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Field characteristics, micro-morphology and GIS based evaluation of major element geochemistry of calcrete deposits of Vilathikulam and its surrounding villages, Thoothukudi District, Tamilnadu, India

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Abstract

Calcretes is impure carbonate deposit formed with in the vadose zone by pedogenic leaching or phreatic zone by evapotranspiration of groundwater under the arid and semi-arid climatic conditions. It occurs in some places as duricrust outcrop centered on Vilathikulam region, Thoothukudi district of Tamilnadu. The general stratigraphic succession of the area profile is cited. The spatial collection of calcrete samples from the outcrops of various landscape setting were carried out. The Micromorphological characters of calcrete are in the form of gravel, nodular, lumby, massive, hardpan and chalky nature. The Micromorphological illustration reveals the micritic or microsparitic calcite precipitation which makes rimming, peloidal or colloform, veining, displacive and replacive structures. Major element geochemical analysis of calcrete indicates that CaO, MgO, SiO_2, Fe_2O_3 and Al_2O_3 are in elevated concentration (>1%), whereas MnO, Na_2O, K_2O, TiO_2 and P_2O_5 are in low level concentration (<1%). The GIS based major element geochemical iso-quality spatial contour maps illustrate the distributional quality of the area which helps to demarcate the suitability of the mining site of calcrete. Further, major element geochemistry delineates the geochemical environmental of the study area.

Keywords: Authigenic, Macromorphology, Micromorphology, Micritic, Microsparitic, Major element geochemistry.

Introduction

Calcrete is a secondary source of impure limestone deposits formed within the regolith part in the both sedimentary and metamorphic terrains. Sometimes it occurs as sub aerial duri-crust exposures associated with thick profile section. Calcrete development is resulted either by soil leaching or by evapotranspiration of groundwater of alkaline rich groundwater under the arid and semi arid climatic conditions[1]. They normally occur as a nodular, hardpan, gravel, lumby, honeycomb and chalky forms etc and microscopically classified as alpha and beta calcrete[2]. Many research works have been concentrated on calcrete deposit, not only in India, but also in various parts of the world[3-10]. The topography of the area is almost flat and plain within the maximum elevation of 46 m above the MSL. The area receives an average rainfall of 600 mm per year and prevails the arid and semi arid climatic conditions. But previously, no much research work has been carried out by any author on calcrete deposit from the areas centered around the Vilathikulam town and its surrounding villages, in Thoothukudi district of Tamilnadu, India Vilathikulam is a located at 56 km from thoothukudi city. This area has been well connected with various national and state high way road networks. The geographic co-ordination lies within the latitude between from 78°0´ to 78°05´ and longitude from 09°10´ to 09°15´ Figure-1. The major part of vaippar river basin is located within the study area. Drainage patterns of the study area are generally sub dentritic and its major flow directions are generally running towards the south east direction towards of Gulf of Mannar.

Geological setting: Proterozoic basement rocks of the study area consists of quartzite, calc-granulites, crystalline limestone, hornblende-biotite-gneiss which enclaves pyroxene granulite or charnockite and granite. The basement rocks are overlain by recent flood plain deposits of black soil with isolated coarse detrital quartz sand. The profiles of calcrete occur as intervening deposits between black soil and weathered basement rocks. In many places, it occur as a sub-aerial duri crust exposure with a thick profile, ranging the thickness from the 1m to 1.25 mm. The general stratigraphic succession of the study area is given in Table-1.

Methodology

Ten calcrete samples were collected spatially from the exposed surface outcrops in and around Vilathikulam region. A part of the samples were used for the thin section analysis and the thin sections were prepared from Indian Institute of Technology (IIT) at Mumbai. The photomicrographs were taken from the thin sections under the camera attached binocular visioned

petrological microscope from the laboratory of Alagappa govt Arts College, Karaikudi and V.O. Chidambaram College, Tuticorin. Another part of the same samples were used for the major element geochemical analysis through XRF (X-Ray Fluorescence Spectrometry) method by the instrument Philips-Magix PRO-PW 2440 at the National Geophysical Research Institute (NGRI), Hyderabad. International geochemical reference materials from the US Geological Survey, the international working group (France) and NGRI (India), were used to prepare calibration curves for the major oxides[11]. Then, the geochemical data was used to prepare spatial iso-quality contour maps of the study area, through the software of Arc-GIS 9.3.

Table-1: Stratigraphic succession of the study area.

Strata	Thickness	Age	Depth
Black cotton soil	1.25 m	Recent	1.25 m
Calcrete layer	1.20 m	Holocene to Pleistocene	1.25 – 2.45m
Sap rock or basement rock	Infinitive	Proterozoic	Below 2.45 m

Field observation: The calcrete deposit occurs as thick profiles deposits within the soil outcrops. In some places, it is formed as concordant or discordant penetrative intrusive forms such as veins or banded layers within the weathered sap rock and soil. In many places, they expose as a sub aerial duri crust outcrops and associated with thick profiles of 1 m in thickness. The penetrative forms of calcrete vein and layers have been observed from the regolith part of the areas of Yilgarn Craton, in Western Australia[12]. Calcrete occurs as a granular or gravel layer at the top of the soil profiles section, whereas the alternate layer of massive, nodular, hardpan, lumby and chalky forms occur in the calcrete profile section above the basement rock. Such above field observation of regolith carbonate occurrences has been already discussed from the metamorphic terrains area of Coimbatore region[13] and from the Pandalgudi region[14]. Regolith carbonates are widespread in many areas of arid and semi arid region of Australia and its regional distribution is mainly controlled by the degree of leaching of carbonate from soil and availability of dissolution of carbonate sources in groundwater in the regolith[15]. The dissolution and weathering process from the calc-alkaline and per-alkaline group of metamorphic basement rocks contributes of alkaline rich groundwater which causes for the formation of calcrete in the regolith part. Such similarity of observation has already pointed out from the study area in Pandalgudi region[14] and also in Coimbatore region[13]. The alkaline rich groundwater is drawn up through soil by capillary action. The occurrence of granular calcrete in the black soil above the full calcrete profiles indicates the evidence for capillary rise and evapotranspiration process. The filed relationship of calcrete and the basement rocks of the study area are presented in photographs Figure-2(a-d).

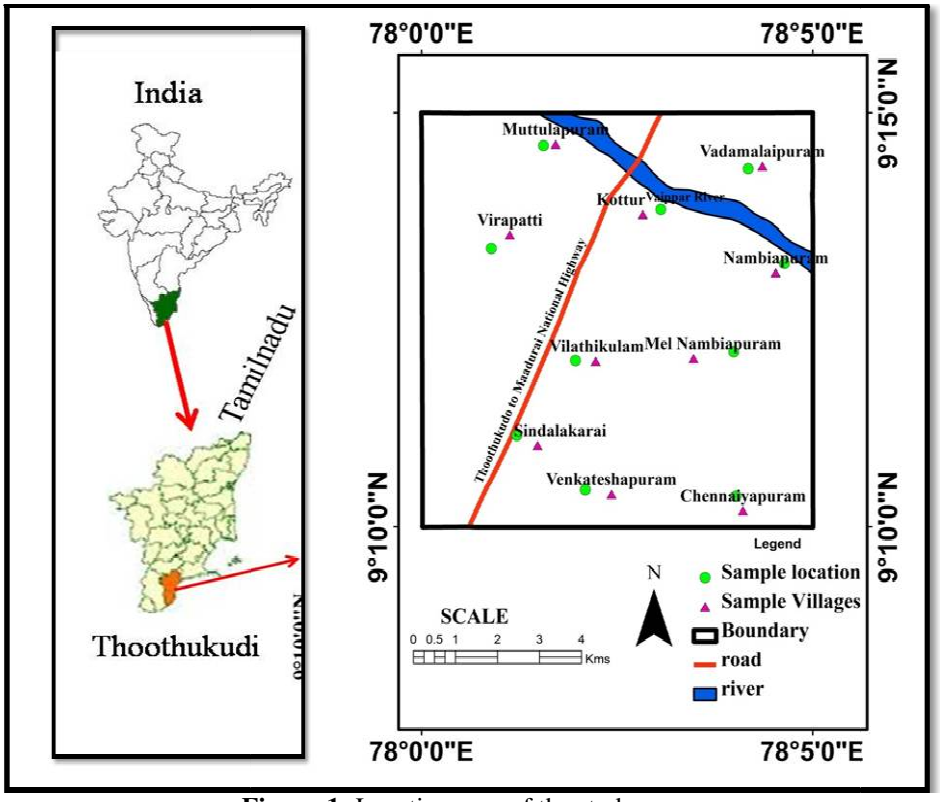

Figure-1: Location map of the study area.

Figure-2(a-d): a-The field photographs show a surfacial outcrop of black soil and thick calcrete profile deposits in the river section. b-The field photographs show the chalky deposits within fracture zone of exposed weathered sap rock. c-The field photograph shows the calcrete deposits as discordant form in the exposed weathered sap rock. d-The field photographs show the bottom weathered sap rock of granite and charnockite followed by calcrete profile and top black soil.

Results and discussion

Micromorphological observation: The calcrete shows the gravel, chalky, lumby, nodular, massive or laminated forms. The Veins, dark spots and vugs could also been seen from the samples under naked eye. The microscopic study reveals that the micritic or microsparitic calcite precipitation which surrounds the phenocryst of unaltered quartz and feldspar grains. This results causes for the rimming, colloform, peloidal, veining, filamental vein and meshwork precipitation of micritic calcite. Sometimes, the micritic calcite deposition shows the displacive or replacive structures in minerals grains of biotite, quartz, and feldspar and clay matrix. The formation of calcrete in the regolith part involves two stages. At the first stage, neomorphic clay mineral such as palygorskite or sepiolite is deposited in the voids, cracks in the soil and weathered saprolite. Then the clay components in the soil or saprolite are replaced by micritic calcite precipitation. Dissolution and simultaneous removal or replacement of aluminium silicate is accompanied by the deposition of carbonate. Such similar replacive and displacive structure have been observed in the regolith part of Cobar-Girilambone region, Australia[6], Coimbatore region[13], Pandalgudi region[14] and Sathankulam region[16]. The veining of microcrystalline calcite precipitation may be due to the vaccum or void created by the rhizome of Prosopis Julifera Mimosacea and Palmyra tree in the soil outcrops. The dark brown dendritic impregnation which is believed to be a clay minerals sesqui-oxide in calcitic matrix is also observed in thin section. Such similar characters have been illustrated in the calcrete of Coimbatore region[13], Pandalgudi region[14] and Sathankulam region[16]. The microscopic observations are shown in photographs from Figure-3 (a-f).

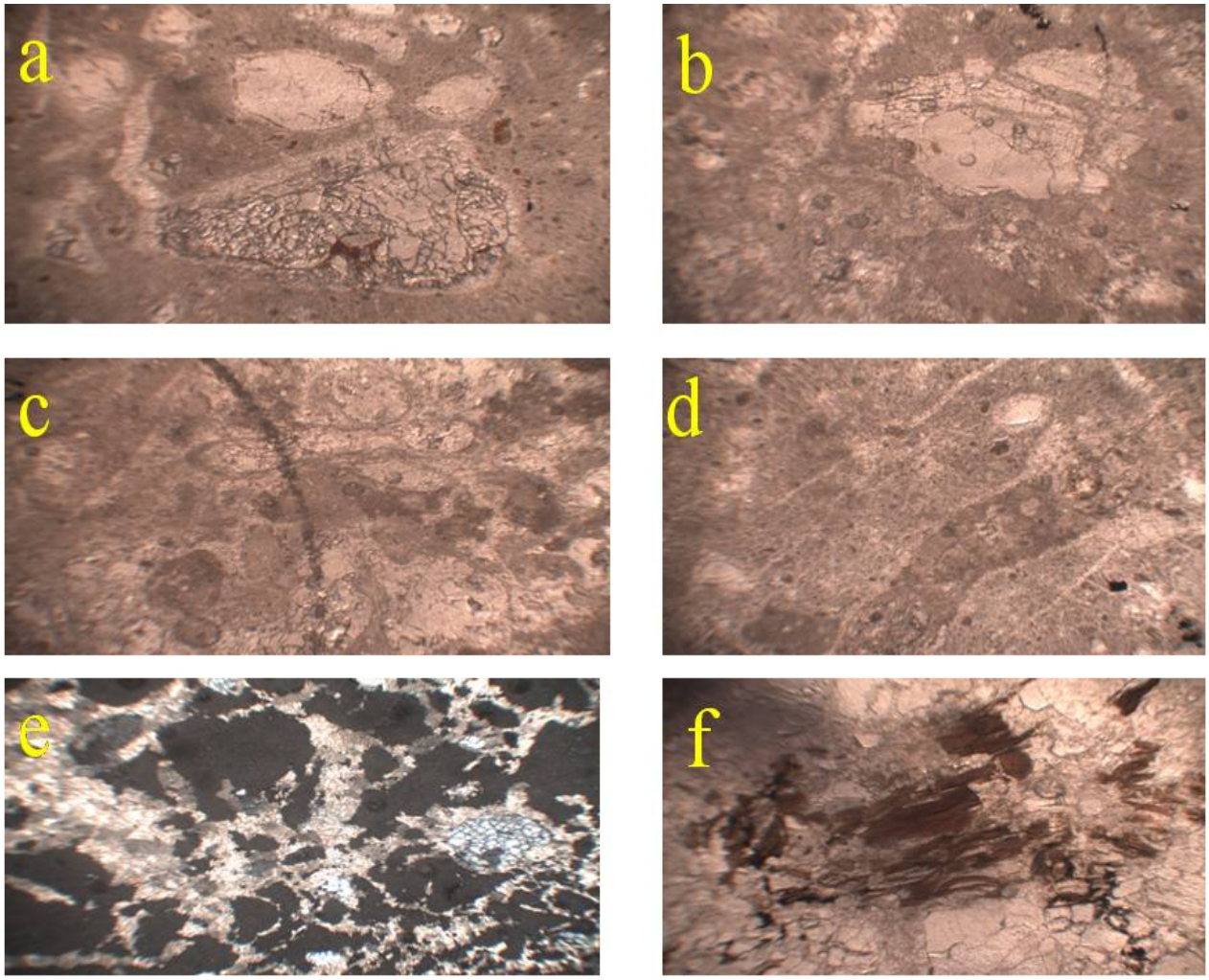

Figure-3(a-f): a-Photomicrographs show rimming of micritic calcite development around weathered feldspar grains and veining structure in voids formed by rhizome. b-Photomicrographs show displacive structures by calcium carbonate deposition along the cleavage plane of unaltered feldspar. c-Photomicrographs show peloidal, colloform structures and micro cystis preservation in the soil profile along with micritic calcite development. d- Photomicrographs show filamental and veining structures development in the voids or vaccum created by the rhizome. e- Photomicrographs show meshwork of micritic calcite development within the clay relict. f-Photomicrographs show displacive micritic calcite development in biotite flaks in hornblende biotite gnesis.

GIS Based evaluation: Major element distribution of calcrete of the study area indicates that the CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 and TCO_3 are greater concentration (above 1%) when compared to the other oxides such as MnO, Na_2O, K_2O, TiO_2 and P_2O_5 Table-2. The CaO and TCO_3 values of the study area range from 40.18% to 48.52% and 61% to 76.69% respectively. Major element geochemistry of the samples shows the similarity in the distribution trend Figure-4. The geographic information system is a quite useful tool in evaluating spatial chemical variation in calcrete deposition of Vilathikulam region. The spatial contour maps of major elements constructed using the Arc GIS 9.3 are presented Figure-5(a-d) and Figure-6(e-f). Theses contour maps illustrate the distribution of TCO_3, CaO, MgO, SiO_2, Al_2O_3 Fe_2O_3 rich calcrete sources at various landscape setting of the study area. The cement industry especially, Ramco group of cement industry requires raw material quality of calcrete with TCO_3.55-75%, CaO-34.20%, MgO.6.30%, SiO_2-17.16%, Al_2O_3-4.53% and Fe_2O_3-2.09%[16]**.** The Total carbonate (TCO_3) and Calcium Oxide (CaO) are prime criteria for cement manufactures. The TCO_3 and CaO anomalies delineated potential quality zones of the respective quality contour maps that may be useful for cement manufactures to locate the TCO_3 and CaO rich area of calcretes in the study area. The villages Kottur, Vilathikulam, Nambiapuram, Virapatti, Muthulapuram, Mel Nambiapuram and Vadamalaipuram villages are inferred as high quality rich prospecting areas of calcrete, representing the values of TCO_3 from 61.23% to 76.90% and the values of the CaO from 41.23 to 48.52%. These areas are highly suitable for mining of calcrete raw material for cement manufacture.

Table-2: Major element geochemistry of calcrete samples of the study area.

Sample village	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	TCO_3
Nambiapuram	22.3	4.98	1.88	0.2	1.98	42.6	3.48	0.35	0.14	0.12	72.6
Chennaiyapuram	25.93	9.99	4.41	0.18	3.59	45.8	7.09	1.78	0.66	0.32	75.83
Virappatti	28.52	3.13	1.71	0.17	1.42	47.2	4.87	0.67	0.19	0.12	75.72
Vilathikulam	21.84	4.26	1.06	0.16	1.24	41.2	3.13	0.28	0.11	0.09	61.23
Venkateshapuram	23.72	10.3	4.8	0.17	3.82	46.9	6.92	1.82	0.53	0.28	76.9
Vadamalaipuram	26.2	3.06	1.69	0.12	1.34	46.8	4.63	0.58	0.17	0.09	75
Muthulapuram	27	4.26	2.58	0.24	2.65	48.5	8.67	1.35	0.27	0.23	75.52
Melnambiapuram	26.53	5.8	2.58	0.13	16.1	46.6	8.07	1.21	0.49	0.06	73.2
Sindalakarai	24.35	5.17	2.09	0.09	15.5	45.6	7.39	1.09	0.37	0.05	70.62
Kottur	20.52	3.16	1.02	0.11	1.13	40.2	3.05	0.21	0.07	0.04	75.18

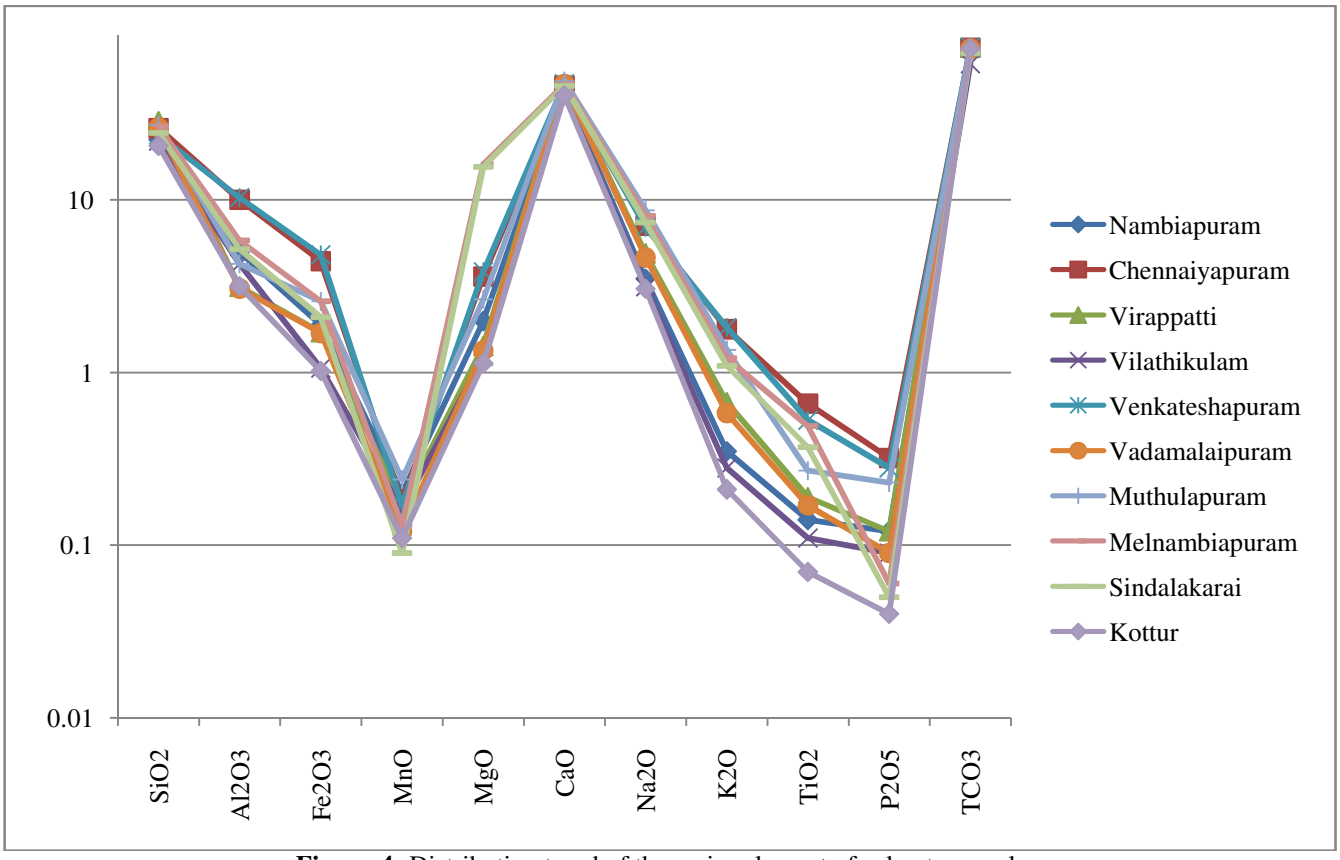

Figure-4: Distribution trend of the major element of calcrete samples.

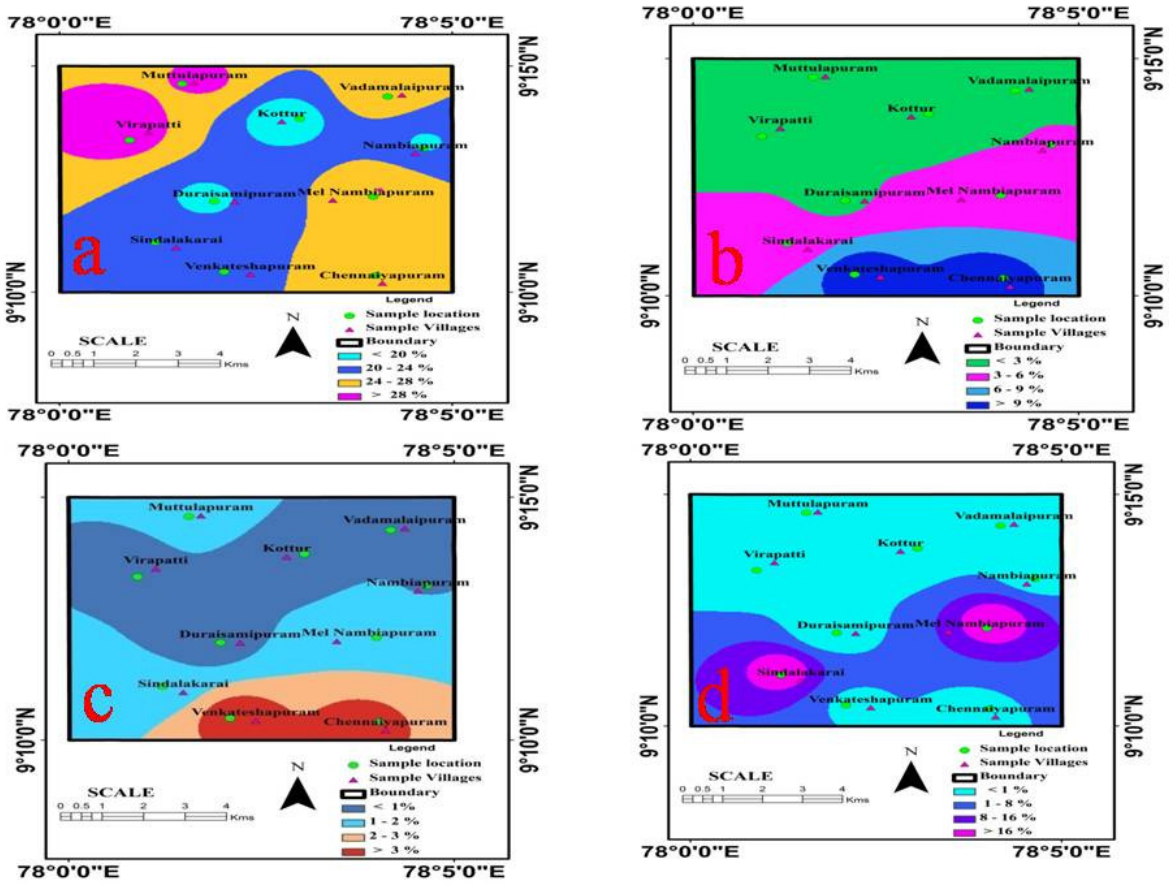

Figure-5(a-d): Iso-quality spatial map of a- SiO_2, b- Al_2O_3, c- Fe_2O_3 and d- MgO.

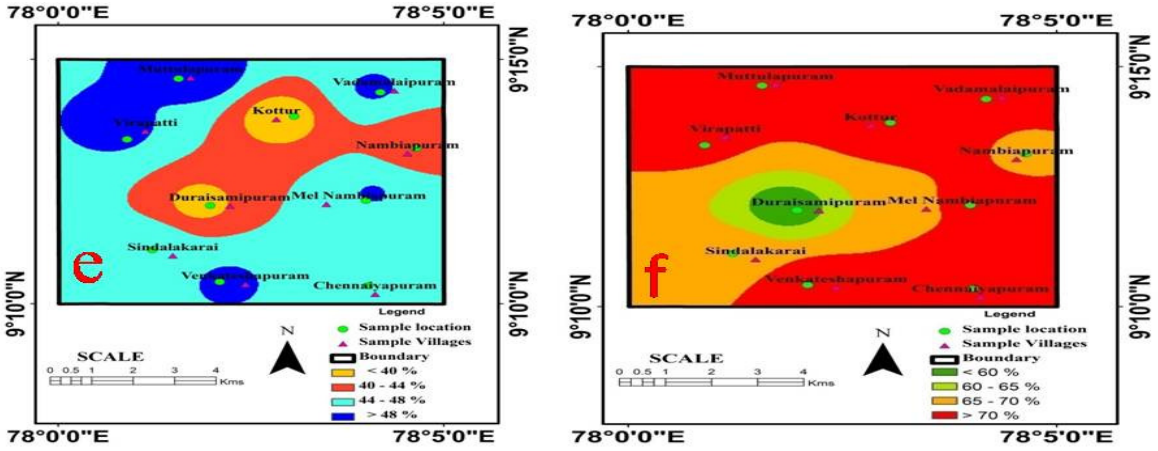

Figure-6(e-f). Iso-quality spatial map of a- CaO, b- TCO_3.

Geochemical environment: Calcrete is a mixture of authigenic carbonate mineral containing with pre-existing phases of the paleosols, such as a sap rock grains, iron oxide and oxy hydroxide impurities. The correlation of major element geochemical study of calcrete is highlighted in various areas in Southern Australia[17], Cobar – Girilambone region, Australia[6], and also in Pandalgudi region, in India[18]. The multiple correlation data of major element geochemistry of calcrete of the study area is given the Table-3. The proportion of the carbonate content generally varies from the pure carbonate (calcite) to low magnesium carbonate (low dolo calcite) in the study area. The variation of high content of $CaCO_3$ in the profile samples may be due to the change in pH, CO_3 and landscape setting[1]. The contact zone of groundwater movement along the bed rock and soil boundary in deeper pedogenic calcrete profile may reflect the high magnesium content in carbonate genesis[6].

Table-3: Multiple correlation coefficients of the major elements of calcrete samples.

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
SiO_2	1									
Al_2O_3	0.01	1								
Fe_2O_3	0.27	0.94	1							
MnO	0.25	0.20	0.31	1						
MgO	0.19	0.17	0.14	-0.47	1					
CaO	0.89	0.25	0.53	0.29	0.26	1				
Na_2O	0.61	0.46	0.64	0.19	0.60	0.79	1			
K_2O	0.45	0.82	0.93	0.26	0.34	0.69	0.86	1		
TiO_2	0.37	0.87	0.90	0.07	0.48	0.53	0.76	0.93	1	
P_2O_5	0.27	0.77	0.85	0.66	-0.30	0.45	0.44	0.77	0.64	1

But in the study area, all the samples show more calcium carbonate ($CaCO_3$) content than the magnesium. This indicates more evapotranspiration process prevailing in the study area, which implies the arid environments. Correlation of CaO with SiO_2, Al_2O_3, Fe_2O_3, K_2O, P2O5 and TiO_2 generally shows the high negative correlation which indicates lithogenic association and calcretes are formed from different sources. CaO and MgO shows low degree positive correlation (r = 0.2), which indicates that may be obtained from the same groundwater sources. The less concentration of magnesium compared to calcium may be due to the less dissolution from the source rocks Figure-7. CaO and MgO is derived from the dissolution and weathering of the calc-alkaline and per-alkaline nature of the source rock materials[14,18]. This same condition is also existed in the study area.

The neoformed clay minerals of palygorskite and sepiolite are commonly associated with pedogenic calcrete. The vadose conditions leading to calcrete development are favorable for insitu palygorskite and sepiolite formation[17]. The calcrete samples obtained from the villages Melanambiapuram and Sindalakarai samples show high concentration of Mg. This may be due to the association of more magnesium bearing unaltered basement rock mineral grains, such as hypersthene and hornblende associated with calcrete deposition in the regolith. The average K_2O concentration of the study area is 0.93 %, whereas average Al_2O_3 concentration is 5.41 %. The distribution of potassium and aluminium reflect the clay mineral impurities[14,18]. The correlation between K_2O and Al_2O_3 in the calcrete of the study area is highlighted as high degree of positive correlation (r = 0.8). The bulk sample analysis proves that the K and Al content of all calcrete samples fall in the montmorillonite and illite composition field Figure-8.

The correlation between iron oxide and TCO_3 is observed as positive (r = 0.5) which indicates that iron oxide may be in carbonate phases. Iron oxide and oxy hydroxide and blue green algal mats from the soil normally contribute iron content to the calcrete[6,17]. But, they are limited in the study area. The clay minerals sesqui-oxide preservation in the calcrete may be due to the water logging which may favour for mobility of ferrous iron[6,14]. The correlation of Fe_2O_3 and Al_2O_3 shows positive correlation (r = 0.9). This may be due to preservation of sesqui – oxide (Fe_2O_3 and Al_2O_3) in calcrete[13,14]. Such above similar conditions are concentrated in the study area. The presence of the silica concentration may be due to the unaltered detrital quartz and feldspar grain in the soil profile. The other oxides MnO, Na_2O, TiO_2 and P_2O_5 are less significance in geochemical interpretation of calcrete of the study area. In general, alkaline groundwater derived from the source rocks of the calc-alkaline and per-alkaline basement rocks and black soil under the arid and semi arid climatic conditions are responsible for the formation of calcrete in the study area.

Conclusion

Calcrete occur as a widespread deposit as sub aerial duri crust exposure with a thickness of profile from 1m to 1.25m and it rest over the weathered metamorphic rocks. The occurrence of calcretes in the study area is in the form of gravel, massive, hardpan, lumby and chalky nature. The microscopic study reveals that the micritic and microsparitic calcite deposition which makes rimming, veining, void, colloform, peloidal, displacive and replacive structure with the sap rock minerals grains. Sesqui-oxide features are common features which observed in the calcitic matrix of calcrete. Geochemistry of calcrete illustrates that CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 and TCO_3 are in the elevated concentration than the other oxides. The GIS based spatial contour maps of CaO and TCO_3 would definitely help for the industrial people to locate the source of the high $CaCO_3$ content calcrete sources in the study area. The $CaCO_3$ rich water derived from the sources of calc-alkaline and per-alkaline rocks and black soil under the influence of arid and semi arid climatic condition which makes calcrete development in the study area.

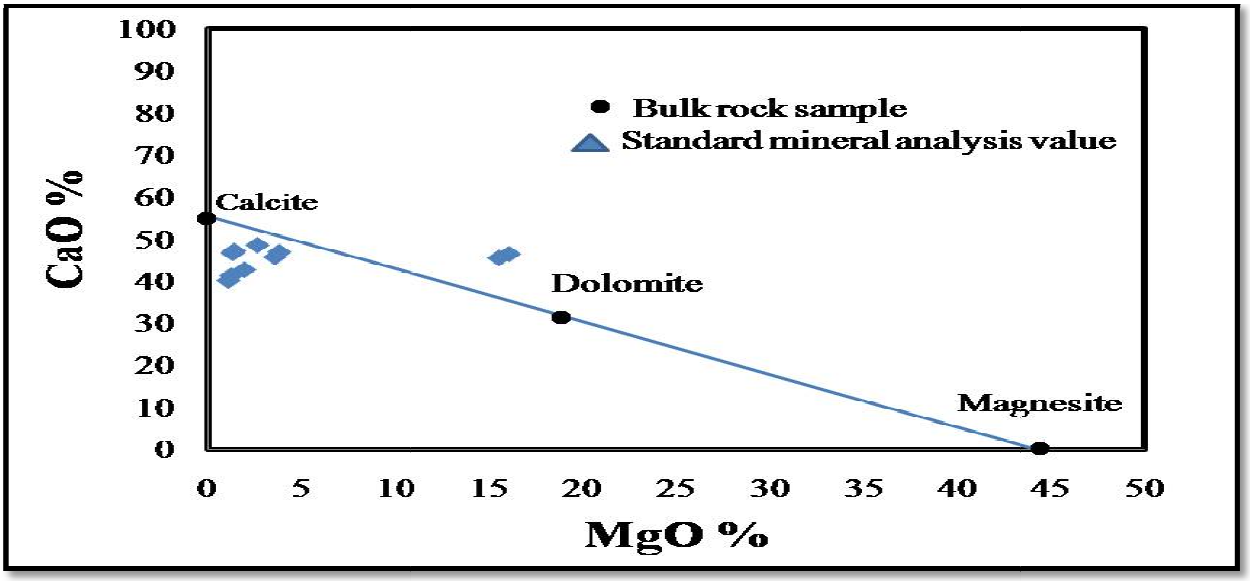

Figure-7: Bivariate plot MgO Vs CaO [6,14,19].

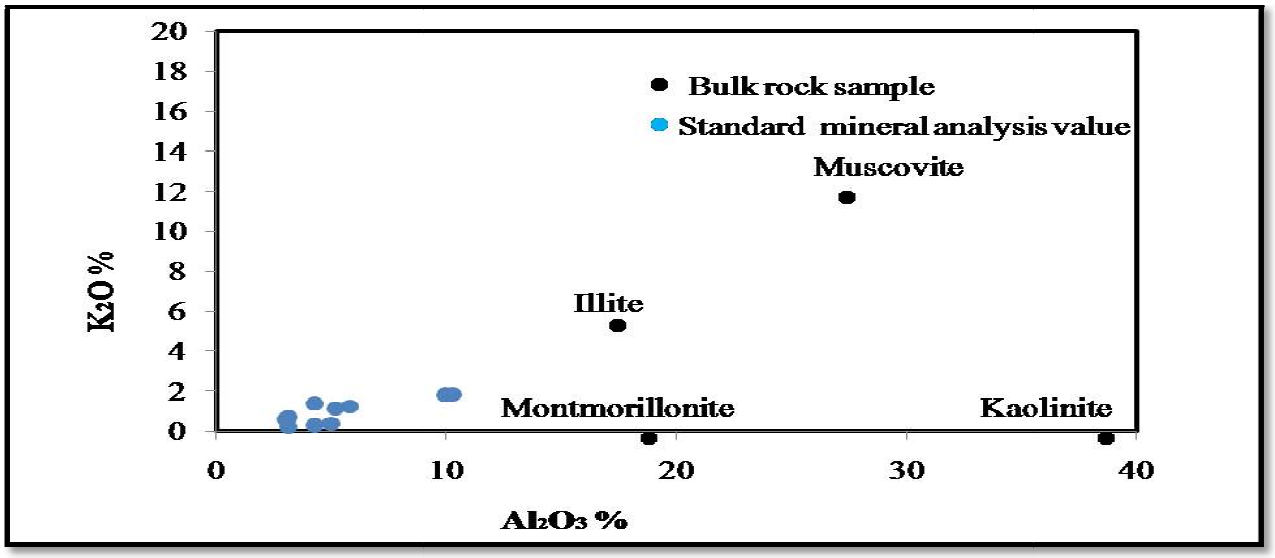

Figure-8: Bivariate plot K_2O Vs Al_2O_3 [6,14,19].

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