Geochemical Characterization of Garudamangalam Limestone Cretaceous of Ariyalur Tamilnadu, India

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Abstract: ***Geochemical studies were carried out from the Garudamangalam (Trichinopoly) formation Cretaceous of Ariyalur, Tamilnadu, India. For this idea, major, minor and Trace elements were resolute by XRF from the limestone samples. Difference of CaO contented with other oxides is ascribed to the variation in the physico-chemical condition throughout the period of deposition. Higher proportion of Ca with the occurrence of Fe_2O_3 indicates a blocked basin under dipping environment. Occurrence of iron oxide also indicates reducing environment. Ca/Mg ratio was used to determine the salinity and evaporation condition. The higher percentage of Ca/Mg ratio in the limestones signifies lower salinity in the area of deposition near to the shoreline. MgO against Fe_2O_3, Al_2O_3 shows negative correlation against CaO. SiO_2 shows positive correlation with MgO and Fe_2O_3 while that of CaO shows negative correlation. Increase of SiO_2 content with the influx of terrigenous material indicates change of depositional environment. The limestones of different units are categorized as Magnesium and Pure Limestone on the basis of high Ca/Mg ratio. Presence of phosphate and manganese in the limestone is indicative of warm and humid climate. The higher amount of Fe_2O_3 in limestone lowers the absorption capacity with lowers the rate of ignition. The trace elements data indicate the formation of the limestones in the proximity of the shoreline***

Keywords: Geochemistry, Limestone, Garudamangalam, Cretaceous, Correlation.

1. Introduction

Chemical investigation is of extraordinary amount and assists in determining the share and shared relationship of the mixture of component elements of limestone. Such investigation moreover help in classification and in determining the ecological circumstances that prevailed through the deposition of the limestone for it's a combination of feasible uses. Performance the further than cooperation in cleverness chemical analysis of a little samples of limestones from Garudamangalam formation. Limestones were conceded out for purpose of chemical composition, classification, share and mutual relationships of the elements and to decipher ecological state throughout the instance of deposition of calcareous sediments. These types of studies were made by dissimilar research workers from time to time (Singh and Anand, 1991; Das et.al, 2004, Das and Das, 2010, Bhattacarjee and Das, 2008 and Moloi Bora et.al, 2013).

1.1 GEOLOGICAL SETTING

The Trichinopoly Group (later redesignated as Garudamangalam) has unconformable relationship with underlying Uttatur Group and is divided into lower Kulakanattam formation and upper Anaipadi Formation (Sundaram and Rao, 1986). The Kulakanattam Formation comprises of conglomerate bands, hard calcareous sandstone, fossilliferous limestone, pebbly and cobbly sandstone, soft sandstone, clays, shales and silt. The lower portion is mainly composed of hard calcareous sandstone bands which are conglameratic in nature. The middle portion is predominantly clays while the upper one is made up of sequences of shell limestone, soft sandstone, Calcareous shales and clays. The maximum width of 5.5km is noticed in the southern portion of the basin, which gradually narrows down towards the north-east (50 to 100m). A conglomerate band with 700 m width is noticed near Kottarai which is formed due to Kottarai which is formed due to intense drag folding (Sundaram and Rao, op.cit).Anaipadi Formation is further divided into two members, the lower member comprises of shale, silt, sandy clays, limestone bands and calcareous sandstone. It is well developed near Anaipadi village and the total thickness is about 164 m. The upper member is mainly composed of yellowish or reddish sands/sandstone with minor bands of fossiliferous grit. The total thickness is around 75 m and these two members merge towards the northern end. As a result an yellowish sandy clay and lenses of highly fossiliferous calcareous sandstone occur alternatively. These two members merge into a sequence of alternating shale, clay and soft argillaceous sandstone beds towards its southern extremity.

In the Tiruchirapalli Cretaceous, the outcrops of Ariyalur Group are exposed over a greater areal extent than any other group in this area. These rocks unconformably lie over the Trichinopoly Group in the central and southern part while in the northern part it directly rests on the Archaean rocks overlapping the Trichinopoly and Uttatur Groups. These rocks are succeeded by the Niniyur Group in the northeastern side and by the Cuddalore Sandstone (Mio-Pliocene) towards east. For the present study, lithostratigraphic classification of Garudamangalam Formation (Trichinopoly Formation) as proposed by Ramasamy and Banerji (1991) has been followed. This scheme is much appropriate for the description of litho-units in the field and can be effectively used for sedimentological studies across litho-units. Garudamangalam Formation consists three formations, namely Kottarai, Anaipadi and Kulattur Members (Ramasamy and Banerji, 1991). The lower most Kottarai Member is a gritty calcareous sandstone containing some fossil fragments and is exposed in the form of a linear band Sundaram and Rao (1979). The middle Anaipadi Member consists of Yellowish brown sandy limestone crowded with large shells of pelecypods and other molluscus and echinoderms. The Upper most-Kulattur Member is composed of Yellowish calcareous sandstone.

The rocks of the Garudamangalam Formation show a transgressive onlap relationship with the Uttatur and Dalmiapuram Formations (Banerji, 1972). The upper contact with the overlying Ariyalur Formation is marked by an angular unconformity. The study area map shown in fig.1.

1.2 METHODOLOGY

Geochemical (XRF) analysis of 10 limestone samples for Major oxide proportion and Trace element (ppm) from the study area was done Table 1&2. XRF study was carried out by R&D Center, India Cements, Dalavoi, Ariyalur. The qualitative and quantitative estimations of different oxides present in the samples were made. The shared associations of dissimilar oxides were studied and the Mg:Ca ratios were utilized to categories the limestone and to realize their surroundings deposition.

Oxides and their shared relationships:

Some oxides and their shared relations are shown below:

Silicon di-oxide (SiO_2), comfortable varies from to % Table1. Bivariant plots of SiO_2 Vs CaO fig.1 show negative correlation, which thus indicates that the SiO_2 proportion decrease with add to of CaO.

1.3 Calcium Oxide (CaO)

Calcium Oxide (CaO), vary from to % Table 1. Bivariant plots of SiO_2 with MgO Fig.2 show negative relationship, its indicate MgO percentage add to with reduce of CaO.

1.4 *Magnesium Oxide (MgO)*

Magnesium Oxide (MgO), % to in Garudamangalam Limestone Table.1. Concentration of SiO_2 Vs MgO and Fe_2O_3 (Fig.3) shows optimistic correlation, and with Fe_2O_3 it shows pessimistic correlation, which thus indicates that, the MgO proportion increases with leakage of CaO &Fe_2O_3 by resolution (Chilinger, 1956).

1.5 Aluminium Oxide (Al_2O_3)

Aluminium Oxide (Al_2O_3) is establish to be changeable from to % Table1. Al_2O_3 Vs CaO plot shows a unenthusiastic correlation fig.5.

1.6 Iron Oxide (Fe_2O_3)

Iron Oxide (Fe_2O_3), the allocation of Fe_2O_3 is establish to be unreliable from to % in Garudamangalam limestone Table1. The bivariant plots of Fe_2O_3 adjacent to SiO_2 (Fig.6 B) optimistically corrlelated Fig.6 (A,B) while pessimistically with MgO and CaO. The variation (increase and decrease) in Fe_2O_3 contented may be connected with terrigenous incursion linked with elevated Iron behavior solutions. The elevated amount of Fe_2O_3 in carbonate rocks lower the assimilation competence with lower the pace of explosion of the samples.

1.7 Other Oxide

MnO_2, Na_2O, K_2O, TiO_2, P_2O_5, S and LOI are the additional constituent here in the limestone samples. The percentages are shown in Table-1.

2. Chemical Classification

Ca/Mg and Mg/Ca Ratios

The allocation of Ca/Mg and its reciprocal Mg/Ca ratio in Garudamangalam limestone’s were utilized by Todd (1966) Table 3 as a parameter for chemical classification. Table.4 Ca/Mg ratios from 62.68% to 21.17% and Mg/Ca ratios vary from 0.02% to 0.05%. Marshner (1968) pointed that Ca/Mg ratio is indicative of stability condition during the formation of carbonate rocks and any decrease in Ca/Mg ratio is related to corresponding increase in salinity. The high concentration of Ca/Mg ratio indicates comparatively less evaporation of sea water during the time of limestone deposition.

The Ca/Mg ratio of carbonate rocks are balanced to dolomite/calcite ratio and Mg/Ca ratio of carbonate sediments augment on going away from the shoreline which is related with the abundance of Mg rich coralline algae in near shore water. The data in the present case indicates the Garudamangalam limestone falls in both Pure Limestone and Magnesian Limestone category and deposition takes place in the immediacy of the shoreline Moloi Bora et.al.(2013). The data in the present case indicates the samples such as NLR-52, KNM-32 and KKD-62 falls in Pure Limestone category indicates the deposition takes place away from the shoreline. Higher values of Ca/Mg ratio of the studied carbonate indicates comparatively less evaporation of sea water and low salinity that prevailed during the formation of limestone in general.

3. Trace Elements Analysis

The elements analysis of carbonate rocks provides important data on the sedimentary and digenetic history. X-ray florescence study (XRF) are used for determining the contents of trace elements in carbonate rocks by whole-rock and selective analyses (Fairchild et.al, 1988). Minor elements in carbonate rocks are important palaeo environmental indicators. The geochemical techniques such as trace elements, in particular, strontium content is considered a helpful tool in understanding the origin and diagenesis of carbonate rocks. Trace element analysis has been used in the differentiation of shallow and deep water limestone. According to Wedepohl (1970) the majority of the trace elements known in carbonate rocks are bounded to the detrital silica oxide fraction of the limestone. The distribution of the abundances of the trace elements of the study area in ppm are measured Table 4.

4. Strontium

Trace elements data have been useful in differentiation of shallow water from deep water limestones. Sr and Mn are linked in specific ways with the carbonate phase. Shallow marine limestones are characterized by low Mn content while those of deeper marine are associated with high Mn content. Shallow water and deep water carbonates also have relatively low Sr (100-400 ppm) and high Sr values respectively (Ofulume, 2012). The average strontium (Sr) concentration of Garudamangalam limestone ranges from with an average 1038 ppm suggesting a relatively deeper environment (500-3000ppm; Flugel and Wedepohl, 1967; Bausch, 1968).

The high ppm of Strontium (Sr) concentration in Garudamangalam Limestone might also indicates the formation of the limestone under high salinity environmental condition. Anderson (1974) explained the effect of low water salinity on the depletion of strontium, so precipitations under high saline environment contain high concentration of Strontium.

1.1 Copper

The concentration of Cu is very low in Garudamangalam limestones (16-43ppm). The association of copper with carbonate rocks is very limited and it is generally restricted to the non-carbonate constituents. However, Deurer et.al (1978) suggested a possible association of copper with carbonates. Pyrites seems to represent the most important carrier of Cu, since Cu have strong chalcophile character. Clay minerals may also accommodate some amount of copper in traces. Clay in association with Copper (Cu) is considered a diagnostic mineral indicative of shallow continental shelf marine depositional enviromments with slow rates of accumulation.

1.2 Vanadium

The concentration of Vanadium (V) ranges from (40-99ppm) in Garudamangalam limestone and indicative of shallow continental shelf marine depositional environments. In the scatter plots Vanadium (V) shows a negative (-ve) correlation with CaO and Positive (+ve) correlation with MgO. Fig.6 & Vanadium (V) content of the limestone increases with the increase of MgO content, which suggest that when the CaO decreases, magnesium together with the Vanadium (V) comes out from the solution (Friedman, 1968 a&b).

5. RESULT AND DISCUSSIONS

The allocation of Ca/Mg ratio in the Garudamangalam formation limestone samples descend two categories i.e., Magnesian and Pure Limestones. In the present case, the high absorption of Ca/Mg ratio indicates moderately fewer vanishing of marine water throughout the time of limestone deposition. The Ca/Mg ratio of carbonate rocks are in proportion to dolomite/calcite ratio and Mg/Ca portion of carbonate sediments add to continuing absent from the beach which is connected with the profusion of Mg rich coralline algae in close to beach water. The information in the present case indicates deposition in the nearness of the beach. The information in the present case indicate the Garudamangalam formation descend in equally pure limestone and Magnesian limestone category and the deposition takes place in the nearness of the beach.

The Cao content decreases with increase of other oxides present in the limestones. This calcium may due to leaching of calcium by solution and subsequent reprecipitation. Change of environment is indicates by the increase of SiO2 content with the influx of terrigenous material (Baishya and Mahanta, 1994). The high Ca/Mg ratio indicates comparatively less evaporation of sea water and less salinity during the formation of Garudamangalam formation (Marshner, 1968). Presence of Fe2O3 and high Ca indicates reducing environment and deposition in closed basin (Wolf et.al, 1967). Presence of few amounts of phosphate and manganese in the limestone indicats a warm and humid climate during the deposition of carbonate sediments (Kotoky and Kataky, 1993).

Concentration of CaO plotted against SiO_2, MgO,Fe_2O_3, Al_2O_3 (Fig.) shows negative correlation. This thus indicates that the CaO percentage decrease with increase of SiO2/MgO/Fe2O3/Al2O3.

Bivariant plots of Al_2O_3 against CaO shows negative correlation and calcium decrease in magnesium rich limestone (7 localities) as compared to the pure limestone (3 localites) table.3. It indicates magnesium become enriched when the CaO is removed by leaching in the solution process the magnesian limestone formed.

The high ppm of Strontium (Sr) concentration Garudamangalam limestone might also indicates the formation of the limestone under higher salinity environmental condition.

Vanadium (V) content of the limestone increases with the increase of MgO content, which suggests that when the CaO decreases, magnesium together with the vanadium comes out from the solution during diagenesis.

6. Concluson

The geochemistry of the Garudamangalam limestone indicates that extremely little quantity of Cu it's indicate small quantity of argillaceous sediments and the associations surrounded by the major oxide mechanism indicates that the argillaceous sediments were resulting from bioclasts i.e., benthic **foraminifera** during the process of formation and diagensis.

The information in the present case indicate the garudamangalam limestone falls in 3 Pure limestone and 7 Magnesium limestone group and the deposition takes place in the closeness of the beach.

Higher values of Ca/Mg ratio of the studied limestone indicates moderately fewer evaporation of sea water and low salinity that prevailed throughout the formation of limestone.

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References

[1]1 Anderson, J. W., 1974: Influence of salinity and temperature on the O_2 consumption of Neanthes arenaceodentata Moore. Am. Zool. 14, 1260.

[2] Baishya, D. K. and Mahanta, S.K., 1994: A Geochemical Study of Sylhet Limestone around Umrangchu Area, North Cachar Hills District, Assam. Bull. Ind. Geol. Assoc., Vol. 27 (1), pp. 63-67.

[3] Bausc, W. M., 1968: Outlines of distribution of strontium in marine limestones. In: Muller, G. and Friedman, G. M. (Eds.), Recent Developments in Carbonate Sedimentology in Central Europe, Springer, 106 -115.

[4]Bhattacharjee, A. and Das P. K., 2008: Geochemical Study of the Lakadong Limestone occurring in and around Cherrapunjee, Khasi Hills, Meghalaya, Bull.

Geo. Sci., Vol. 3 (1), pp 17-23.

[5] Carver, R. E., 1970: Procedures in Sedimentary Petrology. Wiley Interscience.

[6] Chilinger, G. V. 1956: Relationship between Ca/Mg ratio and geological age. Bulletin of American Association of Petroleum Geology 40, pp2225-2226.

[7] Das, P. K, Barthakur, P and Gogoi, A., 2004: Geochemical study of Lakadong (Tertiary) Limestones occurring in and around Mawsynram, East Khasi Hills District of Meghalaya, Vol. 6(2), pp 373-380.

[8] Das, P. K and Das M.M., 2010: Geochemical Study of the Prang Limestone of Shella Formation occurring in and around Lumshnong of Jaintia Hills, Meghalaya, India, Jour. Assam Sci. Soc., Vol. 51 (2), pp 150-160.

[9] Deurer, R., Forstnor, U., Schmoll, G., 1978: Selective chemical extraction of carbonate-associated metals from recent lacustrine sediments. Geochim. Cosmochimica Acta 42, 425–427.

[10] Flugel, H. W. and Wedepohl, K.H., 1967: Die-vertielung des strontiums in oberjurassicchen karbonatgeserien Der Nordlichen Kalkalpen. Ein Bietrang Zur Dia geneses Von karbonate gesteinen contr Heidelberg. Mineral Petrology 14, 249-299.

[11] Friedman, G. M., 1968a: Geology and geochemistry of reefs carbonate sediments and water, Gulf of Aquba (Elat) Red sea. Journal of Sedimentary Petrology 38, No.3, 893-919.

[12] 12. Friedman, G. M., 1968b: The fabric of carbonate cement and matrix and its dependence on the salinity of water. In: German Muller and Gerald M. Friedman (Eds) Recent Development in Carbonate Sedimentology in Central Europe. Springer-Verlay, 11-26.

[13] Kotoky, P. and Kakaty, T, 1993: Geochemistry of Siju Limestone, West Garo Hills, Meghalaya, Ind. Jour. Geochem. Vol. 8 (1 and 2), pp. 25-36.

[14] Kinsman, D. J. J., 1969: Interpretation of Sr2+ concentration in carbonate minerals and rock. Journal of Sedimentary Petrology 39, 486-508.

[15] Marshner, H., 1968: Ca/Mg Distribution in Carbonates from the Lower Keuper in NW Germany (Development in Carbonate Sedimentology in Central Europe), Ed. pp. 127-135.

[16] Morse, J. W. and Mackenzei, 1990: Geochemistry and Sedimentology Carbonates, Elsevier Amsterdam, pp707.

[17] Murthy, M.V.N., Chakraborty, C. and Talukdar, S. C., 1978: Stratigraphic Revision of the Cretaceous – Tertiary Sediments on the Shillong Plateau. Rec. Geol. Sur. India, Vol. 107 (2), pp80-90.

[18] Ofulume, A. B, 2012: Using Geochemical Criterion To Check The Depositional Environment Derived From Fossil Content And Microfacies Of The Shagamu, Mfamosing And Gboko Limestones, Nigeria; Journal of Applied Sciences Research, 8(1): 371-376, 2012 ISSN 1819-544X.

[19] Pettijohn, F. J., 1975: Sedimentary Rocks, Harper and Row, 3rd Edition, New York, pp. 212.

[20] Singh, N. I. and Anand, R., 1991: Major oxide Geochemistry of Carbonates in Ukhrul Area. Ukhrul District, Manipur, 3rd Manipur Science Congress, Vol. 3, pp. 22-26.

[21] Todd. T. W., 1966: Petrographic classification of carbonate rocks. Journal of Sedimentary Petrology 36(2), 317-340.

[22] Wedepohl, K. H., 1970: Geochemistry data on sedimentary carbonates and carbonate rocks and their facies and

[23] petrogenic evaluation. Verh. Geol. Bundesanst. 4, 692-705.

[24] Wolf, K. H., Easton, A.J. and Warne, S., 1967: Development in Sedimentology Techniques of Examining and Analysing Carbonate Skeletons Minerals in Rocks, pp. 253-341.

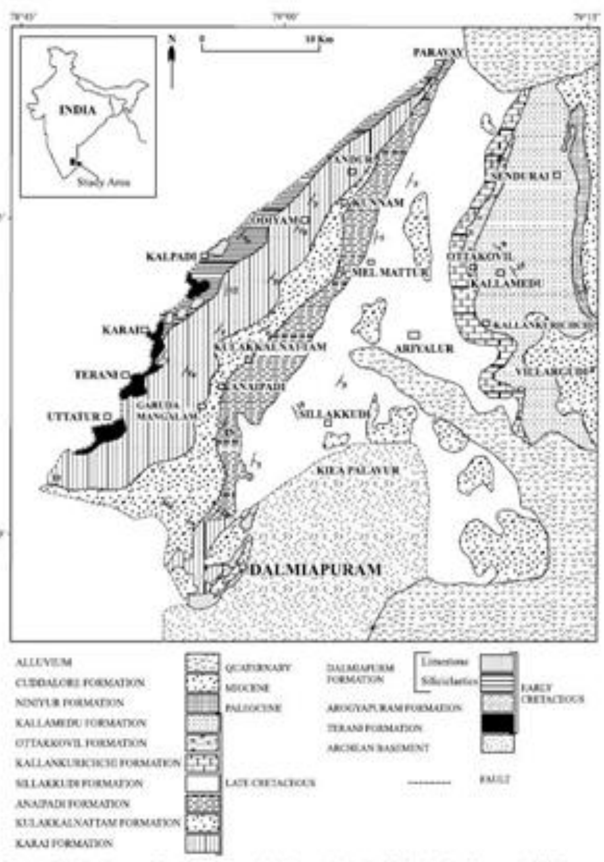

Figure 1. Geological map of the Ariyalur area of the Cauvery basin (modified after Sundaram et al., 2001).

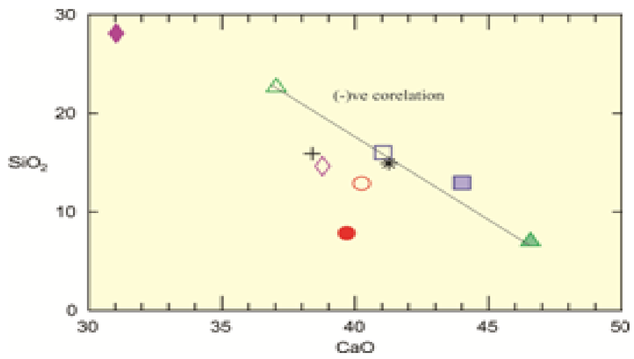

Fig. 2 Mutual Relationship between CaO Vs SiO_2

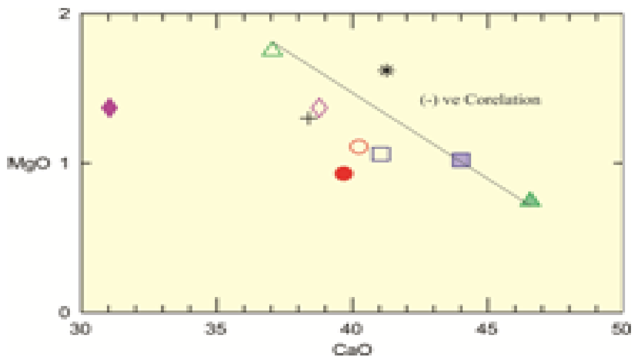

Fig.3 Mutual Relationship between CaO &MgO

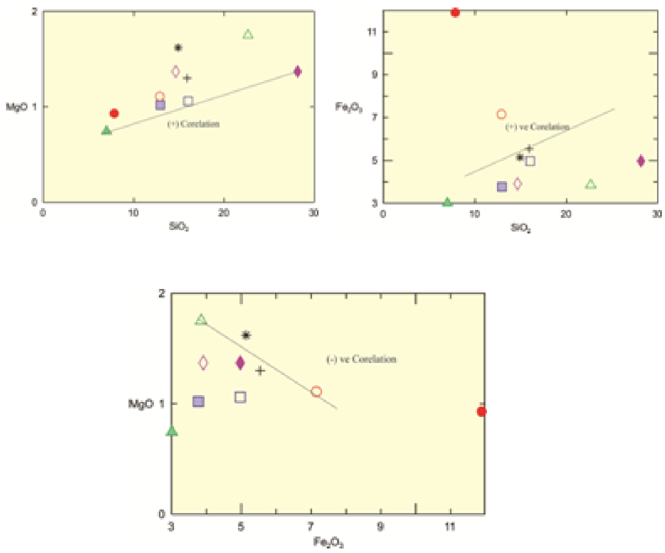

Fig.4: Mutual Relationship between MgO,Fe_2O_3 & SiO_2

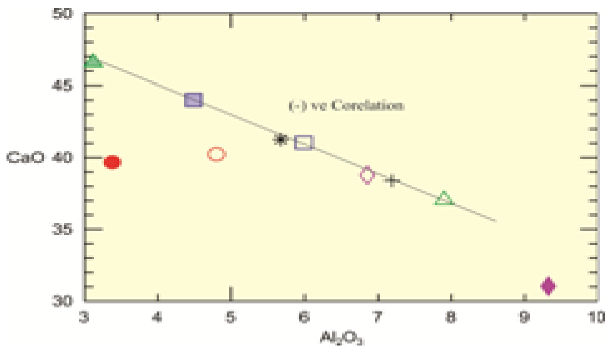

Fig.5 Mutual Relationship between Al_2O_3Vs CaO

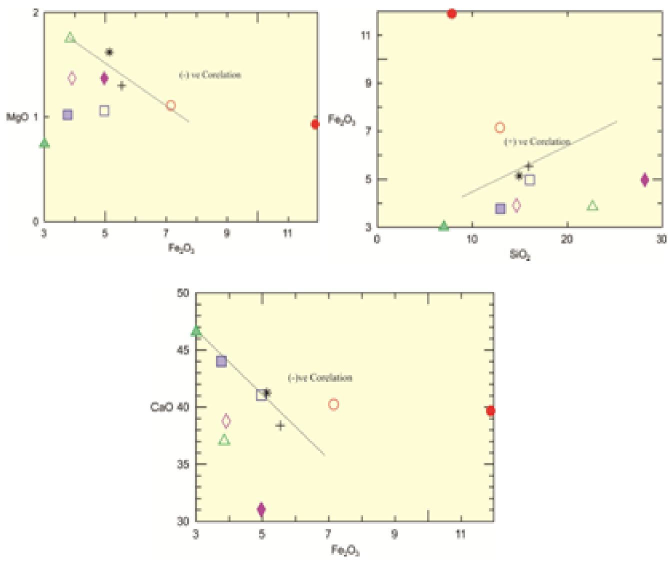

Fig.6 : Shows Mutual Relationship between Fe_2O_3Vs MgO,CaO and SiO_2Vs Fe_2O_3

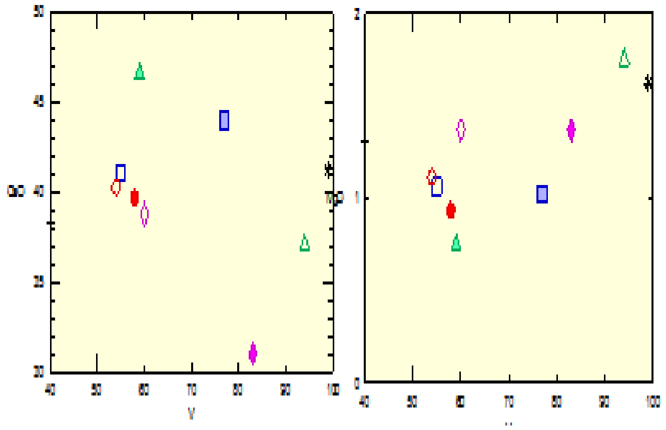

Fig.7 Vanadium Vs MgO and CaO

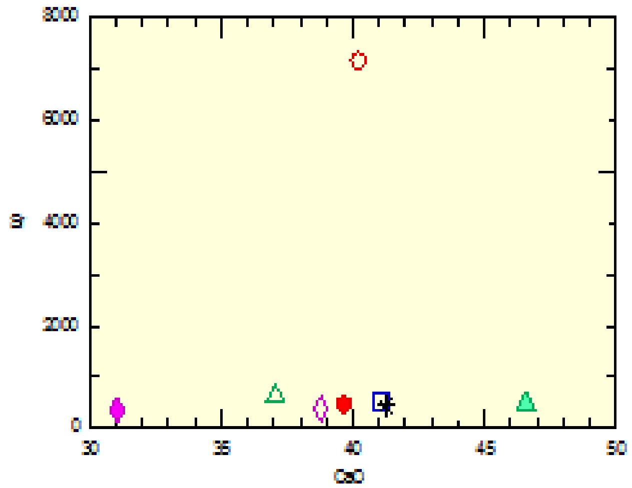

Fig.8 Sr Vs CaO

Table 1: Major Oxides Constituents in Garudamangalam Limestone (XRF Data)

Sample	ADP-51	NLR-52	GDM-46	KNM-32	KMP-1	PL-22	KKM-37	KKD-62	KNM-34	SKR-54
SiO2	22.63	7	16.02	12.95	14.64	28.11	12.89	7.85	15.91	14.92
Al2O3	7.9	3.12	5.99	4.49	6.85	9.32	4.8	3.38	7.19	5.68
Fe2O3	3.85	3.01	4.97	3.77	3.91	4.97	7.15	11.9	5.54	5.14
CaO	37.04	46.57	41.05	44.01	38.78	31.04	40.24	39.68	38.39	41.26
MgO	1.75	0.74	1.06	1.02	1.37	1.37	1.11	0.93	1.3	1.62
S	0.09	0.05	0.08	0.03	0.09	1.73	0.04	0.08	0.07	0.06
Na2O	1.19	0.12	1.08	0.6	0.73	0.7	0.3	0.27	0.61	0.93
K2O	1.14	0.25	0.58	0.54	0.51	0.08	0.58	0.39	0.48	0.78
MnO	0.17	0.47	0.52	0.26	0.24	0.26	0.37	0.45	0.34	0.12
TiO2	0.73	0.19	0.58	0.34	0	0.44	0.25	0.22	0.43	0.46
P2O5	0.11	0.02	0.04	0.03	0.01	0.07	0.04	0.04	0.15	0.12
LOI	22.9	38.21	27.66	31.73	32.24	21.52	31.85	34.71	29.36	28.57
Total	99.5	99.74	99.64	99.78	99.36	99.6	99.62	99.9	99.77	99.65

Table 3: Chemical Classification of Carbonates (after Todd, 1966)

Expressive Name	Average proportion Ca/Mg	Mutual proportion Mg/Ca
Pure Limestone	100.00 – 39.00	0.00 – 0.03
Magnesian Limestone	39.00 – 12.30	0.03 – 0.08
Dolomictic Limestone	12.30 – 1.41	0.08 – 0.18

Table2 Trace element(ppm) constituents of Garudamangalam Limestones

Sample	ADP-51	KNM-34	NLR-52	GDM-46	KNM-32	KMP-1	PL-22	KKM-37	KKD-62	SKR-54
V	94	59	55	77	60	83	54	58	40	99
Zr	295	178	33	234	137	111	76	62	49	126
Ce	-	-	-	104	151	99	-	-	-	-
Ni	61	57	31	46	40	37	58	68	52	131
Co	62	45	-	101	49	40	75	-	46	165
Cr	123	112	47	73	101	83	81	70	40	117
Ga	15	13	8	16	10	9	10	9	9	17
Zn	55	63	29	42	41	59	45	46	0	66
Ba	2516	597	1227	976	329	185	962	0	0	227
Rb	25	13	12	0	16	15	15	24	20	34
Nd	0	0	52	0	46	75	-	-	-	73
Cu	16	25	18	23	18	25	21	-	-	43
Sr	608	476	530	0	374	352	7150	454	-	434
W	151	145	-	285	203	118	408	48	-	489
Cd	88	81	87	86	0	0	70	88	105	-
Y	20	31	-	10	23	13	11	32	37	54
Ag	-	-	-	-	-	-	74	-	-	-
Br	-	-	-	-	-	11	-	-	-	-

Table:4 Chemical Classification of Garudamangalam Formation Limestones

Sample	CaO	MgO	Ca/Mg	Mg/Ca	Name	Locality
ADP-51	37.04	1.75	21.17	0.05	Magnesian Limestone	Anaipadi
NLR-52	46.57	0.74	62.68	0.02	Pure Limestone	Nallur
GDM-46	41.05	1.06	38.73	0.03	Magnesian Limestone	Garudamangalam
KNM-32	44.01	1.02	43.15	0.02	Pure Limestone	Kunnam
KMP-1	38.78	1.37	28.31	0.04	Magnesian Limestone	Kurumbapalayam
PL-22	31.04	1.37	22.66	0.04	Magnesian Limestone	Pilimisai
KKM-37	40.24	1.11	36.25	0.03	Magnesian Limestone	Kulakanattam
KKD-62	39.68	0.93	42.67	0.02	Pure Limestone	Kallakudi
KNM-34	38.39	1.3	29.53	0.03	Magnesian Limestone	Kunnam
SKR-54	41.26	1.62	25.47	0.04	Magnesian Limestone	Sirukalapur