and humid region, the final product of this process is the formation of Karst topography—a kind of landform characterized by the development of isolated hills and disconnected ranges, sink-holes, underground channels as well as caves. It should be noted, however, that, in the formation of Karst topography, the position of beds and the joints, fissures, bedding planes, and all other kinds of cracks in the limestone have no doubt played an important role. The process that forms the Karst topography may be briefly discussed as follows:

Under a hot and humid region, the vegetation is usually in full flourish, and consequently the surface is covered by a thick bed of organic matter. Through the decomposition of organic matter, the concentration of CO_2 both in water and in air under the zone of organic matter would easily become saturated. If this case is true, the partial pressure of CO_2 in such an atmosphere would increase to the greatest extent by conversion of all the oxygen in the air into CO_2; in other words, the air under the zone of organic matter would contain 20 per cent of CO_2 instead of oxygen. The dissolving power of waters in contact with such a kind of CO_2-saturated air would be undoubtedly much stronger than that under ordinary air. This explains why the Karst topography is particularly developed in a hot and humid climate.

Percolation of water in massive limestones is effected in two ways: first, along the joints or fissures and, second, along the bedding planes. Nearly all stratified rocks are cut by roughly vertical cracks or joints. These often occur in two sets or systems which intersect each other at nearly right angles. Such joints offer avenues for the water which has soaked into the soil to penetrate downward to greater depths. As the water descends along the joints, solution takes place, the joints are enlarged and crevices are formed. The intersection of two joints which cross each other is a particularly favorable spot for the penetration of water into limestone. In such a situation more or less circular openings are formed, instead of the long narrow crevices produced along individual joints.

Water which finds its way into the joints of rock descends until its downward progress is brought to a stop. This may be the result of one of two causes: First, a bed such as shale or a massive limestone layer, which is impervious to water, may be encountered; or, second, the ground-water table, or depth at which all the openings in the rock are filled with water, may be reached. In either case, when the downward movement of the water is brought to a stop, lateral movement begins and channels are dissolved out along the bedding planes or porous layers in the limestone.

VI . THE GEOLOGIC SIGNIFICANCE OF CALCITIC LIMESTONES

Except for those of fresh water origin, most kinds of limestone may be regarded as the typical products of marine deposition. Wherever limestones occur, the ancient landforms of marine environment may be reconstructed from the study of their distribution and their thickness represented on isopach maps. These are very important in the study of stratigraphy as well as paleogeography.

According to R. A. Daly (5), the pre-Cambrian seas were lacking of available calcium materials. The conditions were therefore unsuitable for the organisms to develop their skeletal structures. Organisms without skeletal structures are consequently rarely ~~to be~~ preserved as fossils. That is why fossils are so very ~~extremely~~ rarely discovered fom the geological formations of pre-Cambrian age.

On the other hand, somebody (25) explained the scarcity of limestone formations in the Archeozoic by the hypothesis that early pre-Cambrian atmospheres were rich in CO_2 and consequently the sea waters would have been highly charged with CO_2, and large quantities of calcium and magnesium carbonates would have been held in solution until agents or conditions developed to cause precipitation. In the absence of shell-forming organisms and other organic lime-precipitating agencies, the lime and magnesia would remain in solution in large quantities. The advent of green plants led to the breaking down of CO_2, the fixing of carbon in the rocks, and the partial release of oxygen to the atmosphere. As the extraction of the CO_2 was done by plants, rapid precipitation of the carbonates of lime and magnesia must have been initiated and thus arose the great limestone formations of the Proterozoic.

The former two statements, to some extent, may contradict each other. However, they indicate~~, however,~~ how the study of limestone may throw some light to the understanding and explanation of some geological events as well as organic evolution. Since the advent of plants is necessary before the appearance of animal life, and same is true for the shell-forming organisms, the writer is therefore rather inclined to the second theory.

Moreover, a study of the origin of limestone may lead to the understanding of their provenances because the calcareous materials are by and large derived from the rocks containing calcium minerals or their equivalents. According to J. Hanamann's careful investigation (5) of the Bohemian rivers the influence of the kind of rock traversed by a river on the chemical composition of that river is clearly illustrated. His results are in part summarized in Table VI, in which the content of calcium and the content of magnesium in streams issuing from different rock formations are given.

TABLE VI: THE CALCAREOUS CONTENTS OF BOHEMIAN RIVERS

Waters from	Calcium in parts per million	Magnesium in parts per million	Ratio of Ca to Mg
Granite	7.73	2.33	3.32 : 1
Phyllite	5.72	2.41	2.37 : 1
Mica-schist	9.33	3.76	2.48 : 1
Basalt	68.84	19.76	3.49 : 1
Cretaceous (partly limestone)	133.38	31.36	4.25 : 1

It is therefore obvious that the calcareous content of river waters is influenced by the composition of the rocks they pass through. Consequently the provenances of limestone may be traced out by the study of chemical composition and drainages of the streams.

VII. THE PEDOLOGIC SIGNIFICANCE OF CALCITIC LIMESTONES

Two kinds of intrazonal soils are particularly developed from limestone, namely, rendzina and terra rossa. The former is developed from calcareous materials, generally, but not always, soft, and some of the parent material remains in the surface horizon. A typical profile would be five inches of granular friable loam (the color varies from black through brown and yellowish and reddish-brown to gray) containing fragments of soft limestone lying directly upon the soft limestone rock. And the latter, though usually ill-defined, is frequently understood to connote materials which are largely of a residual nature left after the loss by solution of the bulk of a rock which consists almost entirely of carbonates, especially of calcium carbonates. Such a residuum is naturally mainly of a colloidal nature and reddish in color.

PART II. THE ORIGIN OF CALCITIC LIMESTONES

I. THE OCCURRENCE OF CALCITE AND ARAGONITE

As already stated before, calcitic limestone consists mainly of calcite and occasionally of aragonite. Under normal conditions, the former is stable at ordinary temperature, the latter is unstable.

M. J. Schleiden (16) and others have indicated that calcite occurs in the cellular tissue of many phanerogemia—e.g., cycadaceae and cactaceae. The lithothamnia seaweeds have a framework or skeleton of calcite; and the halimeda contain aragonite.

P. F. Kendall (16) found that shells of the pteropoda are mainly aragonite, and they disappear below 1,500 fathoms depth, while the calcite shells of the globigerina are found in the zone of 2,925 fathoms. The following list shows that some organisms have shells composed of calcite and others of aragonite(25):

Calcite	Aragonite
Lithothamnium, Alga	Halimeda, Alga
Lithophyllum, Alga	Galaxaura, Alga
Polytrema, Foraminifera	Millepora, Hydromedusa
Corallium, Alcyonarian	Distichopora, Hydromedusa
Tubipora, Alcyonarian	Heliopora, Alcyonarian
Serpula, Annelid	Spirula, Cephalopoda
Terebratula, Brachiopoda	Sepia, Cephalopoda
Argonauta, Cephalopoda	
Balanus, Crustacean	

The shells of many mollusks are partly calcite and partly aragonite, the latter forming the inner pearly portion. According to O. B. Boggild (25), almost all salt-water forms consist of calcite and aragonite and fresh-water forms are mostly calcite.

H. A. von Vagel (16) found that CO_2 precipitates amorphous calcium carbonate from lime-water, but on standing the precipitate becomes crystalline. By amorphous he undoubtedly meant what now would be called sub-microscopically crystalline which on standing becomes coarsely crystalline. M. Pettenkofer showed that the crystallization is retarded if an excess of calcium hydroxide be present. G. Rose found that if a little CO_2 is passed into a cold solution of calcium hydroxide, calcite is formed, and aragonite if the solution is hot. He reported also that calcite is obtained by the action of CO_2 on lime-water below 30°; aragonite at temperature above 90°; while a mixture of the two is obtained at intermediate temperature. He further found that a concentrated and warm solution of calcium hydroxide furnishes calcite when treated with CO_2; while a very dilute solution at ordinary temperature furnishes aragonite. H. Waston found that if the liquid from which the calcium carbonate is precipitated is above 30°, aragonite is formed, if below that temperature, calcite, and this whether the solution be seeded with these minerals or not.

The addition of an ammonium carbonate solution to a cold solution of calcium chloride furnishes a voluminous flocculent precipitate of calcium carbonate which, according to G. Rose, if immediately filtered and dried, appears under the microscope to consist of opaque granules like grains of chalk; but if this same precipitate be left for some time in contact with the liquid from which it has been precipitated, it collects into microscopic crystals of calcite. Again, if a boiling solution of ammonium carbonate be added to one of calcium chloride, the precipitate consists of aragonite mixed with a little calcite, while if the admixture be made in the reverse order, small crystals of aragonite are alone obtained. If the crystals be not immediately collected on a filter, washed, and dried, but allowed to remain in the cold mother liquid for about a week, they are completely converted into calcite. The transformation goes more slowly under water. In preparation of calcium carbonate from a solution of calcium chloride and ammonium carbonate, the temperature at which the aragonite-form is converted into the calcite-form is increased to a much greater extent by an increase in the concentration of the calcium chloride. Using the ammonium carbonate of such a concentration that on adding the calcium chloride a thick, gelatinous mass is obtained, the upperlimit of temperature for the ammonium carbonate solution is 32°, while the calcium chloride may be used boiling. With dilute solution at the same temperature, the aragonite crystals are at once converted into calcite; the limit of temperature for weak solution is 22°, and the lower the temperature, the smaller and more stable are the crystals of aragonite. The presence of CO_2 in the solution determines the formation of calcite, and this explains the formation of calcite when the ammonium carbonate is at a high temperature, as it is then decomposed, with the formation of CO_2.

The aragonite-form is more stable when the solution is alkaline with an excess of ammonium carbonate, and also when the precipitate is washed with water containing calcium sulphate instead of pure water. When the aragonite prepared from calcium chloride and ammonium carbonate is separated from the mother liquid and heated to 60°, it is converted into calcite; on the other hand, the aragonite precipitated by sodium carbonate can be heated to 100° without change.

According to G. Rose (16), if dilute solution of calcium chloride and sodium carbonate are allowed to diffuse slowly into one another, crystals of aragonite are formed; while if concentrated solution be employed, crystals of calcite are produced. If boiling solution of the two salts are mixed, aragonite is precipitated. He further found that if the turbid liquid obtained by mixing calcium chloride and sodium bicarbonate be boiled, calcite is formed.

L. Bourgeois heated precipitated calcium carbonate with ammonium chloride or nitrate, urea, and water in a sealed tube at 150°-180°, and obtained crystals of calcite and aragonite; and when the urea was omitted, crystals of calcite alone appeared.

M. Miron and M. Bruneau (16) observed that a river-water was used to work an aspirator sucking air charged with ammonia gas, the ammonia neutralized the free carbonic acid in the water, and the calcium carbonate, previous-held in solution, was deposited in the exit tube in the form of crystals of calcite.

According to H. Credner (16), the presence of a little lead or strontium carbonate, or calcium sulphate, favors the formation of aragonite. F. Cornu obtained aragonite by crystallization from an aqueous solution of calcium carbonate in carbonic acid containing a little manganese sulphate. Crystals of calcite, aragonite and dolomite are formed when a solution of calcium carbonate in water saturated with CO_2 is mixed with some magnesium chloride or sulphate and kept at 2°, 20°, and 90°. A larger proportion of aragonite is formed at the higher temperature. On the other hand, H. Leitmeier said that only the aragonite crystallizes from a solution of calcium bicarbonate containing magnesium sulphate; at 20°, the ratio is $H_2O : CaCO_3 : MgSO_3 . 7H_2O = 1,000 : 1 : 10$.

Both calcite and aragonite crystallize at ordinary pressure from solvents. G. Rose and O. Mugge (16) have shown that the transformation of aragonite into calcite proceeds very slowly at 410°, and even as low as 400°. P. N. Laschtschenko found the heats of cooling of aragonite and calcite are the same up to 455°; between 445° and 465° the value for aragonite is greater than for calcite; and the difference increases with the temperature. Above 465° the difference becomes less, and at 470° the two values are identical, thus showing that the transformation of aragonite into calcite begins at 445° and is completed at 470°. The beginning of the transformation is characterized by the crystals becoming turbid, and the turbidity disappears at 470°. The specific gravity determinations at different temperatures are in harmony with this conclusion. It is therefore inferred that at temperature exceeding 470°, calcite is alone stable at atmospheric pressure.

G. Tammann (16) suggested that the transformations with aragonite and calcite resemble those with phenol, and illustrated them by the diagram as shown in Fig. 4. If the temperature exceeds the limits AC, aragonite is converted into calcite; and calcite is converted into aragonite if the temperature exceeds BC, and CD represents the effect of pressure on the transition temperatures.

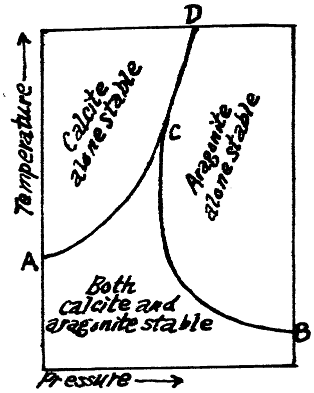


Fig.4. Zones of Stability of Calcite and Aragonite

As stated before, of two modifications of the same substance the more soluble variety is usually the less stable; aragonite is more soluble than calcite, and is therefore the less stable form. Usually also that modification which is stable at higher temperature has the lower density, here, aragonite, the denser form, is that which is less stable at higher temperatures.

From the foregoing statements, some conclusions may be drawn as follows:

1. The range of temperature and pressure for the formation of calcite is much greater than that of aragonite.

2. Aragonite is usually deposited from hot solutions while calcite is formed from cold solutions.

3. At ordinary temperatures, while calcite can be formed under most conditions, aragonite is produced only (a) through organic agencies; (b) by deposition from hot springs; and (c) when an orthorhombic isomorphous carbonate such as sulphates or carbonates of strontium or lead is present to serve as nucleus. These explain therefore why most limestones consist nearly entirely of calcite instead of aragonite.

II. THE ORIGIN OF CALCITIC LIMESTONES

Limestones are formed in various ways, but in all cases the primary action involves the separation of calcium carbonate from its solution in fresh or salt water. The separation of calcium carbonate from its solution are chiefly due to the loss of CO_2.

In general, as discussed before, the loss of CO_2 may be caused by a diminished proportion of CO_2 in the air, or by a higher temperature or both; or it may be due to organisms which make use of the CO_2 in their vital processes, or the production by bacterial action of ammonia, which indirectly achieves the same result; or, in short, it may be in any way in which the concentration of CO_2 may possibly be diminished. Consequently, if the surface layers of the sea are saturated, as we believed they are, precipitation of $CaCO_3$ will be brought about whenever any of the foregoing agencies are operating.

For the convenience of discussion, the processes possible for the formation of limestones are listed as the following scheme:

A. Calcitic Limestones due to Chemical Processes
1. Due to Physicochemical Processes
a. Decrease of CO_2 Content
b. Evaporation of Water
c. Increase in Salinity
d. Mingling of Solutions
2. Due to Biochemical Processes
a. Photosynthesis of Aquatic Plants
b. Activities of Bacteria
c. Deposition in Calcareous Tissues and Shells
B. Calcitic Limestones due to Mechanical Processes

A. CALCITIC LIMESTONES DUE TO CHEMICAL PROCESSES

1. Due to Physicochemical Processes

a. Decrease of CO_2 Content: It is obvious now that the solubilty of calcium carbonate in water decreases as the CO_2 content of the water decreases. Sea water free from CO_2 at 16° dissolves only 0.0131 gram of calcium carbonate per litre (24). Any decrease of CO_2 content of sea water would naturally lead to the precipitation of calcium carbonate or limestone. It has also been shown that removal of CO_2 under aseptic conditions causes a 4 per cent loss of calcium at tropical temperature (10). This appears as crystalline calcium carbonate.

The changes of CO_2 content may be caused by agitation, by rise of temperature, by decrease of partial pressure of the atmosphere, and by decrease of hydrostatic pressure.

Agitation is present wherever the sea water is disturbed by the action of waves and currents, by the inflowing of streams, by the eruptions of volcanoes, and by many kinds of natural disturbances such as earthequakes, landslides, dropping-in of cosmic bodies, etc. Whenever agitation occurs, the escape of CO_2 from the sea water is inevitable, and thus causes the precipitation of calcium carbonate, provided that the sea water is already saturated.

The rise of temperature has naturally the effect of forcing some amount of CO_2 out of the sea water and thus results in the precipitation of calcium carbonate. This may be brought about by the interflowing of warm and cold currents (or, in other words, by the oceanic circulations), by the eruption of submarine volcanoes, and by the solar radiation (particularly in the shallow water bodies such as shores, shallow bays, small lakes, lagoons and swamps). It is concluded (10) that in middle latitudes the sea water should be near the balancing point with respect to solid calcium carbonate, and that in tropical shallow water the chemical conditions may favor the separation of a small fraction of the calcium as carbonate.

Now let us consider what will happen when, in the course of the oceanic circulation, the cold water, which carries more CO_2 and more $CaCO_3$ than the warm surface layers, reaches the surface and is slowly warmed. In the first place, it will gradually lose CO_2 to the air, the residual concentration of free CO_2 being dependent at any moment upon the temperature of the water and the proportion of CO_2 in the air at that place. The consequence of this loss is that the amount of calcium in solution will at some point exceed the concentration which the water is able to hold in solution—or, in other words, the product $[Ca^{++}][CO_3^{=}]$ reaches its characteristic precipitation value—whereupon precipitation occurs. This process is without doubt taking place now in tropical and subtropical regions wherever and whenever conditions are fulfilled. Similar results may be obtained in the case where the warm waters flow into the cold areas.

As exemplifying the quantitative effects of change of temperature in the precipitation of calcium carbonate, Johnston and Williamson

(25) gave the following calculation: A current of sea water of temperature of 15°, is assumed to become saturated with calcium carbonate, and after traveling 600 miles at a rate of about 16 miles per day, to attain a temperature of 20°. This rate of travel would permit new water to be brought completely over the 600 miles ten times each year. On being warmed from 15° to 20°, the water would precipitate 5.4 parts calcium carbonate per million by weight or 2 parts per million by volume. If this calcium carbonate settled to the bottom, it would make an annual deposit over the entire area of two one-millionths of the depth of the current. For a current 100 feet deep the annual deposit over the entire area would be 2 mm., or one foot in 300 years.

Submarine volcanic activity would heat and agitate adjacent waters, thus driving out CO_2 and compelling carbonate precipitation. J. E. A. Kania (25) has theoretically concluded that a lava flow 20 square miles in area and 100 feet thick issuing at a temperature of 900 and accompanied by the usual gas emissions is capable of precipitating a mass of limestone equal to 191 circular lenses, each 500 feet in diameter and 50 feet thick. A similar submarine vent intermittently giving off gases during a period of a million years, thus heating and agitating the sea water with expulsion of CO_2 therefrom during that time, would lead to the precipitation of a mass of limestone 1,000 feet thick, extending over an area of 7,000 square miles.

The figures given above should not be taken too seriously, for events in nature are sometimes too complicated to be explained only by a single condition. In the first case, for instance, the rise of temperature would not be uniform, the currents would transport the precipitate to some places more extensively than others, and if the currents were underlain by colder water with small calcium carbonate content, some of the precipitate would again go into solution. In the second case, the rate of eruption, and the heat and gas issued from the volcanic vent would not be the same through all the time. These discussions, however, do give us a good idea how the limestone may be formed. The effects of the rise in temperature would be more apparent where the warming of waters occurred over shallow bottoms, while the submarine volcanic action may be employed to explain the formation of unfossiliferous limestone which occur interbedded with subaqueous lava flows.

It is established that the quantity of calcium carbonate held in solution is largely dependent upon the quantity of CO_2 in the water. This quantity of CO_2 inturn is almost entirely determined by the CO_2 in the air above the water (or, in other words, the partial pressure, i.e. the proportion of CO_2 in the layer of atmosphere in contact with the water) and the temperature. There is a definite and quickly attained equilibrium between the proportion of CO_2 in the adjacent atmosphere and the concentration of free CO_2 in the water, the factor of proportionality being the solubility of CO_2 in the water at a particular temperature. The effects of variations in the CO_2 content of the atmosphere upon the CO_2 content of the water and the solubility of calcium carbonate are shown in Table VII.

Through the studies of sea water by various workers (25), it is agreed that the surface layer of sea water remains just about saturated with calcium carbonate at 30°. Any decrease of partial pressure of the air, therefore, would cause the loss of CO_2 from the water and thus lead to the precipitation of calcium carbonate.

TABLE VII: THE EFFECTS OF VARIATIONS IN THE CO_2 CNTENT OF THE ATMOSPHERE UPON THE CO_2 CONTENT OF THE WATER AND THE SOLUBILITY OF CALCIUM CARBONATE.

CO_2 in the atmosphere expressed:		Free CO_2 of H_2CO_3 in solution parts per million	Solubility of calcite, parts $CaCO_3$ per million
As partial pressure	As parts per 10,000 by volume		
0.0001	1.0	0.18	44
0.0002	2.0	0.36	55
0.00025	2.5	0.45	59
0.0003	3.0	0.55	63
0.00035	3.5	0.64	66
0.0004	4.0	0.73	69
0.0005	5.0	0.90	75

The hydrostatic pressure increases in proportion to the depth. Water at a pressure of one atmosphere of CO_2 and at a temperature of 14° C dissolves a volume of CO_2 equal to its volume, about twice as much at two atmospheres, about three times as much at three atmospheres, etc. Since the amount of CO_2 increases in accord with the depth, the shallow zone of a water body is naturally a favorable site for the formation of calcium carbonate. The researches of the "Challenger" chemists have shown that at depths greater than 3,000 fathoms, little or no solid calcium carbonate can remain on the sea-floor. In fact, the tendency to the complete solution of this salt is strong at all depths greater than 2,500, if not 2,000 fathoms. This means that the permanent removal of calcium carbonate from the present oceanic solution through the decay of animal carcasses at the bottom seems to be possible only in about one-half of the existing ocean basin—say 70,000,000 square miles. This area is partly neritic (depths less than 100 fathoms) and partly bathyal (depths between 100 and 1,000 fathoms).

b. Evaporation of Water: Limestone may be formed through the evaporation of saline or fresh water. Evaporation takes place in arms of the sea, in caves, about springs, in lakes and playas, and in streams.

The products of evaporation of sea water are known as evaporites. They consist usually of a group of compounds, of which limestone is always an important member. The evaporation of sea water may result into two ways: Firstly, it may become concentrated by the addition of inflowing water which carries plenty of calcium carbonate. Secondly, the communication of the salt water with the sea may be cut off and the amount of the water becoming less and less through evaporation, precipitation of the salts thus results.

According to the bar theory, the formation of a thick bed of evaporites may be explained in the following way: In the area such as the Kara Bobhaz Gulf of the Caspian Sea, where the communication between the gulf and the sea is barred by a more or less elevated, narrow, or shallow waterway, and the sea water inside the gulf thus becomes more and more concentrated in the course of time. During the period of continuous concentration and evaporation, some of the salts may precipitate. The communication between the gulf and the sea may be continuously open or may alternately closed and open due to fluctuations on the level of the water. If the communication was stopped by the change of water level or general subsidence of the region, the sea water in the gulf then begins a second concentration and precipitation. Thus through these repetitions, a thick bed of evaporites is possibly formed in the gulf. It is of course that the gulf or basinal area must have continuously existed long enough to allow the concentration of a large amount of inflowing water.

The carbonates are always among the first to be precipitated, and theoretically a bed of calcium carbonate should lie at the base of each group of evaporites. This is well illustrated by the famous Triassic Keuper deposits of Germany, where the whole sequence of the evaporites is as follows in descending order:

Third cycle	Anhydrite
	Red clay
Second cycle	Common salt
	anhydrite
	salt clay
First cycle	Carnallite
	Kieserite
	Polyhalite
	Common salt
	Anhydrite
	Limestone and dolomite

Many limestone formations that are found in geological columns are of evaporites. They were especially developed during the Silurian, Permain, Triassic, and Cretaceous periods. Recent examples of evaporites may be observed in the Kara Boghaz Gulf of the Caspian Sea, the Great Salt Lake, the Dead Sea, and many other inland water bodies in arid and semiarid areas.

The calcareous deposits about springs are known as tufa, calcareous sinter, and travertine. They are mostly due to the escape of CO_2 and organic activity. The evaporation in some cases is probably of minor importance in their development.

The evaporation of calcareous solution in caves forms the characteristic stalactite, stalagmite, and kindred rocks.

Evaporation of calcareous solution also takes place in the shallow water lakes and playas in arid and semiarid regions. For instance, the tepetate and caliche of the semiarid Southwest United States are lime deposits which occur over the flood plains and alluvial fans and cones of the ephemeral, but often torrential, rivers. The reh of India and the sabath of Eygpt are also lime deposits in similar areas due to evaporation.

Fresh waters flowing toward the equater into the sea, as those of the Rhone and Mississippi, may have a part of their calcium carbonate precipitated as they spread over the surface of the sea because of lower density and become evaporated for some time.

c. Increase in Salinity: The salinity of sea water influences the solubility of calcium carbonate in the water at least because of its relation to (1) the solubility of free CO_2 in the water, and (2) the quantity of calcium in the water. Like the temperature, it effects also the viscosity and density of the water and the growth of living organisms. Owing to its effect on the density of water, it influences the circulation of masses of water in the ocean, with the result that bodies of warm or cold water are moved from their places of formation; and thus the salinity indirectly affects the temperature of the water. In this paragraph, however, we concentrate our discussions only on its relations to (1) the solubility of free CO_2 in the water, and (2) the quantity of calcium in the water.

CO_2 is less soluble in NaCl and $NaSO_4$ solutions than in fresh water. The solubility of CO_2 in water decreases as the salinity of the water increases. This may be well illustrated by the studies of Great Salt Lake water by A. J. Eardley as shown in the following Table VIII.

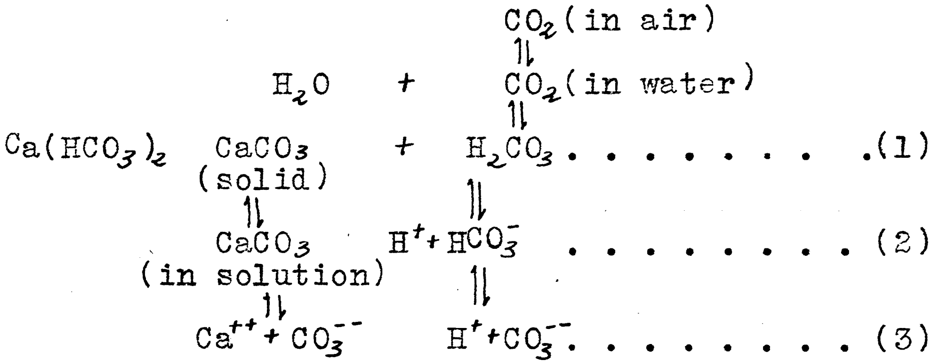
TABLE VIII: SOLUBILITY OF CO_2 IN WATER, SODIUM CHLORIDE SOLUTION, AND VARIOUS CONCENTRATIONS OF GREAT SALT LAKE WATER, AT 0° AND 25°C.

Lake level in feet	Salinity grams per 100 c.c.	Density	Solubility			
			Great Salt Lake Water		Pure NaCl Solution	
			0°C	25°C	0°C	25°C
15	15.13	1.104	0.887±.005	0.418±.005		
6.2	23.98	1.159	0.614±.005	0.338±.005	0.678	0.352
-1.2	27.60	1.224	0.440±.01	0.263±.01		
——	(saturated)					

Distilled Water	1.713	0.759

The solubility figures are unit volumes of gas sbsorbed in a unit volume of solution. The figures for the NaCl solution are those for a 3.44 normal solution which corresponds in gram equivalents of Na to Great Salt Lake water of 23.98 per cent salinity. The pH of Great Salt Lake water ranges from 7.4, when saturated with NaCl and $NaSO_4$, to 8.48, when diluted with 6 to 7 parts of water.

The table shows the solubility of CO_2 in various solutions to be affected as strongly by a 25°C change in temperature as by doubling the salinity. It indicates that pure water can absorb four times as much CO_2 as can the Great Salt Lake brine when saturated with NaCl and $NaSO_4$. It indicates also that the brine is less absorbent than a gram-molar solution of pure NaCl. The reaction for calcium might be written as follows:



$$\begin{array}{cccccl}
 & & & CO_2\text{(in air)} & & \\
 & & & \upharpoonleft\downharpoonright & & \\
 & H_2O & + & CO_2\text{(in water)} & & \\
 & & & \upharpoonleft\downharpoonright & & \\
Ca(HCO_3)_2 & \underset{\text{(solid)}}{CaCO_3} & + & H_2CO_3 & \ldots\ldots\ldots & (1) \\
 & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \\
 & \underset{\text{(in solution)}}{CaCO_3} & & H^+ + HCO_3^- & \ldots\ldots\ldots & (2) \\
 & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \\
 & Ca^{++} + CO_3^{--} & & H^+ + CO_3^{--} & \ldots\ldots\ldots & (3)
\end{array}$$

With the removal of CO_2 from the solution, some of the H_2CO_3 would necessarily break up into H_2O and CO_2 to supply the deficiency of CO_2 thus created. In turn, some of the ions of stage (2) would unite to form molecular H_2CO_3. To supply the HCO_3^- ions taken from stage (2), the ions of stage (3) would unite, thus removing CO_3^{--} ions from the solution. Inasmuch as these CO_3^{--} ions are attracted as much by the Ca^{++} ions as the H^+ ions, some of the ionized $CaCO_3$ will revert to the molecular condition and hence into solid state as a precipitate.

On the other hand, since the salinity decreases the solubility of CO_2 in water, it would seem to follow that the normal carbonate stream waters entering the brine of Great Salt Lake would lose part of their CO_2 content and the precipitation of $CaCO_3$ which had been held in solution as bicarbonate would result.

With respect to salinity, the solubility of calcium carbonate increases as the salt content increases. As stated before, the solubilty of calcium carbonate rises with increased salinity to a certain limit with NaCl and then begins to fall at a concentration of 10 grams per 100 c.c., but with $NaSO_4$ it continues to rise to the limits of the experimental work at a concentration of 250 grams per litre.

P. D. Trask (23) has presented data suggesting that the quantity of calcium carbonate in marine sediments increases as the salinity of the surface water rises, and the rate of increase is greatest between salinities of 34 to 36 parts per thousand. Areas where the salinity of the surface water is less than 34 parts per thousand generally contain less than 5 per cent calcium carbonate, whereas, where the salinity is more than 36 parts per thousand, the sediments contain, as a rule, more than 50 per cent calcium carbonate. The precipitation may be due to the increased salinity, and perhaps, it may be that the increased salinity influences in some way the organic precipitation of calcium carbonate. However, the concentration of calcium at any given depth depends almost entirely upon the salinity, because the salinity represents the concentration of total solids in solution, and if the salinity changes, then it follows that the concentration of all the salts, including those of calcium, likewise changes.

d. Mingling of Solutions: Certain calcareous deposits are formed through the mingling of different kinds of solutions that produces reactions leading to precipitation. However, little is known about the precipitation of calcium carbonate in this way except where fresh water loaded with calcium carbonate enters bodies of water of high salinity. According to A. J. Eardley (8), considerable sodium carbonate and carbonic acid were discharged into the Great Salt Lake by streams draining areas of eruptive rocks in the region, and calcium, in solution as the chloride, probably was precipitated as the carbonate according to the following equation:

$$CaCl_2 + Na_2CO_3 \longrightarrow CACO_3 + 2NaCl$$

Certain calcium carbonates may have been formed in this way wherever and whenever conditions were fulfilled.

2. Due to Biochemical Processes

The abstraction of free CO_2 from fresh and saline water by growing plants, the production of ammonia in sea-water by decaying organisms or by bacteria, and the utility of calcium by shell-forming animals have all the effects of disturbing the equilibrium in a solution originally saturated with $CaCO_3$, and hence lead to the production of calcium carbonate. These may be separately discussed in the following headings:

a. Photosynthesis of Aquatic Plants: All green plants require CO_2. Aquatic plants satisfy their needs for CO_2 from the bicarbonates in the water, reducing these to carbonates, which may then precipitated. The precipitation takes place upon adjacent surfaces, thus covering leaves, stems, and the bases to which the plants are attached. The precipitated carbonates are in very finely divided forms and seem to consist of small crystals of calcite. Work of this kind by green plants is known as photosynthesis and occurs at all depths in which plants containing chlorophyll grow. Green plants are known in the

Caribbean to the depth of 284 meters, but it is thought that the lower limiting depth of much carbonate precipitation by photosynthesis is about 80 meters.

It is probable that algae do this work to the greatest extent, particularly those belonging to the Chlorophyceae, or green algae, and the Rhodophyceae, or red algae: the former including HALIMEDA and UDOTEA and the latter CORALLINA, JANIA, MELOBESIA, LITHOTHAMNIUM, and LITHOPHYLLUM. The lime appears to form at first as tiny separate crystals, which ultimately develop into star-like clusters, and these by enlargemant unite to form solid masses or layers.

In the process of photosynthesis, the cellulose of plants is formed according to the following equation:

$$12CO_2 + 11H_2O \longrightarrow C_{12}H_{22}O_{11} + 12O_2 \ldots\ldots\ldots (1)$$

From this equation, it is obvious that, in order to make one molecule of cellulose, 12 molecules of CO are required. As already stated before, the aquatic plants acquire this CO from the bicarbonate in solution, and the chemical reaction is:

$$Ca(HCO_3)_2 \rightleftharpoons CO_2 + CaCO_3 + H_2O \ldots\ldots\ldots (2)$$

This means while one molecule of CO_2 is taken by the plants, one molecule of $CaCO_3$ would precipitate. If 12 molecules of CO_2 were removed, as shown in equation (1), then 12 molecules of $CaCO_3$ would precipitate. The molecular weight of cellulose and $CaCO_3$ is 342 grams and 100 graams respectively, we may say, therefore, that in the formation of 342 grams of celluose, 1,200 grams of $CaCO_3$ would form. In other words, for each gram of cellulose formed by phtosynthesis when CO_2 comes from bicarbonate, approximately 3.5 grams of $CaCO_3$ would precipitate.

So far as plants are concerned the CO_2 required for photosynthesis is acquired from bicarbonate ions in solution. If several positive ions are present some of each may be precipitated, depending upon equilibrium and solubility relations.

b. Bacterial Activities: The precipitation of calcium carbonate in the sea through the activities of bacteria is a rather complex and controversial problem. The bacterralogical process of calcium carbonate precipitation is confined only to certain localities. As stated by R. M. Field (9), the marine bacteria are probably negligible in the precipitation of calcium carbonate and all bacteria are relatively more important in the muds and fresh and brackish waters of Andros Island than in the marine muds covering the banks. Among the various forms of bacteria, the sulphate-reducing bacteria, ammonifying-bacteria, denitrifying bacteria, and the agar-liquefying bacteria are important but indirect agents in the precipitation of calcium carbonate.

G. H. Drew (7) suggested and attempted to prove that denitrifying bacteria are indirectly responsible for certain fine-grained calcium carbonate sediments that have extensive distribution at Tortugas and were actually observed by J. F. McClendon (25) in process of precipitation.

N. R. Smith (22) placed the bacteria found in sea water and sea bottom muds in six groups, among which are denitrifiers and strong ammonifiers, which dominate in the muds of the bottom where their activities ultimately lead to the formation of calcium carbonate from calcium sulphate.

W. Bavendamm (2) found relatively few bacteria in the white calcium carbonate muds covering the sea bottom and banks west of Andros Island, but he found that in muds of the coast and in mangrove swamps bacteria are abundant, the surface muds of the mangrove swamps on Williams Island containing 16 million bacteria per gram and, at the depth of 4 feet, 2 million per gram, leading to the view that the formation of the carbonate takes place in the muds of mangrove swamps and similar places at the surface. As to the organisms which may be responsible for the precipitation of calcium carbonate, he also reported as follows:

" Apart from the types which Drew and others have erroneously termed 'calcium bacteria', going so far as to attach special names to them, there were found in many places numerous ureabacteria which to this day have escaped observation. These bacteria, like the denitrifying forms observed by Drew, are able to precipitate calcium carbonate under certain conditions. Also the strictly anaerobic, sulphate-reducing bacteria, which are probably important in the process of calcium carbonate precipitation, were found to exist everywhere. The presence of very active cellulose- and hemicellulose-destroying bacteria attracted special attention. These organisms were notable for their ability to dissolve agar-agar made from brown and red algae, and are ao abundant that they are believed to be not only responsible for the decomposition of the abundant organic matter in the mangrove swamps but together with other bacteria they might well aid in the precipitation of calcium carbonate (2). "

Besides, putrefaction of organic matter under some conditions producing ammonia may indirectly lead to the formation of calcium carbonate. The process is that ammonia may combine with CO_2 to form ammonium carbonate, which, reacting with calcium salts in solution, converts the calcium to the carbonate. This carbonate in saturated waters is then precipitated. Experiments by J. Murray and R. Irvine and others (25) have shown that sea water in which organic matter decays has all its calcium salts changed to carbonates and precipitated to extent possible.

Three ways have been postulated by whcih bacteria may precipitate calcium carbonate. They are:

(1). Nitrates in solution are first reduced to nitrites, which ultimately are changed to ammonia. This ammonia react with CO_2 to form ammonium carbonate, which, reacting with calcium ions in solution, leads to precipitation of calcium carbonate. It was stated by G. Linck (25) that this calcium carbonate is in the form of aragonite. This may need confirmation, although the finegrained carbonate studied by Drew was in that form. The bacteria studied by F. T. Williams and E. McCoy (25) formed calcite. That ammonia is formed in decompositional processes is well known, and there is little doubt that some calcium carbonate may be precipitated in this way. The equations are:

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

$$(NH_4)_2CO_3 + H_2O + Ca^{++} \longrightarrow CaCO_3 + 2NH_4OH$$

(2). Ammonia may act directly with calcium bicarbonate, combining with the CO_2 and precipitating the carbonate as follows:

$$2NH_4OH + Ca(HCO_3)_2 \longrightarrow (NH_4)_2CO_3 + CaCO_3 + 2H_2O$$

(3). Organic salts of calcium are used by bacteria for food. This releases calcium hydroxide, which may unite with CO_2 and precipitate calcium carbonate.

It should be noted, however, that the precipitation is an indirect process and is not directly connected with the vital activities of the organisms but is a by-product of those activities.

c. Deposition in Calcareous Tissues and Shells: The formation of calcareous tissue and shell limestone may be regarded as due to the compound processes. Firstly, the formation of calcareous tissues and shells by lime-secreting or lime-depositing organisms is a biochemical process. Secondly, the accumulation of tissues and shells after death of the organisms is chiefly a mechanical process. And lastly, the cementation of tissues and shells into a rock is a physicochemical process. The formation of calcareous tissues and shells is therefore, only the first stage in the formation of some kinds of limestone.

LITHOTHAMNIUM is an extremely important contributor to coral reefs, and in the materials derived from the boring on Funafuti it was the most abundnat organic substance. HALIMEDA was second in abundance.

Many higher green plants also do the same kind work in fresh water. For instance, CHARA in Green Lake, Wisconsin, contains within its tissue structure about 70 per cent calcium and magnesium carbonates on a sand-free and air-dry base, of which about 2.5 per cent is magnesium carbonate. It is estimated that the plant deposits in Green Lake about 1,000 tons of calcium carbonate annually.

So far as to the formation of calcareous shells, the appearance of shell-forming organisms after the advent of green plants, as stated before, was of initial importance to the rise of the great limestone formations of the Proterozoic. Since then, the contributions of shell-forming organisms to the formation of limestones is forever increased through all geological periods. Among the different groups of shell-secreting animals, foraminifera, corals, bryozoans, brachiopods, mollusks, and crinoids are the most important contributors to the formation of shell limestones and limestone reefs.

According to the analyses by F. W. Clarke and W. C. Wheeler (4), as given in the Table IX, most of marine organisms have a high content of calcium carbonate in their hard parts.

TABLE IX: THE INORGANIC CONSTITUENTS OF MARINE INVERTEBRATES

Organisms	Percentages					
	$CaCO_3$	$MgCO_3$	SiO_2	Ca_3PO_4	$(Al,Fe)_2O_3$	$CaSO_4$
Foraminifera	77–90	1.8–11	T–15	T	T–5.0	0
Calcitic sponges	71–85	4.6–14	T–8	?–10	T–5.7	0
Corals	73–99.9	0.1–16	T–2	T–9	T–1.0	T–5.4
Annelids	90–92	0.0–10	0	T–1	0	T–0.13
Echinoderms	78–93	5.0–15	0–10	T–1.9	0.1–5.2	T–4.2
Bryozoa	63–97	0.6–11	0.2–6.7	T–2.7	0.–2.3	0.3–2.8
Calcareous brachiopods	89–99	0.5–8.6	0.06–0.5	T–0.6	0.04–0.5	0.4–1.7
Phosphatic brachiopods	12–80	0.8–0.67	0.5–0.9	75–92	0.3–1.2	2.9–8.6
Mollusks	94–99.9	0 –6	0 –2.2	0 –0.9	0.4–1.9	0 –0.2
Barnacles	96–98	0.8–2.5	0.03–2.1	0 –0.8	0.15–0.7	. . . .
Crustaceans	29–83	3.7–16	0 –3.8	8.7–2.7	0.06–8.9	T–5.3
Calcareous algae	74–99	10.9–25	0.02–2.1	T–0.4	0.001–1.6	0.03–1.4
Average	83.30	6.36	2.02	5.60	1.14	1.11

T equals trace.

From this table, it is quite clear that most of marine invertebrates play an important role in the abstraction of calcareous materials from the sea water and ultimately lead to the formation of the great sequences of limestone.

B. CALCITIC LIMESTONES DUE TO MECHANICAL PROCESSES

Now let us complete our discussion on the origin of limestone by consideration of certain kinds of limestones owing their origin to the mechanical processes.

Limestones are by and large products of chemical origin. The mechanical processes that are responsible in the formation of limestone in general are not important. There are, however, mechanically transported and deposited calcium carbonate that have formed limestones in the past, and the ripple-marked and cross-laminated limestones so common in many geological sections also indicate calcium carbonate sediments of mechanical deposition.

There also appears to be considerable finely divided calcium carbonate carried in suspension, and some of this may be of colloidal dimensions. The deposition of this materials apart from calcium carbonate of other derivation would lead to fine-grained limestone.

The deposition of a great deal of the shell limestone is as truely mechanical as that of gravels and quartz sands, and the deposits are really sands and gravels of shell matter. After such organic matter is thrown on a beach, it may be picked up by wind and transported inland to be deposited in dunes. Thus there are dunes on Bermuda composed entirely of coral fragments, shell fragments, and shells of foraminifera. An older similar lime deposit of Bermuda now consolidated is known as a sandstone, although nearly pure calcium carbonate. On the shores of the Arabian Sea is a limestone of eolian deposition known as the Miliolitic formation because of the abundance of shells of MILIOLA. The Junagarh limestone overlying the Decan trap in the Kathiawar district of western India is also ascribed to this origin. In Ireland are dunes on the coast of Galway which are composed of the shells of foraminifera.

Besides, the limestone breccias sometimes occurred in the piedmont areas and along the faulted zones may also be regarded of mechanical origin.

The agents that bring about to the accumulation of skeletal and protective structures of organisms may be streams, winds, currents, waves, and scavengers. Among them the waves and scavengers are the most important. They reduce shell matter to sand dimension, after which the shell sands may be accumulated in water or on land. The sands of some streams are composed of particles of limestone. These may lead to the formation of limestone, though the case is rare.

III. ENVIRONMENTS OF LIMESTONE DEPOSITION

According to the recent study of L. L. Sloss (21), the environments of limestone deposition may be summarized as follows:

A. PLATFORM LIMESTONES

Platform limestones are deposited under conditions of marine inundation of tectonically neutral areas of the continental interior when adjacent positive areas are either peneplaned, submerged, or too far distant to supply significant quantities of clastics. Such shallow seas should be sufficiently warm to promote the growth of large numbers of carbonate-secreting or depositing organisms and the precipitation of inorganic carbonates from solution.

The resulting limestones are typically of three types: (1) normal marine, when precipitation by inorganic processes or algae exceeds contributions by macroscopic forms; example—Mission Canyon limestone (Mississippian) of central Montana. (2) fragmental, when major contributions are made by benthonic animals (limestones of Osage age in the Mississippi Valley). (3) foraminiferal, an accumulation of tests of pelagic foraminifera plus inorganic precipitates (Cretaceous chalk) or an accumulation of tests of benthonic foraminifers (Pennsylvanian fusulinid limestones).

B. BASIN LIMESTONES

Basin limestones accumulate in intracratonic basins of the type termed "autogeosynclines" by Marshall Kay and of which the Michigan basin is an example. For long periods of time, such areas are tectonically negative, sinking as their loads of sediments accumulate, and during these negative periods distinctive basin deposits are formed.

Basin environments may be divided into three types: (1) Basins with open access to the sea—The chemistry and population of the sea occupying an open basin are unaffected by the negative tectonic potential of the underlying earth's crust, so long as deposition and subsidence are equal and coincident. Therefore open basin limestones tend to be lithologically and biologically identical with platform types and distinctions must be drawn on the basis of relative thickness and lithologic associations. Isopach maps of limestone intervals indicate the location, extent, and shape of open basins in the absence of lithologic criteria, with thickness in the center of the basins being two or three times as great as those on the adjoining platform areas. (2) Barred or Confined basins—Carbonate deposition in barred basins inevitably gives way to evaporite deposition if restricted waters prevail for a sufficiently long time. Under ideal conditions the following sequence of deposits leads from open basin deposits to evaporites: a, normal marine or fragmental limestone; b, dense limestone, sometimes associated with oolitic limestone; c, dense and saccharoidal dolomite; and d, evaporites. (3) Basin margins—The zones of demarcation between tectonically neutral platforms and tectonically negative areas, apparently meet the requirements for persistent biohermal growth more frequently than other areas of epicontinental sedimentation. Narrow but fairly continuous zones of reef limestones characteristically mark the margins of active basins, and, when mapped, serve as one of the readiest means of defining the limits of such basins.

C. GEOSYNCLINAL LIMESTONES

Geosynclinal limestones accumulate in extracratonic linear belts of marked negative tendency. Such deposits must have formed when sinking of the trough took place independent of any rising and emergence of associated positive belts, or, less likely, when detritus from emergent positives was incapable of reaching the site of carbonate deposition. When the normal negative tendency of a geosyncline prevails carbonate deposition may occur under either of the following environments:

(1) subsidence equal to, and coincident with deposition—When subsidence and deposition are equal the limestones do not markedly differ in charater from platform limestones, as has been discussed for the equivalent situation in basins. Here, again, relative thicknesses and isopach mapping are the clues to the identification of the geosynclinal environment. Aside from information gained from associated clastic rocks and regional structures, isopach maps of limestome intervals make it possible to delineate geosynclinal borders and separate basinal from geosynclinal environments. Geosynclinal limestones are recognized by their considerable linear extent and by their great increase in thickness (five to ten times) over adjacent platform deposits.

(2) subsidence in excess of rate of deposition—Excess of subsidence over deposition, rare in the intracratonic basins, appears to be fairly common in geosynclines. At least, this is true if the dense, organic, cherty and sparsely fossiliferous limestones can be so interpretted.

The two types of geosynclinal limestones often occur interbedded with one another, suggesting an alternation of deep and shallow conditions with some evidence of cyclical deposition.

PART III. THE CLASSIFICATION OF CALCITIC LIMESTONES

The classification of limestones may be based on their mode of origin, their texture, and their chemical composition. In the classification based on the mode of origin, we have:

A. Orga~~i~~nic limestones which comprise all limestones contoning mainly or entirely organic remains, such as

1. Shell-fragment limestones or Coquina.
2. Reef limestones.
3. Fossiliferous limestones.
4. Chalks.
5. Calcareous oozes.

B. Precipitated limestones which include all limestones owing their origin either directly to the physicochemical processes or indirectly to biochemical processes, such as

6. Ordinary dense limestones.
7. Non-metamorphosed crystalline limestones.
8. Oolitic and Pisolitic limestones.
9. Travertines and Tufas.
10. Stalactites and stalagmites and cave pearls.
11. Onyx.
12. Aragonite muds and calcite mudstones.
13. Marls.
14. Miscellaneous.

C. Clastic limestones include all limestones owing their origin to the mechanical processes, such as

15. Conglomeratic and brecciatic limestones.

In the classification based on the texture we have exactly the same kinds of limestones as those listed in the classification based on the mode of origin, except our discussions here are emphasized on the formation and characteristics of the particular texture. For instance, while the shell-fragment limestone is one type of organic limestones, it is also a type of limestones which shows a particular shelly texture. To make the classification more complete and clear, we may list in the following a scheme for the classification of limestones based on the texture:

1. Shelly limestones.
2. Reef limestones.
3. Fossiliferous limestones.
4. Chalky limestones.
5. Calcareous oozes.
6. Ordinary dense limestones.
7. Non-metamorphosed crystalline limestones.
8. Oolitic and pisolitic limestones.
9. Travertines and tufas.
10. Stalactitic and stalagmitic limestones.
11. Onyx.
12. Aragonite muds and calcite mudstones.
13. Marly limestones.
14. Conglomeratic and brecciatic limestones.
15. Miscellaneous.

Since both the classification based on the mode of origin and the classification based on the texture deal with exactly the same subject, we shall combine them together in the discussion.

In the classification based on the chemical composition, we have all kinds of limestone which are distinguished from one another by the presence of some chemical elements or impurities that give them a more or less distinctive nature. Thus we have:

1. High calcium limestones.
2. Dolomitic limestones.
3. Argillaceous limestones.
4. Arenaceous and siliceous limestones.
5. Cherty limestones.
6. Carbonaceous and bituminous limestones.
7. Phosphatic limestones.
8. Glauconitic limestones.
9. Ferruginous limestones.
10. Miscellaneous.

THE CLASSIFICATION OF CALCITIC LIMESTONES BASED ON THE MODE OF ORIGIN

A. ORGANIC LIMESTONES

1. Shell-fragment Limestones or Coquina: The shell-fragment limestone consists usually of broken or disintegrated fragments of large calcareous skeletons mixed with the complete shells of smaller organisms, and cemented together by comparatively clear recrystallized calcite. It consists also of a lithified shell-sand which forms a matrix enclosing the more complete remains of larger organisms.

The typical limestone of the Mississippian system provides a good example. Among the recognizable fragments in this rock are bits of crinoids, bryozoa, and brachiopods, mixed in various proportions with complete shells of foraminifera and ostracods. These are set in a cement of recrystallized calcite. It will be noticed that all the recognizable fragmental remains are those of calcitic organisms, and this is a general characteristic of the older, well-lithified shell-fragment limestones. Presumably the disintegrated shells of aragonitic organisms have suffered redistribution, and their material has been recrystallized to form the secondary calcite cement in which the identifiable shell-fragments are embedded.

Recent example of shell-fragment limestone is the so-called COQUINA. It is a whitish, fragile limestone now forming on the coasts of Florida and consisting of shells and their fragments of all sizes somewhat loosely packed and cemented together. The name coquina is derived from the Spanish word for shell. It has been suggested (25) that it should be extended to include all shell-fragment limestones no matter what the position in the time scale.

In addition, the shell-fragment limestones in some cases may contain abundant fragments of stony algae.

2. Reef Limestones: Reef limestone differs from the majority of fragmental and organic limestones in the fact that it is built up in a solid coherent form from the first, and thus presents a considerable resistance to erosion during its accretion. The foundations of many reefs, however, are found to consist of cemented fragments of coral rock, and it appears that such reefs have grown outwards upon a foundation of their own debris. In some cases, the bulk of the underlying deposit probably consists of submarine scree, with a thin veneer of autochthonous coral rock on top. In a single specimen, the reef limestone may look like that of shell-fragment limestone. It is distinguished, however, from the latter by the presence of some characteristic features of sessile benthonic organisms.

Although corals are commonly the dominant and controlling builders of ancient and modern reefs, the remains of other invertebrates such as stromatoporoids, crinoids, and bryozoans in the past have contributed a large proportion of the reef material, sometimes they even replaced the corals as the controlling organisms of the reef communities. For example, the Silurian bioherms around the Michigan basin were built up chiefly of stromatoporoids. Some calcareous plants such as the calcareous algae are also important contributors to the reef materials. According to M. A. Howe (12), at the Atoll of Funafuti the relative abundance of the organisms composed the reef rock was found to be (1) LITHOTHAMNIUM (algae), (2) HALIMEDA (algae), (3) foraminifera, and lastly (4) corals. A typical reef limestone, therefore, does not consist by any means exclusively of coral. There are always present numerous shells and skeletons of marine invertebrates which either have played a part in building up the rock, or lived in the reef as shelter.

The formation of reef limestone represents a complicated and interesting problem in geology and stratigraphy. Take the formation of coral reef as an example, we may describe it briefly as follows:

Each coral reef is the site of intense organic activity, and nearly every available spot is inhabited. The coral heads are attacked by boring animals, and the more delicate forms are devoured by fishes. The work of organisms and the grinding of waves reduce much shelly matter to sands and muds. These and organic matter fill the pockets and interstices between the coral growths, and ultimately a compact mass is formed. The great volume of decaying organic matter, the warmth of water, and the wave activity over the reefs lead to strong diagenetic activity in the reef rock, and many reef limestones have been changed to dolomite.

Reef limestones seem to have a high degree of purity, with an almost complete absence of insoluble matter. They consist almost entirely of calcite and aragonite, with practically no terrigenous minerals.

Modern reefs are confined to shallow water, but the majority of them stand at or near the edges of steep submarine slopes, so that their debris is often deposited in deep water. Reefs situated entirely in shallow-water areas, such as the Alacran Reef, are of less importance at present day than those facing deep water, but the fossil reefs of Mesozoic and Paleozoic limestones appear to have grown principally in areas of shallow epicontinental seas.

3. Fossiliferous Limestones: This type of limestone is so named from the presence of a noticeable quantity of organic remains. It

differs from the shell-fragment limestone by the predominance of a fine-grained matrix and by the comparatively complete preservation of organic remains. The matrix is usually composed of extremely minute crystals of calcite or calcite mudstone. Embedded in this matrix are considerable amounts of complete organic skeletons or comparatively larger fragments. Hollow shells such as those of brachiopods are frequently found to be partly filled with a similar calcite mudstone, sharply marked off with a level upper surface from clear, coarsely crystalline calcite, which fills the rest of the shell. In other cases, the internal spaces of shells contain no mudstone, but are partially or wholely filled with coarse calcite crystals. Observations of this kind show that the clear cement in many organic limestones arises, not from the recrystallization in situ of calcareous mud, but from the redistribution of calcium carbonate in solution within the rock.

Deposits of this kind were probably formed in quiet or sheltered water, where fine-grained carbonate mud could settle, and organic remains were entombed in an unbroken condition, irrespective of size or fragility. Calcite fossils, such as the guards of belemnites and the aptychi of ammonites, are usually preserved in an uncorroded condition.

4. Chalks: Chalk is a soft, white, and friable limestone. Most of chalk is pure white, but some is gray, flesh color, or buff. It consists of a fine calcareous powder, which under the microscope is found to be made up of organic remains which consist of the disintegrated calcareous skeletons of invertebrates, mixed with a varying

proportion of extremely fine-grained material composing complete and fragmentary cocoliths. It consists also but in minor amount of amorphous material, spheres, and inorganic matter such as clay, sand, glauconite, etc.

As shown by the chemical analyses, most chalks contain more than 95 per cent of calcium carbonate. The calcium carbonate is entirely in the form of calcite, and the so-called amorphous material is in fact finely divided calcite.

The texture of chalk may vary considerably from place to place. For instance, in the Chalk formation of England, a high proportion of INOCERAMUS prisms in some beds gives rise to a perceptibly gritty-textured rock, while a reduced quantity of molluscan debris, and a correspondingly large bulk of cocoliths, results in the finest and most impalable varieties of chalk. Foraminifera are usually present, and since they are the most easily recognized objects in coarse washings examined under a low or medium power of the microscope, it has sometimes been claimed that the chalk is essentially a foraminiferal limestone. This is not the case, however, and these fossils r rarely make up more than a small proportion of the rock. Some chalk contain abundant spherical bodies which are most probably the remain of some planktonic organisms of unknown affinites.

As a whole, the lithology of chalk suggests deposition under the moderately deep and quiet conditions characteristic of the modern mud belts—that is, below the level at which wave action is capable of repeatedly stirring up the finest sediment. This would put a minimum depth limit for the finest varieties of the chalk at about 100 fathoms.

5. Calcareous oozes: Ooze is a recent deep sea deposit. There are two kinds of ooze which are mainly composed of calcareous material, namely, globigerina ooze and pteropod ooze.

J. Murray and A. F. Renard (17) designated as globigerina oozes those deposits which contain over 30 per cent of the dead shells of foraminifera. The color of globigerina ooze ranges from white to brown, depending on the nature of the other substances mixed with the shells. The prevailing color is milky white or rose far from land, and dirty white, blue, or gray near land. The texture is very fine-grained and homogeneous, and in tropical regions many foraminifera are visible to the eye. In addition to foraminifera, shells of many other organisms may present, among which mollusks, pteropods, and calcareous algae are important.

Pteropod ooze is composed of dead shells of pteropods and heteropods along with the shells of other pelagic mollusks or larval forms. Foraminifera are also present. It is limited below by the depth of about 1,500 fathoms, although shells of pteropods occur to depths of 2,000 fathoms. Compared with globigerina ooze, pteropod ooze is more friable and granular, less homogeneous and uniform, and has a higher calcareous content.

B. PRECIPITATED LIMESTONES

6. Ordinary Dense Limestones: The ordinary dense limestone is aphanitic in appearance. It has frequently conchoidal fracture and is normally unfossiliferous. It may be designated as a normal marine deposit. It is formed either by chemical precipitation or by mechanical deposition in quiet waters, at some distance from the shores, where only fine-grained particles would be delivered and avoids the detrital materials of terrigenous origin and the larger organic skeletons.

A variety of this type of limestone is the lithographic limestone. It is a fine-grained compact rock of uniform texture and composition. The lithographic stone from the neigbourhood of Solenhofen, near Munich, is specially prized—it readily receives delicate markings from engraver's tools, and by etching acids, and it is porous enough to receive and retain the greasy preparation used by the lithographer in transferring and printing.

7. Non-metamorphosed Crystalline Limestones: This type of limestone is probably formed by a mixture of mechanical and chemical processes of deposition. It is composed of coarse crystals of calcite without obvious organic structures. There is frequently present crystals of dolomite. The crystalline structure is either due to recrystallization through the agency of water, or to dolomitization.

Recrystallization probably begins with many sediments at the time of deposition. Permeating waters dissolve some parts of the sediments, and other mineral particles take from the waters the substances they require to continue growth, or new minerals develop as reactions to new environment. Thus, a fine-grained lime mud may become crystallized to form an interlocking system of calcite or dolomite crystals, as illustrated by the Hoburgen "marbles" of Gotland or the Chicotte "marbles" of Anticosti.

Dolomitization may take place either by replacement of calcium carbonate by magnesium carbonate through addition of magnesium carbonate solution, or by leaching of calcium carbonate. If the process is complete, the limestone then becomes entirely dolomite.

8. Oolitic and Pisolitic Limestones: The oolitic and pisolitic limestone possess a characteristic texture somewhat resembling the

roe of a fish (oolite), or in the coarse forms a heap of peas (pisolite). In general, oolite is referred to those particles of less than 2 mm. in diameter, and pisolite to those of more than 2 mm. in diameter. Both oolite and pisolite has spheroidal and ellipsoidal shapes with concentrically laminated internal structure. Some laminae have also radiate structure. The laminae may be indicated by different colors or different states of crystallization. When examined under the microscope, all the concentric laminae are usually observed to arranged around a nucleus which may consist of a piece of shell, or a grain of any kind of mineral. The material which makes up each of these concentric laminae consists, in most modern oolitic limestones, of aragonite crystals laid tangentially to the surface of the oolitic grain or oolith. In many of the older oolitic limestones, on the other hand, the ooliths are found to be made up of little radiating prisms of calcite, set at right angles to the concentric rings.

Oolitic limestone is undoubtedly of saline water sediment. It is found in all geological ages, but in England it is specially prominent in Middle and Upper Jurassic, which on this account were formerly known as the Oolitic system.

Recent ooliths occur in the Red Sea, on the shallow submarine platforms of Florida and the Bahamas, and on the shores of the salt lakes of the western United States, such as the Great Salt Lake of Utah, and Pyramid Lake of Nevada. Most of these examples agree in consisting of aragonite, laid down in concentric coats around some nucleus, which may be a sand-grain, or, more usually, a shell chip or fragment of limestone. When first formed, they show a tangential arrangement of the component crystals, but in places where sedimentation has continued from Pleistocene times, some of the older ooliths have been partially or wholly recrystallized, the aragonite being converted to radial prisms of calcite.

Ooliths and pisoliths of aragonite have been recorded in the deposits of natural hot springs, the best-known examples being the pisolitic sinters of Karlsbad of Germany and Vichy of France.

The modern marine ooliths appear to be forming in very shallow water where the dissolved salts become slightly concentrated by strong evaporation. Vigorous movement of the water, particularly by tidal currents and waves, keeps the nuclei in motion, and makes the ooliths approximate ultimately a spherical form, whatever the shapes of the orginal nuclei may have been. There is considerable evidence that the Pleistocene and older oolitic limestones were also formed in quite shallow, well-stirred water, and it seems reasonable to suppose that strong evaporation from warm sea-water was responsible for precipitating the calcium carbonate of which they are formed.

9. Travertines and Tufas: Travertine and tufa are calcareous deposits either about springs or in salt lakes and playas due to evaporation. Tufa is more porous, and travertine is more compact and sometimes banded in appearance. In some cases, the precipitation is aided by agitation. For instance, in the places where agitation is adjacent to the fast water as falls and rapids in streams carrying carbonate water, the precipitation would take place readily.

The name TRAVERTINE is derived from an old Roman designation of the town of Tivoli near Rome, where an extensive deposit of it occurs. Travertine has usually a highly porous and in part vesicular texture.

It shows also a remarkable development of concentric and botryoidal structures, resembling those of oolitic and pisolitic limestones. In some cases, nearly spherical concretionary masses have been formed in it with diameter of six or eight feet, and consist of innumerable, thin concentric layers of calcium calcium carbonate.

Tufa or calcareous sinter is somewhat similar to travertine but with more porous texture. It is extensively developed around some of the desiccated lakes of the Great Basin region of western America. The best example is the shore deposits of Lake Lahontan in northern Nevada. This lake was formerly fed by streams bringing in a large quantity of dissolved calcium carbonate; and this substance now constitutes great sheets and terraces along the former shores of the lake, and on the buttes which were once islands in it. According to I. C. Russell (20), there are three distinct types of tufa in the Lake Lahontan, which he calls LITHOID, THINOLITIC, and DENDRITIC respectively. The lithoid tufa is gray and compact, and much more stone-like than the others. It occasionally contains shells of gastropods. It occurs as beds and dome-shaped masses with banded structure and not infrequently constitutes the cores of other tufa masses. The thinolitic tufa, second in order of deposition, is composed of orthorhombic prisms 6 to 8 inches long and about half an inch thick. It has a banded structure. The dendritic tufa usually occurs in spheroidal and mushroom, or dome-shaped, masses with concentric arrangement and an internal dendritic structure. It may be of algae origin and not due to evaporation.

Some of the tufa masses are large and form crags, castle-like structures, towers, shafts, etc., and in Pyramid Lake there is an island formed wholly of tufa. Some of the towers and shafts of tufa are 50 to 60 feet high. The large masses have a central portion of compact lithoid tufa. This is surrounded by a band of thinolitic tufa, and over the outside and constituting the major portion is a covering of dendritic tufa.

10. Stalactites, Stalagmites, and Cave Pearls: Stalactite and stalagmite are the best-known purely calcareous deposits extensively developed in the limestone caves due to evaporation. The water percolating through the overlying limestone becomes charged with calcium carbonate, which is deposited when the CO_2 is given off in contact with the air. The process is assisted by the evaporation of the water. A film of calcium carbonate forms over drops hanging from the roof, and, by gradual accretion long, pendant icicle-like bodies with radial or concentric structure are produced. Similarly, the drops falling on floor build up masses which often take the form of pillars. The pendant mass is called stalactite, the floor material, stalagmite. They occur in nearly all limestone caves. According to the experimental work by V. C. Allison (1), the growth of stalactite and stalagmite may briefly described as follows:

A stalactite forms as a slender tube, which increases in diameter until the drip and evaporation reach equilibrium. The increase in diameter is affected partly by the creeping of the lime solution up over the rim of the stalactite and partly by the lime solution percolating from the inside of the tube outward through small channels in the stalactitic wall. After drip-evaporation equilibrium is attained, the stalactite continues to grow symmetrically with uniform diameter unless conditions change. The removal of CO_2 from the pendant drop of lime solution causes the precipitation of calcium carbonate as a thin, translucent film on the surface of the drop. If evaporation is good, this film is repeatedly broken and the pieces go spinning up to the rim of the tube—the drop is alive. This spinning motion is due to surface tension and also to the fact that the down-flowing current is at the center of the drop and the up-flowing current at the periphery. Preceeding the break away of the drop, there is a periodic, vertical oscillation which increases in frequency and amplitude until the actual break occurs.

A stalagmite is, at the start, limited to a circle bounded by the splash of the drops hitting the floor. Good evaporation and rapid drip cause the formation of a saucer at the limit of the circle. The bottom of the saucer slowly rises as lime is deposited in it, and the excess solution cascades down over the rim and down the sloping sides of the stalagmite until such a diameter and convex surface are realized that the resulting evaporation surface will be just sufficient to evaporate the solution it receives. The stalagmite will now continue to grow vertically in a symmetrical form unless conditions change. Poor evaporation and high concentration (or both) mean that the spattering drops will eventually form a small mound which will increase in height and decrease in diameter until the drip and evaporation surface is in equilibrium.

Cave pearls are pisoliths, sometimes of large size, found in the underground waters of limestone caves, where they are closely associated with deposits of stalactite or stalagmite. They are formed in pools and streams in which the water is in sufficiently vigorous motion to roll over the growing concretions, so that the precipitate is deposited more or less uniformly on all sides. Cave pearls are exceptional among recent pisoliths in consisting of calcite rather than aragonite—a difference which is probably partly due to the low temperature at which precipitation takes place, and partly to the low content of salts, other than calcium carbonate, in the precipitating solution.

11. Onyx: Onyx may be regarded as a variety of cave deposits with remarkable banded texture. It is formed by the slow evaporation or loss of carrying power of thermal spring waters and the waters of limestone caverns. The compact translucent product may be beautifully banded by deposition of sucessive layers of calcium carbonate, mainly present as aragonite, with varying proportions of color-goving impurities. From the nature of their formation onyx may be expected to be small and highly irregular in structure. The beautiful banding effects and the softness of color characteristic of onyx make it highly desirable for ornamental purposes despite its high cost.

12. Aragonite Muds and Calcite Mudstones: Aragonite mud is now forming on the Great Bahama Bank where the extreme shallowness of the sea over the shoals effectively reduces circulation, and the water in the centre of the bank is virtually isolated from that of the open sea. Under the strong subtropical sun the water rises in temperature, and increased evaporation takes place. Since the rainfall there is insufficient to make up for the loss by evaporation, water is drawn in from the sea, and there is a slight concentration of salts in the centre of the bank. The surface water of the open sea in these latitudes is already saturated with respect to calcium carbonate, and any rise in temperature reduces the solubility of

the salts. Consequently, as the solution becomes warmed and concentrated in its passage across the shoals, the excess calcium carbonate crystallizes out. In quiet and sheltered parts of the bank, the precipitate takes the form of minute needles of aragonite, usually from one to five microns in length, forming a white, muddy-textured sediment of almost pure calcium carbonate. Such a sediment is known as aragonite mud. Aragonite mud is also precipitated in coastal mangrove swamps of the same region through the activities of bacteria living upon the organic debris which abounds in these swamps (11).

Calcite mudstone is the older and lithified representative of the modern aragonite mud. In North America, two remarkably persistent bands of calcite mudstone occur in the Ordovician of the Appalachians, and form conspicuous parts of the Lowville and Mosheim Limestones. The pure calcite mudstone is pale gray in color, and has a smooth, almost conchoidal fracture, but small quantities of impurities may impart darker or more brilliant colors. Thin sections show that the rock consists of extremely minute crystals of calcite, the individuals being so small that they render the slice semi-opaque. Running through this fine-grained rock are irregularly branching little veins of clear calcite, in comparatively coarse crystals. These are probably formed at the time of conversion from aragonite mud to a solid calcite rock. Aragonite mud behaves, in many respects, like a clay sediment, and retains a considerable amount of water enmeshed in the network of acicular crystals. On lithification, the aragonite recrystallizes as a dense and tightly welded mass of calcite granules. The carbonate is thus compacted into a smaller volume, and innumerable shrinkage cracks are formed into which the water of the aragonite mud is expelled. These spaces later become filled with coarsely crystalline calcite, deposited slowly from solution (11).

13. Marls: Marl is loose, earthy materials consisting chiefly of calcium carbonate or dolomite intermingled with more or less clay. It is commonly gray, but some is yellow, green, blue, or black, and some has pronounced colors due to special impurities, such as iron oxide and organic matter. It shows all gradations into clays and shales. In fact, the marl may be regarded as a transition type between limestone and clay. Marl is formed both in the fresh-water lakes and in the shallow marine waters. We have thus two types of marl: fresh-water marl and marine marl.

Fresh-water marl is a mixture of calcium carbonate with a variable content of impurities. Colors are various. Most are gray to white or pale blue, but red and black marls are not uncommon. Some marls have the calcium carbonate in the form of broken shells, wheras in others there is no evidence of shells. Marl has been stated to form only in the epilimion—the upper zone of the lake water—and this may be the case in some lakes, but bacteria that precipitate calcium carbonate may be present in muds beneath the hypolimion—the lower zone of the lake water—to depths of 18 or more meters, and it is known that extensive deposits have been made at that and greater depths. The plant CHARA, which often grows in great profusion in environments of comparatively small and shallow lake, deposits calcium carbonate within its tissues, and thus builds up a skeleton which is almost wholly calcareous. In most lake marls, the calcium carbonate deposited by plants is mixed with argillaceous sediment and plant debris, and encloses the calcareous shells of invertebrates such as pond snails.

Marine marl is formed in the shallow zones of the sea such as the sheltered lagoons and mangrove swamps. It is, in some instances, impure calcareous organic deposits, which owes much its calcareous nature to an abundance of shell fragments. In many deposits of marly character the ingredients lime, silica, and alumina are mixed in such proportions that they are suited directly for the manufacture of hydraulic or Portland cement.

14. Miscellaneous: In the semiarid regions, the calcium carbonate is formed through evaporation into a characteristic feature which is collectively designated as duricrust. The process may be shortly described as follows:

The ground-water table in a semiarid area is relatively deep, and the frequent excess of water permits removal of considerable material in solution, so that waters flowing from such a region tend to have a large content in parts per million of soluble materials. These are chiefly carbonates and sulphates. Movement of the ground water is upward during dry seasons, and there is much deposition of soluble and colloidal substances in and on surface materials. The soluble substances consist mostly of calcium, magnesium, and sodium carbonates and sulphates. They deposit in the surface materials and parallel the surface, and may attain a thickness of several feet. These are called duricrusts. The duricrusts are so firm in places that they may be used for stones. They occur in all semiarid regions of the world, such as mentioned before, the tepetate and caliche of

Southwest United States, the reh of India, and the sabath of Eygpt are all duricrusts but different in names.

C. CLASTIC LIMESTONES

[illegible]

15. LIMESTONE CONGLOMERATES AND BRECCIAS: Limestone conglomerates frequently occur in the geological columns. It is usually found to be a constituent of intraformational conglomerates or tillites. This is probably due to the fact that the limestone pebbles are comparatively easily dissolved and eroded by the water, and therefore they can not be transported for a long distance to form the basal or interformational conglomerate unless conditions are exceptionally favorable.

Limestone breccias commonly occur along faulted zones, in the glacier deposits, and in piedmont areas. It is always deposited in close proximity to the parent rock so that the irregularities of the pebbles could be preserved to most extent. Some limestone breccias are so firmly consolidated that they may be used for ornamentation and construction after polishing. The so-called puddingstone marble is probably of such a type of limestone breccia.

THE CLASSIFICATION OF CALCITIC LIMESTONES BASED ON THE CHEMICAL COMPOSITION

1. High Calcium Limestones: This is an exceptionally pure limestone, being almost free from magnesium, as well as other impurities. It contains from 93 to 99 per cent or even more of calcium carbonate, and may embrace all the textural varieties.

2. Dolomitic Limestones: Limestone which contains magnesium carbonate in any quantity up to 45.65 per cent may be refferred to dolomitic limestone if the magnesium carbonate is present in the

form of the double carbonate of calcium and magnesium; otherwise it is called plainly magnesium limestone. If the quantity of magnesium carbonate excesses 45.65 per cent of the total rock, it becomes a dolomite. The dolomitic limestone may include all textural types.

3. Argillaceous Limestones: Argillaceous limestone contains a varying proportion of clay minerals. A good example of this type of limestone is the so-called hydraulic limestone or cementstone which is extensively used as raw material in the manufacture of hydraulic or Portland cement. It is in fact the harder part of a marly deposit. Indurated rocks of this kind do not always form continuous beds, but often show a tendency to occur as nodular masses developed at some particular horizon, or distributed irregularly throughout a thicker deposit of less calcareous clay or shale. It is believed that in such occurrence the calcium carbonate has been segregated from the surrounding sediment into the nodules, where it has crystallized between the clay particles without causing any increase in the original volume of the sediment. Since marl by definition is a limestone containing more or less quantity of clay, it is, therefore, the loose type of argillaceous limestone.

4. Arenaceous and Siliceous Limestones: Arenaceous limestone contains fine particles of siliceous sand or quartz deposited with the calcareous sediments. The silica may be deposited as quartz in the form of veins and geodes. Siliceous limestone is consolidated by a siliceous cement. In some cases, the siliceous cement is so developed that the calcium carbonate may be replaced by silica, and the limestone becomes wholly silicified.

5. Cherty Limestones: Chert and its darker variety, flint, frequently occur in limestones. Flints are mostly in chalk and cherts in other varieties of limestone. Both chert and flint are aphanitic rocks composed of cryptocrystalline quartz mostly in the form of microfibrous chalcedony. They occurred in the limestones as nodules, lenses, concretions, and rarely as beds. They are of both organic and inorganic origin.

Organic precipitation of silica as chert and flint takes place through the agency of organisms with siliceous shells, such as diatoms, radiolaria, and siliceous sponges. These organisms extract the silica orginally from sea water. After death, their remains were deposited in the accumulating calcareous mud and underwent partial solution. The dissolved silica may then travel some distance and be deposited in the gelatinous state around certain nuclei; and subsequently this gelatinous silica crystallizes into chert and flint.

The colloidal silica in suspension, on the other hand, may be precipitated as a gel by electrolytes in solution in sea water or through bacterial elimination of stabilizing organic colloids. The gel settles to the bottom and assumes spheroidal or ellipsoidal form. If a large quantity is precipitated, a lens or bed is formed. Accumulating overburden flattens spheroidal and ellipsoidal bodies and changes shapes to lenticular. Dehydration and crystallization take place in course of time, and the gels change to chert and flint.

6. Carbonaceous and Bituminous Limestones: Limestone may contain more or less amount of carbonaceous materials, which always give it a dark or black color. If the carbonaceous materials in limestone

consists chiefly of cellulose and ligneous substances, and have no particular odor, the limestone is named carbonaceous. If, on the other hand, the carbonaceous matters are rich in hydrocarbons, with a distinct odor, the limestone then belongs to the bituminous variety.

7. Phosphatic Limestones: Limestone may occasionally contain a small amount of calcium phosphate, especially those limestones of organic origin. This gives rise to phosphatic limestones.

8. Glauconitic Limestones: Glauconitic limestone is so named because it contain in more or less amount the mineral of glauconite. Glauconite is a sedimentary mineral of iron silicate, $FeK. Si_2O_6 . nH_2O$. Its presence in sediments is generally considered good evidence that the depositing waters were marine. It is commonly associated with limestones due to the fact that it is formed in the shallow zones of the sea waters, which are also favorable for the formation of calcium carbonate.

9. Ferruginous Limestones: Limestone frequently contains iron-bearing minerals of which sedimentary iron carbonate and iron sulphide are the most common. These minerals are particularly common in those limestones formed by bacterial activity. Both sedimentary iron carbonate and iron sulphide are also formed by the same bacterial activity that form the limestones. They are, therefore, frequently associated with one another. The presence of iron in limestones may be indicated by red colors.

10. Miscellaneous: Some limestones contain a special kind of gaseous inclusion, and this may give them a particular name. For instance, a bed of calcite in Chatham Township of Canada contains 0.016 per cent of hydrogen sulphide. A cubic foot of the rock contains about 500 cubic inches of the inclosed gas. When struck, it gives an

offensive odor. This rock is called the fetid limestone or "stinkstone".

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