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Geochemistry of the Dalmiapuram Formation of the Uttatur Group (Early Cretaceous), Cauvery basin, southeastern India: Implications on provenance and paleo-redox conditions

Jayagopal Madhavaraju and Yong Il Lee

ABSTRACT

Major, trace and rare earth elements (REE) study was carried out on the Lower Cretaceous Dalmiapuram Formation in southeastern India in order to understand the geochemical variations among various litho-units. Coral algal limestone (CAL) shows high content of CaO (53 ± 0.5, n=4) than the bedded limestone (BL) (42 ± 2, n=4) and gray shales (GS) (19 ± 6, n=3). The limestones are depleted in most of the trace elements when compared with the Post-Archean Australian Shale (PAAS). Likewise, gray shales are also depleted in many trace elements (Co, V, Rb, Ba, Zr, Y, Nb, Hf and Th), whereas few elements (Ni, Cr, Sr, Pb and U) show similar concentrations with respect to PAAS. The observed large variations in ΣREE contents among CAL (18 ± 8, n=4), BL (59 ± 17, n=4) and GS (157 ± 49, n=3) are mainly due to the amount of terrigenous matter present in them. The Eu and Ce anomalies were calculated from the PAAS-normalized values. The limestones (CAL and BL) and gray shales show small variations in Eu anomalies (Eu/Eu*: 1.23 ± 0.10, n=4, 1.16 ± 0.10, n=4 and 1.17 ± 0.10, n=3, respectively). The observed positive Eu anomalies in the limestones and gray shales may be due to the presence of plagioclase feldspar. The CAL shows a negative Ce anomaly (Ce/Ce*: 0.90 ± 0.06, n=4) whereas BL shows a positive Ce anomaly (Ce/Ce*: 1.05 ± 0.14, n=4; except KI15) and gray shales show no Ce anomalies (Ce/Ce*: 0.98 ± 0.02, n=3). Variations in Ce anomalies in these limestones may be due to the mixing between sediment components and a seawater end member. The characteristics of non-seawater-like REE patterns, elevated REE concentrations, high La/Nb/YbN ratios and low Y/Ho ratios suggest that the observed variations in ΣREE contents are mainly controlled by the amount of detrital sediments in the limestones of the Dalmiapuram Formation. The REE patterns and La/Sc, La/Co, Th/Co, Th/Cr, Cr/Th, and Th/Sc ratios suggest that the terrigenous materials present in the Dalmiapuram Formation were mainly derived from intermediate to felsic rocks. The limestones (CAL and BL) show positive values of Mn* and low V/(V+Ni) ratios (≤0.50) suggesting that these limestones have been deposited under oxic condition whereas gray shales show negative Mn* values and high V/(V+Ni) ratios (≥0.50) which support that these shales were deposited under reducing conditions. 

Key words: rare earth elements, provenance, paleo-redox conditions, Dalmiapuram Formation, Cauvery basin, southeastern India.
RESUMEN

Se llevaron a cabo estudios geoquímicos de elementos mayores, traza y tierras raras (ETR) en la Formación Dalmiapuram del Cretácico Inferior en el sureste de la India, para entender las variaciones geoquímicas entre diversas unidades litológicas. Una caliza de corales y algas (CAL) muestra alto contenido de CaO (94.6 ± 1, n=3) que una caliza estratificada (BL) (75.8 ± 4, n=4) y lutitas grises (GS) (33.6 ± 11, n=4). Las calizas están empobrecidas en la mayoría de los elementos traza respecto a la Lutita Australiana Postarquea (PAAS, por sus siglas en inglés). De igual forma, las lutitas grises están empobrecidas en muchos elementos traza (Co, V, Rb, Ba, Zr, Y, Nb, Hf y Th), mientras que algunos elementos (Ni, Cr, Sr, Pb y U) tienen concentraciones similares a la PAAS. Las grandes variaciones observadas en el contenido de ΣETR entre CAL (18 ± 8, n=4), BL (59 ± 17, n=4) y GS (157 ± 49, n=3) se deben principalmente a la cantidad de materia terrígena presente en ellas. Se calcularon anomalías de Eu y Ce a partir de los valores normalizados a PAAS. Las calizas (CAL y BL) y lutitas grises muestran pequeñas variaciones en las anomalías de Eu (Eu/Eu*: 1.23 ± 0.10, n = 4, 1.16 ± 0.10, n = 4 y 1.17 ± 0.10, n = 3, respectivamente). Las anomalías positivas de Eu observadas en las calizas y lutitas grises pueden originarse por la presencia de plagioclasa. CAL muestra una anomalía negativa en Ce (Ce/Ce*: 0.90±0.06, n=4), mientras que BL muestra una anomalía de Ce positiva (Ce/Ce*: 1.05 ± 0.14, n=4; excepto KI15) y las lutitas grises no muestran anomalías en Ce (Ce/Ce*: 0.98 ± 0.02, n=3). Las variaciones en la anomalía en Ce en estas calizas pueden deberse a la mezcla entre componentes de los sedimentos y un miembro terminal de agua marina. Las características de los patrones ETR distintos a los de agua marina, las elevadas concentraciones de ETR, las proporciones altas de La/Yb y las proporciones bajas de Y/Ho sugieren que las variaciones observadas en ΣETR están principalmente controladas por la cantidad de sedimentos detríticos en las calizas de la Formación Dalmiapuram. Los patrones de ETR y las relaciones La/Sc, La/Co, Th/Co, Th/Cr, Cr/Th y Sc sugieren que los materiales terrígenos presentes en la Formación Dalmiapuram se derivaron principalmente de rocas intermedias a felsícas. Las calizas (CAL y BL) muestran un valor positivo de Mn* y proporciones bajas de V/(V+Ni) (≤0.50) sugiriendo que estas calizas se depositaron en condiciones ricas en oxígeno mientras que las lutitas grises muestran valores negativos de Mn* y proporciones altas de V/(V+Ni) (≥0.50), lo que apoya que estas lutitas se depositaron bajo condiciones reductoras.

Palabras clave: elementos de las tierras raras, proveniencia, condiciones de paleo-redox, Formación Dalmiapuram, cuenca Cauvery, sureste de India.

INTRODUCCIÓN

El comportamiento de los elementos raros (REEs) en suelos, sedimentos y rocas carbonatadas ha sido discutido por muchos trabajos (Ronov et al., 1967; Piper, 1974; Klinkhammer et al., 1983; De Baar et al., 1988; Elderfield et al., 1990). La concentración de REE en suelos e internos se ve influenciada por factores relacionados con diferentes fuentes de entrada (p.e., aporte de tierras raras), la erosión y transporte de la actividad diagenética (Elderfield, 1988; Piepgras y Jacobsen, 1992). La distribución de REE, particularmente la anomalía de Ce en sedimentos de carbonato y rocas carbonatadas, proporciona información útil sobre los cambios de la formación deposicional en diferentes ambientes marinos (Liu et al., 1988; German y Elderfield, 1990; Murray et al., 1991a), variaciones en la productividad de sedimento (Toyoda et al., 1990), condiciones de carbonato-marino (Liu et al., 1988), proximidad a la fuente (Murray et al., 1991a), litología y diagenesis (Nath et al., 1992; Madhavaraju y Ramasamy, 1999a; Armstrong-Altrin et al., 2003) y coloides Fe-organicos de fuentes de susstrato (Sholkovitz, 1992).

El comportamiento de los REE es uniforme en el ambiente terrestre, excepto para Ce y Eu. El Eu exhibe un comportamiento de Ce3+ y Ce4+ y Ce4+, mientras que el Eu exhibe un comportamiento de Ce3+ y Ce4+. Las anomalías de Ce en rocas carbonatadas se usan como indicadores para entender las condiciones de paleo-redox (Liu et al., 1988). Sin embargo, mucha gente ha expresado preocupaciones sobre el uso de Ce anomalías como un indicador de condiciones de paleo-redox (German y Elderfield, 1990), litología y diagenesis (Nath et al., 1992; Madhavaraju y Ramasamy, 1999a; Armstrong-Altrin et al., 2003) y coloides Fe-organicos de fuentes de susstrato (Sholkovitz, 1992).

El comportamiento de los REE en suelos e internos se ve influenciado por factores relacionados con diferentes fuentes de entrada (p.e., aporte de tierras raras), la erosión y transporte de la actividad diagenética (Elderfield, 1988; Piepgras y Jacobsen, 1992). La distribución de REE, particularmente la anomalía de Ce en sedimentos de carbonato y rocas carbonatadas, proporciona información útil sobre los cambios de la formación deposicional en diferentes ambientes marinos (Liu et al., 1988; German y Elderfield, 1990; Murray et al., 1991a), variaciones en la productividad de sedimento (Toyoda et al., 1990), condiciones de carbonato-marino (Liu et al., 1988), proximidad a la fuente (Murray et al., 1991a), litología y diagenesis (Nath et al., 1992; Madhavaraju y Ramasamy, 1999a; Armstrong-Altrin et al., 2003) y coloides Fe-organicos de fuentes de susstrato (Sholkovitz, 1992).

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of terrigenous materials masking the seawater signatures in marine carbonate rocks. The objective of this study is to understand the behavior of elements in marine environments, the causes of variations in Ce anomalies, and the usefulness of trace elements and their ratios in predicting the paleoredox conditions in the Dalmiapuram Formation.

GEOLGY AND STRATIGRAPHY

In India, the Cauvery basin is known as a Mesozoic extensional basin formed all along the eastern continental margin of Peninsular India and has been classified as a pericratonic rift basin (Biswa et al., 1993). It contains thick sedimentary sequences of around 6 km, which were deposited on the Archaean basement (Rangaraju et al., 1993). The sedimentary rocks in the Cauvery basin are well exposed in five isolated areas, i.e., Pondicherry, Vridhachalam, Ariyalur, Tanjore, and Sivaganga (Banerji, 1972). Among these areas, the Cretaceous-Tertiary sedimentary rocks are well exposed in the Ariyalur area (Figure 1). Numerous studies on stratigraphy, sequence stratigraphy, paleontology, clay mineralogy, geochemistry, depositional environments and tectonic evolution of the Cauvery basin have been carried out.

Figure 1. Geological map of the Ariyalur area of the Cauvery basin (modified after Sundaram et al., 2001).
out by many researchers (Sastry et al., 1972; Sundaram and Rao, 1986; Ramasamy and Banerji, 1991; Govindan et al., 1996; Madhavaraju and Ramasamy, 1999a, 1999b, 2001, 2002; Sundaram et al., 2001; Nagendra et al., 2002; Madhavaraju et al., 2002, 2004, 2006).

Blanford (1862) first studied and mapped sedimentary rocks in the Ariyalur area and divided them into three distinct groups, i.e., Uttatur, Trichinopoly and Ariyalur. Detailed lithostratigraphic classification of Cretaceous-Tertiary rocks was given by many workers (e.g., Srivastava and Tewari, 1969; Banerji, 1972; Sastry et al., 1972; Sundaram and Rao, 1986; Ramasamy and Banerji, 1991; Sundaram et al., 2001). For the present study, we have followed the lithostratigraphic classification proposed by Sundaram et al. (2001).

The Cretaceous Uttatur Group has been subdivided into four formations, i.e., Terani Formation, Arogyapuram Formation, Dalmiapuram Formation and Karai Formation (Sundaram et al., 2001). The first three formations have been dated to be Early Cretaceous and the last formation to be Late Cretaceous. The Dalmiapuram Formation is well exposed in the Kallakudi limestone quarry in Dalmiapuram. On the basis of the lithology, the Dalmiapuram Formation was divided into two members, viz. gray shale member in the lower part and limestone member in the upper part (biothermal limestone, bedded biostromal limestone/marls and marls).

The gray shale (GS) member (3.5 m thick) is exposed in the northern part of the Kallakudi limestone quarry (Subbaraman, 1968). The color of shale varies from ash gray to dark gray depending upon the presence of organic matter. The gray shale contains coaly matter along with few pyrite grains (Ramasamy and Banerji, 1991). The gray shale is overlain by a 35 m thick coral algal limestone (CAL), bedded limestone (BL) and marl (Nagendra et al., 2002). The coral algal limestone (CAL) is massive, hard, pinkish to flesh red color and is characterized by the presence of vugs and cavities. The vugs are filled with microsparite and sparry calcite cement. The CAL has abundant algal and coral grains, bioclastic fragments of crinoids and brachiopods, with packstone and boundstone textures. The CAL is overlain by a thick succession of rhythmically bedded limestone (BL) and marl, which shows soft, off-white to brownish yellow in color and grades vertically upward into very thin bedded marls. The BL contains abundant foraminifers. The bedding contact between BL and marls is well defined in the outcrop. The alternating sequence of bedded limestone and marls resulted from cyclic carbonate building activity (Figure 2).

The significant difference between CAL and BL is that the latter encloses more terrigenous matter (around 20%) and is stratified. The terrigenous materials are quartz, feldspar and clay particles. The CAL includes calcareous algae, coral fragments and bryozoans, which suggests a shallow marine environment (Banerji et al., 1996). The presence of abundant benthic foraminifera in the BL indicates that it was deposited along rocky shores in a moderately deep water shelf (>50 m water depth) facies (Ramasamy and Banerji, 1991; Ramasamy et al., 1995; Yadagiri and Govindan, 2000). Ramasamy and Banerji (1991) assigned an Early to Middle Albian age to the limestone member of Dalmiapuram, based on the abundant foraminifers and ammonites.

MATERIALS AND METHODS

Samples were collected from a 40 m thick section of the Dalmiapuram Formation, in the Kallakudi limestone...
quarry near the Dalmiapuram village. Eleven representative samples were selected and analysed – four from the coral algal limestone (CAL), four from the bedded limestone (BL) and three from the gray shale (GS). Samples were air dried and then ground in an agate mortar. Then fused glass beads were prepared for major element analyses.

Major, trace and rare earth element analyses were performed at the Korea Basic Science Institute. The major oxides were analyzed with a Phillip PW 1480 X-ray fluorescence spectrometer with a rhodium X-ray source (see Norrish and Hutton, 1969; Giles et al., 1995). The United States Geological Survey (USGS) sedimentary reference material MAG-1 was used to determine data quality (Table 1). The analytical accuracy was better than ±1% for SiO₂, Al₂O₃ and K₂O, better than ±2% for MnO, and better than ±4% for Fe₂O₃, CaO and MgO. The accuracy of Na₂O, P₂O₅ and TiO₂ was better than ±6%.

Trace elements (Ba, Cr, Sc, Sr, V and Zr) were analysed with a Jobin Yvon 138 Ultrace ICP-AES. Rare earth elements (REEs) and additional trace elements (Co, Cu, Hf, Y, Nb, Ni, Pb, Rb, Th and U) were measured with a VG elemental PQ II plus ICP-MS (see Jarvis, 1988). For these analyses, as is customary, the mass calibration and intensities were daily checked with a tuning solution. Calibration was achieved from standard solutions of different concentration levels prepared from Spex quality stock solutions. As for the major-elements, the USGS sedimentary geochemical standard MAG-1 was used for evaluation of the accuracy of analytical data. The analytical results for the MAG-1 obtained in the present study are compared with the published values compiled by Govindaraju (1994) and those available at the USGS internet site (Table 1). The analytical precision for trace elements such as Co, Zr, Rb, Th and U were better than ±3%, whereas Cu and Hf were better than ±6% and Ba, Cr, Nb, Pb, Sr, Ni, V and Y better than ±10%. The accuracy of all rare earth elements were better than ±4%, except Tb, Dy, Ho, Tm and Lu for which it was better than ±10%. The detection limits for the method used in this study are also presented in Table 1. They generally obey the findings suggested by Verma et al. (2002), Santoyo and Verma (2003), and Verma and Santoyo (2005).

All samples were run in triplicate and the three analyses were then averaged and reported. The results of major oxides, trace and rare earth elements are given in Tables 2 and 3. Yttrium is inserted between Ho and Dy in the REE pattern according to its identical charge and similar radius (REE+Y pattern, Bau, 1996). Post-Archaean Australian Shale (PAAS) values given by Taylor and McLennan (1985) were used for REE-normalized diagrams.

For some of the data interpretation, we have used a statistical basis (Bevington and Robinson, 2003; Verma, 2005) although in future more quantitative significance tests can be incorporated (Verma, 2009).

### RESULTS

#### Major elements

The concentrations of major oxides in the limestones and gray shales of the Dalmiapuram Formation are given

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**Table 1. Comparison of data of major oxides, trace and rare-earth elements for USGS reference sample MAG-1 (marine sediment) with the literature USGS certificate of analysis (Govindaraju 1994; see also USGS website) as well as limits of detection (LOD) data for XRF, ICP-AES and ICP-MS.**

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>Mean (this study) *</th>
<th>Literature Mean</th>
<th>Standard deviation</th>
<th>LOD **</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50.72</td>
<td>50.4</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.48</td>
<td>16.4</td>
<td>0.30</td>
<td>0.0287</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.11</td>
<td>6.8</td>
<td>0.60</td>
<td>0.0552</td>
</tr>
<tr>
<td>CaO</td>
<td>1.42</td>
<td>1.37</td>
<td>0.10</td>
<td>0.0007</td>
</tr>
<tr>
<td>MgO</td>
<td>3.11</td>
<td>3.0</td>
<td>0.10</td>
<td>0.0012</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.59</td>
<td>3.55</td>
<td>0.17</td>
<td>0.0053</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.60</td>
<td>3.83</td>
<td>0.11</td>
<td>0.0053</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.098</td>
<td>0.009</td>
<td>0.0053</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.70</td>
<td>0.75</td>
<td>0.07</td>
<td>0.0053</td>
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<tr>
<td>P₂O₅</td>
<td>0.17</td>
<td>0.16</td>
<td>0.021</td>
<td>0.0053</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>14.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Mean (this study) * and Literature Mean ± standard deviation. LOD ** limit of detection three times the standard deviation of seven blank measurements; for major elements in µg/L and for trace elements in ng/L. - : not determined or not reported.

* Major elements in wt. % are by XRF (average of 43 measurements); trace elements in µg/g by ICP-AES and ICP-MS (average of six measurements). Data were not tested for possible discordant outliers before calculating the mean values; this could be done in future (Barnett and Lewis, 1994; Verma, 2005; Verma and Quiroz-Ruiz, 2006a, 2006b, 2008; Verma et al., 2008).

** LOD (limit of detection) three times the standard deviation of seven blank measurements; for major elements in µg/L and for trace elements in ng/L. - : not determined or not reported.
in Table 2. Low concentration of SiO₂ is observed in CAL (2.20 to 3.58%), whereas high concentrations are found in BL (11.92 to 19.46%). Small variation is found in CaO contents in CAL (52.48 to 53.70%) and BL (40.64 to 45.33%). A higher concentration of Al₂O₃ is observed in BL (2.61 to 5.52%) than in CAL (0.57 to 1.06%). The Fe₂O₃ content in CAL and BL varies from 0.32 to 0.85% and from 1.36 to 2.68%, respectively. The contents of K₂O and Na₂O are low in both CAL and BL (Table 2). A high concentration of SiO₂ is observed in GS, which varies from 34.82 to 46.12%, whereas their CaO content is lower (13.05 to 25.30%). Maximum concentrations of Al₂O₃, Fe₂O₃, K₂O and Na₂O are also found in the GS (Table 2).

Trace elements

Trace element concentrations of limestones and gray shales were normalized against PAAS values (Taylor and McLennan, 1985) and are plotted in Figure 3. In limestones, the large-ion lithophile elements such as Rb and Ba show depletion compared to PAAS (Figures 3a, 3b). When compared to PAAS, CAL (Figure 3a) has low concentration of Sr, whereas BL (Figure 3b) has similar concentration of Sr. The ferromagnesian trace elements (Co, Ni, Cr and V) and the high field strength elements (HFS: Zr, Y, Nb, Hf, Th and U) are depleted with respect to those of PAAS.

PAAS-normalized patterns of gray shales show moderate depletion of Co, V, Rb, Ba, Zr, Y, Nb, Hf and Th, whereas Ni, Cr, Sr, Pb and U exhibit similar concentrations as PAAS (Figure 3c). The observed variations in the trace element abundances in CAL, BL and GS may be due to their lithology.

Rare earth elements

REE content is low in CAL (10.8 to 28.9 ppm) and relatively high in BL (38.5 to 75.9 ppm) and GS (108.5 to 206.7 ppm). ΣREE contents in CAL, BL and GS average 18, 59 and 157 ppm, respectively. The concentration of REE is less in limestones than in shales, consistent with the observation that marine carbonate phases contain significantly less REE than terrigenous materials (Piper, 1974). The variations in REE concentrations in the different litho-units of the Dalmiapuram Formation are probably controlled by the amount of biogenic calcite. This is supported by the strong negative correlation between CaO and ΣREE contents (r = -0.96, n = 11, at a significance level of 0.01, Bevington and Robinson, 2003; Verma, 2005).

PAAS-normalized REE+Y patterns of CAL, BL and GS are shown in Figure 4. CAL shows more or less flat REE+Y pattern with positive La and slightly negative Ce anomalies (Ce/Ce*: 0.83 to 0.97; Table 4) and chondritic Y/Ho ratios (16.11 to 32.20, average 25.8, Table 4; Y/Ho chondrite ratio = ~28). BL samples exhibit LREE-enriched but HREE-depleted patterns with positive Ce anomalies (Ce/Ce*: 1.03 to 1.17) and chondritic Y/Ho ratios (18.80 to 28.64, average 23.6). One sample from BL (K115) shows a negative Ce anomaly (Ce/Ce*: -0.86). Like BL, GS also shows flat LREE and depleted HREE pattern. La, Gd and Ce anomalies are completely absent in GS. The limestones (CAL and BL) and gray shales of the Dalmiapuram Formation show positive Eu anomalies (Table 4).

DISCUSSION

Source of REE

Large variations in ΣREE content are noticed among different litho-units of the Dalmiapuram Formation (Table 5). The average ΣREE content of the limestones from the Dalmiapuram Formation is lower than that of the shallow marine Maastrichtian Limestones (Table 5) of the Cauvery basin (Madhavaraju and Ramasamy, 1999a) and Kudankulam Limestones of southern India (Armstrong-Altrin et al., 2003; Table 5). Nevertheless, the average ΣREE content in gray shales of the Dalmiapuram Formation is higher than that of the Neoproterozoic shales (gray shales)
<table>
<thead>
<tr>
<th>Sample No</th>
<th>K14</th>
<th>K17</th>
<th>K19</th>
<th>KI10</th>
<th>K11</th>
<th>KI14</th>
<th>K15</th>
<th>KI19</th>
<th>GS1</th>
<th>GS2</th>
<th>GS3</th>
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</thead>
<tbody>
<tr>
<td>Ba</td>
<td>14</td>
<td>0.405</td>
<td>22</td>
<td>0.740</td>
<td>23</td>
<td>0.726</td>
<td>23</td>
<td>0.780</td>
<td>233</td>
<td>4.627</td>
<td>222</td>
</tr>
<tr>
<td>Co</td>
<td>1.20</td>
<td>0.028</td>
<td>1.01</td>
<td>0.023</td>
<td>1.33</td>
<td>0.030</td>
<td>1.45</td>
<td>0.026</td>
<td>4.56</td>
<td>0.011</td>
<td>4.42</td>
</tr>
<tr>
<td>Cr</td>
<td>8.07</td>
<td>0.380</td>
<td>7.20</td>
<td>0.362</td>
<td>-</td>
<td>-</td>
<td>9.40</td>
<td>0.420</td>
<td>17.03</td>
<td>0.662</td>
<td>94.69</td>
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<tr>
<td>Cu</td>
<td>10.44</td>
<td>0.162</td>
<td>12.97</td>
<td>0.109</td>
<td>12.19</td>
<td>0.094</td>
<td>6.81</td>
<td>0.065</td>
<td>25.33</td>
<td>0.322</td>
<td>12.35</td>
</tr>
<tr>
<td>Hf</td>
<td>0.05</td>
<td>0.002</td>
<td>0.08</td>
<td>0.005</td>
<td>0.28</td>
<td>0.005</td>
<td>0.12</td>
<td>0.005</td>
<td>0.73</td>
<td>0.002</td>
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</tr>
<tr>
<td>Sc</td>
<td>0.91</td>
<td>0.040</td>
<td>0.82</td>
<td>0.040</td>
<td>0.87</td>
<td>0.041</td>
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<td>0.049</td>
<td>1.99</td>
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<tr>
<td>Ti</td>
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<td>0.167</td>
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<td>Y</td>
<td>1.61</td>
<td>0.022</td>
<td>0.94</td>
<td>0.009</td>
<td>1.45</td>
<td>0.017</td>
<td>2.81</td>
<td>0.006</td>
<td>6.30</td>
<td>0.067</td>
<td>5.93</td>
</tr>
<tr>
<td>Zr</td>
<td>3.98</td>
<td>0.017</td>
<td>3.30</td>
<td>0.011</td>
<td>8.55</td>
<td>0.380</td>
<td>4.06</td>
<td>0.021</td>
<td>15.87</td>
<td>0.633</td>
<td>11.23</td>
</tr>
<tr>
<td>Nb</td>
<td>0.62</td>
<td>0.004</td>
<td>0.71</td>
<td>0.005</td>
<td>0.88</td>
<td>0.016</td>
<td>1.77</td>
<td>0.008</td>
<td>3.92</td>
<td>0.045</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni</td>
<td>18</td>
<td>0.375</td>
<td>16</td>
<td>0.350</td>
<td>12</td>
<td>0.220</td>
<td>18</td>
<td>0.048</td>
<td>22</td>
<td>0.240</td>
<td>19</td>
</tr>
<tr>
<td>Pb</td>
<td>1.15</td>
<td>0.007</td>
<td>1.34</td>
<td>0.008</td>
<td>2.55</td>
<td>0.018</td>
<td>0.97</td>
<td>0.008</td>
<td>4.36</td>
<td>0.056</td>
<td>5.11</td>
</tr>
<tr>
<td>Rb</td>
<td>1.54</td>
<td>0.058</td>
<td>1.75</td>
<td>0.065</td>
<td>3.93</td>
<td>0.137</td>
<td>2.66</td>
<td>0.082</td>
<td>11.47</td>
<td>0.475</td>
<td>10.41</td>
</tr>
<tr>
<td>Th</td>
<td>0.62</td>
<td>0.004</td>
<td>0.57</td>
<td>0.003</td>
<td>0.54</td>
<td>0.002</td>
<td>0.84</td>
<td>0.003</td>
<td>2.50</td>
<td>0.024</td>
<td>2.32</td>
</tr>
<tr>
<td>U</td>
<td>0.14</td>
<td>0.003</td>
<td>0.12</td>
<td>0.002</td>
<td>0.17</td>
<td>0.002</td>
<td>0.13</td>
<td>0.001</td>
<td>0.95</td>
<td>0.002</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 3. Trace and rare earth elements concentrations (ppm) in limestones and gray shales of the Dalmiapuram Formation.
of southern India (Nagarajan et al., 2007; Table 5). The REE content in the limestones are related to the amount of terrigenous particles present in them (Madhavaraju and Ramasamy, 1999a). Likewise, an increase in the REE content may be due to the increasing supply of terrigenous contaminants. Carbonates and authigenic marine phases mainly record the seawater-like REE pattern (Piper, 1991). PAAS-normalized REE patterns of CAL show more or less flat pattern, whereas BL and GS show LREE-enriched and HREE-depleted patterns. Both CAL and BL show non-seawater-like REE+Y patterns, i.e., absence of LREE depletions, La and Gd anomalies and superchondritic Y/Ho ratio. The non-seawater-like patterns in the carbonate rocks can result from the incorporation of terrestrial materials (Elderfield et al., 1990), Fe and Mn oxides (Bau et al., 1996) and phosphates (Byrne et al., 1996). In the studied sediments, the lack of HREE enrichment and the low concentration of REE preclude the possible significant contamination by Fe and Mn oxides and phosphates.

The inclusion of terrigenous materials in the limestones may be assessed by determining the relative abundance of $\text{Al}_2\text{O}_3$, Th and Sc. The concentrations of $\text{Al}_2\text{O}_3$ is lower in CAL (0.82 ± 0.2, n=4), but BL (3.39 ± 1.4, n=4) shows higher concentration of $\text{Al}_2\text{O}_3$ than the siliciclastic-contaminated carbonates ($\text{Al}_2\text{O}_3$ concentration of 1.59%, in Veizer, 1983). In the Dalmiapuram limestones, the $\text{Al}_2\text{O}_3$ contents show positive correlation with LREE depletion ($\text{Nd}_n/\text{Yb}_n$ ratio) (statistically significant at a significance level of 0.001; linear correlation coefficient $r=0.85$, n=8) and ΣREE contents (statistically significant at a significance level of 0.01; linear correlation coefficient $r=0.65$, n=8). Furthermore, $\text{Al}_2\text{O}_3$ content have significant positive correlation with trace elements such as Th and Sc (statistically significant at a very strict significance level of 0.001; linear correlation coefficient $r=0.79$ and $r=0.93$, respectively, n=8) which suggest that the presence of terrigenous materials can be considered as the dominant source of REE in these limestones.

The PAAS-normalized La$_n$/Yb$_n$ ratios vary slightly between limestones (CAL and BL) and gray shales. The limestones and gray shales show higher La$_n$/Yb$_n$ ratios (CAL: 1.8 ± 0.2; BL: 2.01 ± 0.2; GS: 1.82 ± 0.2; Table 4) than the terrigenous input values proposed by Condie (1991; about 1.0) and Sholokovitz (1990; about 1.3). The La$_n$/Yb$_n$ ratios of the Dalmiapuram limestones are generally similar to that of the shallow marine Maastrichtian Limestones (Table 5) of the Cauvery basin (Madhavaraju and Ramasamy, 1999a) and Kudankulam Limestones of
southern India (Armstrong-Altrin et al., 2003; Table 5). Y/Ho ratio has been considered as a proxy of seawater chemistry (Bau, 1996; Nozaki et al., 1997). Carbonates free from terrigenous materials display Y/Ho ratio between 44 and 74, but terrestrial materials and volcanic ash have constant chondritic Y/Ho values of ~28. The limestones (CAL and BL) of the Dalmiapuram Formation show low values of Y/Ho (25.8 ± 7.5, n=4; 23.6 ± 4.2, n=4; respectively) similar to that of GS (average 25.3). These values are more or less similar to chondritic values (~28). High REE contents, non-seawater-like REE patterns, the large presence of certain trace elements such as Sc, Th and Hf, high La/Yb, ratios and low Y/Ho ratios collectively suggest that the REE signals were mainly influenced by the incorporation of terrigenous materials in the limestones of the Dalmiapuram Formation.

The La/Sc, La/Co, Th/Sc, Th/Co, and Th/Cr ratios show significant variations in felsic and mafic rocks and are most useful in understanding the provenance composition (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995). La/Sc, La/Co, Th/Co, Th/Cr, Cr/Th, and Th/Sc ratios of limestones and gray shales of the Dalmiapuram Formation are compared with felsic and mafic rocks (fine fraction) as well as to upper continental crust (UCC) and PAAS values (Table 6), which suggest that these ratios are within the range of intermediate to felsic rocks. The REE patterns in the sedimentary rocks provide useful information regarding the source rock characteristics (Taylor and McLennan, 1985; McLennan, 1989). In the present study, PAAS-normalized values exhibit flat patterns and slight LREE enrichment, which suggest that the terrigenous materials present in the limestones and gray shales were mainly derived from the intermediate to felsic source rocks.

**Eu anomaly**

The limestones (CAL and BL) and gray shales from the Dalmiapuram Formation show small variations in Eu anomalies (Eu/Eu*: 1.23 ± 0.1, n=4, 1.16 ± 0.1, n=4 and 1.17 ± 0.1, n=3, respectively; Table 4). The limestones and gray shales show typical positive Eu anomalies. PASS-normalized positive Eu anomalies are found in sediments affected by hydrothermal solutions (Michard et al., 1983; German et al., 1993; Kurian et al., 2008), intense diagenesis (Murray et al., 1991b; MacRae et al., 1992), variations in plagioclase content (Nath et al., 1992) or as result of eolian input (Elderfield, 1988). Hydrothermal activity generally

![PAAS normalized REE diagrams for limestones and gray shales of Dalmiapuram Formation (a: CAL, b: BL and c: GS).](image-url)
Geochemistry of the Dalmiapuram Formation, Cauvery Basin, southeastern India

Table 4. Element ratios in limestones and gray shales of the Dalmiapuram Formation.

<table>
<thead>
<tr>
<th>Rock</th>
<th>Coral-algal Limestone</th>
<th>Bedded Limestone</th>
<th>Gray Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KI4 KI7 KI9 KI10</td>
<td>KI11 KI14 KI15 KI19</td>
<td>GS1 GS2 GS3</td>
</tr>
<tr>
<td>La/Sc</td>
<td>4.54</td>
<td>3.65</td>
<td>3.45</td>
</tr>
<tr>
<td>La/Co</td>
<td>3.44</td>
<td>2.96</td>
<td>2.26</td>
</tr>
<tr>
<td>Th/Sc</td>
<td>0.68</td>
<td>0.70</td>
<td>0.62</td>
</tr>
<tr>
<td>Th/Co</td>
<td>0.52</td>
<td>0.56</td>
<td>0.41</td>
</tr>
<tr>
<td>Th/Cr</td>
<td>0.08</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Cr/Th</td>
<td>13.02</td>
<td>12.63</td>
<td></td>
</tr>
<tr>
<td>V/(V+Ni)</td>
<td>0.36</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn*</td>
<td>0.355</td>
<td>0.258</td>
<td>0.384</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>1.16</td>
<td>1.20</td>
<td>1.35</td>
</tr>
<tr>
<td>Ce/Ce*</td>
<td>0.86</td>
<td>0.83</td>
<td>0.93</td>
</tr>
<tr>
<td>La/Sc/YbN</td>
<td>1.83</td>
<td>2.00</td>
<td>1.60</td>
</tr>
<tr>
<td>Nd/Sc/YbN</td>
<td>2.17</td>
<td>1.75</td>
<td>1.80</td>
</tr>
<tr>
<td>Y/Ho</td>
<td>32.20</td>
<td>23.50</td>
<td>16.11</td>
</tr>
</tbody>
</table>

occur in the deep-sea regions, but the samples from the Dalmiapuram Formation were deposited under shallow marine environments. So far, no eolian materials were reported from the limestones of Dalmiapuram Formation. MacRae et al. (1992) mentioned that the sediments can attain positive Eu anomalies due to diagenesis. The extent of diagenetic alterations in limestones can be assessed by using immobile trace elements. CAL and BL samples exhibit a positive correlation between Eu and immobile trace (Zr, Y and Th) elements (statistically significant at a significance level of 0.001; linear correlation coefficient $r=0.74$, $r=0.99$ and $r=0.96$, respectively, n=8) supporting the non-diagenetic origin of Eu.

The inclusion of detrital feldspar in the bulk sediments may produce significant positive Eu anomalies (Murray et al., 1991a). Element ratios such as K/Al and Na/Al are useful to distinguish the type of feldspars in the bulk sediments. In the present study, the K/Al ratios do not show any significant correlation with Eu/Eu* ($r=0.44$, n=11; not significant at a significance level of 0.001) whereas Na/Al ratios have significant positive correlation with Eu anomalies (statistically significant at a significance level of 0.001; linear correlation coefficient $r=0.86$, n=11) (Figure 5). Hence, the positive Eu anomalies in the limestones and gray shales may be due to the presence of plagioclase feldspar, rather than to a regional phenomenon like eolian input or hydrothermal events.

**Variation in Ce anomaly**

Numerous studies have been carried out on the behaviours of Ce in marine sediments to infer paleoceanographic conditions (Grandjean et al., 1987; German and Elderfield, 1990; Nath et al., 1997; Madhavaraju and Ramasamy, 1999a). The depletion of Eu in oceanic water results from redox changes relative to the rest of REE series (Elderfield, 1988; Piepgras and Jacobsen, 1992; Nath et al., 1994). Variations in Ce fractionation has been observed in the Cariaco Trench (De Baar et al., 1988), Chesapeake Bay (Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1992), anoxic Bannock (Schiift et al., 1989), Tyro basins (Bau et al., 1997), Saanich Inlet (German and Elderfield, 1989), and Oxygen Minimum Zone (OMZ) of northwestern Indian Ocean (German and Elderfield, 1990) and Black sea (German et al., 1991).

The Ce/Ce' values in CAL range from 0.83 to 0.97 (average 0.90 ± 0.06, n=4) whereas the Ce/Ce' values in BL vary between 0.86 and 1.17 (average 1.05 ± 0.14, n=4). In gray shales, the Ce/Ce' values ranging from 0.96 to 1.00

Table 5. Average geochemical values of the Dalmiapuram Formation compared to shallow and deep marine sediments.

<table>
<thead>
<tr>
<th>Rock</th>
<th>Dalmiapuram Formation</th>
<th>Maastrichtian Limestone$^2$</th>
<th>Kudankulam Carbonate Limestone$^3$</th>
<th>Arabian Sea Carbonate sediments$^4$</th>
<th>Indian Ocean Carbonate sediments$^5$</th>
<th>Neoproterozoic Gray Shale$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce/Ce'</td>
<td>0.9 ± 0.06</td>
<td>1.05 ± 0.14</td>
<td>0.98 ± 0.02</td>
<td>0.76 ± 0.16</td>
<td>0.9 ± 0.06</td>
<td>0.84 ± 0.06</td>
</tr>
<tr>
<td>La/Sc/YbN</td>
<td>1.8 ± 0.2</td>
<td>2.01 ± 0.2</td>
<td>1.82 ± 0.2</td>
<td>1.8 ± 0.5</td>
<td>2.7 ± 1.4</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>$\Sigma$REE</td>
<td>18 ± 8</td>
<td>59 ± 17</td>
<td>157 ± 49</td>
<td>73 ± 20</td>
<td>80 ± 40</td>
<td>78 ± 40</td>
</tr>
<tr>
<td>CeO</td>
<td>53 ± 5</td>
<td>42 ± 2</td>
<td>19 ± 6</td>
<td>42 ± 8</td>
<td>49 ± 3</td>
<td>29 ± 12</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>1.23 ± 0.1</td>
<td>1.16 ± 0.1</td>
<td>1.17 ± 0.1</td>
<td>0.58 ± 0.14</td>
<td>0.78 ± 0.31</td>
<td>1.15 ± 0.08</td>
</tr>
</tbody>
</table>

$^a$, $^b$, $^c$, $^d$, $^e$, $^f$: Present study, n=4, n=3, respectively; $^2$ Madhavaraju and Ramasamy (1999a), n=8; $^3$ Armstrong-Altrin et al. (2003), n=9; $^4$ Nath et al. (1997), n=9; $^5$ Nath et al. (1992), n=9; $^6$ Nagarajan et al. (2007), n=3.
Table 6. Range of element ratios of the Dalmiapuram Formation compared to felsic rocks, mafic rocks, Upper Continental Crust (UCC) and Post-Archaean Australian Shale (PAAS).

<table>
<thead>
<tr>
<th></th>
<th>CAL1a</th>
<th>Dalmiapuram Formation1</th>
<th>BL1b</th>
<th>Gray Shale1c</th>
<th>Range of sediments2</th>
<th>UCC3</th>
<th>PAAS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu/Eu*</td>
<td>1.20 – 1.35</td>
<td>1.08 – 1.22</td>
<td>1.10 – 1.22</td>
<td>0.40 – 0.94</td>
<td>0.71 – 0.95</td>
<td>0.63</td>
<td>0.66</td>
</tr>
<tr>
<td>La/Sc</td>
<td>3.45 – 6.23</td>
<td>3.98 – 8.04</td>
<td>3.23 – 3.86</td>
<td>2.50 – 16.3</td>
<td>0.43 – 0.86</td>
<td>2.21</td>
<td>2.40</td>
</tr>
<tr>
<td>La/Co</td>
<td>2.26 – 4.21</td>
<td>1.49 – 3.87</td>
<td>1.59 – 2.99</td>
<td>1.80 – 13.8</td>
<td>0.14 – 0.38</td>
<td>1.76</td>
<td>1.65</td>
</tr>
<tr>
<td>Th/Sc</td>
<td>0.62 – 0.86</td>
<td>0.81 – 1.28</td>
<td>0.81 – 1.15</td>
<td>0.84 – 20.5</td>
<td>0.05 – 0.22</td>
<td>0.79</td>
<td>0.90</td>
</tr>
<tr>
<td>Th/Cr</td>
<td>0.41 – 0.58</td>
<td>0.48 – 0.73</td>
<td>0.39 – 0.97</td>
<td>0.67 – 19.4</td>
<td>0.04 – 1.40</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>Cr/Th</td>
<td>0.07 – 0.08</td>
<td>0.02 – 0.20</td>
<td>0.10 – 0.11</td>
<td>0.13 – 2.7</td>
<td>0.018 – 0.046</td>
<td>0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

1a,1b,1c Present study, n=4, n=4, n=3, respectively. 2 Cullers (1994, 2000); Cullers and Podkovyrov (2000); Cullers et al. (1988). 3 Taylor and McLennan (1985).

In oceanic water, Ce/Ce* values range from <0.1 to 0.4 (Elderfield and Greaves, 1982; Piepgras and Jacobsen, 1992), whereas in average shale Ce/Ce* is 1 (Murray et al., 1991b). A remarkable variation in Ce/Ce* values is observed between CAL and BL. CAL shows a negative Ce anomaly whereas BL exhibits a distinct positive anomaly. The observed negative Ce anomalies in CAL are smaller than in the Arabian Sea sediments (Nath et al., 1992) and in deep-sea carbonates from the Indian Ocean (Nath et al., 1992), and these values are more or less comparable to shallow marine Maastrichtian limestones of the Cauvery basin (Madhavaraju and Ramasamy, 1999a) and Kudankulam Limestones of southern India (Armstrong-Altrin et al., 2003; Table 5). The absence of negative Ce anomalies is noticed in BL. The positive Ce anomalies occur as result of lithological input and diagenesis (Nath et al., 1992; Madhavaraju and Ramasamy, 1999a; Armstrong-Altrin et al., 2003), paleo-redox conditions (German and Elderfield, 1990) and Fe-organic-rich colloids from riverine input (Sholkovitz, 1992). In the studied limestones, Ce/Ce* values are not correlated with U content (r=0.48) and Ce/Ce* values show negative correlation with the amount of CaO (r=-0.60), which suggest that the variations in Ce/Ce* values in these limestones are not related to the paleo-redox conditions. In addition, Ce/Ce* values do not show any correlation with scavenging-type particle reactive elements (Ce/Ce* vs. Pb: r=0.03), in agreement with shallow marine depositional environments, where scavenging processes are negligible when compared with deep marine environments.

CAL exhibits high content of CaO, low contents of SiO₂ and Al₂O₃ and negative Ce anomaly, whereas BL show comparatively low content of CaO, high contents of SiO₂ and Al₂O₃ and positive Ce anomaly. The content of terrigenous components are low in CAL when compared with BL. The absence of Ce anomalies in BL may have resulted from the increasing supply of detrital materials. In the studied limestones, Ce is positively correlated with detrital elements such as Zr, Th, Y, Rb and Hf (statistically significant at a very strict significance level of 0.001; linear correlation coefficient r=0.66, 0.86, 0.98, 0.76 and 0.86, respectively, n=8). Like Ce, Ce/Ce* values also exhibit a positive correlation with Zr, Th, Y, Rb and Hf (statistically significant at a significance level of 0.05; linear correlation coefficient r=0.53, 0.66, 0.60, 0.63 and 0.62, respectively, n=8), but there is no significant correlation between Ce/Ce* values and Fe₂O₃ (r=0.14). Therefore, the observed variations in Ce contents and Ce anomalies between CAL and BL can be explained by the simple mixing between different proportions of detrital components (with Ce/Ce* values of 1) and seawater end members (Ce/Ce* <1).

Paleo-redox conditions

Manganese is highly sensitive to environment redox conditions. Low Eh conditions generally support the production of reduced, soluble forms (Mn²⁺) that migrate to an oxic zone where re-oxidised manganese can precipitate
(Calvert and Price, 1972; Balzer, 1982; Force and Cannon, 1988). Accordingly, for sediments deposited in pelagic and hemipelagic environments, which are subjected to a transition from anoxic to oxic conditions, the reducing condition initiate the enrichment of Mn in the pore waters of reducing layers and the subsequent upward distribution of dissolved manganese may precipitate in the solid phase, just below or above the redox boundary (Bellanca et al., 1996). The limestones (CAL and BL) and gray shales show little variations in MnO content (0.01 to 0.02%; 0.022 to 0.05%; 0.02 to 0.05%; respectively). The fluctuation in manganese values in the Dalmiapuram Formation may be due to the variations in the environmental conditions.

The variations in the solubility of reduced iron and manganese may lead to significant fractionation of these metals across the redox boundaries, with most of the iron being fixed in sulphide under low Eh conditions, while manganese tends to be incorporated under more oxygenated conditions above the redox boundary (Krauskopf, 1979; Bellanca et al., 1996). Based on these phenomenon, Machhour et al. (1994) and Bellanca et al. (1996) proposed the relationship Mn\(^{m^-}\) = log([Mn\(_{shale}\)/Mn\(_{shale}\)]/[Fe\(_{shale}\)/Fe\(_{shale}\)]) to find out the redox potential of the depositional environment. The mean values used for Mn\(_{shale}\) and Fe\(_{shale}\) are 600 and 46,150 ppm, respectively (Wedepohl, 1978). Both limestones (CAL and BL) of Dalmiapuram Formation show significant positive Mn\(^{m^-}\) values (0.258 to 0.462; 0.014 to 0.451; respectively; Table 2), whereas the gray shale show significant negative Mn\(^{m^-}\) values (-0.073 to -0.334). The limestones of Dalmiapuram Formation show significant positive Mn\(^{m^-}\) values suggesting that these limestones have been deposited under oxic condition. The more negative Mn\(^{m^-}\) values of gray shales suggest that they formed under reducing conditions.

Significant variations in vanadium content are observed in the Dalmiapuram Formation, where limestones exhibit low values (CAL: 5.1 to 10 ppm; BL: 14.49 to 40.85 ppm) and gray shales show slightly higher values (66.25 to 102.07 ppm). Likewise, Ni content also fluctuates in a similar manner (CAL: 12 to 18 ppm; BL: 19 to 22 ppm; 30 to 59 ppm). The proportionality of vanadium to nickel, mainly expressed as V/(V+Ni), has been commonly used to find out information on Eh, pH and sulphide activity in the depositional environment (Lewan and Maynard, 1982; Lewan, 1984; Brett and Wanty, 1991; Hatch and Leventhal, 1992; Tribovillard et al., 1994). The solubility of vanadium in natural waters, its extraction from seawater and absorption onto sediments are mainly influenced by redox conditions (Bellanca et al., 1996). Dissolved vanadium is readily bound to high molecular metallo-organic complexes (Lewan and Maynard, 1982) or absorbed onto biogenic materials (Prange and Kremling, 1985). During the early diagenetic alteration of sediments, vanadium tends to mobilize from the biogenic materials under oxic environments, whereas the mobilization of vanadium is very restricted in anoxic conditions (Shaw et al., 1990). In addition, nickel, along with Cu and Cr, is mainly enriched in organic-rich sediments where these metals are trapped with organic matter (Leventhal and Hosterman, 1982; Gilkson et al., 1985). Nevertheless, vanadium accumulates relative to nickel in reducing environments, where sulphate reduction (production of H\(_2\)S) is more efficient and Ni\(^{3+}\) may be partially delayed by NiS complexes (Lewan and Maynard, 1982; Lewan, 1984; Odermatt and Curiale, 1991; Huerta-Diaz and Morse, 1992).

The limestones (CAL and BL) show low V/(V+Ni) ratios (0.29 to 0.48, except K119 which show a high value of 0.67; Table 4) when compared with gray shales (0.61 to 0.69). V/(V+Ni) ratios of limestones of Dalmiapuram Formation are similar to those of normal marine systems (V/(V+Ni) ratio ≤0.5) calculated by Lewan (1984). The gray shales generally show V/(V+Ni) ratios higher than 0.5, which strongly suggest that these shales were deposited under dysoxic/anoxic conditions. If V/(V+Ni) ratios are greater than 0.8, they would indicate the presence of significant dissolved H\(_2\)S in highly reducing bottom waters of a marine environment (Hatch and Leventhal, 1992). The V/(V+Ni) ratios in gray shales (0.64, n=3) are lower than 0.8, which indicates the moderate frequency in the redox state of the depositional environment of the gray shale member of Dalmiapuram Formation.

**CONCLUSIONS**

The concentrations of major, trace and REE are significantly varied between different litho-units of the Lower Cretaceous Dalmiapuram Formation distributed in southeastern India. The limestones exhibit high REE contents, non-seawater-like REE patterns, high La\(_{o} \)/Yb\(_{n}\) ratios and low Y/Ho ratios, indicating that the REE concentrations in these limestones were mainly influenced by the incorporation of terrigenous materials. The limestones and gray shales show a positive Eu anomaly, which suggests the enrichment of detrital feldspar anomaly, particularly plagioclase feldspar. The limestones show significant variations in Ce anomalies. The observed variations in Ce anomalies in the limestones are mainly controlled by the input of detrital materials. Geochemical parameters such as La/Sc, La/Co, Th/Co, Th/Cr, Cr/Th, and Th/Sr ratios are within the range of intermediate to felsic rocks. The limestones (CAL and BL) show positive Mn\(^{m^-}\) values and high V/(V+Ni) ratios suggesting that they formed in an oxidizing environment whereas negative Mn\(^{m^-}\) values and high V/(V+Ni) ratios in the gray shales suggest that they were deposited under reducing conditions.

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