

## GEOCHEMICAL STUDY OF LIMESTONES OF SHELLA FORMATION OCCURRING IN AND AROUND SHELLA-ISHAMATI AREA, EAST KHASI HILLS DISTRICT, MEGHALAYA, INDIA

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### ABSTRACT

Geochemical studies were carried out from the three Limestone Members (Lower Tertiary) of Shella Formation, Jaintia Group occurring around Shella-Ishamati area of East Khasi Hills District of Meghalaya. For this purpose, major, minor and trace elements were determined by XRFS from the limestone samples. Variation of CaO content with other oxides is attributed to the fluctuation in the physico-chemical condition throughout the period of deposition. Higher percentage of Ca with the presence of Fe<sub>2</sub>O<sub>3</sub> indicates a closed basin under reducing environment. Presence 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 shore line. MgO against Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> shows negative correlation against CaO. SiO<sub>2</sub> shows positive correlation with MgO and Fe<sub>2</sub>O<sub>3</sub> while that of CaO shows negative correlation. Increase of SiO<sub>2</sub> content with the influx of terrigenous material indicates change of depositional environment. The limestones of different units are categorized as Magnesium and Pure Limestones on the basis of high Ca / Mg ratio. Presence of phosphate and manganese in the limestones is indicative of warm and humid climate. The higher amount of Fe<sub>2</sub>O<sub>3</sub> in limestones 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 Members, Shella Formation, Shella, Ishamati (Meghalaya)

### INTRODUCTION

Chemical analysis is of tremendous importance and aid in determining the distribution and mutual relationships of the various constituent elements of limestones. Such analysis also helps in classification and in determining the environmental conditions that prevailed during the deposition of the limestones for its various commercial uses.

Keeping the above usefulness in mind chemical analyses of a few samples of limestones from three limestone members namely Lakadong, Umlatdoh and Prang Limestones were carried out for determination of chemical composition, classification, distribution and mutual relationships of the elements and to decipher environmental condition during the time of deposition of calcareous sediments. These types of studies were made by different research workers from time to time (Singh and Anand, 1991; Das et. al, 2004, Das and Das, 2010, Bhattacharjee and Das, 2008).

The geochemical analysis gives a precise idea about the qualitative and quantitative aspects of different major oxides such as SiO<sub>2</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, S (as SO<sub>2</sub>) and LOI. Moreover, different trace elements such as Sr, Mn, Cr, Cu, Ni, V, etc. Trace element analysis has been used in the differentiation of shallow and deep water limestone.

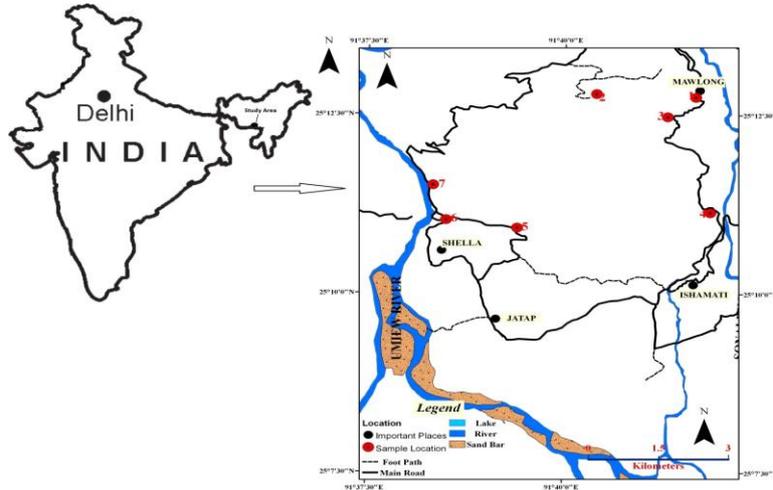


Figure 1: Location Map of the Study Area from Mawlong to Ishamati up to Shella, Meghalaya, India

**GEOLOGICAL SETTING**

Shella Formation of the Jaintia Group of lower Tertiary age (Eocene) is well exposed in and around Shella-Ishamati area, Khasi Hills District, Meghalaya. The location map of the study area is shown in Figure 1.

Shella Formation is the lowermost lithounit of the Jaintia Group and comprise of three alternating sandstone and limestone members. The lowermost member of the formation is the Therria Sandstone. This sandstone member is characterised by coarse grained sandstones with intercalated limestone. This member is overlain by Lakadong Limestone which is composed of hard, massive and bedded, compact, ash-grey, fossiliferous limestone. The Lakadong Limestone Member is overlain by Lakadong Sandstone which is dirty white, light yellow, and occasionally buff in colour, course grained to medium grained, fining upwards which takes more argillaceous character towards top. The Lakadong Sandstone is overlain by Umlatdoh Limestone and is composed of hard, compact, fine grained, dark-grey, massive, limes tones and less fossiliferous. The Umlatdoh Limestone is overlain by Narpuh Sandstone which is dirty white, fine grained to coarse grained with calcareous girt and occasional thin limestone. Narpuh Sandstone is overlain by Prang Limestone which is the uppermost Shella Formation. It is characterized by hard, compact, grey colored, highly fossiliferous, massive limestone Figure 2.

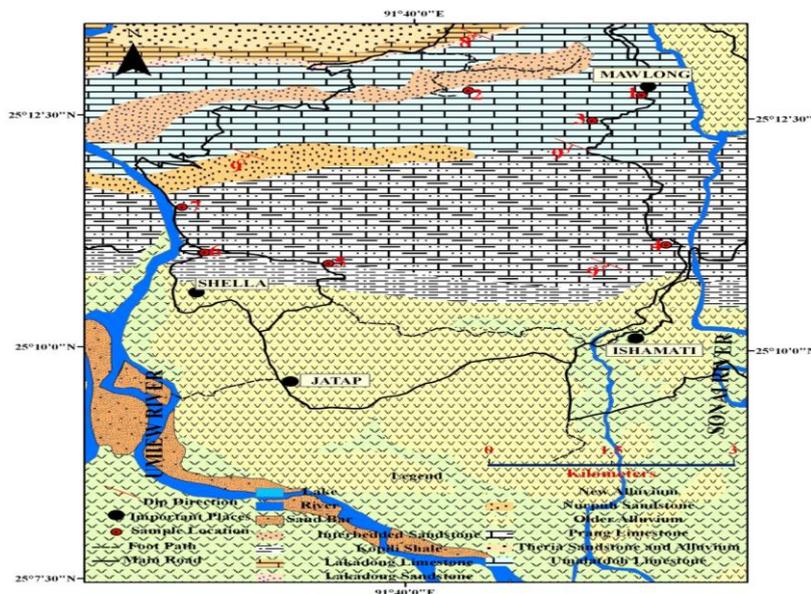


Figure 2: Geological Map of the Study Area from Mawlong to Ishamati up to Shella

**METHODOLOGY**

Geochemical (XRFS) analysis of 28 samples for Major oxide percentage and 18 samples for Trace elements of limes tones from the study area was done Table 1&2. X-ray Fluorescence spectroscopic study was carried out by Spectrometer at USIC, Gauhati University. The qualitative and quantitative estimations of different oxides present in the samples were made. The mutual relationships of different oxides were studied and the Mg: Ca ratios were utilized to categorise the limes tones and to understand their environment of deposition.

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

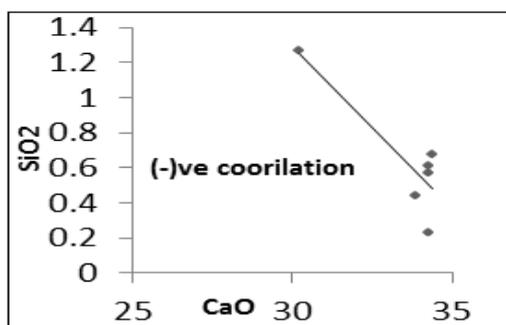
| Sl. No. | Sample_No. | CaO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | TiO <sub>2</sub> | Mn <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | S*   | LOI** |
|---------|------------|-------|------------------|--------------------------------|--------------------------------|------|------------------|--------------------------------|-------------------------------|-------------------|------------------|------|-------|
| 1       | PRL 1      | 51.04 | 0.27             | 0.35                           | 0.12                           | 1.26 | 0.01             | 0.02                           | 0.02                          | 0.06              | 0.02             | 0.08 | 46.75 |
| 2       | PRL 2      | 50.99 | 0.26             | 0.39                           | 0.16                           | 1.48 | 0.01             | 0.02                           | 0.02                          | 0.06              | 0.01             | 0.05 | 46.55 |
| 3       | PRL 3      | 48.98 | 0.43             | 0.32                           | 0.25                           | 1.18 | 0.01             | 0.02                           | 0.02                          | 0.41              | 0.02             | 0.22 | 48.14 |
| 4       | PRL 4      | 34.69 | 0.34             | 0.38                           | 0.26                           | 2.57 | 0.01             | 0.02                           | 0.01                          | 0.06              | 0.03             | 0.03 | 61.6  |
| 5       | PRL 5      | 34.41 | 0.27             | 0.48                           | 0.28                           | 2.06 | 0.01             | 0.02                           | 0.01                          | 0.07              | 0.03             | 0.02 | 62.34 |
| 6       | PRL 6      | 50.08 | 0.83             | 0.56                           | 0.39                           | 1.38 | 0.02             | 0.02                           | 0.04                          | 0.07              | 0.03             | 0.05 | 46.53 |
| 7       | PRL 7      | 29.58 | 6.59             | 1.98                           | 0.95                           | 2.11 | 0.12             | 0.03                           | 0.02                          | 0.04              | 0.48             | 0.02 | 58.08 |
| 8       | PRL 8      | 29.34 | 3.39             | 1.36                           | 0.53                           | 2.75 | 0.12             | 0.06                           | 0.01                          | 0.03              | 0.26             | 0.01 | 62.14 |
| 9       | PRL 9      | 30.1  | 0.03             | 1.98                           | 1.61                           | 1.75 | 0.46             | 0.23                           | 0.14                          | 0.15              | 0.07             | 0.01 | 63.47 |
| 10      | PRL 10     | 48.79 | 1.78             | 0.75                           | 0.87                           | 1.28 | 0.04             | 0.02                           | 0.05                          | 0.26              | 0.08             | 0.14 | 45.94 |
| 11      | PRL 11     | 49.6  | 1.32             | 0.36                           | 0.52                           | 1.21 | 0.03             | 0.02                           | 0.03                          | 0.04              | 0.03             | 0.05 | 46.79 |
| 12      | PRL 12     | 50.69 | 2.01             | 0.71                           | 0.96                           | 1.27 | 0.05             | 0.02                           | 0.04                          | 0.06              | 0.08             | 0.19 | 43.92 |
| 13      | UML 1      | 50.96 | 0.59             | 0.72                           | 0.27                           | 1.71 | 0.02             | 0.02                           | 0.04                          | 0.06              | 0.05             | 0.43 | 45.13 |
| 14      | UML 2      | 34.37 | 0.16             | 0.58                           | 0.38                           | 1.71 | 0.01             | 0.02                           | 0.02                          | 0.13              | 0.04             | 0.04 | 62.54 |
| 15      | UML 3      | 33.59 | 0.08             | 0.56                           | 0.23                           | 1.78 | 0.01             | 0.02                           | 0.03                          | 0.06              | 0.02             | 0.13 | 63.49 |
| 16      | UML 4      | 49.23 | 0.26             | 0.31                           | 0.28                           | 1.12 | 0.01             | 0.02                           | 0.01                          | 0.05              | 0.01             | 0.2  | 48.5  |
| 17      | UML 5      | 50.44 | 0.23             | 0.29                           | 0.37                           | 1.06 | 0.01             | 0.02                           | 0.01                          | 0.05              | 0.02             | 0.02 | 47.48 |
| 18      | UML 6      | 49.88 | 0.23             | 0.28                           | 0.43                           | 1.17 | 0.01             | 0.02                           | 0.02                          | 0.06              | 0.02             | 0.06 | 47.82 |
| 19      | UML 7      | 49.96 | 0.18             | 0.87                           | 0.37                           | 1.24 | 0.01             | 0.03                           | 0.03                          | 0.05              | 0.03             | 0.1  | 47.13 |
| 20      | UML 8      | 49.68 | 0.23             | 0.67                           | 0.59                           | 1.06 | 0.01             | 0.02                           | 0.01                          | 0.05              | 0.04             | 0.02 | 47.62 |
| 21      | UML 9      | 30.43 | 6.88             | 1.63                           | 0.69                           | 1.93 | 0.03             | 0.1                            | 0.07                          | 0.31              | 0.06             | 0.04 | 57.83 |
| 22      | UML10      | 29.83 | 6.15             | 1.98                           | 1.47                           | 1.75 | 0.02             | 0.02                           | 0.12                          | 0.27              | 0.14             | 0.07 | 58.18 |
| 23      | LDL 1      | 33.87 | 0.44             | 0.79                           | 0.42                           | 1.41 | 0.05             | 0.02                           | 0.05                          | 0.14              | 0.36             | 0.06 | 62.39 |
| 24      | LDL 2      | 34.38 | 0.68             | 0.39                           | 0.49                           | 1.4  | 0.02             | 0.02                           | 0.02                          | 0.01              | 0.11             | 0.19 | 62.29 |
| 25      | LDL 3      | 34.27 | 0.57             | 0.59                           | 0.48                           | 1.12 | 0.02             | 0.02                           | 0.02                          | 0.01              | 0.08             | 0.05 | 62.77 |
| 26      | LDL 4      | 34.26 | 0.61             | 0.57                           | 0.79                           | 1.37 | 0.02             | 0.02                           | 0.02                          | 0.01              | 0.08             | 0.2  | 62.05 |
| 27      | LDL 5      | 34.27 | 0.23             | 0.75                           | 0.78                           | 1.84 | 0.01             | 0.02                           | 0.01                          | 0.01              | 0.04             | 0.02 | 63.02 |
| 28      | LDL 6      | 30.19 | 1.27             | 1.99                           | 0.88                           | 1.73 | 0.04             | 0.09                           | 0.02                          | 0.01              | 0.05             | 0.08 | 64.65 |

\*\*LOI = Loss of Ignition, \*S = SO<sub>2</sub>

Oxides and their Mutual relationships:

Some oxides and their mutual relationships are shown below:

**Silicon di-Oxide (SiO<sub>2</sub>)**



**Figure 3: Mutual Relationship between CaO & SiO<sub>2</sub> (Lakadong Limestone)**

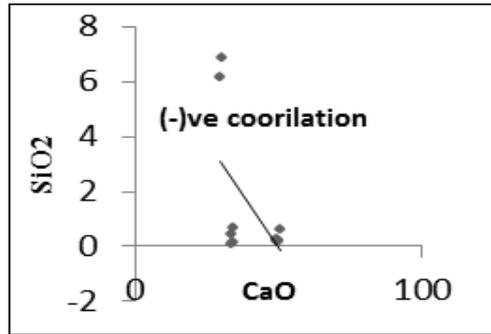


Figure 4: Mutual Relationship between CaO & SiO2 (Umlatdoh Limestone)

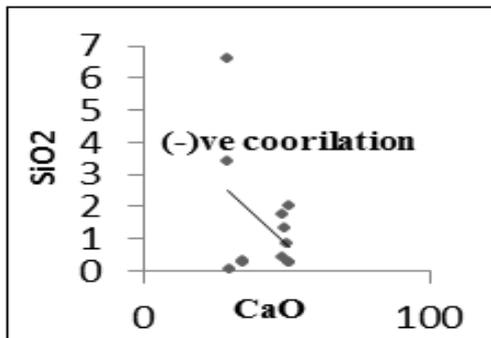


Figure 5: Mutual Relationship between CaO & SiO2 (Prang Limestone)

Silicon di-oxide (SiO<sub>2</sub>), content varies from 0.23% to 6.27% in Lakadong Limestone, in Umlatdoh Limestone 0.08% to 6.88% and in Prang Limestone 0.03% to 6.59% Table 1. Bivariant plots of SiO<sub>2</sub> with MgO and Fe<sub>2</sub>O<sub>3</sub> Figures 3, 4 & 5 show positive correlation, while that with CaO shows negative correlation, which thus indicates that the SiO<sub>2</sub> percentage decreases with increase of CaO.

**Calcium Oxide (CaO)**

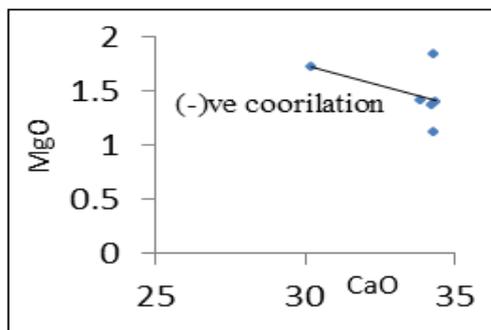


Figure 6: Mutual Relationship between CaO & MgO (Lakadong Limestone)

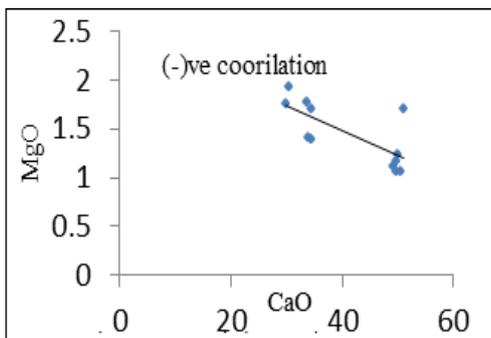
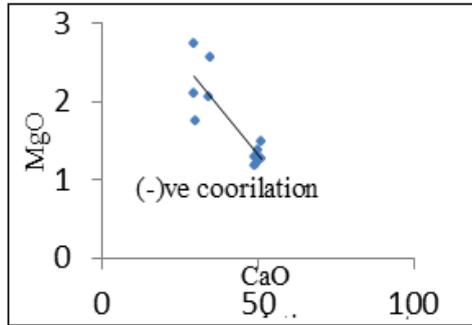


Figure 7: Mutual Relationship between CaO & MgO (Lakadong Limestone)



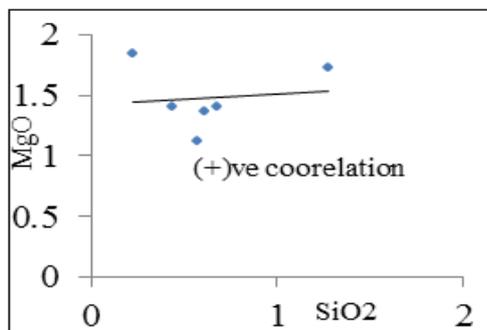
**Figure 8: Mutual Relationship between CaO & MgO**

Calcium Oxide (CaO), 30.19% to 34.38% in Lakadong Limestone, in Umlatdoh Limestone 29.83% to 50.96% and in Prang Limestone 29.34% to 51.04% Table 1.

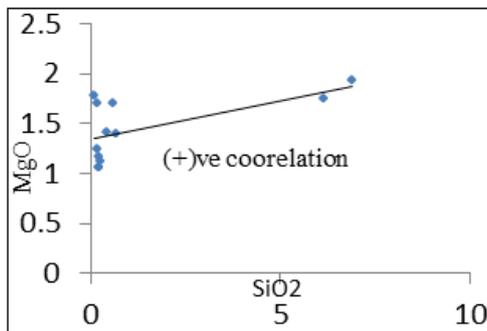
Concentration of CaO plotted against SiO<sub>2</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> Figures 6, 7, 8 shows negative correlation.

This thus indicates that the CaO percentage decreases with increase of SiO<sub>2</sub>/MgO/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.

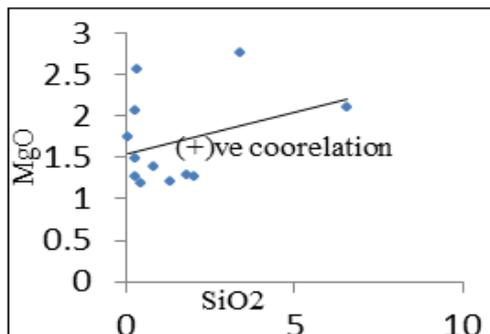
**Magnesium Oxide (MgO)**



**Figure 9: Mutual Relationship between SiO<sub>2</sub> & MgO (Lakadong Limestone)**



**Figure 10: Mutual Relationship between SiO<sub>2</sub> & MgO (Umlatdoh Limestone)**



**Figure 11: Mutual Relationship between SiO<sub>2</sub> & MgO (Prang Limestone)**

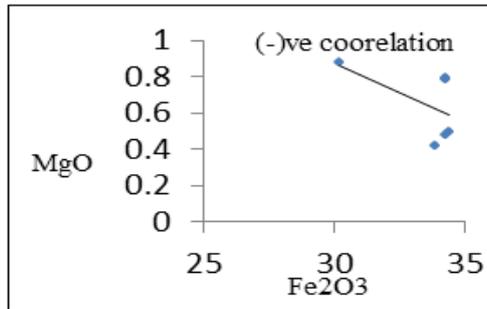


Figure 12: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub>& MgO (Umlatdoh Limestone)

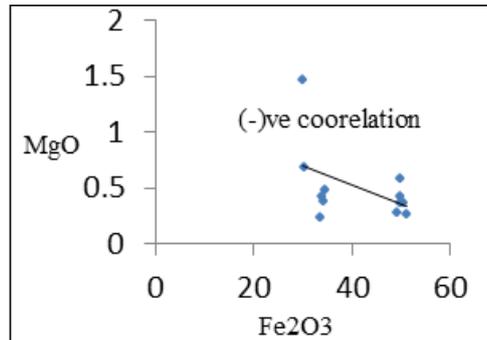


Figure 13: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & MgO (Umlatdoh Limestone)

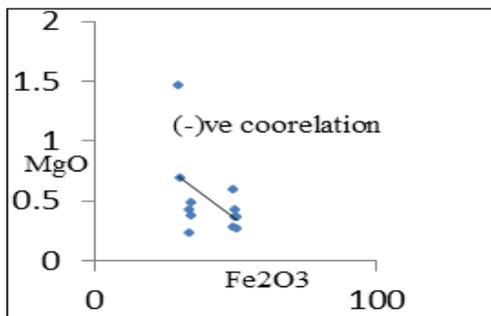


Figure 14: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & MgO (Umlatdoh Limestone)

Magnesium Oxide (MgO), 1.12% to 18.40% in Lakadong Limestone, in Umlatdoh Limestone 1.93% to 14.53% and in Prang Limestone 1.18% to 2.75% Table 1.

Concentration of MgO plotted against SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>, Figures 9, 10, 11 and 12, 13, 14 shows Positive Correlation and with Fe<sub>2</sub>O<sub>3</sub> it shows Negative Correlation, which thus indicates that, the MgO percentage increases with leaching of CaO & Fe<sub>2</sub>O<sub>3</sub> by solutions (Chilinger, 1956).

**Aluminium Oxide (Al<sub>2</sub>O<sub>3</sub>)**

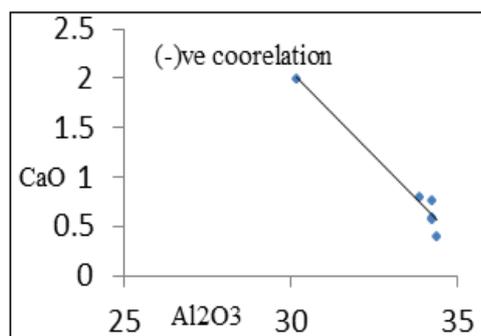


Figure 15: Mutual Relationship between Al<sub>2</sub>O<sub>3</sub> & CaO (Lakadong Limestone)

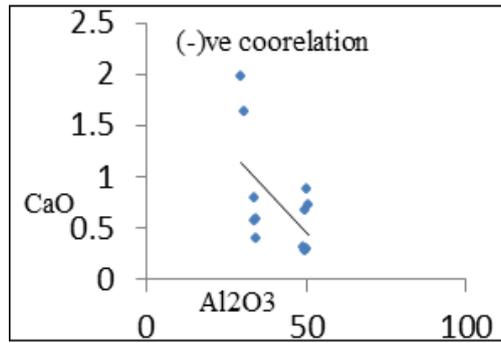


Figure 16: Mutual Relationship between Al<sub>2</sub>O<sub>3</sub> & CaO (Lakadong Limestone)

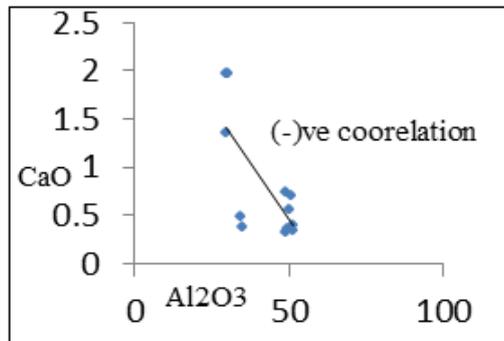


Figure 17: Mutual Relationship between Al<sub>2</sub>O<sub>3</sub> & CaO (Prang Limestone)

Aluminium Oxide (Al<sub>2</sub>O<sub>3</sub>) is found to be varying from 0.28% to 1.99% in Lakadong Limestone, in Umlatdoh Limestone 0.28% to 1.98% and in Prang Limestone 0.32% to 1.98% Table 1. Aluminium Oxide Al<sub>2</sub>O<sub>3</sub> shows a negative (-ve) coorelation with Calcium oxide (CaO) for all three members Figures 15, 16 & 17.

**Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>)**

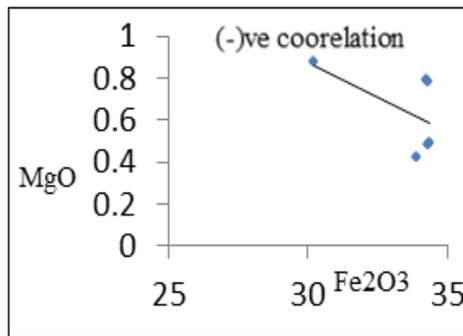


Figure 18: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & MgO

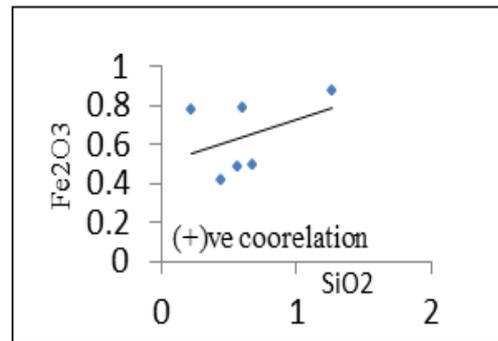


Figure 19: Mutual Relationship between SiO<sub>2</sub> & Fe<sub>2</sub>O<sub>3</sub>

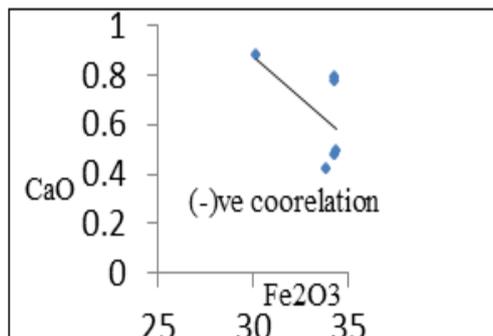


Figure 20: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & CaO

Figures 18, 19 & 20: Shows Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/MgO/CaO in Lakadong Limestone

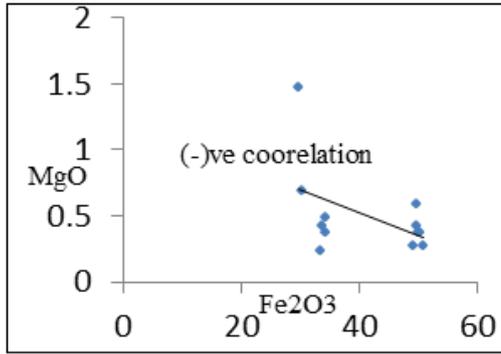


Figure 21: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & MgO

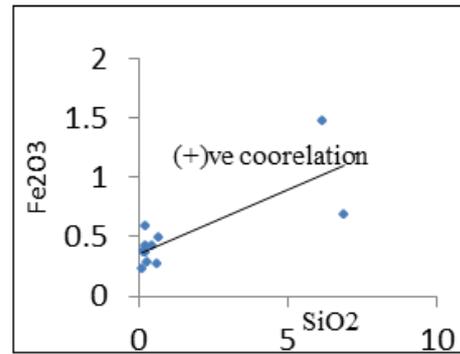


Figure 22: Mutual Relationship between SiO<sub>2</sub> & Fe<sub>2</sub>O<sub>3</sub>

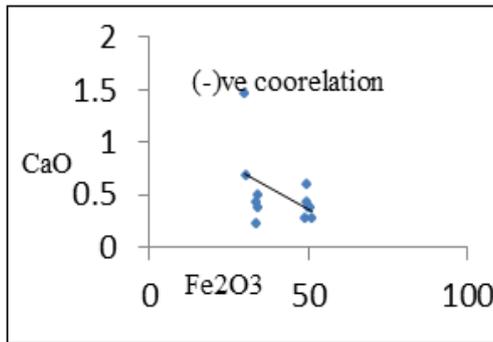


Figure 23: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & CaO

Figures 21, 22 & 23: Shows Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/MgO/CaO in Umlatdoh Limestone

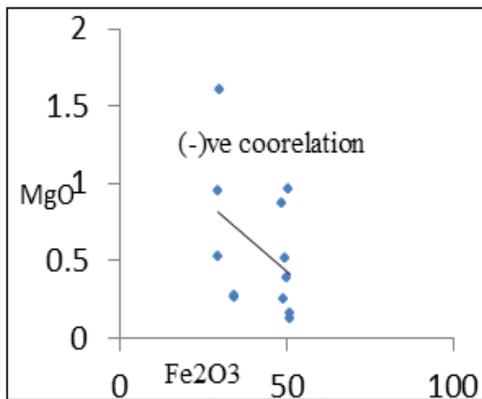


Figure 24: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & MgO

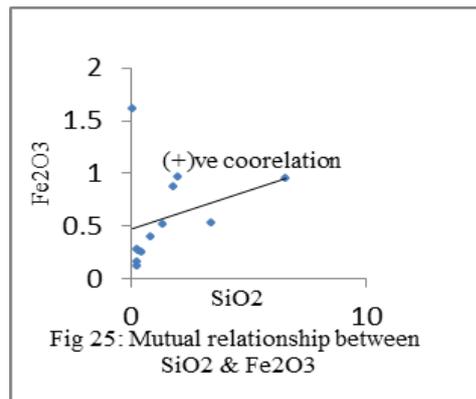


Fig 25: Mutual relationship between SiO<sub>2</sub> & Fe<sub>2</sub>O<sub>3</sub>

Figure 25: Mutual Relationship between SiO<sub>2</sub> & Fe<sub>2</sub>O<sub>3</sub>

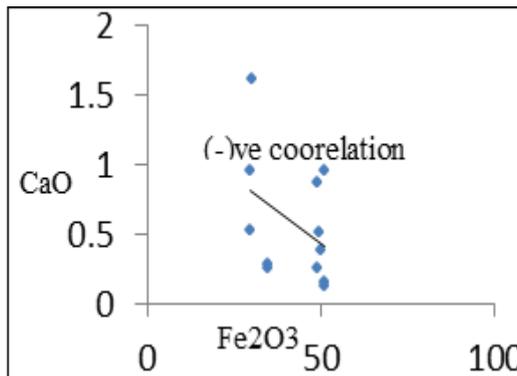


Figure 26: Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> & CaO

Figure 24, 25 & 26: Shows Mutual Relationship between Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/MgO/CaO in Prang Limestone

Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>), the distribution of Fe<sub>2</sub>O<sub>3</sub> is found to be varying from 0.42% to 0.88% in Lakadong Limestone, in Umlatdoh Limestone 0.23% to 1.47% in Prang Limestone 0.12% to 0.61% Table 1.

The bivariant plots of Fe<sub>2</sub>O<sub>3</sub> against SiO<sub>2</sub> (+)vely correlated Figures 19, 22 & 25 while (-)vely correlated with MgO and CaO Figures 18, 21 & 24 and 20, 23, & 26. The fluctuation (increase or decrease) in Fe<sub>2</sub>O<sub>3</sub> content may be related with terrigenous influx associated with high Iron bearing solutions. The higher amount of Fe<sub>2</sub>O<sub>3</sub> in carbonate rocks lowers the absorption capacity with lowers the rate of ignition of the samples.

**Other Oxide**

Mn<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>2</sub>, and LOI are the other constituents present in the limestone samples. The percentages are shown in Table-1.

**Ca/Mg and Mg/Ca Ratios**

The distribution of Ca/Mg and its reciprocal Mg/Ca ratio in the three limestones were utilized by Todd (1966) as a parameter for chemical classification. Table 5 Ca/Mg ratios vary from 40.79% to 80.62% in Lakadong Limestone, 2.62% to 46.86% in Umlatdoh Limestone and 1.41% to 80.45% in Prang Limestone Table 4. Mg/Ca ratios vary from 0.012% to 0.024% in Lakadong Limestone, 0.032% to 0.382% in Umlatdoh Limestone and 0.012% to 0.0707% in Prang Limestone Table 4. 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 proportionate to dolomite/calcite ratio and Mg/Ca ratio of carbonate sediments increase 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 deposition in the proximity of the shoreline. The data in the present case indicates the upper two formations i.e. Umlatdoh and Prang falls in both Pure Limestone and Magnesian Limestone category and deposition takes place in the proximity of the shoreline. The lower part i.e. Lakadong Limestone falls in Pure Limestone category indicates the deposition takes place away from the shoreline.

The Ca/Mg ratio also corresponds to stability condition during the formation of carbonate rock (Marshner, 1968). He pointed out that the degree of salinity increases with decrease of Ca/Mg ratio. 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.

**CHEMICAL CLASSIFICATION**

Limestones are classified by different workers (Pettijhon, 1957; Rodger, 1954; Twenhofel, 1950 on different basis. Here, the classification of Limestones of the investigated area is made after Todd, 1966. The Ca/Mg ratio and Mg/Ca ratios were utilized by Todd (1966) as a parameter for Chemical Classification Table 3. Limestone samples having 1.41%-12.30% is grouped as Dolomitic Limestone, limestone samples having 12.30%-39.00% Ca/Mg are grouped as “Magnesian Limestone” and Limestone samples having 39.00% to 100% are grouped as “Pure Limestone” Table 2.

**Table 2: Chemical Classification of Shella Limestone (after Todd, 1966)**

| Descriptive Term    | Standard Ratio Ca/Mg | Reciprocal Ratio Mg/Ca |
|---------------------|----------------------|------------------------|
| Pure Limestone      | 100.00 – 39.00       | 0.00 – 0.03            |
| Magnesian Limestone | 39.00 – 12.30        | 0.03 – 0.08            |
| Dolomitic Limestone | 12.30 – 1.41         | 0.08 – 0.18            |

**Table 3: Chemical Classification of Shella Carbonates**

| Sl. No. | Sample No. | CaO   | MgO  | Ca/Mg | Mg/Ca | Name                | Members            | Types            |
|---------|------------|-------|------|-------|-------|---------------------|--------------------|------------------|
| 1       | PRL 1      | 51.04 | 1.26 | 40.50 | 0.02  | Pure Limestone      | Prang Limestone    | Pure & Magnesian |
| 2       | PRL 2      | 50.99 | 1.48 | 34.45 | 0.02  | Magnesian Limestone |                    |                  |
| 3       | PRL 3      | 48.98 | 1.18 | 41.50 | 0.02  | Pure Limestone      |                    |                  |
| 4       | PRL 4      | 34.69 | 2.57 | 13.49 | 0.07  | Dolomitic Limestone |                    |                  |
| 5       | PRL 5      | 34.41 | 2.06 | 16.70 | 0.05  | Dolomitic Limestone |                    |                  |
| 6       | PRL 6      | 50.08 | 1.38 | 36.28 | 0.02  | Magnesian Limestone |                    |                  |
| 7       | PRL 7      | 29.58 | 2.11 | 14.01 | 0.07  | Dolomitic Limestone |                    |                  |
| 8       | PRL 8      | 29.34 | 2.75 | 10.66 | 0.09  | Dolomitic Limestone |                    |                  |
| 9       | PRL 9      | 30.1  | 1.75 | 17.20 | 0.05  | Dolomitic Limestone |                    |                  |
| 10      | PRL 10     | 48.79 | 1.28 | 38.11 | 0.02  | Magnesian Limestone |                    |                  |
| 11      | PRL 11     | 49.6  | 1.21 | 40.99 | 0.02  | Pure limestone      |                    |                  |
| 12      | PRL 12     | 50.69 | 1.27 | 39.91 | 0.02  | Pure limestone      |                    |                  |
| 13      | UML 1      | 50.96 | 1.71 | 29.80 | 0.03  | Magnesian Limestone | Umlatdoh Limestone | Pure & Magnesian |
| 14      | UML 2      | 34.37 | 1.71 | 20.09 | 0.04  | Dolomitic Limestone |                    |                  |
| 15      | UML 3      | 33.59 | 1.78 | 18.87 | 0.05  | Dolomitic Limestone |                    |                  |
| 16      | UML 4      | 49.23 | 1.12 | 43.95 | 0.02  | Pure Limestone      |                    |                  |
| 17      | UML 5      | 50.44 | 1.06 | 47.58 | 0.02  | Pure Limestone      |                    |                  |
| 18      | UML 6      | 49.88 | 1.17 | 42.63 | 0.02  | Pure Limestone      |                    |                  |
| 19      | UML 7      | 49.96 | 1.24 | 40.29 | 0.02  | Pure Limestone      |                    |                  |
| 20      | UML 8      | 49.68 | 1.06 | 46.86 | 0.02  | Pure limestone      |                    |                  |
| 21      | UML 9      | 30.43 | 1.93 | 15.76 | 0.06  | Magnesian Limestone |                    |                  |
| 22      | UML 10     | 29.83 | 1.75 | 17.04 | 0.05  | Dolomitic Limestone |                    |                  |
| 23      | LDL 1      | 33.87 | 1.41 | 24.02 | 0.04  | Magnesian Limestone | Lakadong Limestone | Pure & Magnesian |
| 24      | LDL 2      | 34.38 | 1.4  | 24.55 | 0.04  | Magnesian Limestone |                    |                  |
| 25      | LDL 3      | 34.27 | 1.12 | 30.59 | 0.03  | Magnesian Limestone |                    |                  |
| 26      | LDL 4      | 34.26 | 1.37 | 25.00 | 0.03  | Magnesian Limestone |                    |                  |
| 27      | LDL 5      | 34.27 | 0.84 | 40.79 | 0.02  | Pure Limestone      |                    |                  |
| 28      | LDL 6      | 30.19 | 0.73 | 41.35 | 0.02  | Pure Limestone      |                    |                  |

The percentage (%) of the major oxides present in the pure limestone and magnesium rich limestone reveals that the percentage of Aluminium Oxide (Al<sub>2</sub>O<sub>3</sub>) is found to be varying from 0.15% to 1.99% in Lakadong Limestone, in Umlatdoh Limestone 0.07% to 1.98% and in Prang Limestone 0.08% to 3.31%, Magnesium Oxide (MgO), 0.64% to 20.75% in Lakadong Limestone, in Umlatdoh Limestone 1.06% to 12.78% and in Prang Limestone 0.62% to 1.78% and Calcium Oxide (CaO), 29.34% to 51.83% in Lakadong Limestone, 29.83% to 50.96% in Umlatdoh Limestone and in Prang Limestone 30.16% to 50.44% Table 1.

### TRACE ELEMENTS ANALYSIS

The elements analysis of carbonate rocks provides important data on the sedimentary and diagenetic history. X-ray fluorescence 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 rock (Kinsman, 1969). The combined use of major oxides data Table 1 and trace elements Table 4 and their relations are used in facies and a palaeoenvironmental analysis continues to evolve in current studies.

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 as Cr(1-47), Cu(1-16), Ni(1-173), Sr(150-1375), V(2-232). In lowermost Lakadong Limestone Cr(12-14), Cu(9-16),

Ni(4-173), Sr(380-785), V(2-8), in middle Umlatdoh Limestone Cr(1-16), Cu(1-16), Ni(3-11), Sr(288-1124), V(2-232), and in uppermost Prang Limestone Cr(4-47), Cu(9-16), Ni(1-13), Sr(150-1375), V(5-232), Table 4.

However, the following elements are more useful for chemical studies of carbonate rocks of the area.

**Table 4: CaO and MgO Percentage (%) with Some Trace Elements (ppm) Constituents in Shella Limestone (XRF Data)**

| Sl. No | Sample No. | CaO % | MgO% | Cr(ppm) | Cu(ppm) | Ni(ppm) | Sr(ppm) | V(ppm) |
|--------|------------|-------|------|---------|---------|---------|---------|--------|
| 1      | PRL 1      | 51.04 | 1.26 | 7       | 13      | 0       | 331     | 17     |
| 2      | PRL 6      | 50.08 | 1.38 | 0       | 14      | 6       | 371     | 32     |
| 3      | PRL 8      | 29.34 | 2.75 | 6       | 11      | 0       | 308     | 19     |
| 4      | PRL 9      | 30.1  | 1.75 | 32      | 9       | 0       | 150     | 32     |
| 5      | PRL 10     | 48.79 | 1.28 | 10      | 15      | 0       | 276     | 43     |
| 6      | PRL 11     | 49.6  | 1.21 | 12      | 11      | 1       | 285     | 27     |
| 7      | PRL 12     | 50.69 | 1.27 | 15      | 13      | 1       | 320     | 59     |
| 8      | UML 1      | 50.96 | 1.71 | 5       | 12      | 3       | 562     | 19     |
| 9      | UML 2      | 34.37 | 1.71 | 4       | 16      | 11      | 564     | 30     |
| 10     | UML 3      | 33.59 | 1.78 | 14      | 11      | 7       | 488     | 10     |
| 11     | UML 4      | 49.23 | 1.12 | 13      | 9       | 17      | 785     | 18     |
| 12     | UML 5      | 50.44 | 1.06 | 12      | 14      | 4       | 616     | 15     |
| 13     | UML 6      | 49.88 | 1.17 | 15      | 11      | 5       | 472     | 20     |
| 14     | UML 8      | 49.68 | 1.06 | 16      | 14      | 0       | 560     | 11     |
| 15     | LDL 2      | 34.38 | 1.4  | 12      | 16      | 7       | 978     | 18     |
| 16     | LDL 3      | 34.27 | 1.12 | 1       | 16      | 9       | 665     | 41     |
| 17     | LDL 4      | 34.26 | 1.37 | 14      | 16      | 11      | 524     | 29     |
| 18     | LDL 6      | 30.19 | 0.73 | 14      | 10      | 0       | 577     | 42     |

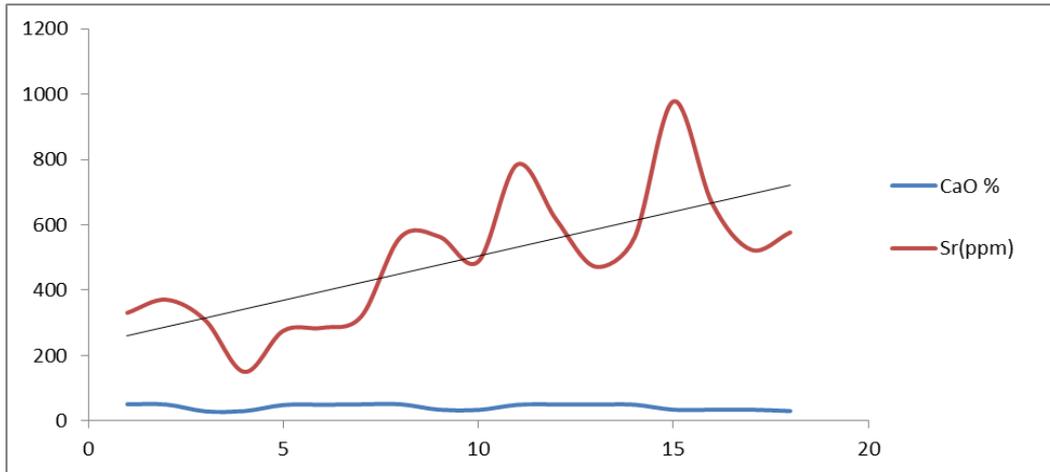
### Strontium

Trace elements data have been useful in the 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 Shella carbonates ranges from 271-1124 ppm with an average of 634 ppm indicating a shallow marine environment of deposition (Flugel and Wedepohl, 1967). Occurrence of Mn in the limestone indicates a warm and humid climatic condition during the deposition of carbonate sediments (Kotoky and Katakya, 1993).

In Lakadong Limestone, the concentration of strontium ranges from 524-978 with an average of 686 ppm suggesting a relatively deeper environment (500-3000 ppm; Flugel and Wedepohl, 1967; Bausch, 1968) than the Umlatdoh carbonate deposition environment.

In Umlatdoh Limestone, the concentration of strontium ranges from 472-785 ppm with an average of 578 ppm suggesting a relatively shallower environment (500-3000 ppm; Flugel and Wedepohl, 1967; Bausch, 1968) than the Lakadong carbonate deposition environment. In Prang Limestone, the concentration of strontium ranges from 150-371 ppm with an average of 291ppm suggesting a relatively shallower environment (500-3000 ppm; Flugel and Wedepohl, 1967; Bausch, 1968) than the Umlatdoh carbonate deposition environment.

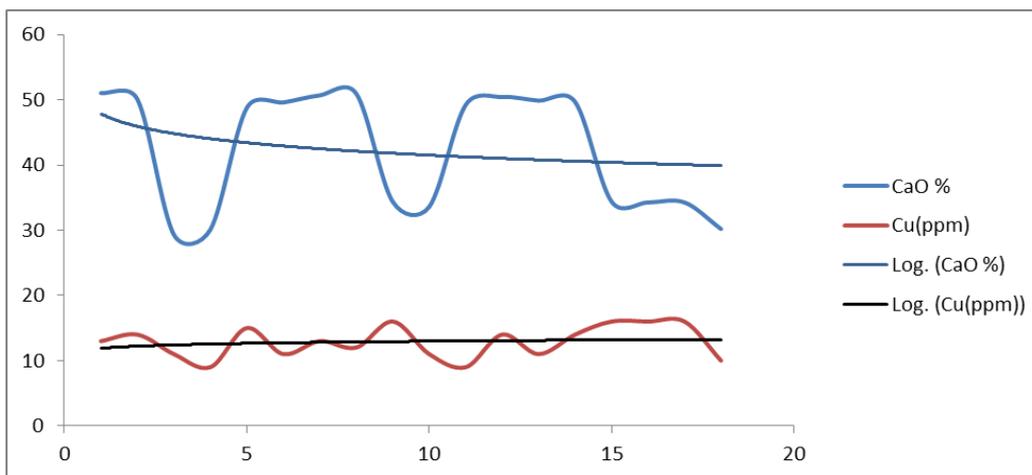
The high ppm of strontium (Sr) concentration in Lakadong Limestone and Umlatdoh Limestone, might also indicates the formation of the limestone under higher salinity environmental conditions in comparison to Prang Limestone. Anderson (1974) explained the effect of low water salinity on the depletion of strontium, so precipitations under high saline environment contain high concentration of strontium Figure 27.



**Figure 27: Shows a Positive (+ve) Correlation with CaO (%) Vs Strontium (ppm), through Prang Limestone, Umlatdoh Limestone and Lakadong Limestone**

**Copper**

The concentration of Cu is very low in Shella Carbonates (1-16 ppm) and in Lakadong Limestone, it ranges from 10-16 ppm, in Umlatdoh Limestone it ranges from 9-16 ppm and in Prang Limestone it is 9-15 ppm. 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. Pyrite seems to represent the most important carrier of Cu, since Cu have very 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 Figure 28.



**Figure 28: Shows that the Entire Carbonates are Basically Shallow Marine Because the Distribution of Cu is Almost Homogeneous and Parallel with CaO, Represented by the Trend Lines**

**Vanadium (V)**

The concentration of Vanadium (V) ranges from 2-59 ppm in the Shella Carbonates and indicative of shallow continental shelf marine depositional environments. In Lakadong Limestone, it ranges from 18-42 ppm, in Umlatdoh Limestone it ranges from 10-30 ppm and in Prang Limestone it is 17-59 ppm. In the scatter plots Vanadium (V) shows a negative (-ve) correlation with CaO and positive (+ve) correlation with MgO. Figures 29 & 30 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 (V) comes out from the solution (Friedman, 1968 a & b).

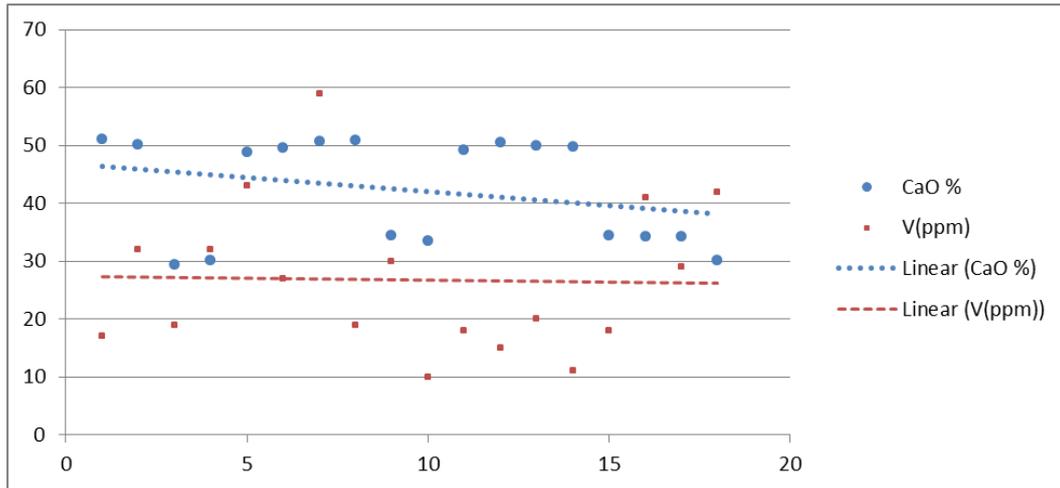


Figure 29: Vanadium (V) a Shows Negative (-ve) Correlation with CaO

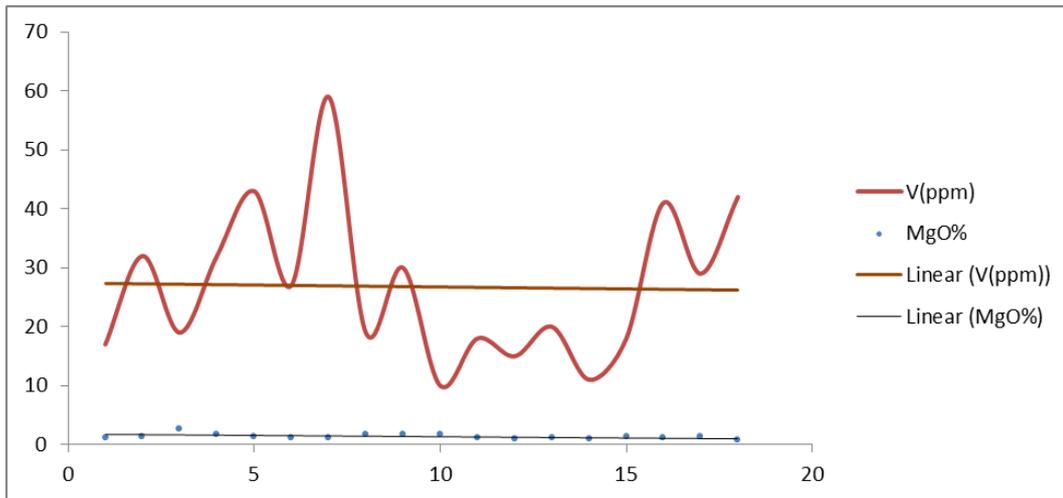


Figure 30: Vanadium (V) a Shows Positive (+ve) Correlation with MgO; Vanadium (V) Content of the Limestone Increases with the Increase of MgO Content Towarda Shore-Line of the Depositional Basin

## DISCUSSIONS AND INTERPRETATION

The distribution of Ca/Mg ratio in the limestone area suggests that limestone samples of three members fall two categories i.e., Magnesian and Pure Limestones. In the present case, 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 proportionate to dolomite/calcite ratio and Mg/Ca ration of carbonate sediments increase 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 deposition in the proximity of the shoreline. The data in the present case indicate the upper two formations i.e., Umlatdoh and Prang fall in both Pure Limestone and Magnesian Limestone categories and the deposition takes place in the proximity of the shoreline. The lower part i.e., Lakadong Limestone falls in Pure Limestone category indicates the deposition takes place just away from shoreline. (Marshner, 1968).

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 SiO<sub>2</sub> 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 these three Limestone Members of Shella Formation (Marshner, 1968). Presence of Fe<sub>2</sub>O<sub>3</sub> 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 limestones indicates a warm and humid climate during the deposition of carbonate sediments (Kotoky and Katakya, 1993).

Concentration of CaO plotted against SiO<sub>2</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> Figures 6, 7, 8, 9 shows negative correlation. This thus indicates that the CaO percentage decreases with increase of SiO<sub>2</sub>/MgO/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.

Bivariant plots of Al<sub>2</sub>O<sub>3</sub> against CaO shows negative correlation and calcium decreases in magnesium rich limestone (i.e. Umlatdoh and Prang Limestone) as compared to the pure limestone (i.e. Lakadong Limestone), it indicates magnesium become enriched when the CaO is removed by leaching in the solution process the magnesium limestone formed.

The high ppm of the strontium (Sr) concentration in Lakadong Limestone and Umlatdoh Limestone, might also indicates the formation of the limestone under higher salinity environmental conditions in comparison to Prang Limestone.

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 (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.

## CONCLUSIONS

The geochemistry of the Shella carbonates indicates that they contain very low amount of argillaceous sediments (except top of Prang Limestone) and the relationships among the major oxide components indicates that the argillaceous sediments were derived from bioclasts i.e., benthic foraminifera during the process of formation and diagenesis.

The data in the present case indicate the upper two formations i.e., Umlatdoh and Prang falls in both Pure Limestone and Magnesian Limestone category and the deposition takes place in the proximity of the shoreline. The lower part i.e., Lakadong Limestone falls in Pure Limestone category indicates the deposition takes place away from the shoreline.

Prang Limestone was deposited a shallow marine near shore environment which is suitable environment to receive some terrigenous materials. Increase volume of MgO in these limestones possibly results due to enriching of MgO by gradual removal of CaO during the diagenesis.

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.

Substantial amount of Terrigenous sediment input into the basin is also indicated by the concentration of trace elements data. The data in the present case indicate deposition in the proximity of the shoreline.

The trace elements data indicate the formation of the limestone under shallow continental shelf marine depositional environment.

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