CHAPTER II

L I M E S T O N E A S R O C K

GENERAL:

Generally the limestones represent calcareous rocks of sedimentary origin only, but now-a-days many workers prefer to include calcitic and dolomitic metamorphic rocks also under this name. Even the carbonate rocks of igneous origin (carbonatites) could also be considered as limestone. So in a broad way, the term "LIMESTONE" may include any rock, in which the carbonate fraction exceeds the non-carbonate constituents irrespective of the mode of origin.

It should, however, be pointed out that except for the small group of "igneous" limestones, those belonging to the metamorphic group, have essentially been derived by the recrystallisation of pre-existing sedimentary limestones only. The author, in this chapter, has briefly touched upon these crystalline calcitic and dolomitic rocks also, before proceeding with a systematic account of the typically sedimentary limestone, the most widespread and the common variety.

IGNEOUS LIMESTONES:

These are better known as carbonatites. The main constituents of most carbonatites is calcite or dolomite. In addition, a great variety of other minerals may be present in variable amounts; among them are apatite, monazite, barite, pyrochlore, perovskite, fluorite, iron and titanium, oxides, various sulphides, rare-earths, etc. As the mineralogical, chemical and field characteristics of carbonatites have become more clearly defined and since their genetic connection with basic alkaline rocks has been established, opinion in favour of magmatic origin of carbonatites has grown. Many writers now advocate the existence of some kind of liquid carbonatite magma - either a primary magma rising from the depths, and reacting with crustal rocks on the ascent, or a carbonatite liquid differentiate from a parent peridotite, pyroxenite, ijolite, or shonkinite magma.

Some of the limestones around the Amba Dungar (near Chhota Udepur, District Baroda) in which famous fluorite deposits of Gujarat occur are classified as carbonatites by Sukeshwala and Udas (1963).

<u>METAMORPHIC LIMESTONES</u>:

Crystalline limestones, marbles, calc-gneisses, etc., are the metamorphosed equivalents of originally sedimentary carbonate rocks - changed by contact and regional metamorphism. Depending upon the original composition, the marbles may be calcitic, or dolomitic. Impurities may occur as various calc-silicates and other minerals.

SEDIMENTARY LIMESTONES:

The word limestone conveys a meaning of a rock composed mainly of the mineral calcite. When pure, the contents are 56 percent calcium oxide, and 44 percent carbon dioxide. But generally limestones contain a varying proportion of magnesium oxide and in practice pure limestones and dolomites are included together. The solution, transportation and deposition of calcium and magnesium carbonates give rise to deposits of limestone and dolomite. Apart from calcite and magnesium constituents, there are impurities, ferruginous, argillaceous or siliceous, depending upon the environments under which it is formed.

In general the term limestone is applied to those rocks in which the carbonate fraction exceeds the non-carbonate constituents. Limestones are a polygenetic group of rocks. Some are fragmental or detrital and are mechanically transported and deposited; others are chemical or biochemical precipitates and having grown in place. Both types may be profoundly modified by various postdepositional changes so that the original characters are obscured or even erased. Rocks of such diverse origins are all designated as limestone, and the following rock types fall under the category of limestones:

(i) Limestone: Carbonate fraction is composed primarily of calcite.

(ii) Magnesian limestone: Limestones with 1 to 2 percent MgO. However, Rodgers (1954) would restrict this term to those rocks containing several percent MgO, but without the mineral dolomite. Except in calcite deposited by living organisms, not more than 2% $MgCO_3$ (less than 1% MgO) in solid solution is possible. The solid solution is unstable, so that fossil calcite invariably contains less than 1 or 2 percent of $MgCO_3$ (Chave, 1952).

(iii) Dolomite: Dolomite is a type of limestone containing dolomite mineral over 50 percent. Many dolomites are not sedimentary, but are epigenetic replacements of limestones. Sedimentary dolomites are generally considered to be sea-floor replacement of calcareous ooze.

(iv) <u>Chalk</u>: White earthy limestone, deposited mainly in shallow waters. It has been suggested that the chalk was precipitated as calcite instead of aragonite, and owing to the greater stability of this substance, it failed to become a dense hard rock.

(v) <u>Marl</u>: It consists of many kinds of semifriable mixtures of clays with 30 to 50 percent calcareous matter. The better indurated rocks of like composition are marlstones or marlite, and are more correctly an earthy or impure limestones. Marl has 35 to 65 percent carbonate and remaining clay.

Limestones are deposited by inorganic, organic and mechanical means. In inorganic process, carbon dioxide plays a dominant role, as the solution of the calcium carbonate in the sea is dependent upon it. If it escapes, calcium carbonate is precipitated. The amount of carbon dioxide in the sea depends upon the water temperature and its amount in the air, which is in equilibrium with that in water. More CO_2 is held in cold water than in warm water. Warmed sea water loses CO_2, and since it is practically saturated with $CaCO_3$, precipitation takes place.

Limestones may be formed mechanically through the deposition of broken shell matter and coral sand, which become cemented into compact limestone. Most limestones are deposited in shallow to moderately deep sea water, free from terriginous sediments.

Organic deposition is brought about by algae, bacteria, corals, foraminifera and larger shells. There are foraminiferal limestone beds consisting only of nummulitic shells, or corals, or larger shell forms (coquina). Calcium carbonate is also deposited by the photosynthesis of plants.

Since many limestones are composed of skeletal structures or debris derived therefrom, the composition of such rocks is an expression of the bulk composition of the skeletal constituents. The composition of shell and other hard parts varies with the nature of the organism and the conditions under which it lived.

The calcareous algae are richer in $MgCO_3$ than are the molluscs; the carapaces of the crustaceans are notably phosphatic. Chave (1952, 1954) has made a special study of the magnesian content of the carbonates of the marine vertebrates. He found magnesium to decrease with the level of organization of the organism, those of the higher phylla being less rich in MgO. The content of magnesium was also a function of the temperature of formation and was generally higher in the shells living in the warmer waters. Aragonitic shells are poor in magnesia; calcitic shells commonly are rich in this constituent.

The most common type of limestone, with less than 4% $MgCO_3$ must either be (i) an inorganic precipitate of calcite (or aragonite), (ii) an accumulation of organic detritus of only those organisms which secrete magnesium-poor skeletons, or (iii) the material if produced by other organisms, has lost its magnesia.

Composition:

The main constituents of a limestone are as follows, the content of which varies widely depending upon the environments:

Chemical composition

Silicon dioxide, SiO_2

Aluminium oxide, Al_2O_3

Ferric and Ferrous oxide, Fe_2O_3 (including FeO)

Calcium oxide, CaO

Magnesium oxide, MgO

Carbon dioxide, CO_2.

There are also other minor constituents such as TiO_2, MnO, Na_2O, K_2O, P_2O_5, SO_3, H_2O_+, H_2O_-, Cl, S, BaO, SrO, Li_2O and organic matter present in negligible quantities.

Mineralogical composition

The essential minerals of limestones are calcite, aragonite and dolomite. Rock building organisms use both calcite and aragonite in their skeletal structures. Certain genera are aragonitic and others are calcitic.

Algae contribute large and important quantities of lime carbonate to present reefs, and therefore, to the clastic lime deposits that are derived from such reefs. Some algae are believed to be the agents for the entrapment of precipitated carbonate.

Aragonite is an unstable form of calcite, and is found, therefore, only in recent materials. Even the aragonite of recent shell materials may change into calcite in the course of a few years (Lowenstam,1954). Aragonite is also presumably precipitated as minute needles as well as oolites. These undergo a recrystallization as do the aragonitic shells, and are converted to a mosaic of calcite.

Most dolomites appear to be a post-depositional product and show replacement relations with calcite. In the dolomites proper the entire rock as such is a mosaic of dolomite crystals. In part the dolomite may be a product of the unmixing of the solid solutions of calcite-dolomite, found in the hard parts of many marine invertebrates (Chave, 1952); in part it is the product of reaction of magnesium - bearing waters with the original carbonate.

Silica occurs in limestones and dolomites as detrital quartz, chalcedonic silica or chert.

Felspar is a common minor constituent of many limestones and dolomites.

Clay minerals are one of the most common contaminants of the carbonate rocks. Clay is not conspicuous in thin sections because of its fine grained and disseminated state, but it is readily apparent in the acid-insoluble residues obtained from limestones.

Other minor constituents of limestones are glauconite, collophane, and pyrite.

Textures and Structures

Because of the polygenetic origin of the carbonate rocks - in part detrital, in part chemical and biochemical, and in part metasomatic - they exhibit a variety of textures and structures unequalled by any other group of rocks; the important ones are as follows:

(a) Mechanically deposited limestones - Current sorting and stratification, cross-bedding, and graded bedding seen in many limestones.

(b) Biochemical - Biohermal (domelike, moundlike, lenslike, or otherwise circumscribed mass, built exclusively or mainly by sedentary organisms and enclosed in a normal rock of different lithologic character) and reef structures.

(c) Chemical - Pisolitic and oolitic structures - and unique structures, notably the banding of some travertines and spongework of some tufas.

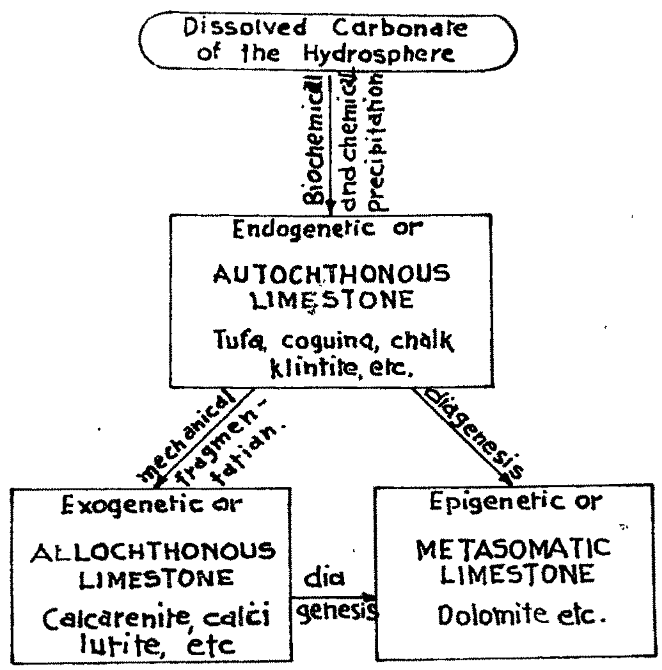
(d) Metasomatic - Principally dolomites - granoblastic textures of rocks recrystallized in the solid state.

Classification

Like all other rocks, the classification of limestones has a genetic basis. Unlike the usual clastic sediments, these are not waste products of a landmass undergoing erosion. Instead, the debris of which these are composed, is derived from within the basin in which they are accumulating. These are, thus intraformational-intrabasinal deposits.

The classification of limestones given by

Pettijohn on the basis of genesis is as fig.10.



GENETIC CLASSIFICATION OF THE LIMESTONES

Fig.10

The criteria for distinguishing between Autochthonus and Allochthonous limestones is as given below:

Authochthonous Limestone.	Allochthonous Limestone.
1. Associated with shales.	1. Associated with orthoquartzites.
2. Grades into calcareous shales and mudstones.	2. Grades into and is interbedded with orthquartzites.
3. Interstics between fossiles filled with lime muds.	3. Interstices filled with clear calcite cement.
4. Bryozoan - incrusted fossils.	4. Contains rolled fossils.
5. Unsorted as to size.	5. Sorted as to size.
6. Fossils articulated.	6. Fossils disarticulated.
7. Reef structures.	7. Cross - bedded.

Any given limestone formation may be a composite of the two above fundamental types.

Autochthonous limestones are accretionary and

Autochthonous limestones

biochemical in origin and have grown in place. If of restricted extent, they are biohermal limestones; if of extended character, they are biostromal.

These are in a sense primary carbonate deposits. It is from these deposits that much or most of the transported or redeposited (allochthonous) limestone are derived.

The algae were important rock builders in the Pre-Cambrian period, and were equally dominant limestone builders throughout the subsequent age also. Pelagic limestones are formed by the accumulation of the tests of pelagic or floating organisms. Chalk is formed mainly by the accumulation of the tests of planktonic calcareous organisms, chiefly foraminifera.

Some minor varieties such as travertine, and calcareous tufa are also formed in place. These are purely chemical precipitates from supersaturated solutions and are the products of localized precipitation in springs and lakes or in the soil profile.

Allochthonous limestones

Allochthonous limestones are detrital in origin (allochthonous: without roots). These are formed by transporting the calcareous sediments and redeposited. The terminology for limestones under this group is evolved on the basis of the grain size of particles.

Calcirudite is a mechanically deposited carbonate rock with sand-grain size more than 2 mm in diameter. When the grain-size is between 2 to 0.0625 mm in diameter, it is termed as calcarenite which is composed of 50 percent or more of carbonate detritus. The calcirudite and calcarenite are cemented by clear calcite.

With the decrease in grain size the calcarenites grade into calcisiltites (carbonate silts) and calcilutites (consolidated carbonate muds). If calcilutites are exceptionally fine grained, dense, homogeneous and exhibit conchoidal or sub-conchoidal fracture, they are termed lithographic limestones.

Some of the detritus is biofragmental, some strictly clastic, and in part both biochemical and chemical carbonate. All of it, however, is current transported and sorted, and mechanically deposited so that the accumulation has the structure of a detrital sediment.

The distinction between materials of biofragmental, fragmental, and even chemical origin is arbitrary. Some of the fossil debris is coated with one or more layers of precipitated carbonate; many of the oolites proper have nuclei of detrital carbonate or quartz. Some calcarenites are nearly all oolites; others wholly fossil debris. Still others consist mainly of granules of calcilutitic material and contain only a few scattered oolites or recognizable fossil materials.

The term coquina is most commonly applied to the more or less cemented coarse shell debris. Micrococquina is made up of finer shell detritus of calcarenite grade. Crinoid coquinas are termed as encrinites.

The oolitic texture almost certainly is a primary feature that is characteristic of shallow, strongly agitated waters.

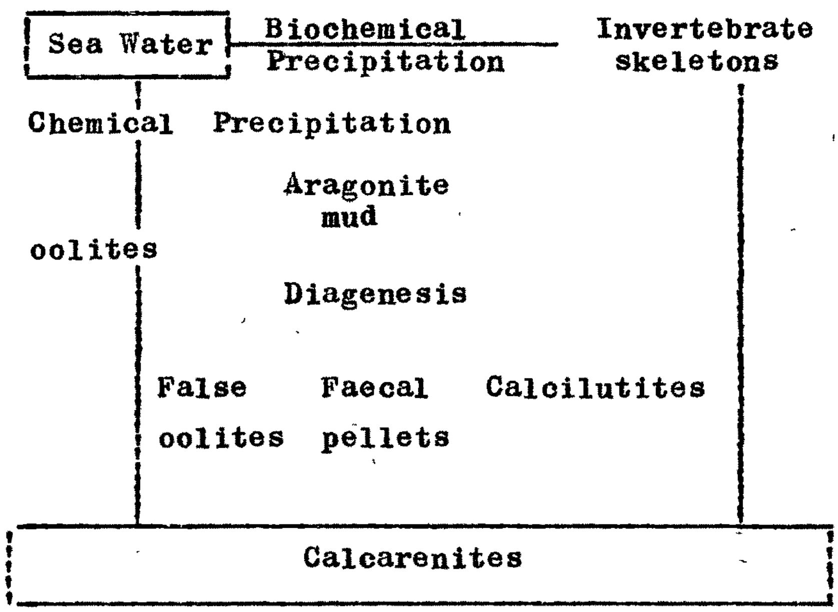


Diagram showing provenance of calcarenites.

Ammonia produced by bacterial action reacts with carbonates to form ammonium carbonate; the ammonium carbonate reacts with the Cas04 of sea water in tern to precipitate $CaCO_3$.

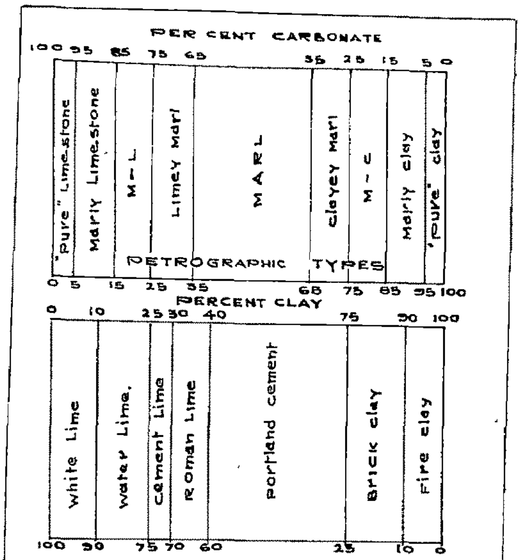
Very shallow marine waters, partially isolated, may become saturated and from such waters carbonate may be precipitated as aragonite. Under turbulent conditions oolites may form; in tranquil waters aragonite is precipitated as minute acicular crystals.

Miscellaneous Chemical Limestones:

Tufa and travertine - These are formed by the evaporation of spring and river waters. They are seldom extensive and restricted mainly to Recent or Quaternary deposits. Tufa is a spongy, porous rocks which forms a thin, surficial deposit around springs and seeps, and exceptionally in rivers. Travertine is a more dense, banded deposit especially common in limestone caverns where it forms the well-known flowstone and dripstone, including stalactites and stalagmites.

Caliche - It is a lime-rich deposit formed in the soils of certain semi-arid regions. Capilary action draws the lime-bearing waters to the surface where by evaporation, the lime-rich caliche is formed. Caliche, if found in the geologic record, is important as a climatic index. It forms only in regions of limited rainfall.

Marl - Friable carbonate earths accumulated in recent or present day fresh-water lakes. Certain plants are able to obtain CO_2 for photosynthesis from calcium bicarbonate. Calcium carbonate, therefore, is precipitated as a crust on the leaves and stems of the plant. The fresh-water marls are somewhat argillaceous and are commonly used as an ingredient in the manufacture of Portland cement. <u>Marlstone</u> (also Marlite) is a better indurated rock of about the same composition as marl. The following figure gives the classification of clay-lime carbonate mixtures and their commercial products.



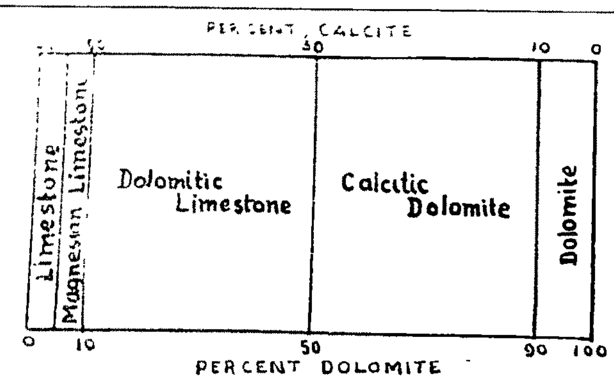
CLASSIFICATION OF CLAY-LIME CARBONATE MIXTURES

Fig.11

DOLOMITE:

Dolomites are those varieties of limestones which contain more than 50 percent carbonate, of which more than half is dolomite. In general rocks in which calcite exceeds dolomite are called dolomitic limestone, and those in which dolomite exceeds calcite are called limy, calcitic, calciferous dolomites.

The figure below gives the classification of calcite - dolomite mixtures.



CLASSIFICATION OF CALCITE-DOLOMITE MIXTURES

Fig.12

Textures and Structures:

Dolomitization tends to destroy earlier textures and structures. Although dolomites are characteristically unfossiliferrous, in some examples fossil remains are visible to the'unaided eye as internal and external moulds.

Dolomitization involves large-scale recrystallization. The end results in a granoblastic texture.

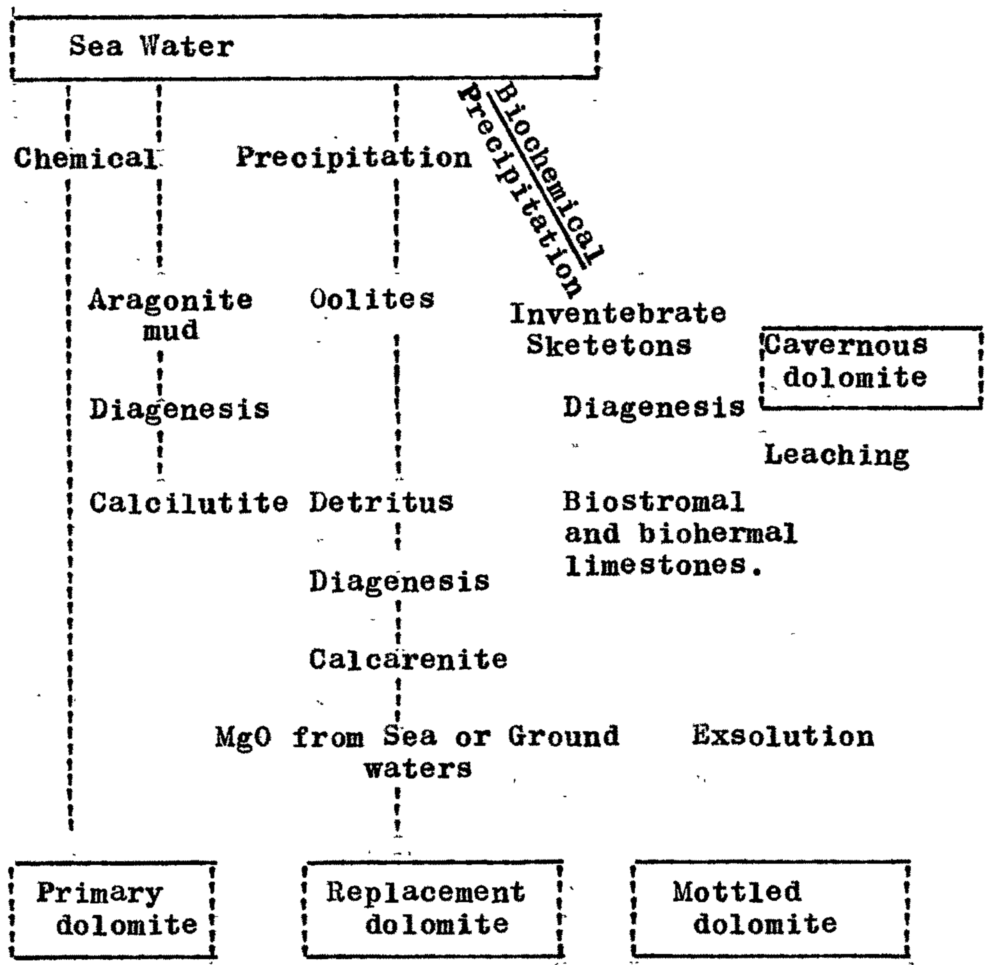
Occurrence and Association:

Dolomitization usually occurs in warm shallow, more saline waters, and is often associated with submarine "Highs", and more commonly a near-shore facies, while limestone is a product of off-shore and deep water sedimentation.

Dolomite is more common among the older rocks. It is closely associated with limestones, with which it may be interbedded. Sometimes dolomites grade laterally into limestone.

Origin:

Most dolomites are replaced limestones; the evidence is that no organism secret dolomite, yet whole coquinas or coquinoid beds are now all dolomites.



Provenance of Dolomite.

Dolomite replacement appears to have been nearly volume for volume rather than for molecule for molecule.

Daly and Steidtmann (1911) took the view that the composition of the early seas was different from that of later times and hence the earlier rocks were more dolomitic than the younger ones.

FOLK'S CLASSIFICATION:

Though the author adopted the Pettijohn's classification of limestones for study, the new approach put forth by Folk (1965) also was kept in view, as is interesting and useful depending upon the purpose for which investigations are carried out; his new classification of carbonates is given below. He suggests two basic components of limestones viz.,-

1. Orthochemical: These are normal chemical precipitates formed within the basin of deposition, and have two constituents -

(a) Microcrystalline calcite ooze (grains 1 - 4 microns in dia.)

(b) Sparry calcite cement (grains or crystals 10 microns or more in dia.)

2. <u>Allochemical</u>: These are differentiated from "Normal" chemical precipitates, and have 4 types, viz., intraclasts (broken from within the formation), oolites, fossils and pellets.

Thus the classification of limestone is based upon the relative proportions of three end members -

(1) Allochems (indicating framework of rock),

(2) Microcrystalline ooze (indicating clay size matrix).

and (3) Sparry calcite cement (replacement of matrix by chemical precipitate).

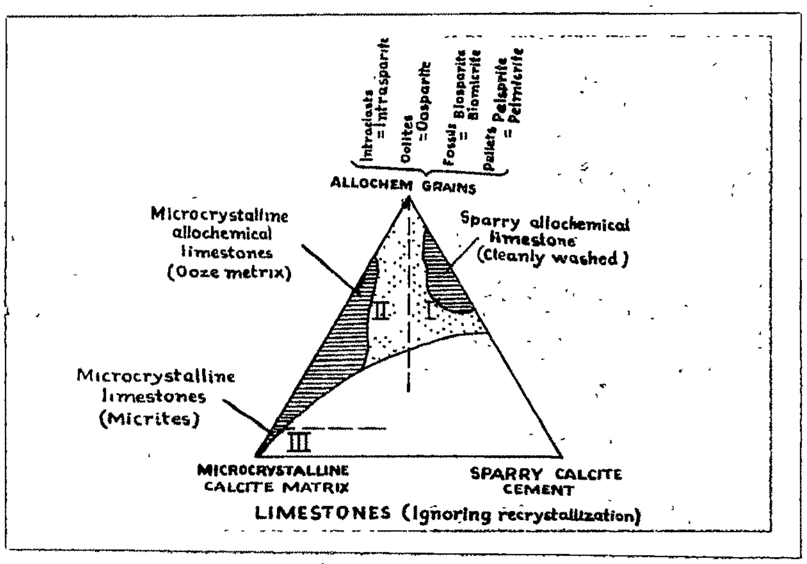


Fig.13

The grain size of allochems mentioned below is indicated in the compositional classification of limestone.

1 mm	Calcirudite
0.0625 to 1 mm	Calcarenite
0.0625 mm	Calcilutite

TABLE No.1

Compositional Classification of Limestones.

	Sparry Allochemical rocks. I	Microcrystalline Allochemical rocks. II	Microcrystalline rocks. III
Intraclastic rocks(i)	Intrasparite and Intrasparrudite(Ii)	Intramicrite and Intramicrudite (IIi)	Micrite(IIIm) If 1-10% Allochems, Intraclast-bearing Micrite(IIIi)
Oolitic rocks (o)	Oosparite and Oosparrudite (Ii)	Oomicrite and Oomicrudite (IIo)	Oolite-bearing micrite(IIIo)
Fossiliferous rocks (b)	Biosparite and Biosparrudite (Ib)	Biomicrite and Biomicrudite (IIb)	Fossiliferous Micrite(IIIb)
Fossiliferous Pellet rocks (bp)	Biopelsparite(Ibp)	Biopelmicrite(IIbp)	
Pellet rocks (p)	Pelsparite (Ip)	Pelmicrite (II p)	Pelletiferous Micrite(III p)
			Dismicrite(IIIx)

Folk (1965) suggested the following methods to examine carbonate rocks:

1. Etching: Immerse specimen in dilute hydrochloric acid for five minutes. This reveals distribution of relatively insoluble constituents such as sand, silt, clay, glauconite, phosphates, authigenicquartz, felspar, chert, pyrite and dolomite, and also reveals the morphology of calcite, whether ooze, spar, fossils, intraclasts, etc.

2. Peels: An acetate impression is made on the slightly etched surface; under a petrographic microscope in transmitted light a wealth of textural detail is brought out in calcite.

3. Insoluble residue: The rock is dissolved and insoluble constituents described under binocular and petrographic microscope.

4. Examination of thin section:

5. Staining: Ramsdan (1954) suggests staining method for differentiating dolomites as follows:

Solution:

2.5 to 3 gm Anhydrous aluminium chloride.

+ 1 gm methyl red

+ 1 Litre water

Few drops of liquid on rock powder in watch glass -

(a) Limestone (0 to 15% $MgCO_3$) -- will turn the solution yellow within a minute.

(b) Dolomitic limestone (16 to 40% $MgCO_3$) - will have a slight effect according to the $MgCO_3$ content.

Colour change within 3 minutes - Limestone.

Colour change within 5 to 10 minutes - Dolocalcite.

Maximum delay - 30 minutes - Dolomite.