CHAPTER - IV
FIELD AND PETRO-MINERALOGICAL OBSERVATION

4.1. Characteristics of Primary Limestone

4.1.1. Introduction

Limestones are one of the important sedimentary rocks in which the carbonate fraction exceeds 50% of non-carbonate fraction. It is primarily made up of minerals of calcite or aragonite and minor level of dolomite. The common impurities are chert, clay and small amount of iron bearing carbonate. The origin of limestone is polygenetic in nature. Limestone are classified into many groups, based on origin such as 1. Shell limestone 2. Chemical limestone 3. Detrital or Clastic limestone 4. Limestone formed by magmatic origin or carbonatite 5. Meta-Sedimentary crystalline limestone.

Some limestone is formed either by chemical leaching or by biological activities, (example - shell limestone). The others are fragmental or detrital and are mechanically transported and deposited. The limestone is showing modified texture and structure, like hydrodynamic fabrics, due to post-depositional changes. The epigenetic and diagenetic limestones have their typical distinctive fabrics. The detrital carbonate is called as calc-arenite (Grabau, 1904). The crystalline limestone and marbles are treated as meta-sedimentary limestone, as they formed in the calc-granulite facies of metamorphism. The carbonate rocks are also obtained from the alkali magmatic origin and evolved through volcanic deposition as carbonatites. Limestones are very common sedimentary rocks which occur in all ages. It makes up about 10% of the total volume of sedimentary rocks. The oldest limestone was obtained from Precambrian and has been dated as 2.6 billion years old. Limestones
are widely noticed in Mio-geosynclinal basin. But, it tends to be absent in Eugeosyncline.

4.1.2. Texture of Limestone

The texture of limestone can be studied under three heading 1. Allochem 2. Micrite and 3. Sparry Calcite. Folk (1956 & 1962) has applied this term ‘Allochem’. The carbonate sediment which is formed by chemical or biochemical precipitation within a depositional basin is called as ‘Allochem’. It includes interclasts, fossil fragments, pellets and oolites.

Folk (1959) defined the term micrite as clay sized carbonate which has the size ranges from 1 µm to 4 µm. The term ‘micrite’ is used to avoid the ambiguity of term used for various fine grained carbonate. In hand specimen, the micrite is dull and ultra-fine grained nature material. They show the various color ranges such as white, black and grey. But, the constituent grains in hand specimen are more or less equant and irregularly rounded under microscope. The limestone which contains coarse crystalline calcite is termed as “spar”. The calcite displays a good rhombic cleavage with clear crystal boundary and more or less vitreous luster. The size of the spar crystals depends on the coarseness of the frame work net and intervening pores. In limestone, the average size of the microspar varies between 0.02 mm to 0.01 mm. When the sparry nature of limestone character can be studied only under the microscope, the term microspar is commonly used.

4.1.3. Structure of Limestone

The structure of limestone can be classified into two kinds such as 1. Hydrodynamic structure 2. Stylolites. Hydrodynamic structures are caused by the
Transportation and deposition of carbonates. The Aeolian carbonate shows large scale of cross bedding. The carbonate formed by turbidity currents shows graded bedding. The limestone formed as nodules which is called as nodular limestone. Argillaceous limestone shows the clay preservation with shell fragments. Garrison and Fischer (1969) thought that nodular limestone is formed in the bathyal region. Such limestone consists of alternate layers of wavy bedded to nodular layer, separated by argillaceous partings or seams. It is caused by flowage and by the solution.

Stylolites are serrated surface marking by the interlocking of grains or mutual interpenetration of grains on two sides. They are abundant in many limestones. Stylolites are generally parallel to bedding. Some stylolites are transverse and perpendicular to bedding plane, as a result of tectonic activity.

4.1.4. Genetical Classification of limestone

The limestones are classified based on genesis, as 1. Allochthonous limestone 2. Autochthonous limestone. The carbonates which are formed by mechanical transportation from elsewhere and are re-deposited by waves and currents. These carbonates are called as Allochthonous. The limestones are formed insitu origin by an accumulation of organically or chemically precipitated materials. These limestones are termed as accretionary or autochthonous limestone. The calcretes are called as autochthonous deposits, because of chemical origin.

4.2. Field observation of calcrete of the study area

4.2.1. Introduction

The study area Sathankulam and its surrounding villages encompassa widespread regolith calcrete deposit in the Eastern and South-Eastern coastal
sedimentary plain, Western and North-Western hard metamorphic terrain. Calcretes occur especially within the sandy soil, black soil and red teri soil. In some places, especially in lacustrine and riverine environment, the calcrete is exposed as surface outcrop and its profile resting over either in sedimentary or metamorphic rock basement. The capillary action draws the lime-bearing groundwater to the surface where by evaporation, lime-rich calcite or dolomite is deposited in the regolith part over the sap rock. The pedogenic leaching from the black soil by surface water also has high carbonate sources which is also responsible for the formation of calcrete in the regolith part. The various factors such as temperature, rainfall, evapotranspiration, humidity, wind, vegetation, alkaline rich groundwater derived from source rock are favorable for pedogenic carbonate in the study area. Nettenberg, (1980) classified the calcrete based on CaCO$_3$ content and fabric pattern such as, 1. Calcareous soil 2. Calcified soil 3. Powder calcrete 4. Honey Comb calcrete 5. Hardpan calcrete and 6. Calcrete boulder and cobbles.

The calcrete facies normally occur in the regolith part as, 1. Nodular carbonate within the regolith 2. Carbonate hardpan structure of nodular massive laminated where the ponding of groundwater over the sap rock 3. Carbonate hard pan forming coating or vein in bed rock 4. Powder carbonate associated with hard pan facies (Hill et al., 1999). Horea Bedelean, (2004) discussed the soil calcrete which shows the morphology of earth to nodular types upto indurated level.

In the study area, the calcrete deposit is well exposed as surface outcrop in Karamanayar river basin, Pannamparai and Ittamozhi lake areas. In many of the places, it occurs as inter bedded deposits between alluvium and bed rock boundary. The calcrete appear as gravel, nodular or oolitic form in the upper profile in the study area, whereas massive laminated, brecciated and chalky form in the lower profile.
Numerous researchers have concentrated their research on alluvial and colluvial pedogenic calcrete, not only in India, but also in various parts of the world. (Khadkikar et al. (1999); Pangaj Srivastava, 2001; Alonso Zarza and Silva, 2002; Peter Felix Henning son et al., 2003; Mark D. Bateman et al. (2003); Rosaria Jimenez - Espinosa and Juan Jimenez - Millan, 2003; Dhir et al., 2004.

In the Western and North-Western side to Sathankulam, the distribution of calcrete is observed below the black soil and sandy soil resting over the basement rock of calc-alkaline and per-alkaline metamorphic rocks of granite, hornblende-biotite gneiss, charnockite, calc-granulite and crystalline limestone. The cavernous structure in calc-granulite and granite outcrop below the calcrete deposit is observed near Nedungkulam village (Fig. 4.1.19) near Sathankulam.

Many researchers have discussed the calcrete profile resting over the hard rock basement. The pedogenic calcrete resting over the granite basement is discussed from Toledo Mountain, Spain (Arnaud Chiquet et al., 2000) David Nash et al. (2004) discussed the calcrete-silcrete intergrade duricrust resting over granite basement at Central Kalahari, Botswana. The calcrete profile containing ferricrete horizon resting over Archaean gneiss in Chennai is observed (Hema Achyuthan, 2004). Durand et al. (2006) explained the thick and extensive outcrops of calcrete within vertisol horizon resting over the Precambrian hornblende-biotite gneissic basement rocks of Coimbatore region. They found hardpan, laminar, massive, brecciated, nodular, coalesced nodules, isolated nodules and penetrative forms in the cracks and joints in the basement rock.

The pedogenic calcrete profile containing powder, massive, brecciated and laminar form of calcrete resting over the Archaean granitic basement were discussed
(Navin Shankar and Hema Achyuthan, 2007). Udayanapillai et al. (2014) observed the regolith calcrete containing gravel, lumpy, nodular, hardpan and chalky nature, resting over the Proterozoic granite and hornblende-biotite gneissic basement at Pandalgudi, Viruthunagar district, Tamilnadu. The non-pedogenic calcrete possessing the abundance of uranium content from the host rock of granite in Paterson region in West Australia, is reported (Songfa Liew and Subash Jaireth, 2011).

Many researchers have discussed calcrete profile resting over limestone basement (Susan Ringrose, 1996; Insung Paik and Hyinkin, 2003; Quilong et al., 2004; Dixon, 2010; Stuart A. Rabinson et al., 2012). In some area, the calcrete profile occurs resting over the sandstone basement are discussed (Lawrence Tanner and Spencer Lucas, 2006; Moussavi-Harami et al., 2009).

In the eastern and southeastern sedimentary terrain of Sathankulam region, the distribution of calcrete is observed within the red teri soil and marine clayey soil. The formation of calcrete below teri sandstone is the ubiquitous feature in the sedimentary terrain. The rhizo calcrete occurrences below the red teri sand dune surface outcrop is already discussed in Bheemunipattinam bad land topography near Vishakapatnam by Jaganatha Rao et al. (2012). Udayanapillai and Ganesha Moorthy, (2013) described the occurrence of calcrete deposit below the black and red soil of Tuticorin district.

The Calcrete outcrop feature below the Teri soil in the study area shows some pot hole like irregular bad land topographic features (Fig. 4.1.5). This may be due to the differential rate of evapotranspiration of alkaline rich groundwater derived from marine calcareous sandstone formation of tertiary and quaternary aquifer, which replaces teri soil and makes calcrete zone. It could be inferred from calcrete replacing teri sandstone at the bottom profile shows the relict feature of red teri deposit.
These bad land topography features are observed in the Thoppukulam and Arasur mines below Teri Soil as Sivalingam shape (Fig. 4.1.9, 4.1.10). The irregular stylolite banding is also a ubiquitous feature in calcrete deposition replacing teri sand which was observed in mines section at Thoppukulam (Fig. 4.3).

In the Western side to Sathankulam near Ittamozhi and North-Eastern side near Naganai village, the reworked calcrete is observed with laterite rock grain derived from the Charnockite source (Fig.4.1.29 and 4.1.30). But laterite and calcrete are formed by various origins such as residual concentration and groundwater respectively. Some time, reworked calcrete is associated with hornblende-biotite genesis and charnockite which was observed in Amuthunnakudi village (Fig.4.1.22). Brecciated, oolitic or honey comb calcrete, massive, laminated friable calcretes are observed in the river basin near Sathankulam and in the lakes of Pannamparai and Ittamozhi villages (Fig.4.1.15, 4.1.16, 4.1.17, 4.1.18, 4.1.21, 4.1.22, 4.1.24, 4.1.25). Oolitic or gravel or granular calcretes are observed in the top profile section of calcrete in the Nedungkulam mines profile section (Fig.4.1.15).

### 4.2.2. Field Profile Studies

The following profile section of calcrete is observed in the Nedungkulam granite mines section (Fig. 4.2a) and Thoppukulam India cement limestone mines section (Fig. 4.2b). The Nedungkulam regolith calcrete profile rest on the granitic and charnockite basement, whereas the Thoppukulam regolith calcrete rest on sedimentary basement of calcareous sandstone and shell limestone.
4.2.3. Macro-Morphology

**Gravel or granular**

Discrete gravel or granular calcrete is observed in the top soil profile section as disseminated deposit above the full calcrete profile. The size of the gravel is ranging from 2 mm to 2.5 cm.

**Hardpan Calcrete**

They occupy the full calcrete profile area above the sap rock. The hardpan calcrete may be nodular, lumpy, laminated, massive, bedded, brecciated, pisolitic, or honey comb structure and penetration form within basement rock.

**Calcrete Below teri soil**

These calcretes are formed at the bottom of the red teri soil formation above the sedimentary limestone basement rock. It is formed by differential rate of evapotranspiration of groundwater and shows some relict character of teri sand feature.

**Powder or Chalky calcrete**

Loose powder calcrete are observed as inter bedded deposit in the calcrete profile between any two hardpan calcrete zones in the hard rock terrain. The size may be silty or clayey or fine sandy mixture.

**Reworked calcrete**

The association of calcrete concentration with other unaltered rock grain is treated as reworked calcrete deposits. Laterite, Hornblende-biotite gneissic grains and Charnockite rock fragments are associated with calcrete cementation. These deposits are observed in the river basin and lacustrine environment.
4.3. Petro-Mineralogy or Micro-Morphology

4.3.1. Micro-Thin section studies of the study area

Texture and fabric are the important terms used by geologists and pedologists to describe different aspects of size, shape and constituents of rocks and soil at high magnification. The micro-morphological classifications of calcrete are described as alpha calcrete and beta calcrete. The dense micro fabric nodules, complex cracks and crystallaria, circum granular cracks, sparry calcite nature, floating sediment grain pattern in calcrete are grouped as alpha calcrete; whereas microbial coating, needle fibre calcite, calcified microbial tubules, alveolar septal fabric, microcodium and calcified pellets are grouped as beta calcrete (Wright, 1990, Wright and Tucker 1991, Horea Bedelean, 2004).

The entire study area is generally covered with both alpha and beta calcrete microstructure. Generally, the pedogenic calcrete resting over the hard rock basement possess the characteristics feature of alpha calcrete in the study area. The calcrete formed in the bottom of the regolith part resting over the sedimentary basement generally shows beta calcrete, because of biogenic activities. But it is not a hard and fast rule in possessing these characteristics.

Numerous research workers have concentrated their research on micromorphology of calcrete association with different lithological basement, not only in India, but also in various parts of the world (Wiliam and Krause 1998; Esref Atabey et al., 1998; Bernard Lauriol and Ian Clare 1999; Pierre Jultras et al., 1999; Arnaud Chiquet et al., 2000; Pangaj Srivastava, 2001; Dhir et al., 2004; Moussavi-Hirami et al., 2004; Qilong et al., 2004; Alon Zarza and Jones 2007; Macropfeiffer et al., 2011; Yu Horiuchi et al., 2012; Owaliaie, 2012; Udayana pillai et al., 2012;
Ceren Kucukuysal and Selim Kapur, 2014; Ersel Goz et al., 2014; Francis et al., 2014).

The detailed microscopic observation of calcrete deposits in the study area reveals that calcrete deposition shows both displacive and replacive textures. The carbonate deposition involves two stages such as initial deposition of carbonate in voids, pores and cracks in regolith part and later replacement of clay component from regolith part by deposition of fine grained carbonate. During this replacement, it removes aluminium silicate by dissolution and then fine grained carbonate is deposited as a gel based material. Such similar observation is also reported in Cobar-Girilambone region of Australia (Queen, 2006). The detrital quartz grain in the soil is unaffected by the process, despite some evidences for grain etching figure by alkaline water. Such similar observation is also observed in the Coimbatore region (Durand et al., 2004; Navin Sankar and Hema Achyuthan 2007). The sesquioxide is formed from the weathering of iron source basement minerals such as biotite, hornblende and hypersthene (Fig. 4.4.2, 4.4.5, 4.4.7, 4.4.24). The textural evidence indicates that carbonate accumulation occur as void lining, some time with collowform, peloidal and lensoidal form (Fig. 4.4.7, 4.4.8, 4.4.9). In some calcrete, micritic carbonate has recrystallized into small coarse grained aggregates which make rimming around quartz, feldspar and other detrital sap rock clast and clay clast (Fig. 4.4.6, 4.4.12, 4.4.13). This above feature seems to be a type of nucleation effect. This character is obtained by the floating mechanism of alkaline groundwater and detrital grain contact. Such characters are reported from areas of calcrete in Khorat Basin, North-Eastern, Thailand (Yu Horiuchi et al., 2012), Coimbatore, India (Navin Sankar and Hema Achyuthan 2007) and Pandalgudi, India (Udayana pillai et al., 2012).
Dendritic impregnation of clay mineral sesquioxide ($\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$) which is thick brown color in micritic grain matrix of calcite is observed in calcrete of Coimbatore region which indicate arid climate (Hema Achyuthan, 2004, Navin Sankar and Hema Achyuthan 2007) and in Khorat Basin, North-Eastern, Thailand (Yu Horiuchi et al., 2012) and Pandalgudi in India. (Udayanapillai and Thirugnana Sambandam, 2012. Such similar observation is also observed in the study area. The Thoppukulam and Nedungkulam – calcrete profile section samples, and Sathankulam – River basin surface outcrop samples of the study area show such type of dendritic impregnation in the micritic calcite matrix. Further, this preservation is also believed to be formed by freshwater golden brown algal mats of chrysophyta in southern Australia (Paul Grevenitz, 2006). Some calcrete thin section of study area displays wavy lamination and colonial cyst preservation. The wavy calcified preservation in calcrete may be attributed by the accumulation of organic matter preservation under the influence of blue green algal mats of cyanophyta. The calcified microcystis, trislender shaped calcified microcystis and calcified fungal hype or tubules were noticed from some thin section of the study area (Fig. 4.4.17, 4.4.18, 4.4.21 and 4.4.22). Such calcified algal mats and fungal hypae were also observed in the Australian calcretes (Paul Grevenitz, 2006; Queen, 2006). The calcified globular cyst preservation forms peloidal and collowform texture and septarian nodules (Fig. 4.4.23, 4.4.24).

In many oolites, nucleus is a silicate sand grain especially quartz. The oolite is sometime associated with sesquioxide preservation. In some thin section, the sap rock grains or basement rock such, as orthoclase, microcline, plagioclase, biotite and hypersthene shows micritic calcite development along the cleavage and cracks in the sap rock grains. The veining structure, calcitic microspar rimming or coronas around
sub-spherical quartz and calcification in interstices in teri soil were observed from the Surangudi teri sand deposit (Udayanapillai and Ganesa Moorthy, 2013). Such similar character is also observed in the calcrete of the study area of teri soil. The veining characters of calcrete in teri soil is observed in the Thoppukulam thin section. In some lacustrine massive calcrete thin section of Ittamozhi lake area (Fig.4.4.26, 4.4.27), it shows some irregular vugs within the ferruginous calcitic matrix: In this cavity, neomorphic deposition of carbonate mud is deposited (Fig. 4.4.27). In general, the high alkaline condition of groundwater obtained from the Tertiary aquifer and dissolution and weathering sources of groundwater derived from the calc-alkaline and per-alkaline basement rock causes for the formation of calcrete deposits in the study area. This groundwater would appear to be necessary to allow dissolution of clay component of soil and saprolite and simultaneous replacement of carbonate.

4.3.2. XRD - Analysis

The mineralogy of calcrete of the study area was determined by two ways for carbonate and non-carbonate fractions of calcrete samples. The procedure for the preparation of carbonate fraction and non-carbonate fraction sample of calcrete for X-ray diffraction calibration techniques, principles of X-ray diffraction and Instrumental details are discussed in the chapter 3. (Material and Methods). There are two regolith calcrete profile samples which were collected from the study area mines section such as, 1. Thoppukulam village regolith calcrete sample between the sedimentary shell limestone basement and topred teri soil outcrop (Fig. 4.2a). 2. Nedungkalam village regolith calcrete samples occurs between the hard rock granite basement and sandy soil (Fig. 4.26). Each profile powder samples of calcrete is analyzed through XRD which revealed its detailed general mineralogy and clay mineralogy.
The qualitative mineralogy of the clay minerals and other minerals of calcrete samples were determined with the standard procedure of XRD data (Carroll, 1970; Brindley and Brown, 1980; Moore and Reynold, 1989; Carver, 1971; Sachinath Mitra, 1989; Deer et al., 1978; Dana and Ford, 2002; Willie Haris and Norman White, 2007). Apart from these illustration, Numerous researchers not only in India, but also in various part of the world have concentrated their research in qualitative mineralogy of the calcrete samples and other sedimentary rocks (Richard C. Vanden Heuvel, 1964; Adam El-Shahat, 1980; George W. Brindley, 1984; Olga Elvira Alsonso and Covadonga Brime, 1990; Namik Cagatay, 1990; Ivar Murtmaa et al., 1995; Lopez Galindo et al., 1996; Kirsten M. Menking, 1997; Colson et al., 1998; Daniel E. Kile and Dennis D. Eberl, 2000; Lackschewitz K.S et al., 2000; Rosaria Jimenez - Millan, 2003; Mogdalena Koubova et al., 2003; Tetsuya Warangai, 2004, 2005; Tylkowski et al., 2004; Singh and Cornelius, 2005; Juho Junttila et al., 2005, Deepthy and Balakrishnan, 2005; Henlie Hong et al., 2007; Atlhophneng et al., 2007; Arun K. Sreedhar et al., 2008; Moazallah and Farpoor, 2012; Fey et al., 2014).

4.3.2.1. Mineralogy in regolith calcrete profile of Nedungkulam village

The Nedungkulam calcrete profile sample shows the result of following clay minerals and other carbonate & silicate minerals through XRD analysis. The calibrated ‘d’ spacing values (0°-30°, 2 Theta) and (0°-60°, 2 Theta) for clay minerals and other carbonate & silicate minerals respectively, its relative counts and other XRD data are given in the Table 4.1 - 4.12 and its diffractogram patterns are shown in the Fig. 4.5(a-l).

The clay minerals Kaoline, Palygorskite, Smectite, Sepiolite, Illite and Beidellite are confirmed from the samples by their ‘d’ spacing value. The carbonate
minerals calcite is predominantly inferred from the samples along with other silicate minerals Quartz, Microcline, Orthoclase, Albite, Hypersthene, Biotite and the oxide minerals Hematite and Magnetite from the study area.

The low angle 2° position calibrated between the values 0° to 30° were set in the XRD instrument for identification of clay mineral. The distribution trend of X-ray diffractogram patterns of the Nedungkulam profile samples are not only show similar distribution, but also show little variation from upper profile to lower profile. The following clay minerals are identified from their observed ‘d’ spacing values.

**Kaoline**

Kaolinite (Al₂Si₂O₅(OH)₄) is present in all the samples. The X-ray diffraction patterns of Kaolinite are characterized by ‘d’ spacing values of 7Å, 3.575Å, 1.487Å, 2.338Å, 1.126Å and 1.67Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study area for Kaolinite clay minerals are 7.17Å, 7.27Å, 7.29Å, 7.33Å, 7.25Å and 3.73Å. Such similar ‘d’ spacing values for Kaoline are reported from various areas of calcrete samples (Adam El-Shahat, 1986; Colson et al., 1998; Deepthy and Balakrishnan, 2005; Juho Junntila et al., 2005; Henilie Hong et al., 2007; Arun K. Sreedhar et al., 2008; Moazallahi and Farpoor, 2012).

**Palygorskite**

It is otherwise called as Attapulgite. The composition of palygorskite is Mg Al₂Si₄O₁₀(OH)-4(H₂O). The palygorskite is available in all the calcrete samples of the profile of the study area. The X-ray diffraction pattern of palygorskite are characterized by the d spacing values of 10.5Å, 4.5Å, 3.23Å, 2.62Å, 4.46Å, 4.43Å,
4.65Å, 6.46-6.23Å, 4.25Å, 4.13Å, 3.69Å, 3.36Å, 3.27Å, 3.22Å, 3.09Å, 2.69Å, 2.62Å, 2.55Å, 2.53Å, 2.52Å, 2.24Å, 2.17Å, 2.13Å. (Deer et al., 1978; Sachinath Mitra, 1989; Dana and Ford, 2002; Willie Haris and Norman White, 2007).

The observed d spacing values in the study area for palygorskite minerals are 4.22Å, 4.12Å, 3.22Å, 11.34Å, 4.19Å, 3.32Å, 3.25Å, 11.49Å, 3.40Å, 3.26Å, 11.38Å, 4.21Å, 3.31Å, 3.26Å, 4.47Å, 4.25Å, 3.33Å, 4.26Å, 4.20Å, 3.63Å, 3.59Å and 3.32Å. Such similar ‘d’ spacing values are reported for palygorskite from various areas of calcrete samples (Richard C Vanden Heuvel, 1964; Adam El-Shahat, 1986; Namik Cagatay, 1990; Lopez Galindo et al., 1996; Colson et al., 1998; Rosaria Jimenez et al., 2003; Henilie Hong et al., 2007; Moazallahi and Farpoor, 2012; Fey et al., 2014).

**Sepiolite**

The chemical composition of sepiolite is Mg₄Si₆O₁₅(OH)₂. 6H₂O. The clay mineral sepiolite is available in all the calcrete samples of profile of the study area except in the 1st section samples. The X-ray diffractogram patterns of sepiolite are characterized by the d spacing values of 12.77Å, 12.27Å, 6.80Å, 12.36Å, 12.1Å, 9.63Å, 10.10Å, 5.47Å, 5.02Å, 8.07Å, 7.50Å, 4.30Å, 4.10Å, 4.56Å, 7.6Å, 6.85Å, 5.02Å, 4.50Å, 4.30Å, 4.51Å, 4.34Å, 4.03Å, 3.75Å, 3.74Å, 3.57Å, 3.18Å, 3.21Å, 3.06Å, 2.83Å, 2.6Å, 2.62Å, 2.59Å, 2.43Å, 2.46Å, 2.24Å, 2.26Å, 2.06Å, 2.13Å, 1.95Å, 1.89Å, 1.70Å (Deer et al., 1978; Sachinath Mitra, 1989; Dana and Ford, 2002; Willie Haris and Norman White, 2007).

The observed ‘d’ spacing values in the study area for the Sepiolite minerals are 8.13Å, 3.80Å, 8.52Å, 8.18Å, 3.82Å, 8.42Å, 8.18Å, 3.81Å, 3.2Å, 3.15Å, 9.88Å, 3.84Å, 3.22Å, 9.82Å, 4.02Å, 3.19Å. Such similar ‘d’ spacing values are reported for
sepiolite from various areas of calcrete. (Richard C Vanden Heuvel, 1964; Lapez Galindo et al., 1996; Fey et al., 2014).

**Smectite**

The Smectite clay mineral is available only in the 2 and 3 section in the profile. The X-ray diffraction patterns of smectite are characterized by ‘d’ spacing values of 15Å, 17Å, 18Å, 12.5Å, 15.5Å, 19Å, 9.6Å, 21Å. (Deer et al., 1978; Sachinath Mitra, 1989; Willie Haris and Norman White, 2007).

The observed d spacing values in the study area for the smectite minerals are 17.37Å, 17.23Å. Such similar ‘d’ spacing values are reported for smectite from various areas of calcrete (El-Shahat, 1986; Lapez Galindo et al., 1997; Kristen M. Menking, 1997; Colson et al., 1998; Daniel E. Kile and Dennis D Eberl, 2000; Rosario Jimenez-Espinosa and Juan Jumenez-Millan, 2003; Deepthy and Balakrishnan, 2005; Singh and Cornelius, 2005; Juho Junttila et al., 2005; Henilie Hong et al., 2007; Arun K. Sreedhar et al., 2008, Moazallahi and Farpoor, 2012; Fey et al., 2014).

**Illite**

Illite is a non-expanding micaceous clay mineral which has the composition of potassium hydrous aluminium silicate (KH₃O)(Al, Mg, Fe)₂(SiAl)₄O₁₀(OH)₂. The X-ray diffraction patterns of illite are characterized by the ‘d’ spacing values of 9.98Å, 4.47Å, 2.56Å, 1.50Å, 3.31Å, 1.98Å and 1.29Å. (Deer et al., 1978; Sachinath Mitra, 1989; Haris and White, 2007).

It occurs in the 2nd and 4th section samples of the profile. The observed ‘d’ spacing values in the study area for Illite is 4.40Å, 4.41Å. Such similar ‘d’ spacing...
values are reported for Illite from various areas of calcrete. (Moazallahi and Farpoor, 2012; Juho Juntilla et al., 2005; Magdalena Koubova et al., 2003; Colson et al., 1998).

**Chlorite**

The high Mg and low Fe chlorite are characterized by the d spacing values of 14Å. (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed d spacing values in the study area are also having as 14.09Å. So it is believed to be the mineral as Chlorite.

**Halloysite**

It is a Kaoline group of clay mineral which shows the ‘d’ spacing values 2.57Å. (Sachinath Mitra, 1989). The observed ‘d’ spacing value in the study area is also having 2.57Å. So, it is believed to be the mineral as Halloysite.

**Quartz**

The quartz occurs as detrital mineral in calcrete. The X-ray diffraction patterns of quartz are generally represented as great peaks. It characterized by ‘d’ spacing values of 3.33Å, 4.25Å, 1.818Å, 1.541Å, 2.456Å, 2.281Å, 2.127Å, 2.236Å and 1.979Å. (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study area of Quartz is 3.33Å, 3.00Å, 3.01Å, 3.02Å, 2.45Å, 2.27Å, 2.23Å, 2.12Å, 1.97Å, 2.11Å, 1.81Å, 3.01Å, 2.48Å, 2.27Å, 2.08Å, 1.82Å, 3.34Å, 2.49Å and 1.82Å. Such similar ‘d’ spacing values are reported for quartz from various areas of calcrete. (Magdalena Koubova et al., 2003; Horry Bedelean, 2004; Tetsuya Waragai, 2005; Singh and Cornelius, 2005; Fey et al., 2014,)
**Feldspar group minerals**

Minor amount of Feldspar group of minerals are found in the calcrete which may be orthoclase, microcline and albite or anorthite.

**Orthoclase**

The x-ray diffraction patterns of orthoclase are characterized by the ‘d’ spacing values of 3.29Å, 1.81Å, 4.25Å, 2.98Å, 2.90Å and 2.16Å. (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed d spacing values in the study area for orthoclase are 4.24Å, 1.81Å, 3.30Å, 4.23Å, 1.81Å, 3.77Å, 1.82Å.

**Microcline**

The X-ray diffraction patterns of Microcline are characterized by the ‘d’ spacing values of 3.22Å, 1.80Å, 2.16Å, 4.18Å, 1.99Å and 1.459Å. (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study area for Microcline are 1.79Å and 1.73Å.

**Albite and Anorthite**

The X-ray diffraction patterns of albite and anorthite are characterized by the ‘d’ spacing values of 3.179Å, 4.016Å, 3.660Å, 3.206Å, 2.952Å, 3.767Å, 2.952Å and 3.197Å, 3.249Å, 3.164Å, 3.033Å, 3.611Å, 2.519Å, 3.030Å, 3.740Å respectively. (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study area for plagioclase feldspar 2.99Å and 3.19Å. Since it is closer to albite ranges, they are established as albite.
**Hypersthene**

The X-ray diffraction pattern of the hypersthene mineral are characterized by the d spacing values of 3.20Å, 2.890Å, 1.486Å, 1.599Å, 1.389Å, 1.304Å. (Sachinath Mitra, 1989). The observed d spacing values in the study area for hypersthene is 2.83Å.

**Biotite**

The x-ray diffraction pattern of biotite minerals are characterized by the ‘d’ spacing values 10Å, 3.34Å, 2.63Å, 1.541Å, 2.44Å, 1.672Å, 1.363Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study area for biotite are 1.67Å, 1.66Å and 1.56Å.

**Calcite**

Calcite is the most abundant mineral in calcrete. The reflections of the calcite in the x-ray diffractograms are generally represented as great peaks. The x-ray diffractogram patterns of calcite mineral are generally characterized by the ‘d’ spacing values of 3.81 Å, 3.03Å, 1.910Å, 1.873Å, 2.28Å, 2.09Å and 1.600Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed d spacing values in the study area for calcite are 1.60Å, 1.62Å, 1.86Å, 1.90Å, 1.97Å, 2.08Å, 3.01Å, 3.81Å, 1.87Å, 3.82Å, 2.27Å, 3.02Å, 2.28Å, 2.09Å and 1.91Å. Such similar ‘d’ spacing values are also reported for calcite from various areas of calcrete. (Richard C Vanden Heuvel, 1964; Adam El-Shahat, 1986; Ivar Murdmaa *et al.*, 1995; Rosario Jimenez *et al.*, 2003; Tetsuya Waragai, 2004; Teksuya Waragai, 2005; Singh and Cornelius, 2005; Horea Bedelean, 2004; Henilie Hong *et al.*, 2007; Arun K. Sreedhar, 2008; Fey *et al.*, 2014).
4.3.2.2. Mineralogy of Thoppukulam Calcrete profile

Thoppukulam calcrete profile samples above the shell limestone basement shows the results of following clay minerals and other carbonate and silicate mineral through XRD analysis. The observed ‘d’ spacing values, its relative intensity counts and other XRD data are given in the (Table 4.13 – 4.22) and its diffractogram patterns are shown in the (Fig. 4.6m to 4.6v). The clay minerals kaoline, montmorillonite, smectite, palygorskite, sepiolite and beidellite are confirmed from the calcrete samples by their ‘d’ spacing values. The carbonate minerals calcite is predominantly observed from the samples along with silicate minerals quartz, orthoclase, microcline, albite, and biotite from the study area.

**Kaoline**

Kaolinite is generally present in all the samples. The observed ‘d’ spacing values in the study area for kaolinite clay mineral 7.38Å, 7.44Å, 3.49Å. These values are confirmed with kaoline mineral data published by Sachinath Mitra, 1989; Deer et al., 1978; Willie Haris and Norman White, 2007.

**Montmorillonite**

It is a clay mineral of sodium hydrous aluminium Silicate. The observed ‘d’ spacing values in the study area for montmorillonite clay mineral is 9.63Å. These values are confirmed with montmorillonite mineral data published by Sachinath Mitra, 1989; Deer et al., 1978; Willie Haris and Norman White, 2007.

**Palygorskite**

It is a clay minerals magnesium aluminium hydrous silicate. It is normally available in the calcrete samples. The XRD patterns of palygorskite are characterized
by the values of 10.5Å, 4.5Å, 3.23Å, 2.62Å, 4.46Å, 4.43Å, 4.65Å, 6.46Å-6.23Å, 4.25Å, 4.13Å, 3.69Å, 3.36Å, 3.27Å, 3.22Å, 3.09Å, 2.69Å, 2.62Å, 2.55Å, 2.53Å, 2.52Å, 2.24Å, 2.17Å and 2.13Å. (Sachinath Mitra, 1989; Deer et al., 1978, Willie Haris and Norman White, 2007).

The observed ‘d’ spacing values in the study area for palygorskite minerals are 6.36Å, 4.15Å, 4.23Å and 4.45Å.

**Sepiolite**

The clay mineral sepiolite is available in all calcrete samples of the profile of the study area. The XRD patterns of sepiolite are characterized by the ‘d’ spacing values of 12.77Å, 12.27Å, 6.80Å, 12.36Å, 12.1Å, 9.63Å, 10.10Å, 5.47Å, 5.02Å, 8.07Å, 7.50Å, 4.30Å, 4.10Å, 4.56Å, 7.6Å, 6.85Å, 5.02Å, 4.50Å, 4.30Å, 4.51Å, 4.34Å, 4.03Å, 3.75Å, 3.74Å, 3.57Å, 3.18Å, 3.21Å, 3.06Å, 2.83Å, 2.6Å, 2.62Å, 2.59Å, 2.43Å, 2.46Å, 2.24Å, 2.26Å, 2.06Å, 2.13Å, 1.95Å, 1.89Å and 1.70Å. (Sachinath Mitra, 1989; Deer et al., 1978; Willie Haris and Norman White, 2007).

The observed ‘d’ spacing values in the study area for sepiolite are 8.50Å, 8.23Å, 6.89Å, 5.52Å, 3.63Å, 3.85Å, 3.84Å, 8.82Å, 3.49Å, 3.84Å, 3.75Å, 8.74Å, 5.53Å and 3.82Å.

**Smectite**

The smectite is commonly available in the calcrete sample. The X-ray diffraction pattern of smectite are characterized by the ‘d’ spacing values of 15Å, 17Å, 18Å, 12.5Å, 15.5Å, 19Å, 9.6Å, 21Å. (Sachinath Mitra, 1989; Deer et al., 1978; Willie Haris and Norman White, 2007). The observed ‘d’ spacing values in the study
area Thoppukulam calcrete profile samples for Smectite are 16.20Å, 11.55Å, 16.22Å, 11.60Å, 16.02Å, 11.43Å, 16.63Å, 11.74Å and 17.14Å.

**Beidellite**

Beidellite is a montmorillonite group of clay mineral. The established ‘d’ spacing values for the minerals are 15.1Å, 4.45Å, 3.02Å, 2.60Å and 2.49Å (Sachinath Mitra, 1989). The observed ‘d’ space values for beidellite clay mineral in the Thoppukulam samples are 3.02Å, 3.01Å.

**Quartz**

Quartz is a common detrital mineral in calcrete. The x-ray diffraction pattern of quartz are characterized by ‘d’ spacing values of 3.33Å, 4.25Å, 1.818Å, 1.541Å, 2.456Å and 1.979Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed ‘d’ space values in the calcrete of Thoppukulam study area are 3.33Å, 3.31Å, 3.32Å, 3.5 Å, 2.49Å, 2.28Å, 2.12Å, 2.48Å, 2.45Å, 2.23Å and 1.81Å.

**Feldspar (Orthoclase)**

The ‘d’ spacing values of orthoclase mineral are characterized by the ‘d’ spacing values of 3.29Å, 1.81Å, 4.25Å, 2.98Å, 2.9 Å and 2.16Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007). The observed d spacing values for the orthoclase from the calcrete samples of Thoppukulam are 3.32Å, 3.02Å, 3.01Å, 3.27Å, 4.24Å, 1.81Å, 4.25Å, 1.81Å, 1.97Å and 4.24Å.

**Microcline**

The established ‘d’ spacing values for microcline minerals are 3.22Å, 1.80Å, 2.16Å, 4.18Å, 1.99Å, 1.459Å (Sachinath Mitra, 1989; Deer et al., 1978; Willie Haris
and Norman White, 2007). The observed ‘d’ spacing values obtained from the Thoppukulam calcrete samples for microcline are 3.22Å, 4.22Å.

**Albite**

The established d spacing values for albite minerals are 3.179Å, 4.016Å, 3.660Å, 3.206Å, 2.952Å, 3.767Å and 2.952Å (Sachinath Mitra, 1989). The observed d spacing values obtained from the Thoppukulam calcrete samples for albite is 3.82Å.

**Biotite**

The X-ray diffraction pattern of biotite are characterized by the ‘d’ spacing values of 10Å, 3.34Å, 2.63Å, 1.541Å, 2.44Å, 1.672Å and 1.363Å (Sachinath Mitra, 1989). The observed d spacing values for the biotite mineral in the Thoppukulam calcrete sample is 1.62Å.

**Calcite**

Calcite is the abundant minerals in calcrete. The reflections of calcrete in X-ray diffractogram are generally represented as great peaks. The XRD diffractogram patterns of calcite mineral are generally characterized by the ‘d’ spacing values of 3.03Å, 1.910Å, 1.873Å, 2.09Å, 1.600Å and 2.28Å (Sachinath Mitra, 1989; Willie Haris and Norman White, 2007).

The observed d spacing values of calcite in Thoppukulam calcrete samples are 3.03Å, 2.48Å, 2.09Å, 1.91Å, 1.87Å, 1.27Å, 1.62Å, 1.60Å, 2.06Å, 1.91Å, 1.87Å, 1.62Å, 1.60Å, 3.02Å, 2.27Å, 2.08Å, 1.90Å, 1.86Å, 1.62Å and 1.60Å.
4.4. SEM Analysis

Micro-structural features of minerals are identified through Scanning Electron Micrographs (SEM). Numerous researchers identified the micro structural features of clay minerals from the calcrete of various regions. Namik Cagatay (1990) identified the clay minerals and other minerals from calcrete samples from Damman Dome, Saudi Arabia region. He identified micro fabric pattern of palygorskite fibre associated with dolomite and feldspar grain. Microbial precipitations of pedogenic micritic calcite were observed from the calcrete samples from New Mexico region through SEM photographs (Curtis Monger et al., 1991). Rodas et al. (1994) observed the palygorskite fibre developed on the edge of smectite crystal through SEM analysis of calcrete samples from Dureo and Tajo basin, Central Spain Region. Calcified filamental fabric structures were identified through SEM analysis of calcrete from Yucca Mountain, Navada region (Vannimann et al., 1994). Veeracchia and Le Coustumer (1996) established palygorskite mineral derived from soil solution, smectite and illite inherited from bed rock and kaoline is formed by detrital origin through SEM photographs of the calcrete samples from Negev desert, Israel. Susan Ringrose (1996) identified the non-pedogenic calcrete in which quartz clast, calcified filament, fungal hypae and endolithic bacteria and microcrystalline silica string were identified through SEM photographs from the calcrete of Dalmore Downs region, Australia. Palygorskite precipitations with smectite association in calcrete were studied through SEM photographs from the Provence Basin, France region (Colson et al., 1998).

Alon Zarza and Silva (2002) observed the mucus films coated by bacteria and needle fibre calcite through SEM analysis of calcrete from the Eastern Canary Island region, Spain. Features of micro borings, spores, peloids, needle fibre calcite,
microrods of micritic and microsparitic calcite, micritic calcite with bioclasts and pisoliths were observed through SEM analysis from the calcretes of Gran Cayman region from Spain (Alonso Zarza and Jones, 2007). Navin Sankar and Hema Achyuthan (2007) observed alveolar septal structure of calcification, calcite and calcified filaments which were observed from the calcrete of Coimbatore region, Tamilnadu, India. Collowform feature and clay mineral identification form soil part were studied through SEM from the regions of Russia (Kuznetsova and Khokhlova, 2012) and in south central Iran (Moazallahi and Farpoor, 2012). Calcified filaments, needle-shaped calcite from calcrete of SW Iran were identified through SEM analysis (Owliaie, 2012). Fibrous, wedge and fan shaped palygorskite associated with at the edge of smectite crystal is observed through SEM from the calcrete of Adona area, Turkish (Kaplan et al., 2014).

In the study area, the non-carbonate fraction of Nedungkulam calcrete sample after acid digestion is subjected to SEM analysis and some characteristic features were identified from top soil to upto weathered bed rock. In the Nedungkulam regolith calcrete profile top section, Kaoline occurs as Spherulitic fabric associated with Quartz grain. Palygorskite fibre has been developed on the edges of Smectite crystal. Sepiolite is characterized by fibrous habit, such as nano composite laminated fibre with fractured surface. In the II\textsuperscript{nd} profile section sample, Smectite crystal end with Palygorskite fibre is observed. Nano composite laminated fiber characters of Sepiolite are observed Kaoline occurs as Spherulitic fabric. Illite tends to occurs as platy nature. In the third profile section, Illite occurs as platy Smectite which bears Palygorskite fibre at edges. In the fourth profile section nano-fabric lamination of Sepiolite, Palygorskite fibre present at the edge of the smectite crystals and platy illite crystal with fibred palygorskite fibre is observed. In the fifth profile section, Kaoline
with Sepiolite fibre and Palygorskite fibre with alveoli, Illite rod like crystal, platy illite crystal with fibred Palygorskite, Kaoline coated with Quartz are observed. In the last bottom profile section, smectite edged with Palygorskite fibre, platy illite crystal, quartz rod coating with Kaolinite and Nano fibrous Sepiolite is observed.

In general, Palygorskite, Smectite, Sepiolite, Kaoline and Illite are important clay minerals identified from the regolith calcrite profile from Nedungkulam calcrite which are formed under arid and semi-arid climatic conditions.

4.5. DTA and TG Analysis

The thermal analysis includes DTA and TG which has been proved as great value for identification and study of the properties of clay minerals and carbonates. These methods depend upon the release of heat or exothermic reaction or absorption of heat or endothermic reaction by the samples during the temperature cycle. These transformations of energy result from either loss of volatile components or changes of entropy with the reorganization of atomic structure in the samples.

4.5.1. History of D.T.A Analysis

The development of DTA has progressed through several stages. Le Chatelier, (1887) described the use of different thermocouples and published DTA curves of Kaolinite. From 1887 to 1935, Orcel began the systematic DTA of clays through twenty research papers. Next stage of researcher began with the advancement of design of good furnaces, sample holders and photographic recording equipment by Norton (1939) and Hendricks (1939). Later, refinements of this design were done by Grim and Rowland (1942). Then, further developments were done by Berkel Hamer and Spiel (1944). Portable apparatus was developed by Hendricks (1946) for use in
studying bauxite deposits in the field. A last development in the basic apparatus was the visual recording of the DTA curves of a number of samples being heated in the same furnace.

Simultaneous development of DTA techniques for the elementary study of carbonate minerals took place in the USA, Japan and USSR. Reconsideration of the thermodynamics of the system gave rise to a very sensitive sample holder (Gruver, 1948; Kaufman and Dilling, 1950) made of platinum foil. Herold (1948) developed a thin sample holder with half platinum and half platinum-10% rhodium in the thermocouple junction in sample holder. Development of static atmosphere control within the furnace was introduced by Saunders and Giedroye (1950) and Rowland and Lewis (1951). Dynamic atmosphere was introduced by Stone (1952). Presently trend is going toward atmospheric control at elevated pressures, where DTA reactions begin to approach equilibrium reactions.

DTA of clays and carbonate are discussed by Richard A Rowland and Rowland C. Mielenz, 1949, based on atmospheric control in DTA. He observed that DTA curves for Siderite has the endothermic values of 600°C with CO₂ and atmosphere control and its exothermic values lies between 800°C to 900°C. He further analyzed DTA values of clay and carbonate. The Kaoline group of minerals such as Dickite, Serpentine, Chrysolite, Kaolinite and Halloysite shows the endothermic values of 700°C, 700°C, 700°C, 600°C and 570°C respectively, while exothermic results of above minerals shows the values of 1000°C, 825°C, 825°C, 1000°C and 950°C respectively, (Richard A Rowland, 1949).

The DTA results of Biotite and Muscovite shows no change in effect of endothermic and exothermic values (Richard A Rowland, 1949). But Lepidolite, Talc,
Pyrophyllite and Prochlorite show the endothermic values of 900°C, 950°C, 800°C and 650°C and 800°C respectively (Richard A Rowland, 1949). The DTA curves for some rhombohedral carbonates were observed by Richard A Rowland, (1949) and established the endothermic values ranging from 500°C to 1000°C. He further established the endothermic DTA curves for Calcite, between 900°C to 1000°C. The DTA curves for Montmorillonite group is established the endothermic values as between 150°C to 200°C and 650°C to 700°C and exothermic values from 900°C to 1000°C (Richard A. Rowland, 1949). Marek Muszynski and Piotr Wyszomirski (2003) published DTA curves for Palygorskite mineral. It has the endothermic values of ranging around 90°C, 130°C, 250°C and 440°C-460°C and exothermic values at 860°C.

DTA curves for the minerals Kaolinite group, Biotite, Muscovite, Montmorillonite, Illite, Sepiolite and Palygorskite are given by (Richard C Mielenz et al., 1949). He observed the endothermic values of Kaolinite group of minerals ranges from 570°C to 720°C, while exothermic values ranges from 820°C to 1000°C. The DTA curve for Biotite and Muscovite show no indication of thermal reaction upto 1100°C and shows the uniformity over the whole range from 100°C to 1000°C. Lepidolite and Tale show the endothermic deflection at 900°C and 950°C respectively, while prochlorite shows the endothermic deflection at 800°C Montmorillonite group shows the endothermic values from 90°C to 260°C, while exothermic ranges from 850°C to 1000°C. Illite has the endothermic deflection at 150°C, 550°C and 900°C, while exothermic values at 950°C. The DTA curves of Sepiolite show the endothermic deflections from 320°C to 360°C, from 360°C to 450°C and possibly from 450°C to 610°C. The exothermic value of Sepiolite occurs
from 750°C to 850°C and from 965°C to 1050°C. Palygorskite shows the endothermic deflection from 100°C to 300°C, while exothermic values at 1000°C.

Brain and Morgan (1969) established DTA endothermic values of Sepiolite as from 122°C to 154°C, 428°C, 531°C, 814°C and exothermic 832°C from 129°C to 175°C, 318°C, 579°C and exothermic 862°C, and Quartz mixture shows the endothermic values from 600°C and 967°C respectively.

Grim R.E and Rowland A.R in part 1, established endothermic deflections for Quartz as 550°C, Geothite endothermic values at 375°C, Gibbsite endothermic values at 350°C, 550°C and exothermic values at 950°C; Kaolinite endothermic values at 300°C, 550°C to 600°C and endothermic values 950°C; Halloysite endothermic values as 125°C, 575°C and exothermic values of 975°C. Illite endothermic values as 150°C, 550°C to 600°C, 875°C to 950°C and exothermic values at 925°C to 950°C. Montmorillonite endothermic values as from 100°C to 250°C, 600°C to 700°C, 800°C to 900°C and exothermic values at 950°C; Bentonite endothermic 150°C, 650°C to 675°C, 850°C to 900°C and exothermic 950°C to 1000°C.

Grim R.E and Rowland A.R (1949) in part 2 established endothermic deflections for Beidellite as 150°C, 550°C and 675°C, 850°C to 900°C and exothermic values 900°C to 950°C; Smectite endothermic values as 175°C, 650°C, 850°C and exothermic values at 350°C; Palygorskite or Attapulgite endothermic values as 150°C, 275°C, 450°C to 500°C and exothermic values as 350°C, 850°C; Kaolinite and Halloysite type clay minerals are characterized by a sharp endothermic reaction between 100°C, 200°C and 500°C and 600°C and exothermic values at about 950°C. Angelica F. Drummond et al., 2001 established Kaoline endothermic dehr-droxylation at 538°C, 490°C, 540°C, 490°C, 280°C.
Thanikachalam and Viswanathan (1973) proved the Kaoline endothermic value as 100°C, 600°C and its exothermic value as 1000. Further, Montmorillonite shows the endothermic values of 150°C, 550°C. Naseerudheen et al. (2013) established the Kaoline endothermic values from 450°C to 650°C, due to dehydroxylation of Kaolinite. Kalinichenko et al. (2002) proved the Tritium accumulation in the structure of clay minerals Kaoline, montmorillonite and Palygorskite through DTA analysis. Lamia Bouchimma et al. (2013) established the DTA result of clay material from Tunisia, Combined DTA and TGA results are published. These curves illustrate predominantly consists of halloysite with minor contents of impurities. The sample is amorphous at 550°C. Shekhavat (2013) studied the TGA and DTA analysis of clay of Western Rajasthan. He interpreted the TGA curve that first step of weight loss occurred around 110°C due to release of adsorbed water. All mineral in the kaoline group undergo dehydration in the temperature range of 400°C-700°C and observed 900°C and 1000°C at exothermic deflection established through D.T.A. Golnaz Jozanikohan et al. (2015) studied the DTA, and TGA analysis of Shurijeh clay minerals from Iran. They established TGA curves by raising the temperature up to 110°C followed by two stage of weight loss. The DTA analysis reveals the endothermic values of Quartz as 573°C and 870°C; carbonate as 600°C and 760°C; Kaoline as 569°C and 988°C; Illite 89°C, 566°C, 966°C, Chlorite 410°C and 720°C; Smectite 110°C, 650°C, 900°C.

4.5.2. DTA and TG Analysis of the study area

The DTA and TG curve of studied non-carbonate fraction of regolith calcrete profile samples of Nedungkulam from top to bottom are shown in the (Fig. 4.7a-f) and the results are given in (Table 4.23). The weight loss of TG values is also given in the same (Table 4.23).
**Kaoline**

Endothermic values of Kaoline in the Nedungkulam profiles are 64°C, 49.3°C, 47.1°C, 54.4°C, 57.6°C and 79.1°C, whereas the exothermic values are 950°C in the profile. Numerous researchers have established the endothermic and exothermic values of Kaoline mineral from various places of research (Grim RE and Rowland A.R., 1942; Richard C Milenz et al., 1949; Brain Morgan, 1969; Thanikachalam and Viswanathan, 1973; Angelia F. Drummond et al., 2001; Maria Foldwari 2011; Nazurutheen et al., 2013; Paul Douglas Archer et al., 2013; Lamia Boucchima et al., 2013). The values of the endothermic reaction of Kaoline mineral in the profile of the study area is coinciding with the established Kaoline endothermic value of 47.1°C to 166°C and exothermic values of 988°C (Golnoz Jozanikohan et al., 2015).

**Sepiolite**

The observed sepiolite endothermic values in the Nedungkulam profile are 349°C, 150°C, 429°C, 430°C, 433°C, 565°C. Numerous researchers established the sepiolite endothermic values and exothermic values (Richard C Milenz et al., 1949; Brain Morgan, 1969). The endothermic values of the sepiolite mineral in the profile are coinciding with the established sepiolite endothermic values of 320°C to 360°C, 360°C to 450°C, 450°C to 610°C. (Richard C Milenz et al., 1949) and also coincide with the endothermic values for sepiolite of 122°C to 154°C (Brain Morgan, 1969).

**Palygorskite**

The endothermic values of palygorskite mineral from Nedungkulam profile are 468°C, 146°C and 717°C. Many researchers established the palygorskite endothermic values and exothermic values (Richard C Milenz et al., 1949; Marex and
Piotr 2003; Brain and Morgan, 1969; Grim R.E and Rowland A.R., 1949). The endothermic values of the palygorskite minerals in the Nedungkulam profile are coinciding with the established palygorskite endothermic values of 100°C to 300°C (Richard C Milenz et al., 1949) and established endothermic values of palygorskite mineral of 440°C to 460°C (Marex and Piotr, 2003) and also coincide with the established endothermic values of palygorskite from 450°C to 500°C (Grim R.E. and Rowland A.K., 1949).

**Smectite**

The observed smectite endothermic values in the Nedungkulam regolith profile is observed as 736°C, 427°C, 753°C, 736.3°C and 717°C. Many researchers established the Smectite endothermic and exothermic values from various areas of researches (Grim R.E. and Rowland A.R., 1949; Maria Foldwari, 2011; Goldnoz Jozani Kohan et al., 2015; Lamia Bouchhima et al., 2013). The endothermic values of the Smectite of the study area are coinciding with the established endothermic values of Smectite of 680°C-750°C (Maria Foldwari, 2011); and also coincide with endothermic values of Smectite of 450°C, 492°C, 493°C (Lamia Bouchiima et al., 2013).