3.1. Introduction

Geology is a very fascinating field science. It could not be studied with in the four walls of a classroom. A proverb is used in the geology field “those who runs in the field reads geology”. Keeping with this aim in the mind, an attempt has been made in this research to concentrate the study of calcrete deposit of Sathankulam and its adjacent surrounding regions. The findings of this study are submitted for Ph.D. research work. The geological background of the Sathankulam region is previously discussed in the first chapter. After a through search on available literature, it is confirmed that no research work is discussed on nature of calcrete outcrop of Sathankulam region, its other source rock associations, geochemistry and depositional environment of the study area. This is the first detailed research work on calcrete deposits of the study area. The flow chart of Research methodology is given in (Table 3.1)

3.2. Field Work

During the year 2012, an intensive field work was planned to investigate the nature of calcrete deposits and its other source rock associations in the study area of Sathankulam and its surroundings. At first, a detailed probe on the literature of calcrete deposits of various regions of national and international status about micromorphology, mineralogy, geochemistry and palaeo-climate thoroughly been studied through available literature. Then, the field survey was carried out on a regional scale. The field survey categorized into two ways such as,
1) At first spatial collection of calcrete samples of different places from the exposed surface outcrops of different landscape setting in and around Sathankulam, between the latitudes from 8°25′1″ to 8°50′0″ N and longitude from 77°75′1″ to 78°00′0″ E.

2) Then, the location of regolith calcrete profile samples from two mine locations, such as Nedungkulam (8°46′0″ N, 77°86′5″ E) granite mine section and Thoppukulam (8°43′8″ N, 77°92′7″ E) sedimentary limestone mines section.

There are six calcrete profile samples from Nedungkulam mine section and five calcrete samples from Thoppukulam mines section were collected. In total, twenty three spatial and eleven profile calcrete samples which were collected for various research purposes (Fig 3.2). The sample locations were makes by using handheld GPS (Global Position System). The collected samples were packed in polythene bags duly labeled with co-ordinate information. While collecting samples, field characteristics of calcrete deposits were observed.

3.3. Laboratory studies

3.3.1. Micro Thin Section Preparation

A part of spatial and profile calcrete samples were used for thin section analysis. These micro-thin sections were prepared from Department of Earth Science, IIT, Mumbai and also at Suschitra polishing Pvt. Ltd., from Ennore, Chennai. Then, the photomicrographs of calcrete and other associated source rocks were taken from Department of Geology, V.O.Chidambaram College, Tuticorin and also from Department of Geology, Alagappa Govt. Arts and Science College, Karaikudi for micromorphology and mineralogical observation study.
3.3.2. X-ray Diffraction Analysis

The selected representative of eleven calcrete profile samples from Nedungkulam mine section and Thoppukulam mine section were subjected to X-ray diffraction analysis through XRD instrument “X-Pertpro” installed in the laboratory of Department of Physics, Manonmaniam Sundaranar University, Tirunelveli. The mineralogy was determined by two ways through XRD on carbonate and non-carbonate fraction of calcrete samples. The non-carbonate fraction of calcrete profile samples were obtained by crushing and sieving (0.2 mm mesh), followed by the dissolution of carbonate in 10% HCl acid. Then, the non-carbonate samples treated by acid digestion were analyzed particularly for clay mineral identification by calibrating 2θ position values from 0° to 30° in the XRD instrument. But, the carbonate fraction of powdered calcrete samples were directly analyzed for general mineralogical studies by setting 2θ position values from 0° to 60° in the XRD instrument. The XRD patterns of the clay minerals and other minerals are identified through their respective ‘d’ spacing values and their intensity (Sachinath Mitra, 1989) and also from published literature.

3.3.3. SEM Analysis

The selected representative of non-carbonate fraction of six Nedungkulam calcrete samples, after acid digestion were studied under Scanning Electron Microscope-Joel JSM-5800 model instrument installed in the National Institute for Interdisciplinary Science & Technology (NIIST), located at Pappanamcode, Trivandrum, Kerala.

The samples were mounted on the brass stub. The mounted grains in the stub were coated with gold in a vacuum evaporator, while the sample was being slowly
rotated. Typical photomicrographs of clay minerals, and its fabric, microstructures, etc., were taken using stereo scan 180 µm at standard magnifications ranging from 100X to 2000X. Then, photomicrographs taken from the SEM lab, are interpreted with SEM mineral atlas and published literatures in the calcrete studies from national and international literatures.

3.3.4. Thermal Analysis

Thermal Analysis (TA) is a group of techniques of Differential Thermal Analysis and Thermal Gravimetric Analysis that study the properties of materials, as they change with temperature. In practice, thermal analysis gives properties like enthalpy, thermal capacity, mass changes and coefficient of heat expansion. Thermal Gravimetric Analysis (TGA) measures changes in weight in relation to changes in temperature. The measured weight loss curves gives information on changes in sample composition, thermal stability and kinetic parameters for chemical reactions in the sample. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. TGA causes mass changes which provide physical information such as gas adsorption, gas desorption phase transitions, such as vaporization and sublimation and chemical information, such as decomposition, breakdown reactions, gas reactions and chemisorptions.

The TGA application involves characterization of thermal stability, material purity and determination of humidity. It examines that corrosion studies, gasification processes and kinetic processes. Calcium oxalate monohydrate is a standard material often used to demonstrate TGA performance. It exhibits 3 weight losses with temperature in an inert atmosphere like N₂. The factors such as heating rate, sample
size, particle size of sample, packing, crucible shape and gas flow rate are the factors affecting TGA curve.

In DTA, differential temperature is plotted against time or against temperature. DTA curve is called as Thermo grams. DTA phenomena cause changes in heat or temperature which provide physical information such as adsorption (exothermic), desorption (endothermic), change in crystal structure. Crystallization and melting and chemical information such as oxidation (exothermic) reduction break down reaction, chemisorptions and solid state reactions.

Combining two techniques, TGA and DTA gives a comprehensive study of material thermal behavior. The sample is usually packed into a deep crucible or pan which accommodates 8 to 10 mg of solid samples. The pans are made up of a different material including aluminum, platinum etc. The sample should be kept on the pan in a uniform manner, so that, weight loss and temperature reproducing is easily obtained. A combined TGA and DTA curve is given in the (Fig. 3.3).

The non-carbonate fraction of Nedungkulam (Fig. 3.3) calcrete profile samples, after digestion of acid treatment, gives endothermic and exothermic values of clay minerals, quartz and biotite etc., through DTA and weight loss information through TGA curves. TGA and DTA analysis experiments were carried out on PERKING ELMAR DR-SII model of combined thermal instrument installed at National Institute of Interdisciplinary Science Institute, Trivandrum, Kerala. The DTA and TGA results of the Nedungkulam non-carbonate fraction of calcrete profile samples curve interpreted with TGA-DTA analysis of clay minerals atlas and from National and International published literatures.
3.3.5. XRF Analysis

The XRF studies are a non-destructive method of qualitative and quantitative analysis of elemental composition of samples. It is based on the measurement of X-ray spectral lines emitted by secondary excitation. Twenty three spatial and eleven profile calcrete samples and selected representative samples of source rock and soil were analyzed for major and minor oxides such as SiO$_2$, Al$_2$O$_3$, MnO, Fe$_2$O$_3$, MgO, CaO, Na$_2$O, $\text{SO}_4$, TiO$_2$, P$_2$O$_5$ and LOI. These representative calcrete samples, source rock and soil samples were analyzed at the XRF lab of National Geophysical Research Institute, (NGRI), Hyderabad. XRF shows high level performance and enables a very sensitive and accurate determination of major elements. International geochemical reference materials from US Geological Survey, the Canadian geological survey, the international working group, France, and NGRI, CSIR lab (India) were used as standards to prepare calibration curves for major oxides (Krishna et al., 2007) to check the accuracy of the analytical data.

3.3.5.1. Sample preparation for XRF

Major element concentrations were determined by X-ray fluorescence spectrometry as per the procedures given in Calvert, (1990). Selected dried calcrete source rock and soil samples were powdered and packed in polyethylene bottles and used for major element analysis by conventional XRF method. The XRF intensities measured from elements in dry samples may increase or decrease due to the XRF absorption and enhancement effects by other elements called the matrix effect (Tertian and Claisse, 1982). In order to evaluate the matrix effect on the XRF intensities, plates of aluminium, titanium, iron and quartz and powdered potassium nitrate and calcium carbonate were prepared as the standard samples. Pressed pellets
are prepared by using collapsible aluminium cups having 12 mm diameter (Govil, 1985). These cups are filled with boric acid and about 1 gram of finely powdered calcrite sample is put on the top of the boric acid and pressed under a hydraulic press at 20 tons pressure to get a pellet. A Phillips Magix PRO model PW 2440, XRF spectrometer coupled with automatic sample change PW 2540, is used for the major element composition determination. The Magix-Pro is a sequential instrument with a single goniometer based measuring channel covering the complete measurement range from few ppms to 100% concentration. The Rubidium (Rh) anode with end window is normally used in X-Ray tube.

3.3.5.2. Total Carbonate (T$CO_3^-$)

Total carbonate (T$CO_3^-$) content of all twenty three spatial and eleven profile calcrite samples were carried out by rapid volumetric titration method of Hutchinson and McLennan (Piper, 1947). This involves treatment of the calcrite samples with a known amount of HCl and estimation of unused HCl by blank titration with and NaOH. The percentage is calculated by the formula $CaCO_3\% = 10(®-S)$ where ® and S are titre values for the blank and sample solutions respectively.

3.3.6. ICPMS Analysis

ICP-MS means Inductively Coupled Plasma Mass Spectrometry. It was developed as a commercial analytical technique in the early 1980 has since been applied to the determination of trace, minor and major elements and REE in almost every analytical field. Virtually, all elements can be measured including alkali and alkaline earth elements, most of halogens and some of the non-metals. Fifteen representative spatial calcrite samples eleven profile calcrite samples selected representative of eight source rocks samples and three soil samples collected from the
study area, were broken and ground into fine powder (-250 meshes) by using Agate Mortar and Pestle. To a 0.05 g (50 mg) of powdered calcrete sample in a 25 ml capacity savillex pipette ® beaker, 10 ml acid mixture of 7 parts of Hydrofluoric acid (HF) (Electronic Grade), 3 part of HNO₃ (distilled) and one part of HCl (AR Grade) was added. Then, 5 ml of 1 mg/ml of 10³ Rh solutions was added as international standard. After tightly closed the Teflon vessels, it is kept it on the hot plate at 140°C for 48 hours.

After two days, Teflon vessels were opened and the contents were evaporated at 200°C to dryness after dropping few drops of HClO₄ (Per-chloric acid) added for complete removal of HF. After completing heating programme, the beakers were cooled to room temperature and carefully vented in fume hood. Then the residue was dissolved in 10 ml of 1:1 NHNO₃ and warm at 70°C for 60 minutes to dissolve the residue. Then, the solution was made up into a final volume of 250 ml with de-ionized water and solution was stored by HDPE bottle. After finally 10 ml solution is pipette out from HDPE bottle and add 1ml concentric HNO₃ (Super pure). Then, solution volume is made up of upto 100 ml by adding de-ionized water.

3.3.6.1. Instrumentation

Solutions were analyzed at CSIR-NGRI, Hyderabad, by high resolution inductively coupled mass spectrometer (HR-ICP-MS) (Nu Instruments Attom®, UK) in the jump-wiggle mode which permits the analyses of interest to be measured accurately. The sample introduction consisted of a standard main hard nebulizer with a cyclonic spray chamber housed in Peltier cooling system. All quantitative measurements were performed using the instrument software (Attolab v.1), while the data processing was done using Nu Quant, which uses knowledge-driven routines in
combination with numerical calculations (quantitative analysis) to perform an automated/manual interpretation of the spectrum of interest. Instrumental parameters for open rating conditions are given in Table 3.1.

Instrument was optimized using 1ppb tuning solution and the sensitivity. In was about 1 million cps. Oxide and oxy-hydroxide ratios were low (< 0.2%) and the double charges ions ratio was < 3%. Mass bias fractionation and several well-known isobaric interferences were addressed by using certified geochemical reference materials. External drift was corrected by repeated analyses of a 1:5000 solution of JG-2 (Japanese standard). Instrument response was corroborated relative to two independent digestions of G-1 and G-2 (USGS standard). Precision and accuracy are better than RSD 3% for the majority of trace elements.

After obtaining eleven major elements, minor, trace elements and REE geochemical data and Total Carbonate (TCO$_3$) data, statistical evaluation of geochemical analysis of calcrete from the result of spatial and profile samples, GIS based evaluation of major element geochemical analysis from 23 spatial samples and geochemical depositional environment of major element from twenty three spatial and eleven profile samples were discussed separately.

Statistical evaluation of major element, minor trace elements and REE geochemistry of spatial and profile samples were subjected to Principal Component Analysis and Cluster Analysis through computer software programme PAST. In the GIS- based spatial evaluation of major element geochemistry studies, Iso-elemental quality contour maps of calcrete deposits of the study area was prepared through (Arc-GIS 9.3) software and these maps help for delineation of high carbonate calcrete
availability area for the suitability of calcrete mining and industrial use in the study area.

3.3.7. Isotope Analysis

Six calcrete samples from Nedungkulam (Fig. 3.2) regolith profile and five calcrete samples from Thoppukulam (Fig. 3.2) regolith profile samples (Total, 11 calcrete samples) have been analyzed for carbon and oxygen isotope study. This analysis was carried out at the stable isotope laboratory at the NEG-LABISE, Departamento de Geologia, Universidad Federal de per nambuco, Brazil. The instrument used for the stable analysis is Triple collector SIRA II mass spectrometer.

3.3.7.1. Methodology

For carbon and oxygen isotopic determination from calcrete samples, CO$_2$ was extracted from powdered calcretes (Carbonates) in a high vacuum line after reaction with H$_2$PO$_4$ at 100% concentration and at 25 $\mu$C, and cryogenically cleared according to the method described by Craig, H (1957). The CO$_2$ gas released by this method was analyzed for carbon and oxygen isotopes in a double inlet, treble collector SIRA II mass-spectrometer using the reference gas BSC (Borboroma Skarn Calcite) calibrated against NBS-18, NBS-19, and NBS-20 has a value of 11.28% POB for $\delta^{18}$O and – 8.58% PDB for $\delta^{13}$C. The results are reported as per ml (%) $\delta^{18}$O and $\delta^{13}$C values relative to Pee Dee Belemnite (PDB international standard of Vienna). The conversion of SMOW values to PDB standard have been attempted by using the following formula $\delta^{18}$O calcite (SMOW) = 1.03086 (Friedman and O Neil, 1977). The uncertainties of the isotope measurements were estimated as 0.1% for C and 0.2% for O, based on multiple analysis of an interval of laboratory standard (BSC).
3.3.8. Ground water study

3.3.8.1. Sampling

Twenty two ground water samples from the various wells of the study area in and around Sathankulam are collected for water quality studies. The water were collected in polyethylene cans which are having the capacity of 1 liter each. The cans were thoroughly rinsed before sampling. A case of borwells or dug wells, sampling was done after flushing in wells for about 10 minutes to ensure representative sampling. The location map of the ground water samples collected from the study area is shown in (Fig. 3.4).

Moreover, the well inventory details like location, rock succession, well shape and dimensions and water table level the thickness of aquifer were also noted while collecting the samples. The water samples were analyzed from the Green Star Fertilizer Pvt. Ltd., (SPIC), Tuticorin, Tamilnadu, India.

3.3.8.2. Analytical Procedures

The water samples were analyzed for pH, Total Dissolved Solids (TDS) and Electrical Conductivity (EC), Calcium, Magnesium, Sodium and Potassium (cations). Chloride, Nitrate, Sulphate, Fluoride and Bicarbonates (anions) as per the APHA (1998) procedures.

\textit{pH}

The pH is measured by determining the voltage developed by two electrodes which are in contact with the solution in a potentiometer. The voltage of one electrode known as a calomel half-cell is fixed, while the voltage of the other electrode varies with the pH sample. The other electrode is glass electrode. The glass electrode system
is based on the fact that a change of 1 pH unit produces an electrical change of 59.1 mV at 25°C.

The pH is measured in systronics 321 pH meter. The instrument was standardized with buffer solutions of pH 4.2 and 9.0 within 0.1 unit of the pH of the buffer solution. Each time temperature was also noted. Then the electrodes were put in the sample and the pH was noted. After each measurement, electrodes were dried by wiping with tissue paper.

**Electrical Conductivity**

To measure the conductivity of a water sample, it is placed in a cell carrying a pair of platinum electrodes coated with spongy platinum black which are firmly fixed in position. Since it is very difficult to measure the area of the electrodes and the distance between them for accurate measurements, the cell constant must be evaluated using the solution of accurately known conductivity. For this purpose 0.01M potassium chloride solution whose conductivity at 25°C is 1408.8 micro siemens / cm. The sample is cooled to 25°C. The conductivity cell is washed with the sample and the conductivity is measured. Elico conductivity meter of model CM 180 is used for measurements.

**Total Dissolved Solids**

TDS is analyzed by residue on evaporation method. A volume of water was passed through a 2 micron porosity filter and the filtrate was collected. A known volume of the filtrate was evaporated on a water bath, in a previously dried, cooled and weighed evaporating dish. After evaporation, the residue was dried at 103°C – 105°C, cooled and weighed. This drying cycle was repeated until the weight loss was less than 0.5 mg. TDS is calculated from the following formula.
\[
\frac{\text{Weight difference (g) } \times 10^6}{\text{Volume of water (mL)}} = \text{TDS mg/L}
\]

**Calcium**

A suitable aliquot of sample is neutralized with 0.02 N hydrochloric acid, boiled for 2-3 minutes to expel the carbon dioxide and cooled to room temperature. 1 ml of 1 N sodium hydroxide is added to maintain a pH of 12-13. Murexide indicator (about 0.2-0.4g) is added and titration is carried out against a standard solution of ethylene diamine tetra acetic acid (EDTA) till the colour changes from red to purple.

\[
\text{Calcium, mg/L as CaCO}_3 = \frac{V \times 0.02 \times 50 \times 1000}{\text{Volume of sample}}
\]

Where \( V \) = Volume of EDTA consumed.

**Magnesium**

The difference between total hardness and calcium hardness is magnesium hardness.

\[
\text{Magnesium, mg/L as CaCO}_3 = \text{Total hardness} - \text{Calcium hardness}
\]

**Sodium and Potassium**

Sodium and potassium are analyzed by photometric technique. In the digital monitor, the sensitivity is adjusted to minimum. Air and fuel are lined up from the burner. The appropriate filter for Na\(^+\) or K\(^+\) is selected. Initially distilled water is aspirated to give a full scale deflection in the galvanometer namely zero reading. If zero is not got, it is adjusted. Then a standard solution of sodium chloride is placed and the
galvanometer is adjusted. Then a standard solution of sodium chloride is placed and the galvanometer is adjusted to give full scale deflection corresponding to the concentration of the standard solution. The zero is again checked using distilled water. Now, the sample is fed and the reading is noted the concentration of sodium corresponding to the reading is obtained from the calibration graph which is a plot of galvanometer reading (abscissa) against the concentration (ordinate) expressed as ppm.

\[
\text{Sodium, mg/L = concentration} \times \text{dilute ratio (if any)}
\]

For potassium, the appropriate filter is selected and the calibration curve is prepared using potassium chloride as standard.

**Alkalinity (Carbonates and Bicarbonates)**

A suitable aliquot of the sample is titrated against standard sulphuric acid (0.05 N) using phenolphthalein indicator. The end point change is pink to colorless. The volume of acid consumed is noted as \( V_1 \). To the colorless solution obtained in the above titration, or if no pink color is produced with phenolphthalein, to the original solution. 1-2 drops of methyl orange indicator solution are added and titrated against the 0.05 N sulphuric acid. The color change is yellow to faint orange. The total volume of acid including that added in titration with phenolphthalein indicator is noted as \( V_2 \).

\[
\text{Carbonates as HCO}_3, \text{mg/mL as CaCO}_3 = \frac{2V_1 \times 0.05 \times 30 \times 1000}{\text{Aliquot}}
\]

\[
\text{Bicarbonates as HCO}_3, \text{mg/mL} = \frac{V_2 \times 0.05 \times 61.02 \times 1000}{\text{Aliquot}}
\]
Bicarbonates as \( \text{HCO}_3^- \), mg/mL

\[
\text{Bicarbonate as } \text{HCO}_3^- \text{, mg/mL} = \frac{V_2 - V_2 \times 0.05 \times 61.02 \times 1000}{\text{Aliquot}}
\]

**Chloride**

Chloride ion concentration is determined by titration method (Vogel, 1968) A suitable aliquot of the sample is taken. If the pH is out of the range 7 – 10 adjust with 1 N sodium hydroxide or 1 N sulphuric acid to the range 7-10. 1 mL of 5% potassium chromate is added. The sample is titrated against 0.02 N silver nitrate. The color change is the appearance of the blackish red silver chromate. The reactions are:

\[
\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}
\]

\[
\text{K}_2\text{CrO}_4 + 2 \text{Ag NO}_3 \rightarrow \text{Ag}_2\text{CrO}_4 + 2\text{KNO}_3
\]

A blank is carried out with 0.5 g of CaCO\(_3\), added to give an inert white precipitate background similar to silver chloride precipitate.

\[
\text{Chloride, mg/L} = \frac{(A-B) \times 0.02 \times 35.46 \times 1000}{\text{Aliquot}}
\]

Where

\[
A = \text{Volume of AgNO}_3 \text{ for sample}
\]

\[
B = \text{Volume of AgNO}_3 \text{ for blank}
\]

**Sulphate**

A suitable portion of the sample is filtered and acidified with drops of concentrated HCl to a pH of 4.5 – 5.0. Then, the sample is evaporated to about 50 ml volume. The sample is filtered and the filter paper is washed with distilled water and the washings are added to the same filtrate. The filtrate is boiled and to the boiling
solution, 10% barium chloride is added with stirring until the entire sulphate is precipitated. The precipitate is kept for overnight for the complete settlement. After, it is filtered through a previously washed dried at 100°C – 110°C and weighed Gooch crucible. Then, the crucible is ignited at 600°C – 800°C in a muffle furnace and cooled then weighed as barium sulphate (BaSO₄).

The sulphate is calculated using the formula.

\[
\text{Sulphate, mg/L} = \frac{\text{Weight of } \text{BaSO}_4\text{ precipitate} \times 10^6 \times 96.07}{\text{Volume of sample} \times 233.40}
\]

**Nitrate**

Nitrate is determined by Brucine method. The reaction between nitrate and brucine produces a yellow colour that can be used for the spectrophotometric estimation of nitrate. Systronics spectrophotometer of model 106 is used for measuring absorbances.

To a portion of the sample containing 0.1 to 8 µg NO₃⁻ – N, 2 ml of 30% sodium chloride is added and the solution is thoroughly mixed. Then, 10mL sulphuric acid is added. Mixing is done thoroughly and cool the solution. Since heat is developed, when H₂SO₄ is added. Then, 0.5mL of brucine sulphate suluric acid reagent is heated in a water bath at 95°C. After 20 minutes, the solution is cooled, the absorbance is measured at 410 nm in a spectrophotometer. A blank is run parallel. Then the results are calculated by following formula.

\[
\text{mg/LNO}_3\text{– N} = \frac{\text{NO}_3\text{– N}}{\text{mL of Sample}}
\]