CHAPTER IX
DIAGENESIS OF LIMESTONE

9.1 INTRODUCTION

Diagenesis is a common process of carbonate rocks. It embraces a large number of factors and mechanisms which tend to alter the original shape of chemical elements, structure of the individual carbonate sediments and depositional texture of the accumulated particles. Diagenetic changes take place at normally low temperature and pressure causing partial to complete lithification of unconsolidated materials into durated rocks (Pettijohn, 1975).

The three principal types of diagenesis of carbonate sediments are recognized by different authors. These are (a) Marine fluid diagenesis proposed by Moshier (1987, 1989), Saller (1984a), Moore and Druckman (1981), (b) Meteoric fluid diagenesis proposed by Ahr (1989), Budd (1989) and Perkins (1989) and (c) Deep burial diagenesis proposed by Dravis (1989). The changes may be selective, such selectivity in part related to the original mineralogy of a skeletal element or cold (Land, 1967). Moreover, the processes are complex because they take place over a period of time, some at the time of deposition and some in the post-uplift stage. The diagenetic history can be very difficult to resolve (Friedman, 1964).
9.2 DIAGENETIC EFFECTS

The petrographical and geochemical studies of the Sylhet limestone show the following diagenetic effects in the investigated area. A two-step process (i.e. early and late) diagenesis is involved during the different diagenetic changes in the present area.

9.2.1 CEMENTS AND CAVITY FILLINGS

The process of cementation consists of chemical deposition of sparry calcite from supersaturated solution on free surfaces of intergranular pore spaces in unconsolidated sediments. Based on the crystallization fabric and compositional difference a variety of cements could be recognized in the present area.

The two phases of cements are observed in both lower and upper horizons of the limestones. They are fibrous and dusty calcite succeeded by clear calcite.

Phase 1: Fibrous and Dusty calcite — The first cement is slightly brown to clear and generally fibrous with strong to week sweeping extinction under cross polarized light. Some cements are columnar and have straight extinction (Photo Pl. X, Fig. 29). It is always having inclusion rich and surrounds all particles as rinds of equal thickness. Crystal boundaries are usually irregular. The fibrous, dusty calcite cement rinds are thickest and most extensive for a centimetre or so just below the zone of sediment infiltration where they have grown.
unimpeded by interstitial peloidal or microbioclastic sediments. Fluid and solid inclusions are the primary cause of the dusty, dirty appearance of these cements.

**Phase 2:** Clear calcite — These limped, equant to columnar crystals with few inclusions are the final phase of calcite precipitation as determined by petrography in all interparticle spaces. They are in optical continuity with the preceding fibrous cements and are the only cements in skeletal molds. They are iron poor and are generally banded-black (Photo PI. VIII, Fig. 23). Although common in lithified layers, clear cements are sporadic in poorly cemented sediments. The fluid inclusions in these crystals are rare.

Granular sparry calcite occurs in interallochem pores and also within the interallochems. It forms a mosaic of more or less equidimensional crystals showing no preferred crystallographic orientation with respect to the surface on which they grow (Photo PI. XI, Fig. 30). Crystals are generally 0.01 mm to 2.00 mm in size and show both plane and curve intergrain boundaries. The calcites locally exhibit zoning with alternating bands of cement of ferroan and non-ferroan types (Photo PI. VII, Fig. 20).

During the early depositional history, the carbonate sediments underwent complete as well as partial diagenetic changes which resulted in the formation of granular mosaic cement in the moldic porosities of the limestone.
According to Bathurst (1966) cementation is formed by sparay calcite when they have been isolated from their parent sea water either by elevation above sea level or by an exchange of brines after deep burial. Skeletal aragonite present in the mud may provide the calcite for cementation of sediments. The minor presence of partially dissolved oolite in the limestone may indicate that oolites may supply a portion of calcium to the solution for reprecipitation processes.

Cementation also takes place after uplift by circulating meteoric waters. The cements so formed tend to be a stable low magnesian calcite and one having more negative oxygen and carbonate isotope values than those found in marine sediments (Bricker, 1971).

The Staining and Infrared studies indicate very minor presence of aragonite. According to Friedman (1964) and Bathurst (1966) leaching is the most effective mechanism for the conversion of aragonite to calcite. Leaching of aragonite material takes place under subaerial conditions early in diagenesis and the resulting moldic porosity is filled with granular calcite cement. The occurrence of low magnesian calcite and aragonite in the shell foraminiferal tests indicates selective neomorphic inversion of aragonite to low magnesian calcite. The relict presence of aragonite nuclei around the low magnesian calcite may be taken as a strong evidence in support of inversion phenomenon. The existence of sharp boundaries between the shells and the surrounding cement may also be taken as the evidence of inversion of aragonite to low magnesian calcite (Photo Pl. VII, Fig. 18).
The limestone exhibits both porphyrotopic and poikilotopic fabric which suggest a competitive growth critarian. Both plane intercrystalline boundary and anfacial trijunction are displayed by the studied limestone. According to Taylor and Illing (1969) the abrupt change in composition between the fibrous calcite and granular calcite mosaic together with the extremely sharp contact defined by the crystal faces of the former suggest a break in calcite precipitation. Aragonite's solubility is substantially different from the solubility of most calcites.

The fibrous aragonite cement has been reported from recent carbonate environment ranging from the intertidal zone to the deep sea environment. The fibrous calcite cement is considered to be a replacement precipitate of metastable calcite (Photo plate V, Fig. 13). The nonplanner intercrystalline boundaries, undulose extinction and markedly elongate habit with inclusions suggest the inheritance of fibrous calcite from the earlier cement.

The gradual increase on the size of the crystals away from cavity walls, the preferred optical and dimensional orientation of crystals are attributed as the result of competitive growth between differentially oriented crystals (Bathurst, 1971). The more favourably orientated crystals obstruct the growth over them (Bathurst, 1975). The growth of crystals not only as space filling cement but also as replacement of micron size fabrics during the growth of neomorphic spar is also discernible under microscope.
The cement appears as syntaxial rims or overgrowths on framework grains of limestone which are single crystals as are the skeletal elements. The secondary overgrowth is a clear calcite distinguished from the original fragment which is clouded with inclusions. Calcite is the usual void filling material, but in some cases dolomite is also present. It has been observed that if calcite and dolomite are both present, dolomite is earlier than calcite (Freeman, 1973).

9.2.2 SOLUTION

Carbonate rocks are especially susceptible to solution. Such solution is commonly made evident by removal of a shell or other skeletal element.

The process of pressure solution increased due to relative increase of chemical potential and thus of solubility more particularly in portion during the diagenetic history of limestone (Bathurst, 1966).

The effect of pressure solution is manifested in the formation of stylolites both on macro and microscale. The stylolites are post cementation in origin in the limestone because they transect the intergranular cement and allochems. The growth of stylolites is obviously the cause of enormous losses of volume in a carbonate succession and also a means of compaction. The insoluble clay and opaque minerals present in the limestone are carried away by the pressure solution and as the growth of stylolites stops with the release of calcium carbonate while insoluble materials are found to be deposited along the path of stylolites (Photo Pl. XII, Fig. 34). In allochem rich
areas the stylolites show bifurcation along grain boundary. The weight of the overlying sediments caused pressure solution along grain contacts during late stages of diagenesis.

The effect of solution is also manifested in the formation of voids in the fossil allochems and subsequent precipitation from pressure solution as ferroan calcite. The carbonic acid produced by the decomposition of organic matter is responsible for the formation of voids which are later on filled by the calcite cement having different optical orientation (Photo Pl. XII, Fig. 33).

9.2.3 NEOMORPHISM

The limestones show clear evidence of increase in grain size or grain diminution and crystallinity. The term "neomorphism" (Folk, 1965) signifies all transformation between one mineral itself or a polymorph transformation or recrystallization. Neomorphic processes can also play an active role in modifying the textural character of carbonate sediments during both early and late stages of diagenesis.

The aggrading and degrading neomorphism have been proposed by Folk (1965). Neomorphic inversion process is displayed by both aggrading and degrading types. Aggrading neomorphism is discernible in the form as the finer crystal mosaic of the same minerals are replaced by the coarser crystal mosaic. The mechanisms underlying this transformation of fine grained carbonate to a coarse carbonate are not clear (Bathurst, 1958). In some cases, the neomorphic mosaic is a product of inversion of
aragonite to calcite as in some shells and in other cases the mosaic is coalescive recrystallization of a carbonate mud or micrite. The process involves the growth of some crystals at the expense of others. Degradig neomorphism leads to the coarsening of the rock fabric to increase in crystal size similar to that which accompanies the conversion of a limestone to a marble. The diagenesis leads to grain diminution or the conversion of larger crystal elements to a mosaic of much smaller grains. The term "micritization" has been proposed to designate this process (Bathurst, 1966).

The Poikilotopic and porphyrotopic fabric give a clear clue to the neomorphic spar rather than a simple recrystallization process. In places the tests of foraminifera and other fossils have been so extremely transacted by spar that only disconnected patches of relics remain. The uniform distribution of crystal size and nature of subhedral to euhedral shape suggest a neomorphic origin. The development of micro or pseudospar is attributed to pregrading neomorphic recrystallization which starts immediately after the initial stages of sediment accumulation and early diagenesis (Mukherjee and Young, 1973). The salinity of the depositional environment and the nature of clay minerals in the sediments might play a significant role in the selective growth of spar in carbonate sediments (Folk, 1965). Due to the growth of neomorphic spar the obliteration of original structure and texture is very prominent. The recrystallization of sparry calcite within the intralallochem areas indicates that such neomorphism occurred during late diagenetic stage. The differences in neomorphic crystal size
of spar in allochems may be thought to be due to variation in composition of the calcium carbonate polymorphs in the original sediments. Diagenetic studies of recent carbonate sediments indicate that nonskeletal aragonite undergoes very slow inversion to low-Mg-calcite as compared to its skeletal counterparts. The presence of water catalyses the inversion process regardless to the nature of aragonite (Land, 1967).

The floating relics (Bathurst, 1971) are also common where the micron size spar is entirely surrounded by spar of relatively larger crystals (Photo Pl.VI, Fig. 17). The replacement of algal matter by sparry mosaic reveals a neomorphic inversion. The inversion has taken in three courses (a) patchy replacement of micron size crystals, (b) sparry replacement of skeletal fabric and (c) syntaxial growth of crystals in walls of allochem.

The irregular distribution of crystal size — general absence of plane intercrystalline boundary and a minor occurrence of enfacial trijunction clearly indicate insitu replacement of calcite cement (Bathurst, 1971). The presence of aragonite spar within the sparry mosaic suggests a polymorphic inversion under wet condition. Passive dissolution precipitation, wet transformation of aragonite to calcite, exchange of Mg$^{2+}$ of high magnesian calcite with Ca$^{2+}$ in the pore solution may be attributed as the probable mechanisms for the neomorphic inversion of crystal mosaic of metastable nature.
9.2.4 COMPACTION

The compaction results from the burial of sediments under the weight of an overlying layer/column of deposited materials. Decrease in porosity, closer packing of grains, deformation of sedimentary structure and fabrics and recrystallization are the results of compaction in accordance to the intensity. The various compaction effects may be of early or late diagenetic nature and depend on the rate of sediment accumulation and supply and the tectonic stability of the depositional area.

The uniform bedded nature and deep water origin of the Sylhet limestone suggest a more or less stable tectonic environment. The preservation of synsedimentary structures like grain contacts — undeformed calcites filled with granular mosaic of cement— undeformed shells and oolites in some slides of the limestone suggest an early lithification of sediments with carbonate precipitation. The very high initial porosity have been greatly reduced by the early diagenetic leaching and cementation. The interallochom spaces are later on filled up by the granular mosaic of cement during neomorphism.

The presence of stylolites and partially dissoluted oolites suggest a significant role of compaction during late diagenesis which affects the porosity and thus resulted in further compaction of the limestone formation.
9.2.5 GLAUCONITIZATION

The Glauconitization is one of the processes of submarine metamorphism and gives rise to the mineral glauconite. The phenomenon is known only in marine sedimentation that formed under anaerobic or reducing environment (Takahashi, 1939). Glauconite may originate from clayey substances incorporated during cementation catalysed by the enhancement of iron bearing solution from the overlying formation by pressure solution.

The glauconites are brownish green to dark grass green and rounded to subrounded in shape. A few grains exhibit yellowish colour. The grains which are present within the foraminiferal tests maintain the configuration of the chambers of the open spaces (Photo Pl.XII, Fig. 35). Its occurrence is seen to be restricted only within the highly fossilised small bands of limestone.

The minor fine dusts of opaque minerals present around the glauconite grains are separated by a thin calcite rim from the grain to which they belong. The period of glauconite shrinkage has been correlated with the formation of microspar or pseudospar under weathering conditions from the study in Gulf areas of Texas (Folk, 1965). The shrinkage of glauconite may be correlated to the uptake of potassium during the late diagenesis (Lindstrom, 1980).

Presence of glauconite suggests that the carbonates are formed in continental shelves and in neritic environment and depth not exceeding
400 fathoms (Cloud, 1955). The yellowish colour of the grain may be attributed to the prevalence of oxidation environment. As a result of selective/or pervasive oxidation glauconites are replaced by calcites and spherulites.

The geological aspects of the origin of glauconite have been reviewed by Cloud (1955) who concluded that it is formed under marine condition of normal salinity, it requires slightly reducing environment, its formation is facilitated by organic matter, it is mainly characteristic of water 10 to 400 fathoms (18 to 700 m) depth, it is formed in areas of slow sedimentation.

9.2.6 DEDOLOMITIZATION

The replacement of dolomite rhombs by calcite termed as "Dedolomitization". It is a process of mineralogical replacement of limestone (Evamy, 1967). De Groot's (1967) experiments on dedolomitization suggested that the process required solutions with a high-Ca-Mg ratio, rapid flow of such waters and temperatures under 50°C.

The replacement may be complete or partial (Brown & Friedman, 1970). The dolomite rhombs are coarsely crystalline (0.02 mm to 1.5 mm) and exhibit an idiotopic fabric within the calcite crystals (Photo Pl. XI, Fig. 31). The occurrence of dolomite within the calcite crystals gives a clear evidence in favour of dedolomitization process.

Brown and Friedman (1970) had revealed that dedolomitization is
a surface phenomenon related to the weathering processes. The dedolomi-
tization is formed by water enriched in calcium sulphate in the
diagenetic history of limestone (Wilson, 1975).

9.2.7 SILICIFICATION

Silicification is a process of mineral replacement by silica in
various forms. The minor amount of quartz is found in the present
limestone. It is very difficult to interpret whether the replacement of
calcite by quartz and of quartz by calcite was early or late diagenesis.
Quartz in the present limestone occurs as a replacement mineral (Photo
Pl. VIII, Fig. 22, 23). On the other hand silica is selectively replaced
by calcite.

9.2.8 AUTHIGENESIS

Most of the chemical reactions pertaining to authigenesis take
place during diagenetic reorganisation and therefore the term diagenetic
mineral is used for minerals produced by authigenesis. Actually
authigenic minerals form at a very early stage of diagenesis and these
do not disrupt the original fabric in the rocks. In contrast the late
diagenetic minerals are replacive nature and tend to destroy initial
fabrics of primary deposition in the rocks.

The late diagenetic mineral in Sylhet limestone is dolomite.
Dolomite is rarely present in the limestone of the investigated area.
The presence of dolomite within the calcite crystals and relict presence
of calcite within the dolomite rhombs suggest a replacive origin of dolomite. It may be inferred that higher concentration of $\text{SO}_4^{2-}$ bearing solution may cause selective leaching of calcite by dolomite.

9.3 DISCUSSION

The diagenetic study of the Sylhet limestone reveals a close relationship between the nature of carbonate cementation and preserved textural fabric. The physical and chemical characteristics of original depositional environment and incorporation of compaction load played a significant role in the evolution of diagenetic textures.

The deposition of limestone with the intervening thin shale beds reveals a deep marine environment of oscillatory characteristics (intertidal/supratidal) where the allochems might have been cemented by the originally deposited aragonite cement. Later on the aragonite cement is converted to stable low-Mg-calcite. The initial high porosity of the carbonates lost during early diagenetic cementation. The early deposited carbonate cements are exposed to subaerial condition immediately following the deposition caused by solution of skeletal aragonite and reprecipitation of low-Mg-calcite in the voids of allochems in the form of dusty mosaic calcite cements. Glauconitization, dedolomitization and silicification may be considered as late diagenetic changes incorporated by the pressure solution and partial dissolution catalysed by the incorporation of iron bearing high magnesian solution from the overlying formation which in turn also caused final elimination of porosity and further compaction of rocks.