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 \( \text{Fe}_2\text{O}_3 \) 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 \( \text{Fe}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 \) shows negative correlation against CaO. \( \text{SiO}_2 \) shows positive correlation with MgO and \( \text{Fe}_2\text{O}_3 \) while that of CaO shows negative correlation. Increase of \( \text{SiO}_2 \) 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 \( \text{Fe}_2\text{O}_3 \) 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.

Key words: Geochemistry, Limestone, Garudamangalam, Cretaceous, Correlation.

INTRODUCTION
Chemical investigation is of extraordinary amount and assists in determining the share and sharedrelationship 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, Bhattacharjee and Das, 2008 and Moloi Bora et.al, 2013).

The geochemical analysis gives a distinct consideration about the qualitative and quantitative aspect of different major oxides such as \( \text{SiO}_2 \), CaO, MgO, \( \text{Fe}_2\text{O}_3 \), MnO, Na,O, K,O, TiO, P2O, S and LOI. In addition, dissimilar trace elements such as Sr, Mn, Cu,Ni, V, etc. Trace element analysis has been used in the purpose of shallow and deep water limestones.

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.

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

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<tr>
<td>SiO₂</td>
<td>22.63</td>
<td>17.30</td>
<td>16.03</td>
<td>12.95</td>
<td>14.94</td>
<td>26.11</td>
<td>12.95</td>
<td>7.85</td>
<td>16.31</td>
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<td>Al₂O₃</td>
<td>7.95</td>
<td>3.18</td>
<td>6.02</td>
<td>4.39</td>
<td>6.85</td>
<td>3.52</td>
<td>4.8</td>
<td>3.38</td>
<td>7.15</td>
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<tr>
<td>Fe₂O₃</td>
<td>3.88</td>
<td>2.01</td>
<td>4.38</td>
<td>3.77</td>
<td>5.91</td>
<td>4.97</td>
<td>7.15</td>
<td>11.90</td>
<td>5.94</td>
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<tr>
<td>CaO</td>
<td>37.69</td>
<td>48.57</td>
<td>51.25</td>
<td>44.51</td>
<td>50.78</td>
<td>47.74</td>
<td>49.24</td>
<td>36.65</td>
<td>51.39</td>
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<tr>
<td>MgO</td>
<td>1.75</td>
<td>0.74</td>
<td>1.06</td>
<td>1.92</td>
<td>1.97</td>
<td>1.37</td>
<td>1.11</td>
<td>0.90</td>
<td>1.90</td>
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<tr>
<td>LOI</td>
<td>0.09</td>
<td>0.05</td>
<td>0.08</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.04</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.18</td>
<td>0.12</td>
<td>0.09</td>
<td>0.60</td>
<td>0.73</td>
<td>0.70</td>
<td>0.3</td>
<td>0.27</td>
<td>0.61</td>
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<td>K₂O</td>
<td>1.14</td>
<td>0.25</td>
<td>0.09</td>
<td>0.64</td>
<td>0.65</td>
<td>0.65</td>
<td>0.06</td>
<td>0.19</td>
<td>0.19</td>
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<td>MnO</td>
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<td>0.26</td>
<td>0.24</td>
<td>0.25</td>
<td>0.97</td>
<td>0.45</td>
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<td>TiO₂</td>
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<td>0.34</td>
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<td>0.34</td>
<td>0.25</td>
<td>0.22</td>
<td>0.43</td>
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<td>P₂O₅</td>
<td>0.11</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
<td>0.15</td>
</tr>
<tr>
<td>LOI</td>
<td>22.9</td>
<td>38.21</td>
<td>27.36</td>
<td>31.73</td>
<td>32.24</td>
<td>21.52</td>
<td>31.85</td>
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<td>Total</td>
<td>95.85</td>
<td>95.74</td>
<td>95.64</td>
<td>95.78</td>
<td>95.36</td>
<td>95.85</td>
<td>95.63</td>
<td>95.90</td>
<td>95.77</td>
</tr>
</tbody>
</table>

LOI= Loss on ignition

Oxides and their shared relationships:
Some oxides and their shared relations are shown below:

Silicon di-Oxide (SiO₂)

- Fig(1) Mutual Relationship between CaO Vs SiO₂
- SiO₂ Vs CaO plot shows a negative relationship, which thus indicates that the SiO₂ proportion decreases with add of CaO.

Calcium Oxide (CaO)

- Fig(2) Mutual Relationship between CaO & MgO
- CaO Vs MgO fig.2 show negative relationship, its indicate MgO percentage add to with reduce of CaO.

Magnesium Oxide (MgO)

- Fig(3) Mutual Relationship between MgO, Fe₂O₃ & SiO₂
- MgO, % to in Garudamangalam Limestone Table 1. Concentration of SiO₂ Vs MgO and Fe₂O₃ (Fig.3) shows optimistic correlation, and with Fe₂O₃ it shows pessimistic correlation, which thus indicates that, the MgO proportion increases with leakage of CaO & Fe₂O₃ by resolution (Chilinger, 1956).

Aluminium Oxide (Al₂O₃)

- Fig(4) Mutual Relationship between Al₂O₃ Vs CaO
- Al₂O₃ is establish to be changeable from to % Table 1. Al₂O₃ Vs CaO plot shows a unenthusiastic correlation.

Iron Oxide (Fe₂O₃)

- Fig(5) (A,B &C): Shows Mutual Relationship between Fe₂O₃ Vs MgO, CaO and SiO₂ Vs Fe₂O₃
Iron Oxide (Fe2O3), the allocation of Fe2O3 is establish to be unreliable from to % in Garudamangalam limestone Table1. The bivariant plots of Fe2O3 adjacent to SiO2 (Fig.6 B) optimistically correlated Fig.6 (A,B) while pessimistically with MnO and CaO. The variation (increase and decrease) in Fe2O3-contented may be connected with terrigenous incursion linked with elevated Iron behavior solutions. The elevated amount of Fe2O3 in carbonate rocks lower the assimilation competence with lower pace of explosion of the samples.

Other Oxide MnO2, Na2O, K2O, TiO2, P2O5, S and LOI are the additional constituents in the limestone samples. The percentages are shown in Table1(1).

The allocation of Ca/Mg and its reciprocal Mg/Ca ratio in Garudamangalam limestone were utilized by Todd (1966) Table (2) as a parameter for chemical classification. Table. 3 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.

Table(2) Chemical Classification of Carbonates (after Todd, 1966)

Table(3) Chemical Classification of Garudamangalam Formation Limestones

Trace Elements Analysis

The elements analysis of carbonate rocks provides important data on the sedimentary and diagenetic 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 palaeoenvironmental 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.

Table(4) Trace element (ppm) constituents of Garudamangalam Limestones.

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.

Copper

The concentration of Cu is very low in Garudamangalam limestones (16-43ppm). The association of copper with carbonate
rally 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 environments with slow rates of accumulation.

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).

**CONCLUSION**

The geochemistry of the Garudamangalam limestone indicates that extremelylittlequantity of Cu it’sindicatesmallquantity of argillaceous sediments and the associationssurrounded 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 moderatelyfewer evaporation of sea water and low salinity that prevailed throughout the formation of limestone.

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**References**