

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

Jayagopal Madhavaraju^{1,*} and Yong Il Lee²

¹ Estación Regional del Noroeste, Instituto de Geología, Universidad Nacional Autónoma de México, Apartado Postal 1039, 83000 Hermosillo, Sonora, Mexico.

² School of Earth and Environmental Sciences, Seoul National University
Seoul 151-747, Korea.

* mj@geologia.unam.mx

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 Σ REE 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 K115) 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 LaN/YbN ratios and low Y/Ho ratios, suggest that the observed variations in Σ REE 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 Postarqueana (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 Σ ETR 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 ($Eu/Eu^*: 1.23 \pm 0.10$, $n=4$, 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 ($Ce/Ce^*: 0.90 \pm 0.06$, $n=4$) mientras que BL muestra una anomalía de Ce positiva ($Ce/Ce^*: 1.05 \pm 0.14$, $n=4$; excepto KI15) y las lutitas grises no muestran anomalías en Ce ($Ce/Ce^*: 0.98 \pm 0.02$, $n=3$). Las variaciones en las anomalías 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_N/Yb_N y las proporciones bajas de Y/Ho sugieren que las variaciones observadas en Σ ETR 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 Th/Sc sugieren que los materiales terrígenos presentes en la Formación Dalmiapuram se derivaron principalmente de rocas intermedias a félsicas. 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.

INTRODUCTION

The behavior of rare earth elements (REEs) in marine waters, sediments and carbonate rocks has been discussed by many workers (Ronov *et al.*, 1967; Piper, 1974; Klinkhammer *et al.*, 1983; De Baar *et al.*, 1988; Elderfield *et al.*, 1990). The REE concentration in seawater is influenced 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; Piegras and Jacobsen, 1992). The distribution of REEs, particularly the Ce anomaly in marine clastic sediments and carbonate rocks, provide useful information on marine depositional environments like marine anoxia (Liu *et al.*, 1988; German and Elderfield, 1990; Murray *et al.*, 1991a), surface productivity variations (Toyoda *et al.*, 1990), oceanic paleo-redox conditions (Liu *et al.*, 1988), proximity to source area (Murray *et al.*, 1991a), lithology and diagenesis (Nath *et al.*, 1992; Madhavaraju and Ramasamy, 1999a; Armstrong-Altrin *et al.*, 2003).

The REEs generally display uniform trivalent behavior, except for Ce and Eu. Europium exhibits Eu^{+2} and Eu^{+3} valences, whereas cerium shows Ce^{+3} and Ce^{+4} valences. Ce anomalies in marine carbonate rocks are used as a reliable

indicator for understanding the paleo-redox conditions (Liu *et al.*, 1988). However, many researchers raised concerns against the usage of Ce anomalies as a paleo-redox indicator (German and Elderfield, 1990; Murray *et al.*, 1991a; Nath *et al.*, 1992, 1997). The variations in Ce anomalies can result from many factors such as paleo-redox conditions (German and Elderfield, 1990), lithology and diagenesis (Nath *et al.*, 1992; Madhavaraju and Ramasamy, 1999a; Armstrong-Altrin *et al.*, 2003) and Fe-organic-rich colloids from river sources (Sholkovitz, 1992).

The chemical signatures, particularly REEs in ancient marine environments, provide information regarding the secular changes in detrital influx and oxygenation conditions at the sediment-water interface (*e.g.*, Holser, 1997; Kamber and Webb, 2001). However, seawater signatures are completely masked by the inclusion of terrigenous materials, which have relatively high, non-seawater-like REE contents (Murray *et al.*, 1992; Webb and Kamber, 2000; Nothdurft *et al.*, 2004). The identification of the incorporation of terrigenous material into marine carbonate as contaminants is important to understand the geochemistry of carbonate rocks. The Lower Cretaceous Dalmiapuram Formation, distributed in southeastern India, is composed of limestones and shales, and provides a good example to identify the role

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 paleo-redox conditions in the Dalmiapuram Formation.

GEOLOGY 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 (Biswas *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

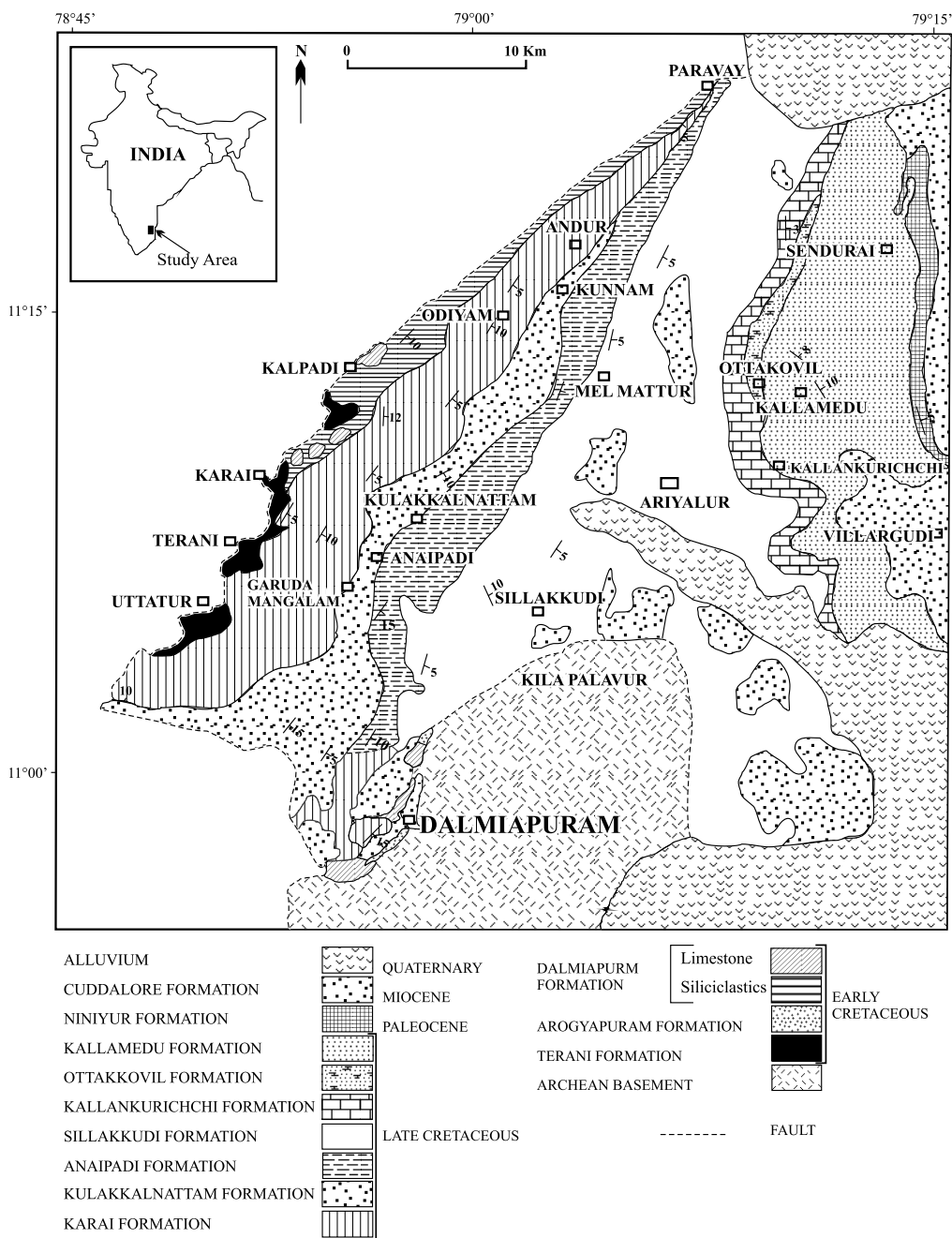


Figure 1. Geological map of the Ariyalur area of the Cauvery basin (modified after Sundaram *et al.*, 2001).

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 (biohermal 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

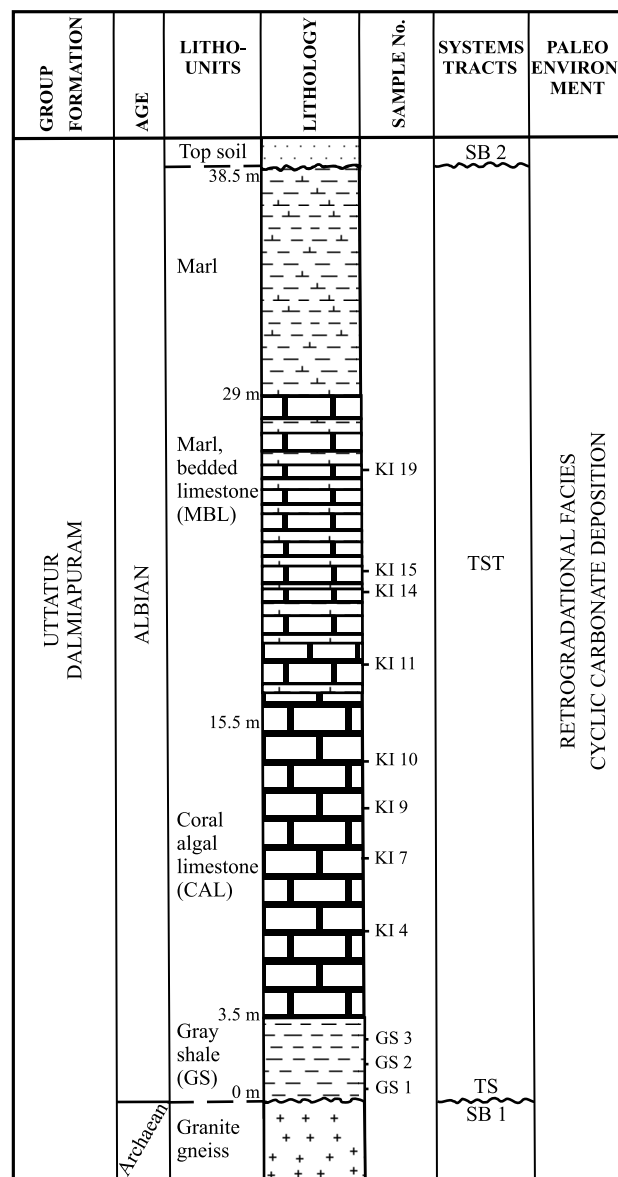


Figure 2. Lithostratigraphy, systems tracts and paleoenvironment of the Dalmiapuram Formation in the Kallakudi quarry II (System tracts and paleoenvironmental interpretation after Nagendra *et al.*, 2002). SB1: Sequence Boundary 1; TS: Transgressive Surface; TST: Transgressive System Tracts; SB2: Sequence Boundary 2.

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

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.

Oxide (%); element (ppm)	Mean (this study) *	Literature		LOD **
		Mean	Standard deviation	
SiO ₂	50.72	50.4	0.96	-
Al ₂ O ₃	16.48	16.4	0.30	5
Fe ₂ O ₃	7.11	6.8	0.60	20
CaO	1.42	1.37	0.10	5
MgO	3.11	3.0	0.10	5
K ₂ O	3.59	3.55	0.17	5
Na ₂ O	3.60	3.83	0.11	50
MnO	0.10	0.098	0.009	5
TiO ₂	0.70	0.75	0.07	15
P ₂ O ₅	0.17	0.16	0.021	15
LOI	14.09	-	-	-
Ba	420.6	480	41	-
Co	20.2	20	1.6	0.0287
Cr	77.1	97	8	-
Cu	34.6	30	3	0.0552
Hf	3.48	3.7	0.5	0.0012
Sc	-	17	1	-
V	128.4	140	6	-
Y	24.91	28	3	0.0075
Sr	133.7	150	15	-
Zr	125.6	130	13	-
Nb	15.01	12	-	0.0053
Ni	47	53	8	0.0466
Pb	28.44	24	3	0.0598
Rb	145.88	150	6	0.0818
Th	11.96	12	1	0.0473
U	2.76	2.7	0.3	0.0008
La	41.46	43	4	0.0044
Ce	87.32	88	9	0.0030
Pr	10.06	-	-	0.0031
Nd	38.10	38	5	0.0034
Sm	7.61	7.5	0.6	0.0034
Eu	1.66	1.6	0.14	0.0031
Gd	5.89	5.8	0.7	0.0036
Tb	1.28	0.96	0.09	0.0024
Dy	5.92	5.2	0.3	0.0024
Ho	1.16	1.0	0.1	0.0027
Er	3.09	3.0	-	0.0024
Tm	0.56	0.43	0.43	0.0023
Yb	2.70	2.6	0.3	0.0029
Lu	0.53	0.4	0.04	0.0018

* 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.

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 Ultracore 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

Table 2. Major oxides concentrations (wt.%) in limestones and gray shales of the Dalmiapuram Formation.

Rock Sample No	Coral-algal Limestone				Bedded Limestone				Gray Shale		
	KI4	KI7	KI9	KI10	KI11	KI14	KI15	KI19	GS1	GS2	GS3
SiO ₂	2.20	2.53	3.21	3.58	11.92	15.74	16.84	19.46	46.12	41.17	34.82
Al ₂ O ₃	0.57	1.06	0.68	0.98	2.61	2.76	5.52	2.68	13.27	10.47	8.92
Fe ₂ O ₃	0.68	0.85	0.32	0.53	1.36	1.38	2.68	1.64	4.95	4.55	3.32
CaO	53.70	52.88	52.76	52.48	45.33	42.91	40.85	40.64	13.05	18.09	25.30
MgO	0.33	0.40	0.46	0.38	0.82	0.84	0.80	0.79	1.67	1.31	1.10
K ₂ O	0.16	0.14	0.03	0.25	0.67	0.26	0.96	0.38	5.34	2.48	3.10
Na ₂ O	0.03	0.03	0.11	0.05	0.11	0.03	0.08	0.03	0.43	0.75	0.19
MnO	0.02	0.02	0.01	0.02	0.05	0.04	0.045	0.022	0.04	0.05	0.02
TiO ₂	0.04	0.02	0.01	0.06	0.14	0.08	0.10	0.07	0.63	0.48	0.36
P ₂ O ₅	0.04	0.12	0.02	0.08	0.09	0.03	0.08	0.02	0.22	0.10	0.13
LOI	42.12	41.60	42.17	41.15	36.93	35.74	31.95	33.95	13.73	18.87	22.20
Total	99.89	99.65	99.78	99.56	100.03	99.81	99.905	99.682	99.45	98.32	99.46

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 (HFSE: 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). Σ REE 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 Σ REE 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 (KI15) 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 Σ REE content are noticed among different litho-units of the Dalmiapuram Formation (Table 5). The average Σ REE 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 Σ REE content in gray shales of the Dalmiapuram Formation is higher than the in the Neoproterozoic shales (gray shales)

Table 3. Trace and rare earth elements concentrations (ppm) in limestones and gray shales of the Dalmiapuram Formation.

Sample No	Coral-algal Limestone										Bedded Limestone										Grey shale					
	K14		K17		K19		K110		K111		K114		K115		K119		GS1		GS2		GS3					
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.				
Ba	14	0.405	22	0.740	23	0.726	23	0.780	233	4.627	222	4.120	162	3.622	91	2.714	472	5.260	543	5.890	313	4.191				
Co	1.20	0.028	1.01	0.023	1.33	0.030	1.45	0.026	4.56	0.011	4.42	0.019	3.13	0.015	5.12	0.104	16.94	0.106	20.34	0.112	7.82	0.087				
Cr	8.07	0.380	7.20	0.362	-	-	9.40	0.420	17.03	0.662	94.69	3.813	11.95	0.439	-	-	111.36	3.748	78.89	3.215	69.79	3.024				
Cu	10.44	0.162	12.97	0.109	12.19	0.094	6.81	0.065	25.33	0.322	12.35	0.084	15.26	0.098	13.14	0.221	27.21	0.211	22.05	0.104	28.31	0.051				
Hf	0.05	0.002	0.08	0.002	0.28	0.005	0.12	0.005	0.73	0.002	0.61	0.015	0.58	0.015	0.53	0.011	2.63	0.003	2.83	0.011	1.20	0.006				
Sc	0.91	0.040	0.82	0.040	0.87	0.041	0.98	0.049	1.99	0.080	2.45	0.089	2.81	0.095	1.92	0.074	10.98	0.422	9.70	0.402	7.22	0.276				
V	10.00	0.198	6.89	0.112	5.10	0.091	8.14	0.167	19.33	0.352	14.49	0.275	17.28	0.307	40.85	0.783	102.07	1.790	78.51	0.831	66.25	0.695				
Y	1.61	0.022	0.94	0.009	1.45	0.017	2.81	0.006	6.30	0.067	5.93	0.046	4.22	0.034	2.82	0.025	16.14	0.051	13.12	0.091	9.09	0.069				
Sr	115	2.920	111	3.010	145	4.126	116	3.500	237	4.11	284	5.57	203	4.06	234	4.19	194	3.570	209	3.430	219	3.400				
Zr	3.98	0.017	3.30	0.011	8.55	0.380	4.06	0.021	15.87	0.633	11.22	0.471	15.89	0.618	16.88	0.640	51.88	2.140	108.40	3.527	37.29	1.248				
Nb	0.62	0.004	0.71	0.005	0.88	0.016	1.77	0.008	3.92	0.045	1.99	0.016	2.04	0.017	1.95	0.018	3.85	0.009	7.35	0.061	6.28	0.030				
Ni	18	0.375	16	0.350	12	0.220	18	0.048	22	0.240	19	0.254	19	0.250	19	0.104	59	0.261	52	0.283	30	0.346				
Pb	1.15	0.007	1.34	0.008	2.55	0.018	0.97	0.008	4.36	0.056	5.11	0.038	4.77	0.031	3.94	0.023	23.63	0.063	17.49	0.053	10.01	0.045				
Rb	1.54	0.058	1.75	0.065	3.93	0.137	2.66	0.082	11.47	0.475	10.41	0.171	12.06	0.221	13.42	0.072	80.33	0.832	52.56	0.398	35.90	0.758				
Th	0.62	0.004	0.57	0.003	0.54	0.002	0.84	0.003	2.50	0.024	2.32	0.015	2.28	0.013	2.46	0.013	12.61	0.121	7.90	0.038	7.60	0.061				
U	0.14	0.003	0.12	0.002	0.17	0.002	0.13	0.001	0.95	0.002	0.63	0.002	0.51	0.002	0.33	0.004	3.56	0.034	3.05	0.018	1.40	0.007				
La	4.13	0.054	2.99	0.037	3.00	0.043	6.11	0.070	15.99	0.083	15.41	0.194	12.11	0.175	7.65	0.053	42.34	0.428	32.41	0.379	23.35	0.210				
Ce	7.42	0.027	4.07	0.013	5.57	0.018	11.86	0.092	29.88	0.106	33.77	0.193	18.94	0.161	16.68	0.159	83.54	0.728	64.44	0.609	44.78	0.455				
Pr	0.85	0.007	0.42	0.005	0.58	0.006	1.29	0.020	2.93	0.032	2.93	0.029	2.20	0.022	1.54	0.020	9.51	0.025	6.90	0.082	4.75	0.094				
Nd	4.28	0.021	2.30	0.011	3.08	0.022	6.65	0.016	15.66	0.083	16.43	0.148	13.15	0.140	8.65	0.088	47.93	0.232	35.64	0.351	24.47	0.308				
Sm	0.50	0.002	0.21	0.002	0.36	0.004	0.78	0.003	1.81	0.008	1.73	0.032	1.50	0.034	0.98	0.023	6.22	0.029	4.34	0.015	3.00	0.054				
Eu	0.12	0.001	0.07	0.001	0.11	0.002	0.19	0.001	0.47	0.003	0.46	0.004	0.36	0.004	0.26	0.007	1.55	0.001	1.12	0.007	0.70	0.010				
Gd	0.47	0.001	0.27	0.001	0.42	0.002	0.74	0.005	1.87	0.019	1.91	0.016	1.42	0.014	0.98	0.014	6.15	0.082	4.32	0.069	3.00	0.011				
Tb	0.05	0.002	0.03	0.001	0.08	0.001	0.05	0.001	0.16	0.002	0.26	0.004	0.13	0.003	0.15	0.001	0.78	0.002	0.56	0.009	0.29	0.003				
Dy	0.31	0.004	0.19	0.002	0.27	0.002	0.49	0.005	1.18	0.005	1.19	0.005	0.81	0.004	0.62	0.006	3.69	0.019	2.77	0.054	1.76	0.032				
Ho	0.05	0.002	0.04	0.001	0.09	0.001	0.09	0.003	0.22	0.002	0.27	0.002	0.17	0.001	0.15	0.002	0.67	0.005	0.56	0.010	0.32	0.002				
Er	0.18	0.001	0.09	0.001	0.16	0.004	0.39	0.003	0.65	0.005	0.68	0.004	0.47	0.002	0.35	0.003	2.01	0.014	1.55	0.018	0.96	0.024				
Tm	0.01	0.0001	0.02	0.001	0.05	0.0004	0.02	0.0003	0.08	0.002	0.12	0.001	0.08	0.003	0.07	0.001	0.26	0.001	0.24	0.005	0.12	0.001				
Yb	0.16	0.001	0.11	0.001	0.14	0.001	0.24	0.004	0.56	0.003	0.62	0.009	0.39	0.007	0.31	0.003	1.83	0.001	1.39	0.030	0.84	0.018				
Lu	0.01	0.0003	0.02	0.001	0.05	0.0003	0.02	0.001	0.07	0.002	0.12	0.002	0.09	0.002	0.07	0.002	0.26	0.001	0.23	0.004	0.11	0.001				
ΣREE	18.5		10.8		14.0		28.9		71.5		75.9		51.8		38.5		206.7		156.5		108.5					

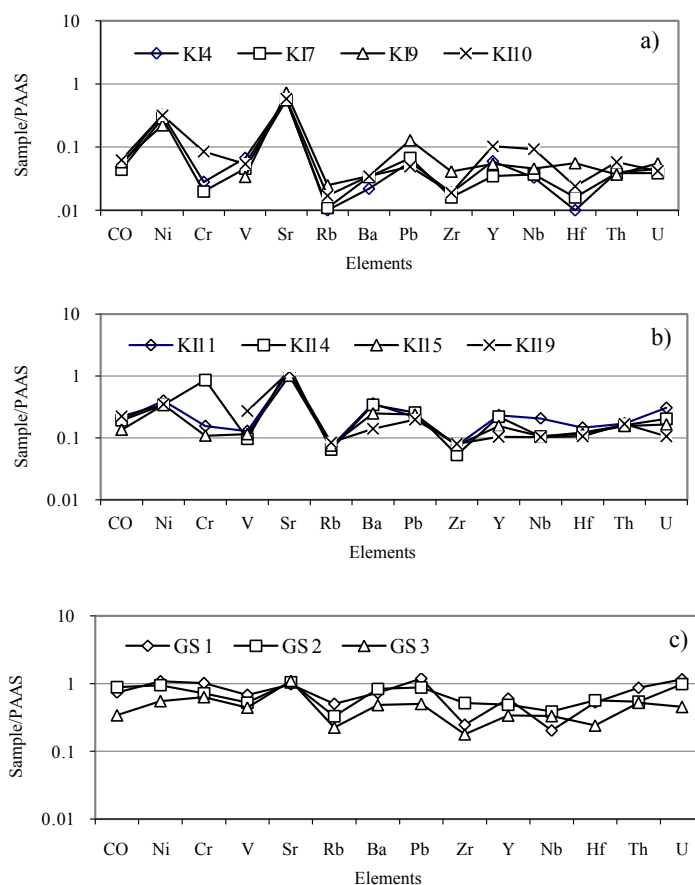


Figure 3. PAAS-normalized trace element diagrams for limestones (a: CAL, b: BL) and gray shales (c: GS) of the Dalmiapuram Formation.

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 depletion, 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 Al_2O_3 , Th and Sc. The concentrations of Al_2O_3 is lower in CAL (0.82 ± 0.2 , $n=4$), but BL (3.39 ± 1.4 , $n=4$) shows higher concentration of Al_2O_3 than the siliciclastic-

contaminated carbonates (Al_2O_3 concentration of 1.59%, *in* Veizer, 1983). In the Dalmiapuram limestones, the Al_2O_3 contents show positive correlation with LREE depletion (Nd_N/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, Al_2O_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 Sholkovitz (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

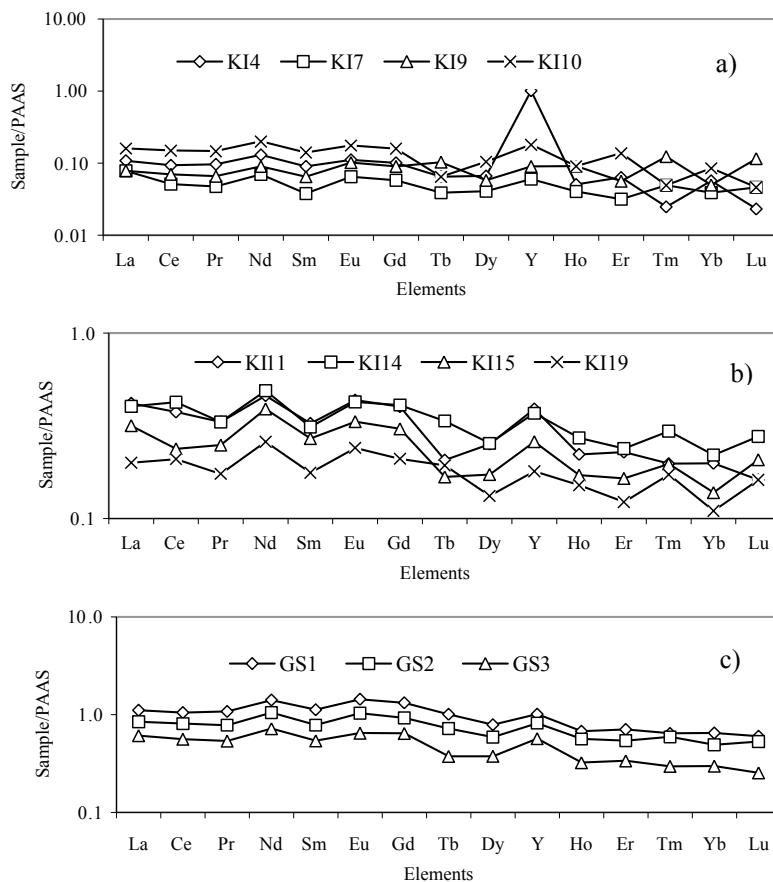


Figure 4. PAAS normalized REE diagrams for limestones and gray shales of Dalmiapuram Formation (a: CAL, b: BL and c: GS).

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_N/Yb_N 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

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

Rock Sample No	Coral-algal Limestone				Bedded Limestone				Gray Shale		
	KI4	KI7	KI9	KI10	KI11	KI14	KI15	KI19	GS1	GS2	GS3
La/Sc	4.54	3.65	3.45	6.23	8.04	6.29	4.31	3.98	3.86	3.31	3.23
La/Co	3.44	2.96	2.26	4.21	3.51	3.49	3.87	1.49	2.50	1.59	2.99
Th/Sc	0.68	0.70	0.62	0.86	1.26	0.95	0.81	1.28	1.15	0.81	1.05
Th/Co	0.52	0.56	0.41	0.58	0.55	0.52	0.73	0.48	0.74	0.39	0.97
Th/Cr	0.08	0.08	-	0.07	0.15	0.02	0.20	-	0.11	0.10	0.11
Cr/Th	13.02	12.63	-	11.19	6.81	40.81	5.24	-	8.83	9.99	9.18
V/(V+Ni)	0.36	0.30	0.30	0.31	0.47	0.43	0.48	0.68	0.63	0.60	0.69
Mn*	0.355	0.258	0.384	0.462	0.451	0.348	0.111	0.014	-0.206	-0.073	-0.334
Eu/Eu*	1.16	1.20	1.35	1.20	1.22	1.19	1.16	1.08	1.18	1.22	1.10
Ce/Ce*	0.86	0.83	0.93	0.97	1.03	1.17	0.86	1.14	0.96	1.00	0.98
La _N /Yb _N	1.83	2.00	1.60	1.78	2.10	1.82	2.29	1.82	1.71	1.73	2.03
Nd _N /Yb _N	2.17	1.75	1.80	2.22	2.30	2.23	2.79	2.36	2.17	2.14	2.40
Y/Ho	32.20	23.50	16.11	31.20	28.64	21.96	24.82	18.80	24.09	23.43	28.41

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 0.01 nor even at 0.05), 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 Ce 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 (Schijf *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.

	Dalmiapuram Formation			Maastrichtian Limestone ²	Kudankulam Limestone ³	Arabian Sea carbonate sediments ⁴	Indian Ocean carbonate sediments ⁵	Neoproterozoic Gray shale ⁶
	CAL ^{1a}	BL ^{1b}	Gray Shale ^{1c}					
Ce/Ce*	0.9 ± 0.06	1.05 ± 0.14	0.98 ± 0.02	0.76 ± 0.16	0.9 ± 0.06	0.84 ± 0.06	0.56	-
La _N /Yb _N	1.8 ± 0.2	2.01 ± 0.2	1.82 ± 0.2	1.8 ± 0.5	2.7 ± 1.4	0.8 ± 0.2	1.03	-
ΣREE	18 ± 8	59 ± 17	157 ± 49	73 ± 20	80 ± 40	78 ± 40	-	125 ± 11
CaO	53 ± 0.5	42 ± 2	19 ± 6	42 ± 8	49 ± 3	29 ± 12	36.6	-
Eu/Eu*	1.23 ± 0.1	1.16 ± 0.1	1.17 ± 0.1	0.58 ± 0.11	0.78 ± 0.31	1.15 ± 0.08	-	0.58 ± 0.25

^{1a,1b,1c} Present study, $n=4$, $n=4$, $n=3$, 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); 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).

	Dalmiapuram Formation ¹			Range of sediments ²		UCC ³	PAAS ³
	CAL ^{1a}	BL ^{1b}	Gray Shale ^{1c}	Felsic rocks	Mafic rocks		
Eu/Eu*	1.20 – 1.35	1.08 – 1.22	1.10 – 1.22	0.40 – 0.94	0.71 – 0.95	0.63	0.66
La/Sc	3.45 – 6.23	3.98 – 8.04	3.23 – 3.86	2.50 – 16.3	0.43 – 0.86	2.21	2.40
La/Co	2.26 – 4.21	1.49 – 3.87	1.59 – 2.99	1.80 – 13.8	0.14 – 0.38	1.76	1.65
Th/Sc	0.62 – 0.86	0.81 – 1.28	0.81 – 1.15	0.84 – 20.5	0.05 – 0.22	0.79	0.90
Th/Co	0.41 – 0.58	0.48 – 0.73	0.39 – 0.97	0.67 – 19.4	0.04 – 1.40	0.63	0.63
Th/Cr	0.07 – 0.08	0.02 – 0.20	0.10 – 0.11	0.13 – 2.7	0.018 – 0.046	0.13	0.13
Cr/Th	11.19 – 13.02	5.24 – 40.81	8.83 – 9.99	4.00 – 15.0	25 – 500	7.76	7.53

^{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).

(average 0.98 ± 0.02 , n=3). 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.*, 1997) 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

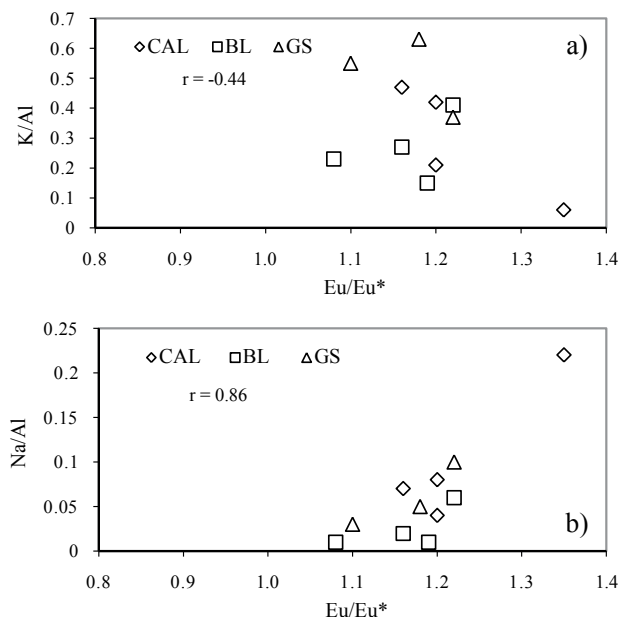


Figure 5. Bivariate plots of Eu/Eu* vs. K/Al and Eu/Eu* vs. Na/Al for the Dalmiapuram Formation.

(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 $Mn^* = \log[(Mn_{\text{sample}}/Mn_{\text{shale}})/(Fe_{\text{sample}}/Fe_{\text{shale}})]$ 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^* values (0.258 to 0.462; 0.014 to 0.451; respectively; Table 2), whereas the gray shale show significant negative Mn^* values (-0.073 to -0.334). The limestones of Dalmiapuram Formation show significant positive Mn^* values suggesting that these limestones have been deposited under oxic condition. The more negative Mn^* 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; Breit 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_2S) is more efficient and Ni^{2+} 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 KI19 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 support 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_2S 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_N/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, 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/Sc ratios are within the range of intermediate to felsic rocks. The limestones (CAL and BL) show positive Mn^* values and low $V/(V+Ni)$ ratios suggesting that they formed in an oxidizing environment whereas negative Mn^* values and high $V/(V+Ni)$ ratios in the gray shales suggest that they were deposited under reducing conditions.

ACKNOWLEDGEMENTS

The first author would like to thank Dr. Thierry Calmus, ERNO, Instituto de Geologia, UNAM for his support and

encouragement during this work. We would like to express our gratefulness to Prof. S.P. Verma for his innovative ideas and useful suggestions. We thank Prof. R.L. Cullers and an anonymous reviewer for critical reviews and constructive comments. This work is partly supported by PAPIIT Project (No. IN121506-3 to JM). This research is also supported by Korea Science and Engineering Foundation (KOSEF) grant (R01-2000-000-00056-0 to YIL).

REFERENCES

- Armstrong-Altrin, J.S., Verma, S.P., Madhavaraju, J., Lee, Y.I., Ramasamy, S., 2003, Geochemistry of Late Miocene Kudankulam Limestones, South India: *International Geology Review*, 45, 16-26.
- Balzer, W., 1982, On the distribution of iron and manganese at the sediment/water interface: thermodynamic versus kinetic control: *Geochimica et Cosmochimica Acta*, 46, 1153-1161.
- Banerji, R.K., 1972, Stratigraphy and micropalaeontology of the Cauvery Basin, Part-I, exposed area: *Journal of Paleontological Society of India*, 17, 1-24.
- Banerji, R.K., Ramasamy, S., Malini, C.S., Singh, D., 1996, Uttatur Group redefined: *Geological Society of India, Memoir* 37, 213-229.
- Barnett, V., Lewis, T., 1994, *Outliers in Statistical Data*: Chichester, UK, John Wiley & Sons, Third edition, 584 p.
- Bau, M., 1996, Controls on fractionation of isoivalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf and lanthanide tetrad effect: *Contributions to Mineralogy and Petrology*, 123, 323-333.
- Bau, M., Koschinsky, A., Dulski, P., Hein, J.R., 1996, Comparison of the partitioning behaviours of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater: *Geochimica et Cosmochimica Acta*, 60, 1709-1725.
- Bau, M., Moeller, P., Dulski, P., 1997, Yttrium and lanthanides in eastern Mediterranean seawater and their fractionation during redox cycling: *Marine Chemistry*, 56, 123-132.
- Bellanca, A., Claps, M., Erba, E., Masetti, D., Neri, R., Premoli-Silva, I., Venezia, F., 1996, Orbitally induced limestone/marlstone rhythms in the Albian-Cenomanian Cison section (Venetian region, northern Italy): sedimentology, calcareous and siliceous plankton distribution, elemental and isotope geochemistry: *Palaeogeography, Palaeoclimatology, Palaeoecology*, 126, 227-260.
- Bevington, P.R., Robinson, D.K., 2003, *Data Reduction and Error Analysis for the Physical Sciences*: Boston, MA, USA, McGraw-Hill, 320 p.
- Biswas, S.K., Bhasin, A.C., Ram, J., 1993, Classification of Indian sedimentary basins in the framework of plate tectonics, in Biswas, S.K., Dave, A., Garg, P., Pandey, J., Maithani, A. Thomas, N.J. (eds.), *Proceedings Second Seminar on Petroliferous Basins of India*: Dehra Dun, Indian Petroleum Publishers, v. 1, 1-217.
- Blanford, H.F., 1862, On the Cretaceous and other rocks of South Arcot and Trichinopoly Districts: *Memoir Geological Survey of India*, 4, 1-217.
- Breit, G.N., Wanty, R.B., 1991, Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis: *Chemical Geology*, 91, 83-97.
- Byrne, R.H., Liu, X., Schijf, J., 1996, The influence of phosphate coprecipitation on rare earth element distributions in natural waters: *Geochimica et Cosmochimica Acta*, 60, 3341-3346.
- Calvert, S.E., Price, N.B., 1972, Diffusion and reaction profiles of dissolved manganese in the pore waters of marine sediments: *Earth Planetary Science Letters*, 16, 245-259.
- Condie, K.C., 1991, Another look at rare earth elements in shales: *Geochimica et Cosmochimica Acta*, 55, 2527-2531.
- Cox, R., Low, D.R., Cullers, R.L., 1995, The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States: *Geochimica et Cosmochimica Acta*, 59(14), 2919-2940.
- Cullers, R.L., 1994, The controls on the major and trace element variation of shales, siltstones and sandstones of Pennsylvanian - Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, USA: *Geochimica et Cosmochimica Acta*, 58(22), 4955-4972.
- Cullers, R.L., 1995, The controls on the major and trace element evolution of shales, siltstones and sandstones of Ordovician to Tertiary age in the Wet Mountain region, Colorado, U.S.A.: *Chemical Geology*, 123(1-4), 107-131.
- Cullers, R.L., 2000, The geochemistry of shales, siltstones and sandstones of Pennsylvanian-Permian age, Colorado, U.S.A.: implications for provenance and metamorphic studies: *Lithos*, 51, 305-327.
- Cullers, R.L., Basu, A., Suttner, L., 1988, Geochemical signature of provenance in sand-size material in soils and stream sediments near the Tobacco Root batholith, Montana, USA: *Chemical Geology*, 70(4), 335-348.
- Cullers, R.L., Podkovyrov, V.N., 2000, Geochemistry of the Mesoproterozoic Lakhanda shales in southeastern Yakutia, Russia: implications for mineralogical and provenance control, and recycling: *Precambrian Research*, 104(1-2), 77-93.
- De Baar, H.J.W., German, C.G., Elderfield, H., Van-Gaans, P., 1988, Rare earth elements distributions in anoxic waters of the Cariaco Trench: *Geochimica et Cosmochimica Acta*, 52, 1203-1219.
- Elderfield, H., 1988, The oceanic chemistry of the rare earth elements: *Philosophical Transactions of the Royal Society of London*, 325, 105-106.
- Elderfield, H., Greaves, M.J., 1982, The rare earth elements in seawater: *Nature* 296, 214-219.
- Elderfield, H., Upstill-Goddard, R., Sholkovitz, E.R., 1990, The rare earth elements in rivers, estuaries and coastal seas and their significance to the composition of ocean waters: *Geochimica et Cosmochimica Acta*, 54, 971-991.
- Force, E.R., Cannon, W.F., 1988, Depositional model for shallow-marine manganese deposits around black shale basins: *Economic Geology*, 83, 93-117.
- German, C.R., Elderfield, H., 1989, Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin: *Geochimica et Cosmochimica Acta*, 53, 2561-2571.
- German, C.R., Elderfield, H., 1990, Application of Ce anomaly as a paleo redox indicator: the ground rules: *Paleoceanography*, 5, 823-833.
- German, C.R., Holliday, B.P., Elderfield, H., 1991, Redox cycling of rare earth elements in the suboxic zone of the Black Sea: *Geochimica et Cosmochimica Acta*, 55, 3553-3558.
- German, C.R., Holliday, B.P., Elderfield, H., 1993, A geochemical study of metalliferous sediment from the TAG hydrothermal mound, 26°08' N, Mid-Atlantic ridge: *Journal of Geophysical Research*, 98, 9683-9692.
- Giles, H.L., Hurley, P.W., Webster, H.W.M., 1995, Simple approach to the analysis of oxides, silicates, and carbonates using x-ray fluorescence spectrometry: *X-ray Spectrometry*, 24, 205-218.
- Gilks, M., Chappell, B.W., Freeman, R.S., Webber, E., 1985, Trace elements in oil shales, their source and organic association with particular reference to Australian deposits: *Chemical Geology*, 53, 155-174.
- Govindan, A., Ravindran, C.N., Rangaraju, M.K., 1996, Cretaceous stratigraphy and planktonic foraminiferal zonation of Cauvery Basin, South India, in Sahni, A. (ed.), *Cretaceous Stratigraphy and Palaeoenvironments*: Geological Society of India, Memoir 37, 155-187.
- Govindaraju, K., 1994, Compilation of working values and descriptions for 383 Geostandards: *Geostandards Newsletter*, 18, 1-158.
- Grandjean, P., Cappetta, H., Michard, A., Albaredo, F., 1987, The assessment of REE patterns and ¹⁴³Nd/¹⁴⁴Nd ratios in fish remains: *Earth and Planetary Science Letters*, 84, 181-196.
- Hatch, J.R., Leventhal, J.S., 1992, Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark shale member of the

- Dennis Limestone, Wabaunsee County, Kansas, USA: *Chemical Geology*, 99, 65-82.
- Holser, W.T., 1997, Evaluation of the application of rare earth elements to paleoceanography: *Palaeogeography, Palaeoclimatology, Palaeoecology* 132, 309-323.
- Huerta-Diaz, M.A., Morse, J.W., 1992, Pyritization of trace metals in anoxic marine sediments: *Geochimica et Cosmochimica Acta*, 56, 2681-2702.
- Jarvis, K.E., 1988, Inductively Coupled Plasma mass spectrometry: A new technique for the rapid or ultra-trace level determination of the rare earth elements in geological materials: *Geological Society of America Bulletin*, 87, 725-737.
- Kamber, B.S., Webb, G.E., 2001, The geochemistry of late Archaean microbial carbonate: Implications for ocean chemistry and continental erosion history: *Geochimica et Cosmochimica Acta*, 65, 2509-2525.
- Klinkhammer, G., Elderfield, H., Hudson, A., 1983, Rare earth elements in seawater near hydrothermal vents: *Nature*, 305, 185-188.
- Krauskopf, K.B., 1979, *Introduction to Geochemistry*: Tokyo, McGraw-Hill Kogakusha, 617 p.
- Kurian, S., Nath, B.N., Ramaswamy, V., Naman, D., Gnaneshwar Rao, Kamesh Raju, K.A., Selvaraj., K., Chen, C.T.A., 2008, Possible, detrital, diagenetic and hydrothermal sources for Holocene sediments of the Andaman backarc basin: *Marine Geology*, 247, 178-193.
- Levanthal, J.S., Hosterman, J.W., 1982, Chemical and mineralogical analysis of Devonian black-shale samples from Martin County, Kentucky; Carroll and Washington counties, Ohio; Wise County, Virginia; and Overton County, Tennessee, U.S.A: *Chemical Geology*, 37, 239-264.
- Lewan, M.D., 1984, Factors controlling the proportionality of vanadium to nickel in crude oils: *Geochimica et Cosmochimica Acta*, 48, 2231-2238.
- Lewan, M.D., Maynard, J.B., 1982, Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks: *Geochimica et Cosmochimica Acta*, 46, 2547-2560.
- Liu, Y.G., Miah, M.R.U., Schmitt, R.A., 1988, Cerium: a chemical tracer for paleo-oceanic redox conditions: *Geochimica et Cosmochimica Acta*, 52, 1361-1371.
- Machhour, L., Philip, J., Oudin, J.L., 1994, Formation of laminate deposits in anaerobic-dysaerobic marine environments: *Marine Geology*, 117, 287-302.
- MacRae, N.D., Nesbitt, H.W., Kronberg, B.I., 1992, Development of a positive Eu anomaly during diagenesis: *Earth and Planetary Science Letters*, 109, 585-591.
- Madhavaraju, J., Hussain, S.M., Guruvappan, M., Ramasamy, S., Mohan, S.P., 2006, Sequence stratigraphy of Lower Niniyur Formation of Cauvery Basin, Southern India: *Journal of the Geological Society of India*, 68, 685-694.
- Madhavaraju, J., Kolosov, I., Buhlak, D., Armstrong-Altrin, J.S., Ramasamy, S., Mohan, S.P., 2004, Carbon and oxygen isotopic signatures in Albian-Danian limestones of Cauvery Basin, Southeastern India: *Gondwana Research*, 7, 519-529.
- Madhavaraju, J., Ramasamy, S., 1999a, Rare earth elements in limestones of Kallankurichchi Formation of Ariyalur Group, Tiruchirapalli Cretaceous, Tamil Nadu: *Journal of the Geological Society of India*, 54, 291-301.
- Madhavaraju, J., Ramasamy, S., 1999b, Microtextures on quartz grains of Campanian – Maastrichtian sediments of Ariyalur Group of Tiruchirapalli Cretaceous, Tamil Nadu – Implication on depositional environments: *Journal of the Geological Society of India*, 54, 647-658.
- Madhavaraju, J., Ramasamy, S., 2001, Clay mineral assemblages and rare earth element distribution in the sediments of Ariyalur Group, Tiruchirapalli District, Tamil Nadu – Implication for paleoclimate: *Journal of the Geological Society of India*, 58, 69-77.
- Madhavaraju, J., Ramasamy, S., 2002, Petrography and geochemistry of Late Maastrichtian - Early Paleocene sediments of Tiruchirapalli Cretaceous, Tamil Nadu - Paleoweathering and provenance implications: *Journal of the Geological Society of India*, 59, 133-142.
- Madhavaraju, J., Ramasamy, S., Alastair-Ruffell, Mohan, S.P., 2002, Clay mineralogy of the Late Cretaceous and Early Tertiary Successions of the Cauvery Basin (southeastern India): Implications for sediment source and palaeoclimates at the K/T boundary: *Cretaceous Research*, 23, 153-163.
- McLennan, S.M., 1989, Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes, *in* Lipin, B.R., McKay, G.A. (eds.), *Geochemistry and Mineralogy of Rare Earth Elements: USA*, Mineralogical Society of America, *Reviews of Mineralogy*, 21, 169-200.
- Michard, A., Albarede, F., Michard, G., Minister, J.F., Charlow, J.L., 1983, Rare earth elements and uranium in high temperature solutions from East-Pacific rise hydrothermal vent field (13°N): *Nature*, 303, 795-797.
- Murray, R.W., Ten Brink, M.R.B., Brumsack, H.J., Gerlach, D.C., Russ III, G.P., 1991a, Rare earth elements in Japan Sea sediments and diagenetic behaviour of Ce/Ce*: Results from ODP Leg 127: *Geochimica et Cosmochimica Acta*, 55, 2453-2466.
- Murray, R.W., Ten Brink, M.R.B., Gerlach, D.C., Russ III, G.P., Jones, D.L., 1991b, Rare earth, major and trace elements in chert from the Franciscan complex and Monterey Group, California: Assessing REE sources to fine grained marine sediments: *Geochimica et Cosmochimica Acta*, 55, 1875-1895.
- Murray, R.W., Buchholtz-Ten-Brink, M.R., Gerlach, D.C., Russ, G.R. III., Jones, D.L., 1992, Interoceanic variation in the rare earth, major and trace element depositional chemistry of chert: Perspective gained from DSDP and ODP record: *Geochimica et Cosmochimica Acta*, 56, 1897-1913.
- Nagarajan, R., Madhavaraju, J., Nagendra, R., Armstrong-Altrin, J.S., Moutte, J., 2007, Geochemistry of Neoproterozoic shales of the Rabanpalli Formation, Bhima Basin, Northern Karnataka, Southern India: implications for provenance and paleoredox conditions: *Revista Mexicana de Ciencias Geológicas*, 24(2), 150-160.
- Nagendra, R., Nagendran, G., Narasimha, K., Jaiprakash, B.C., Nallapareddy, A., 2002, Sequence stratigraphy of Dalmiapuram Formation, Kallakkudi Quarry – II, South India: *Journal of the Geological Society of India*, 59, 249-258.
- Nath, B.N., Bau, M., Ramlingeswara-Rao, B., Rao, Ch.M., 1997, Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone: *Geochimica et Cosmochimica Acta*, 61, 2375-2388.
- Nath, B.N., Roelandts, I., Sudhakar, M., Plueger, W.L., 1992, Rare earth element patterns of the Central Indian Basin sediments related to their lithology: *Geophysical Research Letters*, 19, 1197-1200.
- Nath, B.N., Roelandts, I., Sudhakar, M., Plueger, W.L., Balaram, V., 1994, Cerium anomaly variations in ferromanganese nodules and crusts from the Indian Ocean: *Marine Geology*, 120, 385-400.
- Norrish, K., Hutton, J.T., 1969, An accurate X-ray spectrographic method for analysis of a wide range of geological samples: *Geochimica et Cosmochimica Acta*, 33, 431-453.
- Nothdurft, L.D., Webb, G.E., Kamber, B.S., 2004, Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: Confirmation of a seawater REE proxy in ancient limestone: *Geochimica et Cosmochimica Acta*, 68, 263-283.
- Nozaki, Y., Zhang, J., Amakawa, H., 1997, The fractionation between Y and Ho in the marine environment: *Earth and Planetary Science Letters*, 148, 329-340.
- Odermatt, J.R., Curiale, J.A., 1991, Organically bound metals and biomarkers in the Monterey Formation of the Santa Maria Basin, California: *Chemical Geology*, 91, 99-113.
- Piepgras, D.J., Jacobsen, S.B., 1992, The behaviour of rare earth elements in seawater: precise determination of variations in the North Pacific water column: *Geochimica et Cosmochimica Acta*, 56, 1851-1862.
- Piper, D.Z., 1974, Rare earth elements in the sedimentary cycle, a summary: *Chemical Geology*, 14, 285-304.
- Piper, D.Z., 1991, Geochemistry of a Tertiary sedimentary phosphate

- deposit, Baja California Sur, Mexico: *Chemical Geology*, 92, 283-316.
- Prange, A., Kremling, K., 1985, Distribution of dissolved molybdenum, uranium and vanadium in Baltic Sea waters: *Marine Geology*, 16, 259-274.
- Ramasamy, S., Banerji, R.K., 1991, Geology, petrography and stratigraphy of pre-Ariyalur sequence in Tiruchirapalli District, Tamil Nadu: *Journal of the Geological Society of India*, 37, 577-594.
- Ramasamy, S., Madhavaraju, J., Banerji, R.K., 1995, Paleoenvironmental indicators of the pre-Ariyalur sequence in Tiruchirapalli District, Tamil Nadu, India (abstract), *in* 2nd South Asia Geological Congress, Colombo, Sri Lanka, 158-159.
- Rangaraju, M.K., Agarwal, A., Prabhakar, K.N., 1993, Tectono-stratigraphy, structural styles, evolutionary model and hydrocarbon habitat, Cauvery and Palar basins, *in* Biswas, S.K., Dave, A., Garg, P., Pandey, J., Maithani, A. Thomas, N.J. (eds.), *Proceedings Second Seminar on Petroliiferous Basins of India*: Dehra Dun, Indian Petroleum Publishers, v. 1, 371-388.
- Ronov, A.B., Balashov, Y.A., Migdisov, A.A., 1967, Geochemistry of the rare earths in the sedimentary cycle: *Geochemistry International*, 4, 1-18.
- Santoyo, E., Verma, S.P., 2003, Determination of lanthanides in synthetic standards by reversed-phase high performance liquid chromatography with the aid of a weighted least-squares regression model: estimation of method sensitivities and detection limits: *Journal of Chromatography A*, 997, 171-182.
- Sastry, M.V.A., Mangain, V.D., Rao, B.R.J., 1972, Ostracod fauna of the Ariyalur Group (Upper Cretaceous), Tiruchirapalli District, Tamil Nadu. Part I. Lithostratigraphy of the Ariyalur Group: *Geological Survey of India, Palaeontologica Indica, New Series*, 40, 1-48.
- Schijf, J., De Baar, H.J.W., Hebeda, E.H., 1989, REE in anoxic brines of the East Mediterranean: *EOS*, 70, 601.
- Shaw, T.J., Geiskes, J.M., Jahnke, R.A., 1990, Early diagenesis in differing depositional environments: the response of transition metals in pore water: *Geochimica et Cosmochimica Acta*, 54, 1233-1246.
- Sholkovitz, E.R., 1990, Rare earth elements in marine sediments and geochemical standards: *Chemical Geology*, 88, 333-347.
- Sholkovitz, E.R., 1992, Chemical evolution of rare earth elements: fractionation between colloidal and solution phases of filtered river water: *Earth and Planetary Science Letters*, 114, 77-84.
- Sholkovitz, E.R., Elderfield, H., 1988, Cycling of dissolved rare earth elements in Chesapeake Bay: *Global Biogeochemical Cycles*, 2, 157-176.
- Sholkovitz, E.R., Shaw, T.J., Schneider, D.L., 1992, The geochemistry of rare earth elements in the seasonally anoxic water column and pore waters of Chesapeake Bay: *Geochimica et Cosmochimica Acta*, 56, 3389-3402.
- Srivastava, R.P., Tewari, B.S., 1969, Biostratigraphy of the Ariyalur Stage, Cretaceous of Trichinopoly: *Journal of Paleontological Society of India*, 12, 48-54.
- Subbaraman, J.V., 1968, Surface and subsurface geology of the area around Dalmiapuram, Trichinopoly District: *Geological Society of India, Memoir* 2, 92-98.
- Sundaram, R., Rao, P.S., 1986, Lithostratigraphy of Cretaceous and Palaeocene rocks of Tiruchirapalli District, Tamil Nadu, South India: *Geological Survey of India, Records* 115, 9-23.
- Sundaram, R., Henderson, R.A., Ayyasami, K., Stilwell, J.D., 2001, A lithostratigraphic revision and palaeoenvironmental assessment of the Cretaceous System exposed in the onshore Cauvery Basin, Southern India: *Cretaceous Research*, 22, 743-762.
- Taylor, S.R., McLennan, S.M., 1985, *The Continental Crust: its Composition and Evolution*: Oxford, Blackwell, 349 p.
- Toyoda, D., Nakamura, Y., Masuda, A., 1990, Rare earth elements of Pacific pelagic sediments: *Geochimica et Cosmochimica Acta*, 54, 1093-1103.
- Tribouillard, N.P., Desprairies, A., Lallier-Verges, E., Bertrand, P., Moureau, N., Ramdani, A., Ramanampisoa, L., 1994, Geochemical study of organic-matter rich cycles from the Kimmeridge Clay Formation of Yorkshire (UK): productivity versus anoxia: *Palaeogeography, Palaeoclimatology, Palaeoecology*, 108, 165-181.
- Veizer, J., 1983, Trace elements and isotopes in sedimentary carbonates, *in* Reeder, R.J. (ed.), *Carbonates: Mineralogy and Chemistry*: U.S.A., Mineralogical Society of America, *Reviews of Mineralogy*, 11, 265-299.
- Verma, S.P., 2005, *Estadística Básica para el Manejo de Datos Experimentales: Aplicación en la Geoquímica (Geoguimiometría)*: México, D.F., Universidad Nacional Autónoma de México, 186 pp.
- Verma, S.P., 2009, Evaluation of polynomial regression models for the Student t and Fisher F critical values, the best interpolation equations from double and triple natural logarithm transformation of degrees of freedom up to 1000, and their applications to quality control in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 26(1), 79-92.
- Verma, S.P., Santayo, E., 2005, Is odd-even effect reflected in detection limits?: *Accreditation and Quality Assurance*, 10(4), 144-148.
- Verma, S.P., Quiroz-Ruiz, A., 2006a, Critical values for six Dixon tests for outliers in normal samples up to sizes 100, and applications in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 23(2), 133-161.
- Verma, S.P., Quiroz-Ruiz, A., 2006b, Critical values for 22 discordancy test variants for outliers in normal samples up to sizes 100, and applications in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 23(3), 302-319.
- Verma, S.P., Quiroz-Ruiz, A., 2008, Critical values for 33 discordancy test variants for outliers in normal samples of very large sizes from 1,000 to 30,000 and evaluation of different regression models for the interpolation and extrapolation of critical values: *Revista Mexicana de Ciencias Geológicas*, 25(3): 369-381.
- Verma, S.P., Santoyo, E., Velasco-Tapia, F., 2002, Statistical evaluation of analytical methods for the determination or rare-earth elements in geological materials and implications for detection limits: *International Geology Review*, 44, 287-335.
- Verma, S.P., Quiroz-Ruiz, A., Díaz-González, L., 2008, Critical values for 33 discordancy test variants for outliers in normal samples up to sizes 1000, and applications in quality control in Earth Sciences: *Revista Mexicana de Ciencias Geológicas*, 25(1), 82-96.
- Webb, G.E., Kamber, B.S., 2000, Rare earth elements in Holocene reefal microbialites: A new shallow seawater proxy: *Geochimica et Cosmochimica Acta*, 64, 1557-1565.
- Wedepohl, K.H., 1978, Manganese: abundance in common sediments and sedimentary rocks, *in* Wedepohl, K.H. (ed.), *Handbook of Geochemistry*: Berlin, Springer, v. II/3, 1-17.
- Wronkiewicz, D.J., Condie, K.C., 1990, Geochemistry and mineralogy of sediments from the Ventersdorp and Transvaal Supergroups, South Africa: Cratonic evolution during the early Proterozoic: *Geochimica et Cosmochimica Acta*, 54(2), 343-354.
- Yadagiri, K., Govindan, A., 2000, Cretaceous carbonate platforms in Cauvery Basin: sedimentology, depositional setting and subsurface signatures: *Geological Society of India, Memoir* 46, 323-344.

Manuscript received: August 28, 2008

Corrected manuscript received: December 12, 2008

Manuscript accepted: December 15, 2008