CHAPTER - 3

LABORATORY TECHNIQUES OF STUDY

3-1. TERMS AND SYMBOLS USED:

3-1.1 Sandstone

SYMBOLS:

The following symbols are utilised in the description of sandstone:

\[ \bar{d}_e = \frac{d_{10} + d_{50} + d_{84}}{3} \]  

Graphic Mean diameter

\[ C = \frac{d_{99} - d_{16}}{d_{84} - d_{16}} \]  

Inclusive graphic skewness

\[ K_c = \frac{d_{99} - d_{25}}{2.44(d_{75} - d_{25})} \]  

Graphic kurtosis

C = One percentile, coarsest

M = Median diameter (50th percentile)
3-1.2 Limestone

TERMS:

The following terms or glossary are used in the study of the limestone:

Allochem.--- or "allochemical constituents", It embraces all organized carbonate aggregates that have originated by chemical and/or biochemical precipitation within the basin of deposition, and that have made up the bulk of many limestones due to transportation. Allochems mostly include intraclasts, fossils, oolites or ooids, and pellets (Folk, 1959, p.4).

Anhedral.--- Individual crystals lacking crystal faces or boundaries (Friedman, 1965, p.647).

Biogenic.--- A deposit of organic material or materials formed through the physiological activities of the organisms (Folk, 1959, p.22).

Biomicrite.--- A group of biogenic limestones consisting a significant admixture of the microcrystalline calcite ooze occupying the spaces between fossil tests and fragments (Folk, 1959, p.23).
Biomicrosparite.— Small shell fragments and foraminiferal tests that have radiating fringes of microspar, and original ooze matrix has been completely neomorphosed or recrystallized (Folk, 1959, p.32).

Biosparite.— A foraminiferal limestone composed largely of tests of bottom-dwelling and floating organisms, and lacking the microcrystalline calcite ooze (fine-textural matrix). It is mostly crystalline (Folk, 1959, p.23).

Galcarenite.— It is a special group of allochem particle-size. Physically transported particles range within 0.068 mm. and 1.0 mm. in diameter; predominantly composed of fossil debris of any kind (Folk, 1959, p.16).

Calcilutite.— It represents particles less than 0.068 mm. in diameter, and is composed with little clay-size fossil fragments (Folk, 1959, p.16).

Calcirudite.— Discrete particles are made by fragmental fossiliferous material; individual particles are larger than 1 mm. in diameter, as outlined in Folk (1959, p.16).
Calcistone.— Refers to the limestone as suggested by Twenhofel (1950, p.673) and is used for rocks which are comparable in chemical composition with the mineral calcite.

Carbonate.— Rocks with more than 50% of carbonate minerals by weight. For practical microscopic study, area percentages, which approximate weight or volume percentages, are used (Bissell and Chilingar, 1967, p.153).

Cement.— Clear to opaque, sparry calcite cement termed sparite occurs in the interstices between crystals or grains and matrix, and/or between crystals. This type of calcite generally forms grains 10 microns or more in diameter. The calcite cement in limestones may be of different crystal size-grades: micrite, microsparite, and sparite (Folk, 1959, p.8).

Cryptocrystalline.— Micritic limestone having aphanic crystalline texture, discrete subhedra and euhedra which are less than 0.001 mm. in size (Bissell et al. 1967, p. 153).

Crystalline.— A texture characterized by interlocking crystals in a mosaic, or discrete crystals,
juxtaposed against each other or against grains, fossils, or matrix. It may refer to discrete crystals in micrite (Bissell et al. 1967, p. 154).

Detrital.— Formed from debris of pre-existing rocks. Detrital limestone is one formed from the detritus of older carbonate rocks (Bissell et al. 1967, p. 154).

Diagenesis.— It refers primarily to the reactions and processes that take place within a sediment between one mineral and another or several minerals and the interstitial solutions (Pettijohn, 1957, p. 643; and Bissell et al. 1967, p. 155).

Druzy.— Sparry calcite lining or filling up shells, open spaces such as voids or vugs, pore spaces, interstices, cavities etc. This is crystalline (Bissell et al. 1967, p. 155).

Equant.— Equidimensional calcite crystals may be aphanic or phaneric (Folk, 1968, p. 24).

Equigranular.— Size and mutual relations of crystals are equidimensional, where the depositional texture has been obliterated by recrystallization or to
chemically precipitated sediments, such as chemically deposited cements (Friedman, 1965, p. 647).

Fibrous.--- It refers to needle shaped cryptocrystalline calcite and occurs generally in the molluscan shells. It resembles with aragonite (Bissell et al. 1967, p. 156).

Fossiliferous micrite.--- Rocks containing microcrystalline calcite matrix with 1-10 percent scattered fossils (Folk, 1969, p. 86). It can be termed as a "lithographic limestone".

Grain growth.--- or "grain enlargement", the term is an unhappy substitute for 'recrystallization' because etymologically "grain growth" can equally well refer to growth of crystals from solution in open pore spaces. This process acts in the carbonate sediments usually having high porosity (Folk, 1966, p. 19).

Hypidiotopic.--- It relates to the fabric of diagenetically altered carbonate rocks or to chemically precipitated sediments. Majority of the constituent crystals are subhedral (Friedman, 1965, p. 648).
Intercrystalline porosity.— Subtype of the primary porosity. It occurs as tiny, original pore-spaces between grains and between fossils and grains (Todd, 1966, p.336); synonym of it: 'mud porosity' (Harbaugh, 1967, p.357). It can be termed as "micrite porosity" (Archie, 1952, p.279).

Intraclast.— Represents group of allochems, fragments of penecontemporaneous, usually weakly consolidated carbonate sediment that have been eroded from adjoining parts of the sea bottom and redeposited by current action to form a new sediment (Folk, 1959, p.4; 1962, p.63).

Inversion.— A process by which unstable minerals change to a more stable form, but with different morphology (Folk, 1965, p.20).

Matrix.— The term is employed for fine-grained material (microcrystalline calcite ooze) where fossils, rock fragments, are embedded. It fills the interstices between the larger (sparry) crystals (Folk, 1959, p.8; 1962, p.65).

Micrite.— Rocks include almost microcrystalline calcite under petrographic microscope, as suggested by Folk (1959, p.8; 1962, p.65-66). Micrite is
assigned to the material size between 0.008 mm. (1/μ) and 0.032 mm. (4/μ) in diameter.

Micritic envelopes.— This term is coined by Friedman (1964, p.808) to portray grain coatings which mostly consists of unoriented cryptocrystalline grains (Sorby, 1879, p.62; Illing, 1954, p.76; Newall et al. 1960, p.481-492; Rasmak, 1960b, p. 471-476; Bathurst, 1964, p.360-64; and Sanders and Friedman, 1967, p. 184).

Microsparite.— Finely crystalline limestone with a grain-size between 0.064 mm. and 0.144 mm. The term is derived by combining micrite and spar. In all the cases sparite is more than 40% in volume and micrite is equal or more than sparite (Folk, 1959, p.32).

Neomorphism.— A comprehensive term of ignorance for all transformations between one mineral and itself or a polymorph—whether inversion or recrystallization, whether the new crystals are larger or smaller or simply differ in shape from the previous ones (Folk, 1963, p.21). This term is more applicable to those rocks where the original material is quite unknown. Fibrous aragonite
pelecypod inverts into the solid state by mosaic sparay calcite can also be called 'neomorphism-inversion', as outlined by Folk (1965, p.24).

Neomorphism fabric or 'recrystallization fabric'.--- Mosaic or other crystalline textural features which identify the trend of any sedimentary carbonate that has experienced neomorphism (or recrystallization). This is not the fabric of metasomatically replaced limestones. Generally, mineral species are the same which show their different crystal size and shape due to neomorphism (Folk, 1965, p.21).

Oöd or "Oölite".--- Particles of allochemical components displaying radial and/or concentric structure (Folk, 1959, p.6); ranging in size from 3.5 Ø to 0.0 Ø.

Orthochemical or "Orthochem".--- Normal chemical precipitation, formed within the basin of deposition or within the rock itself, and showing little or no evidence of significant transportation (Folk, 1959, p.7).

Pellet.--- Structureless, spherical to elliptical or ovoid aggregates of microcrystalline calcite matrix,
ranging in size between 0.03 mm. and 0.15 mm., although the most common size is 0.04 to 0.08 mm. (Folk, 1959, p.7; 1962, p.64).

Permeability.--- It is a quantitative measure of the capability of the porous medium to transmit fluids (Pollard and Reicherts, 1952, p.335; and Harbaugh, 1967, p.381). A more appropriate unit of permeability is the millidarcy. Permeability is quantitatively related to the pore-space configuration (size and shape of the pores) in the carbonate rocks (Teodorovich, 1943, referred in Aschenbrenner and Chilingar, 1960, p. 1681).

Pore-size distribution or "Capillary Pressure".--- It refers to the estimation of reservoir potential deposit of incongruity of applying the conventional geometric concept of 'pore-diameter' to many of the void spaces present in carbonate rocks (Archie, 1942, p. 279; Aschenbrenner and Aichauer, 1960, p. 237; Murray, 1960, p. 64; Stout, 1964, p. 331-332; and Robinson, 1966 p. 543; 1967, p.358).
Poikilotopic.--- It relates to the inequigranular fabric in the rocks which have undergone neomorphism, where the constituent crystals are more than one size and in which larger crystals enclose smaller crystals of another mineral (Friedman, 1965, p. 651).

Porosity.--- Porosity of a rock is a ratio of the pore space to its bulk volume. The porosity, thus, is total pore-space, because pore-space is not occupied by calcite minerals, as contrasted to the effective or available pore-space. Total pore-space includes all interstices or voids, whether connecting or not, and hence is larger than the effective pore-space (Pettijohn, 1949, p. 79).

Porphyrotopic.--- It alludes the mutual relationships of mineral crystals in the rocks where the constituent crystals are of more than one size (inequigranular) and in which larger crystals (porphyrotopes) are enclosed in a fine-grained matrix (Friedman, 1965, p. 649).

Recrystallization.--- It is "... a process wherein the mineral species, in the petrographical microscope sense,
remains identical through the change...", for example - high-magnesian calcite changes to low-magnesian calcite and this change is known as recrystallization (Folk, 1966, p.21).

Selective neomorphism.--- It demonstrates partly transformation of fibrous aragonite into a mosaic of coarser, clearer sparry calcite in individual organic material or fossil. Synonym: selective replacement (Bathurst, 1958, p.20; 1959, p.368; and Friedman, 1964, p.307).

Sparry.---or "sparry calcite or sparite".--- It represents clear, transparent, readily cleavable crystals generally having an interlocking mosaic texture (Folk, 1959, p.6; 1962, p.66).

Spherulite.--- Spherical to subspherical, essentially monomineralic components of carbonate rocks that are attributed by exclusively radial internal structure (Bissell et al. 1967, p.167). Spar spherulites are thus easily differentiated from oölites which display both concentric and radial structure. According to Pettijohn (1957, p.202), spherulites resemble smaller bodies of oölitic habit where merely a radial structure is visible.
Stylolite.— A stylolitic seam is a surface marked by interlocking interpenetration of the two sides. The teethlike projections of one side fit into sockets like dimension on the other. In cross section the stylolitic surface resembles a suture (Ger: Drucksuturen) or the tracing of a stylus - an oscillogram (Pettijohn, 1957, p. 213).

Subhedral.— It relates to the shape of crystals and represents mineral with partially developed crystal faces (Friedman, 1965, p.647).

Vuggy porosity.— Characterized by non-filling, filling, and partial filling of calcite crystals and the formation of walls of vugs with aid of matrix or micrite (Waldschmidt et al. 1956, p.953).

Xenotopic.— It is a fabric of diagenetically altered carbonate rocks. It is a descriptive term used in which the majority of the constituent crystals are anhedral (Friedman, 1965, p.648).
SYMBOLS:

The following symbols are used here in describing the characteristics of the limestone:

Ls = Calcarenites, Ll = Calcilutite,

Lr = Calcirudite, type -I = Sparry Allochemical rocks,

type -II = Microcrystalline Allochemical rocks

type -III = Microcrystalline rocks "or lithographic limestone"

Ii = Intrasparite, Ib = Biosparite

IIb = Bionomicite and biomicrosparite

IIIi = Fossiliferous intramicrite

IIIb = Fossiliferous microsparite and micrite

N.E4 = Neomorphic, medium to finely crystalline equant calcite

N.E6 = Neomorphic, medium to coarsely crystalline equant calcite

N.E8 = Neomorphic, medium equant calcite

N.F2 = Neomorphic, very finely fibrous

N.B3 = Neomorphic, finely bladed calcite (where the parent mud might have been aragonite).

Ø = Phi unit, Pd = Initial displacement pressure or entry pressure

C-factor = Measure of the pore-sorting

Sm = Minimum unsaturated mercury or pore volume

md = millidarcys, PSI = Pressure per square inch
\[ \delta^{13}C = \left( \frac{^{13}C/^{12}C}{^{12}C/^{12}C \text{ St.}} - 1 \right) \times 1000 \]

\[ \delta^{18}O = \left( \frac{^{18}O/^{16}O}{^{16}O/^{16}O \text{ St.}} - 1 \right) \times 1000 \]

\[ ^{13}C/^{12}C = \text{Carbon isotope ratios} \]

\[ ^{18}O/^{16}O = \text{Oxygen isotope ratios} \]

\[ 0/\infty = \text{Per mil unit for } \delta^{13}C \text{ and } \delta^{18}O. \]

3-2. TECHNIQUES USED FOR SANDSTONE:

Because of the friable nature of sandstones from the Tura and Rewak formations, it was required to impregnate the sediments with Canada balsam at about 110°C for two days prior to the preparation of thin sections. Volumetric distribution of the petrographic constituents were estimated from the thin sections, using a Swift's point-counting mechanical stage unit (Chayes, 1949, p. 6; 1956, p. 109) and the mineralogical classification was made, following Doty and Hubert (1962, p. 32, fig. 8). Each thin section was further utilized in ascertaining the type of quartz and was counted. Volumetric distribution of the genetic groups of quartz was also estimated (Doty and Hubert 1962, p. 23).
Most usual method adopted in determining the grain-size distribution included sieve analysis and pipette analysis for unconsolidated samples. The samples were first treated with dilute hydrochloric acid to get rid of the ferrous iron cementing materials. After complete disintegration, the finer than 4.0 $\phi$ (0.062 mm.) material was removed by wet sieving. The coarser than 4.0 $\phi$ (0.062 mm.) material (sand fraction) was completely dried and then sieved through a series of nested screens at 1.0 $\phi$ class intervals, using Ro- Tap Automatic shaking machine for 15 to 20 minutes (Krumbein and Pettijohn, 1938, p.139). Each sieve fraction was then weighted. The materials finer than 3.0 $\phi$ (0.125 mm.) were subjected to the pipette analysis, followed the procedure outlined by Krumbein and Pettijohn (1938, p.166-167).

Statistical parameters or textural parameters were graphically obtained from the cumulative curves, drawn against the phi scale on log probability graph paper (Folk and Ward, 1957, p.11-14). Mutual relationships of parameters in the form of scatter diagrams were used to evaluate the characteristics of the tectonic history of the area (Cadigan, 1961, p. 135), and to interpret the depositional environments of the sediments (Passega 1957, p.1964; 1964, p.831; Mason and Folk 1938, p.215; Friedman 1961, p.516; 1962, p.738; 1967, p.328; Folk 1966, p.80; Moiola and Weiser 1968, p.48;
Following the conventional procedure, heavy minerals were separated from the representative bulk samples of the sandstone, using bromoform (Specific gravity 2.89) (Krumbein and Pettijohn, 1938, p. 335). The heavy minerals were mounted on glass slides with Canada balsam. Frequencies of the different mineral species were determined by counting them under the microscope. The Z.T.R. maturity index was determined from the heavy mineral assemblages (Hubert, 1962, p. 443-444). Roundness of zircon, tourmaline, and rutile was determined by adopting Power's visual comparison chart (Powers, 1953, p. 118). Length and breadth measurements of zircon, and tourmaline were measured microscopically with the aid of micrometer scale fitted in the objective and catenae diagrams were constructed (Smithson, 1939, p. 350, fig. 3).

3-3. TECHNIQUES USED FOR LIMESTONE:

For the detail petrographical study of the limestones of the Siju and the Rewak Formations, one hundred and fifty thin sections were utilized. Petrographic components of the limestones were volumetrically measured with the help of automatic point counter (Chayes, 1949, p. 6). Data obtained include allochems, microcrystalline calcite,
and sparry calcite cements, and were utilized in classifying the limestones, (Folk 1959, p.4; 1962, p.64). The size of the allochems measured and counted from thin section, for the allochem particles ignoring the crystal-size of microcrystalline and sparry calcite in the limestones (Folk 1959, p.16). Texture, fabric and microstructures were examined in thin section with the help of polarizing microscope.

In identifying the carbonate minerals and types of carbonate cements for the limestones, uncovered thin sections were stained, followed Friedman (1959, p.88), Dickson (1965, p.588; 1966, p.493), and Evamy (1969, p.788). Before staining, thin sections were etched with 1.5% hydrochloric acid and then examined with universal stage to distinguish between calcite and dolomite minerals (Dickson, 1966, p.493). Different carbonate minerals namely, calcite and aragonite, showed their different intensity of colour relying on the strength of hydrochloric acid used (1.5%) in the solution. An acid solution of two different staining reagents namely, alizarine red-S and potassium-ferricyanide, exhibited their own characteristics, which facilitated in differentiating between calcite and dolomite. The technique was followed from Dickson (1966, p.493) and Evamy (1969, p.788), that became useful to decipher the genesis of the carbonate minerals and to study the distribution of ferrous iron. Two types of calcite cement in the limestones were
identified, applying combine staining reagents: 1) non-ferroan calcite, showing pink stain, and 2) ferroan calcite - showing blue stain. Besides this, staining permits easy identification of fabric and genesis of cementing and replacement mineralization.

Mineralogical analyses of the limestone samples were made by staining techniques, (Friedman 1959, p.89, fig. 1), from thin sections. Prior to stain, all uncovered thin sections were treated with 1.5% hydrochloric acid for five minutes (Lamer, 1950, p.2). Specific stains for aragonite and calcite were obtained by single treatment. Aragonite stained gray and/or black in Feigl’s solution, whereas calcite did not show any colour. Low-magnesian calcite (or calcite) was easily differentiated from high-magnesian calcite, by treating the thin sections in the solution of 30% NaOH + alizarine red-S (Friedman, loc. cit.). Their distribution in the limestones was quantitatively determined, with the help of a Swift’s point-counting stage unit (Chayes, 1949, p.6). Alizarine red-S and Feigl’s solution were prepared separately, as follows:

Alizarine red-S

0.1 gm. of alizarine red-S were dissolved in 100 c.c. 0.2% cold hydrochloric acid.
Feigl's solution

Solid Ag₂SO₄ A/R was poured in a solution of 11.8 gm. MnSO₄ 7H₂O in 100 c.c. of distilled water, and boiled for few minutes (15 minutes). After cooling, the mixture was filtered and one to two drops of dilute NaOH solution were added and the precipitate which formed was filtered off after one to two hours. The solution was kept in a dark bottle (Feigl, 1937, p. 329).

For thin section size-analyses, the long-axis of each allochem grains especially fossils, and crystals were measured by means of a micrometer ocular which was calibrated with a stage micrometer. The recorded measurements of allochem grains and crystals were grouped into ½ phi or 0.5 ½ class (intervals), upto 4.5 ½ for the calculation of the cumulative frequency. The values of selected 5th, 16th, 25th, 50th, 75th, 84th, and 95th percentiles for allochem and crystal size thin section obtained from a straight line plot on probability graph paper using allochem and crystal size distribution data (tables II, III) were converted into allochem and crystal size sieving with the aid of the over-all regression line, as demonstrated by Friedman (1958, p. 408, fig. 4). Finally, the size-size frequency curves for allochem and crystal were plotted on log probability graph paper with the data. Statistical parameters for allochem and crystal were
measured from the sieve-size frequency curves, followed the
derived formulae of Folk and Ward (1957, p. 11-14). Allochon
size (mean size) and standard deviation or sorting of the
samples are most useful to interpret limestone environments
and also to distinguish the limestones between the submerged
and the beach conditions (Folk, 1962a, p. 230; Folk and

In determining the porosity of limestones, two
out of three volumes have been measured with the Ruska
Universal Porameter (Cat. No. 1053 E) by the mercury-injec-
tion method. These volumes are the bulk, solid or grain,
and the pore volumes. The pore volume is the void space or
pore space in the sample. The bulk volume is the sum of
the pore volume and solid volume. The solid volume is the
actual volume of solid material in the sample. There is a
relationship between bulk, solid, and pore volumes:

\[ BV = SV + PV \]

where, \( BV \) is the bulk volume,
\( SV \) is the solid volume, and
\( PV \) is the pore volume.

Before applying the mercury-injection method, the
plugs of limestone were prepared in 1 inch cubic size to
enclose in the pyconometer. The plugs were first cleaned
with brush and then inserted in the pyconometer. The bulk
volume and pore volume of the plugs were evaluated by mercury-displacement in the pycnometer and read directly on the volume scale and pore space scale respectively. The solid volume can be derived from the obtained data of these volumes. The porosity function of the samples were calculated from the derived formula (Pollard and Reicherts, 1952, p.232):

\[
\begin{align*}
BV &= \text{Bulk volume} \\
SV &= \text{Solid volume} \\
PV &= \text{Pore volume} \\
\text{Porosity fraction} &= \frac{PV}{BV} \quad \text{or} \quad 1 - \frac{SV}{BV} \\
\text{Percent porosity} &= \left(1 - \frac{SV}{BV}\right) \times 100
\end{align*}
\]

Pore-size in the limestone rocks was measured from capillary pressure curve obtained from the mercury-injection system (Purcell, 1949, p.42; Robinson, 1966, p.548). In the mercury-injection system, the vacuum designates original water comprised in the samples and mercury (or non-wetting) was the displacing phase which was constrained into the evacuated rock pores. The samples were thoroughly cleaned by brush and its effective porosity was determined.

After making the system to zero PSI, the mercury was injected into the chamber slowly. The mercury volume entering the sample was measured with each increment of pre-
ssure applied to the mercury and the capillary pressure curve was plotted in the graph. The capillary pressure curve stands for invasion of progressively smaller pores with increasing pressure. Pore-diameter was inversely related to capillary pressure.

Capillary pressure curve was analyzed for the following physical parameters: 1) $P_d$, 2) C-factor, and 3) $S_m$. These parameters were measured from a log-log plot of the capillary pressure curve, as outlined by Robinson (1966, p. 555, fig. 13 & 14).

Used samples for porosity and pore-size determinations were utilized to prepare thin sections for the permeability measurement. For calculated permeability of limestones from thin sections, the following factors were essential:

A) type of pore-space, B) percent porosity, C) size of pores, and D) pore shape. An attempt was made to classify the pore-space on the basis of its petrographic characteristics from thin sections. Teodorovich's pore-space types have been outlined by Chilingar (1957, p. 70), and Aschenbrenner and Achauer (1960, p. 237). The pore-size is defined as the diameter of the largest sphere which can fit inside a pore. The average pore-size was measured from 100 pores in each thin section of limestones. Pores were classified on the degree of elongations.
Finally, the permeability of limestones was calculated from thin sections using Teodorovich's techniques and prepared tables of empirical coefficient values, as quoted in Aschenbrenner and Chilingar (1960, p.1421-1423). The permeability of limestones was calculated as,

\[ K = A \times B \times C \times D. \]

where, \( K \) stands for the permeability in millidarcy and factors A to D were shown by empirically derived numericals, as quoted in Aschenbrenner and Chilingar (1960, p. 1482, tables I - IV).

Nearly 40 representative limestone samples from the Siju and the Rewak Formations intended for colorimetric, flame photometric, titration, and isotopic analyses, were first pulverized and sieved through a nested screen of 3 \( \phi \) (0.125 mm.) size. In determination of moisture (\( H_2O \)) and loss on ignition (combined loss of \( CO_2 \) and other organic constituents), the detail technique introduced by Wolf, Easton, and Warne (1967, p.296) was followed. The acid insoluble residue including organic matter and \( SiO_2 \) was analyzed quantitatively using filtering glass-sintered crucible of different pore-sizes and 541 Whatman filter paper, as shown by Bisque and Lemish (1959, p.74), and Wolf et al. (1967, p.297).
The analytical procedure for the determination of $R_2O_3$ group was adopted from Wolf et al. (1967, p.298). Except total iron, the other constituents of the $R_2O_3$ solution (Ti, P, Mn, Al) were measured with a Klett-Summerson Photoelectric Colorimeter. The final readings of these elements from solution $R_2O_3$ and standard solutions were calculated with the calibration factor as specified in the instrument and were expressed in terms of percent. In preparing the standard solution by diluting 1000 ml., the following reagents were used: potassium titanium oxalate for $TiO_2$, manganese sulphate for $MnO_2$, potassium dihydrogen phosphate for $P_2O_5$, and ammonium alum for $Al_2O_3$. Hydrogen peroxide was used as a colour developing reagent in the separation of $TiO_2$ from the solution $R_2O_3$. $P_2O_5$ was measured from the $R_2O_3$ solution with ammonium molybdate as colour developing reagent (Snell and Snell, 1936, p.480). Manganese ($MnO_2$) was determined from the solution $R_2O_3$ by oxidizing to permanganate which gave purple colour with ammonium persulphate in presence of phosphoric acid and silver nitrate. The readings of $Al_2O_3$ were taken from the solution $R_2O_3$ with a solution of 8-hydroxyquinoline in chloroform after iron was complexed with $2', 2'$ dipyridyl.

In determining calcium, magnesium, and iron content of limestone rocks, the E.D.T.A. titration method was followed (Cheng, Kurtz, and Bray 1952, p.1640). It is indeed a rapid, easy, and most accurate technique to test directly calcium,
magnesium, and iron, without precipitation. This method has
been outlined here in detail.

DIGESTION OF SAMPLES

1. Take 1.0 gram sample into a 250 ml. beaker and
add cautiously 10 ml. of perchloric acid.

2. Heat the solution gently until it becomes colour­
less, then evaporate to dryness. After complete evaporation
the sample should be cooled.

3. Dissolve the cooled residue by adding 3 ml. of
1:1 hydrochloric acid and 10 ml. of distilled water. Filter
the solution and dilute to 250 ml. with distilled water. It
is essential that distilled water be used for all aqueous
solutions, and that all equipment be washed thoroughly with
distilled water.

DETERMINATION OF CALCIUM

REAGENTS

Versenate solution.— Dissolve 4 grams of the di­
sodium salt of (ethylenedinitrilo) tetraacetic acid in 1 litre
of water. Standardize this solution against a standard calcium
solution by titrating 10 ml. of the standard calcium solution
with Versenate.
Standard calcium solution.--- Dissolve 2.500 grams of reagent grade calcium carbonate in approximately 5 ml. of 1:1 hydrochloric acid (warm gently) and dilute to exactly 1 litre with water. This solution contains 1 milligram of calcium per millilitre.

Potassium hydroxide.--- Use a 20% aqueous solution.

Calcium indicator powder.--- Mix thoroughly 40 grams of powdered potassium sulphate and 0.2 gram of Murexide.

TITRATION

1. Pipette a 10 ml. aliquot of the solution to be analyzed into a 200 ml. porcelain dish, then add approximately 20 ml. of water, 1 ml. of potassium hydroxide, and a tiny scoop (20-30 mg.) of calcium indicator powder.

2. Stir the solution and titrate with the standardized Versenate. The end point is reached when the colour of the solution changes from pink to violet.

DETERMINATION OF MAGNESIUM

REAGENTS

Versenate solution.--- Prepare as for Calcium Buffer solution.--- Dissolve 60 grams of ammonium chloride in approximately 200 ml. of water, add 570 ml. of strong ammonium hydroxide, and dilute to 1 litre with water.
Potassium cyanide.— Prepare a 10% aqueous solution.

F-241 indicator.— Dissolve 0.15 gram of Eriochrome Black T-(F 241) and 0.5 gram of sodium borate in 25 ml. of methanol.

**TITRATION**

1. Pipette a 10 ml. aliquot of the solution to be analyzed into a 200 ml. porcelain dish; add 25 ml. of water, 2 to 3 ml. of buffer solution, a few drops of potassium cyanide solution, and 8 drops of F 241 indicator.

2. Stir, and titrate the solution with Versenate solution. The end point is reached when the colour of the solution changes from wine-red to clear blue. Standardization of the Versenate solution for magnesium is used standard solution of magnesium sulphate according to the described procedure with the standard calcium solution.

3. The volume of this titration is for both calcium and magnesium; however, magnesium can be calculated by subtracting the calcium value from the value for both calcium and magnesium.

**DETERMINATION OF IRON**

**REAGENTS**

Versenate solution.— as mentioned under Calcium

Sodium Acetate.— Prepare 35% aqueous solution
Indicator. Dissolve 2 grams of Salicylic acid in 100 ml. of methanol.

Standard Iron solution. Dissolve 1.0 gram of electrolytic iron in 10 ml. of 1:1 hydrochloric acid, digest on the steam bath until all iron has been dissolved, and make up to 1 litre with water.

TITRATION

1. Pipette a 100 ml. aliquot of the solution to be analyzed into a 250 ml. beaker. Add sodium acetate reagent to adjust the reaction of the solution to pH 2 to 3, as indicated by pH paper, then add 1 ml. of Salicylic acid solution.

2. Stir and titrate with the Versenate solution. The end point is reached when the colour of the solution alters from purple-red to colourless or light yellow. Titrate until any reddish tint disappears.

3. Versenate solution is standardized against standard iron solution, based on the molality of the Versenate solution as found with the standard calcium solution.

CALCULATIONS

If 1 gram of sample is made up to a 250 ml. solution and a 10 ml. aliquot is taken for titration, calcium and magnesium can be calculated as follows:
Calcium oxide per cent = \[ \frac{A \times 25 \times 1.4 \times B}{1000} \times 100 \]

Magnesium oxide per cent = \[ \frac{C \times 25 \times 1.66 \times (D-E)}{1000} \times 100 \]

If a 100 ml. aliquot of the 250 ml. solution made from the 1 gram sample is taken for iron titration, iron can be calculated as follows:

Ferric oxide per cent = \[ \frac{E \times 2.8 \times 1.45 \times F}{1000} \times 100 \]

A = milligrams of calcium per millilitre of Versenate solution

B = millilitres of Versenate solution used in titration, with murexide as indicator

C = milligrams of magnesium per millilitre of Versenate solution.

D = millilitres of Versenate solution used in titration, with F 241 as indicator

E = milligrams of iron per millilitre of Versenate solution

F = millilitres of Versenate solution used in titration, with salicylic acid as indicator

In determining sodium and potassium content of limestones, the samples were digested according to Wolf et al. (1967, p.311) to determine them separately by using Lange's flame-photometer. Total sulphur was determined quantitatively, followed Vogel (1951) as referred in Wolf et al. (1967, p.313).
Two significant stable isotopes such as carbon and oxygen were analyzed from the powdered limestone samples by using carbon-dioxide which was liberated during the reaction of calcium carbonate with 100% phosphoric acid (MacRae, 1950, p.849; and Sharma et al. 1969):

$$2 \text{H}_3\text{PO}_4 + 3 \text{CaCO}_3 \rightarrow \text{Ca}_2\text{(PO}_4)_2 + 3 \text{H}_2\text{O} + 3 \text{CO}_2$$

The carbon-dioxide was purified and analyzed, the isotopic composition of carbon and oxygen by a 6-inch, 60° RMS-19 mass-spectrometer with an isotope ratio using a double collection system. All the samples were analyzed in the laboratory of the Department of Chemistry, Indian Institute of Technology, Kanpur, (U.P.) India.

Oxygen isotope data were presented as $\delta^{18}O$ values in permil deviation relative to Standard Mean Ocean Water (S.M.O.W.). Samples with a higher $^{18}O/^{16}O$ (heavier) were envisaged as plus $\delta$-values and samples with a lower oxygen isotope ratio (lighter) were taken as minus $\delta$-values. The following mathematical expression was used as,

$$\delta^{18}O = \left( \frac{R}{R_{\text{standard}}} - 1 \right) \times 1000$$

where, $R = ^{18}O/^{16}O$ in sample, and

$R_{\text{standard}} = ^{18}O/^{16}O$ in standard (S.M.O.W.)

Data for the carbon isotope were reported similarly.
as δ 13C values in per mil deviation relative to the University of Chicago Pee Dee Belemnite standard (Urey and Others, 1951, p. 403; and Craig, 1957, p. 133). The plus δ-values was designated with the heavier C13/C12 and minus δ-values was assigned to the lighter C13/C12. The following mathematical expression was used as,

\[ \delta^{13}C = \left( \frac{R}{R_{\text{standard}}} - 1 \right) \times 1000 \]

where, \( R = C^{13}/C^{12} \) in sample, and

\( R_{\text{standard}} = C^{13}/C^{12} \) in standard (P.D.B.)

Obtained δ-values were corrected for mixing in the valve system, and for C13 and O17 variations for oxygen and carbon respectively, adopted the equation derived by Craig (1957, p. 140). The reproducibility of δ 13C and δ 18O values is within ± 0.2 per mil or better.