# RARE EARTH ELMENTS IN LIMESTONES OF MURAL FORMATION OF BISBEE GROUP, NORTHERN SONORA, MEXICO

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## ABSTRACT

Major, trace and rare earth elements concentrations of Aptian-Albian limestones of Mural Formation have been determined to understand the depositional conditions. The limestones show four petrographic types viz. wackestone, packstone, grainstone and boundstone. The limestones from CP and SSJ sections exhibit large variations in $CaCO_3$ content than the CECP section. REE contents are lower in the CECP section than CP and SSJ sections. The limestones from CP and SSJ sections exhibit large variations in Eu anomaly ($Eu/Eu^*$: 0.84 to 1.67, 0.42 to 2.64, respectively) whereas least variations are observed in the CECP section (0.91 to 1.00). Noticeable variations are observed in Ce anomaly in CP, SSJ and CECP sections (0.67 to 1.20, 0.73 to 1.05, 0.63 to 1.00, respectively). CLC, TS and MQ members exhibit non-seawater like REE pattern whereas LC, CLP, CLE, Canova and El Caloso members exhibit seawater like REE pattern. The variations in the Ce/Ce* ratios are mainly influenced by the variations in the detrital and biogenic components.

## INTRODUCTION

Rare earth element (REE) concentrations, REE patterns, Eu and Ce anomalies in marine sediments provide useful information on marine depositional environments. REE concentration in seawater is mainly controlled by factors relating to different input sources (e.g. terrestrial input from continental weathering, hydrothermal input) and scavenging processes related to depth, salinity and oxygen levels (Elderfield, 1988; Greaves et al., 1999). The rare earth elements generally reflect uniform trivalent behaviors except Ce and Eu which exhibit multiple valences. The REE signatures in ancient marine environment provide information on secular changes in detrital influx and oxygenation conditions in water column (e.g. Holser, 1997; Kamber and Webb, 2001). Many seawater proxies are completely invalidated by inclusion of terrigenous materials that have relatively high, non-seawater-like REE contents, irrespective of subsequent diagenesis (Murray et al., 1992; Webb and Kamber, 2000). The purpose of the present study is to document the differences in REE characters in limestones deposited between proximal and distal part of the marine environments; to find out the influence of terrigenous materials on REE characteristics of carbonate rocks; to understand the probable reason for the variation in the Ce anomaly in the limestones of Mural Formation.

## GEOLOGY AND STRATIGRAPHY

The limestones of Mural Formation well exposed in a 300 km long transect which extends from Sierra El Chanate (westernmost part) to Cerro El Caloso Pitaycachi (northeastern most outcrops) localities (Fig. 1) (Gonzalez-Leon et al., 2008). The lithostratigraphic studies of Mural Formation show minor facies changes from west to east. The facies characteristic of different members of Mural Formation suggest that the depositional environments varied from restricted shelf with deltaic and fluvial influence to open shelf with coral rudist buildups, to offshore shelf. The Mural Formation is divided into six members i.e. i) Cerro La Ceja (CLC), ii) Tuape Shale (TS), iii) Los Coyotes (LC), iv) Cerro La Puerta (CLP), v) Cerro La Espina (CLE) and vi) Mesa Quemada (MQ). The Tuape section of Lawton et al. (2004) and the Cerro Caloso Cabullona section of Warzeski (1987) are considered as the representative section of the Mural Formation which serves as reference for the regional correlation. This correlation suggests that the lithological characters of CLC, TS, LC, CLP, CLE and MQ members are easily identifiable with minor facies variations from the Sierra El Chanate to Sierra San Jose. The facies of the Mural Formation deepening towards the eastern part of the basin i.e. towards the Cerro El Caloso Pitaycachi section. In the eastern part of the basin, the Mural Formation is divided into five members i.e. Canova, El Caloso, Angostura, La Aguja and Agua Prieta members (Warzeski, 1987). The base of the Mural Formation is not exposed in the Cerro El Caloso Pitaycachi section. This section mainly consists of Canova member and part of the El Caloso member. The Canova member is considered as a deeper, lateral facies equivalent of Los Coyotes and Cerro La Puerta members and El Caloso member is correlatable with the Cerro La Espina member in the northeastern Sonora (Gonzalez-Leon et al., 2008).

Fig. 1. Location map of the studied sections of the Mural Formation in Sonora.

## MATERIAL AND METHODS

Many sections of Mural Formation exposed in the northern part of Sonora were studied. Among them, carbonate rocks are well exposed in the Cerro Pimas, Sierra San Jose and Cerro El Caloso Pitaycachi sections (Fig. 1). Around seventy thin sections were prepared for petrographic study. Representative samples (Twenty samples from Cerro Pimas, fifteen samples from Sierra San Jose and sixteen samples from Cerro El Caloso Pitaycachi sections) were selected from each member in order to establish the geochemical variations among them. The selected samples were powdered in an agate mortar. Then, fused glass beads were prepared for major element analysis using a Phillip PW 1480 X-ray fluorescence spectrometer with a rhodium X-ray source (see Norrish and Hutton, 1969; Giles et al., 1995). Rare earth elements and certain trace elements were determined by a VG elemental PQ II plus Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (see Jarvis, 1988). The geochemical sedimentary standard MAG-1 (USGS) was used for calibration.

## RESULTS AND DISCUSSION

### PETROGRAHY

In carbonate rocks, four major petrographic types have been identified i..e. *wackestone, packstone, grainstone* and *boundstone*. The *wackestone* contains a small amount (around 2%) of quartz and feldspar grains. Among organics algal and molluscan materials are found in the micritic matrix (Fig. 2A). Few echinoid plates are floating on the micritic matrix. Some cavities are filled with sparry calcite cement whereas some other cavities are filled with poikilotopic cement. The limestone exhibits bedding parallel irregular anatomizing microstylolite set. The clay materials and mineral grains are concentrated along the stylolite interfaces. In Cerro Pimas section, it represents the Cerro La

Ceja, Tuape Shale and Mesa Quemada members; In Sierra San Jose section, this petrographic type represents the Cerro La Ceja, Tuape Shale, Los Coyotes and Mesa Quemada members; In Cerro El Caloso Pitaycachi section, it represents the Canova member. The *packstone* contains framework elements of algal, rudist, coral, and foraminifera (Fig. 2B). Besides some molluscan fragments and echinoid plates are also seen in the micritic matrix. Few echinoid plates show pore structures. It also contains very small quantity of quartz grains. Many bioclasts are coated with micritic layer. Because of micritic envelop over the bioclasts, the internal structure of the shell fragments is not completely destroyed. The cement is both microsparite and sparry calcite. In Cerro Pimas section, this petrographic type represents the lower part of the Los Coyotes and Cerro La Espina members. In Cerro El Caloso Pitaycachi section, it represents the El Caloso member.

The *grainstone* (Fig. 2C) has more than 10% of fragmentary organic remains, which, are embedded in the sparry calcite cement. The organic remains include algal, coral, molluscan and foraminifera. Few echinoid and crinoidal plates are present in the sparry calcite cement. The limestone also exhibits some benthic foraminifera's. Most of the bioclasts are coated with micrite. Because of micrite layer over the bioclasts, the internal structure of the shells is not completely destroyed or altered. The internal part of the moll scan fragments are partly filled with sparry calcite cement. It represents the upper part of the Los Coyotes and Cerro La Espina members in Cerro Pimas Section. The *boundstone* is a type of carbonate rock, which is bound together in the original depositional environment by framework building organism. The framework organisms include bivalves, corals, rudists, echinoderms, intraclasts and foraminifera (Fig. 2D). Many organisms are coated with micritic layer. It represents the Cerro La Puerta and Cerro La Espina members in Sierra San Jose section.

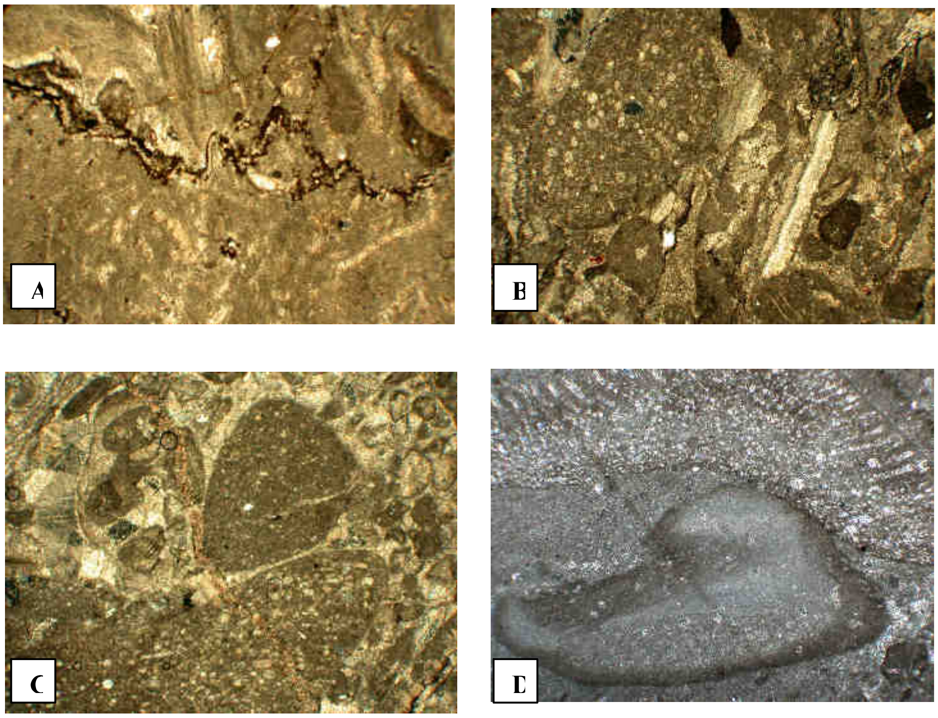


Fig. 2. A. The wackestone contains algal and molluscan grains and also exhibits bedding parallel irregular anatomizing microstylolite set, B. The packstone exhibits framework elements of algal, molluscan and foraminiferal grains, C. The photomicrograph shows algal and foraminifera, D. The boundstone reveals the framework organisms include rudists and foraminifera.

**GEOCHEMISTRY**

In Cerro Pimas section (CP), the $CaCO_3$ in the TS, LC and MQ members show small variations (77.61 to 83.52%, 91.89 to 98.01%, 89.07 to 94.52%, respectively) whereas CLC and CLE members show large variations (67.76 to 95.19%, 68.99 to 95.16%, respectively). In Sierra San Jose section (SSJ), small variations are observed in the CaCO3 contents in the CLC, TS, CLP and CLE members (58.51 to 66.53%, 82.32 to 88.77%, 92.28 to 93.82%, 90.41 to 97.46%, respectively) whereas large variations are observed in the LC member (64.67 to 91.41%). In Cerro El Caloso Pitaycachi section (CECP), both Canova and El Caloso members show least variations in $CaCO_3$ contents (89.11 to 93.75%, 94.36 to 97.76%, respectively). Large variations in Si contents are observed in CP and SSJ sections (0.70 to 10.88%, 0.12 to 14.78%, respectively) whereas least variations are observed in the CECP section (0.26 to 2.61%). Like Si concentrations, the large variations in ΣREE contents are also observed in both CP and SSJ sections (5.22 to 113.96 ppm, 2.28 to 108.58 ppm, respectively) whereas REE contents are lower in the CECP section (1.94 to 17.40 ppm).

PAAS normalized REE+Y patterns of representative limestone samples from CP, SSJ and CECP sections are given in Fig.3. The limestones from CP and SSJ sections show large variations in Eu anomaly ($Eu/Eu^*$: 0.84 to 1.67, av. 1.17 ± 0.22, n=20; 0.42 to 2.64, av. 1.15 ± 0.47, n=15; respectively) whereas least variations are observed in the CECP section (0.91 to 1.00, av. 0.95 ± 0.03, n=16). The limestones from CP and SSJ sections show significant positive Eu anomaly whereas such positive anomaly is absent in the CECP section (Table 1). Noticeable variations are observed in Ce anomaly in CP, SSJ and CECP sections (0.67 to 1.20, av. 0.91 ± 0.15, n=20; 0.73 to 1.05, av. 0.90 ± 0.11, n=15; 0.63 to 1.00, av. 0.80 ± 0.12, n=16; respectively, Table 1). The observed variations in Ce anomaly in these limestones are mainly due to the mixing of various portions of biogenic and detrital materials.

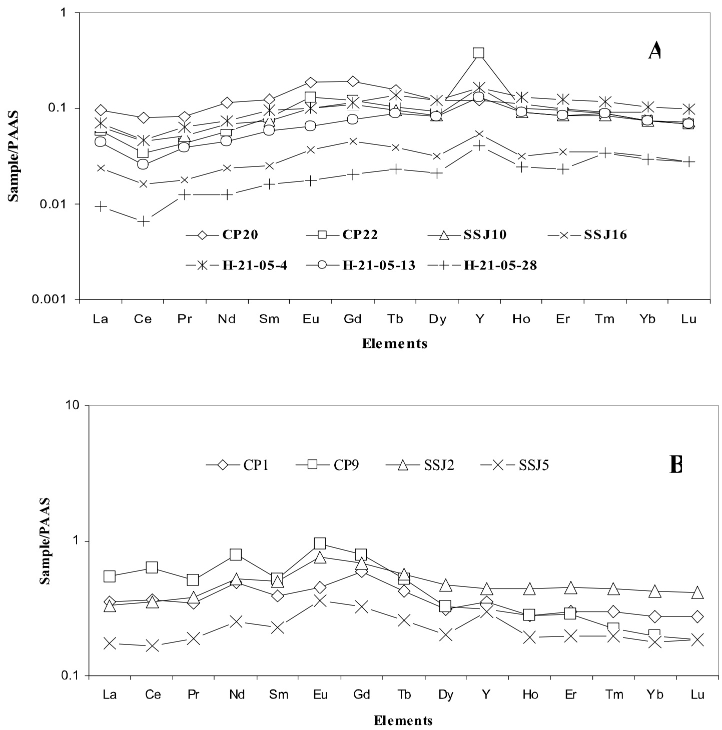


Fig. 3. A. PAAS normalised REE+Y patterns of the Mural Formation show seawater-like signatures, B. PAAS normalised REE+Y patterns of the Mural Formation with non-seawater-like signatures.

The ΣREE contents and $La_N/Yb_N$ ratios of Mural Formation are lower than the shallow marine Maastrichtian Limestones (Table 1) of Cauvery Basin (Madhavaraju and Ramasamy, 1999) and Kudankulam Limestones of Southern India (Armstrong-Altrin et al., 2003). $Ce/Ce^*$ ratios of Mural

Formation are similar to that of shallow and deep marine sediments (Madhavaraju and Ramasamy, 1999; Armstrong –Altrin et al., 2003; Nath et al., 1992, 1997).

| | **Mural Formation[1]** | | | **Maastrichtian Limestone[2]** | **Kudankulam Limestone[3]** | **Arabian Sea carbonate sediments[4]** | **Indian Ocean carbonate sediments[5]** |
|---|---|---|---|---|---|---|---|
| | **Cerro Pimas section[1a]** | **Sierra SanJose section[1b]** | **Cerro El Caloso Pitaycachi section[1c]** | | | | |
| $Ce/Ce^*$ | 0.91 ± 0.2 | 0.90 ± 0.1 | 0.80 ± 0.1 | 0.76 ± 0.2 | 0.9 ± 0.1 | 0.84 ± 0.1 | 0.56 |
| $La_N/Yb_N$ | 1.07 ± 0.6 | 0.91 ± 0.3 | 0.64 ± 0.1 | 1.8 ± 0.5 | 2.7 ± 1.4 | 0.8 ± 0.2 | 1.03 |
| ΣREE | 37 ± 26 | 33 ± 31 | 10 ± 4 | 73 ± 20 | 80 ± 40 | 78 ± 40 | - |
| $CaCO_3$ | 88.4 ± 9 | 85.8 ± 12 | 92.7 ± 2 | 75 ± 15 | 88 ± 5 | 51 ± 22 | 65.3 |
| $Eu/Eu^*$ | 1.17 ± 0.2 | 1.15 ± 0.5 | 0.95 ± 0.03 | 0.58 ± 0.1 | 0.78± 0.3 | 1.15 ± 0.1 | - |

[1a,b,c]Present study, n=20, n=15, n=16, respectively; [2]Madhavaraju and Ramasamy, 1999, n=8; [3]Armstrong-Altrin et al., 2003, n=9; [4]Nath et al., 1997, n=9; [5]Nath et al., 1992.

Table 1: Average geochemical values of the Dalmiapuram Formation compared to shallow and deep marine sediments

In the present study, the limestones deposited in the western and eastern part of the basin show significant variations in ΣREE contents, Eu and Ce anomalies and $La_N/Yb_N$ ratios. The limestones from LC, CLP, CLE, Canova and El Caloso members show low contents of detrital materials which exhibits seawater-like REE+Y patterns whereas CLC, TS and MQ members show non-seawater-like REE+Y patterns. CLC, TS and MQ members show significant amount of terrigenous materials which effectively mask the seawater characters. Hence the limestones deposited under open marine environment are suitable for paleoceanographic studies.

## CONCLUSION

The limestones of Mural Formation show various petrographic types i.e. wackestone, packstone, grainstone and boundstone. The limestones from CP and SSJ sections show large variations in $CaCO_3$ content than the CECP section. Likewise, the large variations in ΣREE contents are also observed in both CP and SSJ sections whereas REE contents are lower in the CECP section. LC, CLP, CLE, Canova and El Caloso members exhibit seawater like REE pattern whereas CLC, TS and MQ members exhibit non-seawater like REE patterns. Variations in the Ce/Ce* ratios are mainly influenced by the variations in the biogenic and detrital contents.

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