DOI: 10.24996/ijs.2022.63.9.13

Iraqi Journal of Science

ISSN: 0067-2904

Depositional Conditions and Nature of Source Rocks of the Upper Part of the Balambo Formation in Northeastern Iraq Based on Rare Earth Elements Data

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Received: 4/10/2021 Accepted: 9/12/2021 Published: 30/9/2022

Abstract

The sequence in the upper part of the Balambo Formation is composed mainly of limestone alternating with marly limestones and dark grey shale in the Bosheen section (eastern Sulaymaniyah, northeastern Iraq) and has been studied in terms of its rare earth element (REE) content. The REEs are very low compared to modern marine sediments. They are depletion in LREEs, and enrichment in HREEs and $(La/Yb)_N$ in the studied rocks, indicating that these sediments retained the REEs pattern of marine waters. The negative Ce anomaly reflects direct sedimentation from marine waters under anoxic conditions with the contribution of terrigenous clays. The positive correlation of ∑REEs with Al, Ti, and Y, and the negative correlation of ∑REEs with CaO, in addition to the variation in Y/Ho ratio, all may indicate the presence of terrigenous fractions as the main source for REEs in the studied strata. The REEs pattern of the upper part of the Balambo Formation mostly shows original characteristics, some of which were modified by detrital input. According to $(La/Yb)_N$ ratios, the sedimentation rate varied during the deposition of the Balambo Formation in the function of its position along the continental margin.

Keywords: REE, conditions of deposition, source rocks, Balambo Formation.

الظروف الترسيبية وطبيعة صخور المصدر للجزء العلوي من تكوين بلامبو في شمال شرقي العراق بالاعتماد على بيانات العناصر الأرضية النادرة

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الخلاصه

تمت دراسة تتابع في الجزء العلوي من تكوين بلامبو الذي يتكون في الغالب من الحجر الجيري يتعاقب مع الحجر الجيري المارلي والسجيل الرمادي الداكن في مقطع بوشين، شرق السليمانية، شمال شرقي العراق من حيث محتواه من العناصر الأرضية النادرة. تبين أن نسبة تلك العناصر قليلة جدًا مقارنة بالرواسب البحرية الحديثة. كما كان هنالك شحة في العناصر الأرضية النادرة الخفيفة وإثراء في الثقيلة منها وفي النسبة (La / Yb) في صخور التكوين قيد الدراسة، مما يشير إلى أن هذه الرواسب احتفظت بنمط العناصر الأرضية النادرة للمياه البحرية. ويعكس الشذوذ السلبي للسيريوم الى الترسيب المباشر من المياه البحرية في ظروف شحيحة الأكسجين مع مساهمة الطين الأرضي في الرواسب البحرية. كما أن العلاقة الموجبة لمجموع العناصر الأرضية النادرة مع Al و Ti و Y ، وعلاقتها السالبة مع CaO بالإضافة إلى التباين في نسبة Y/Ho، قد تشير جميعها إلى وجود القتاتات الأرضية كمصدر لتلك العناصر الأرضية النادرة في الحجر الجيري قيد الدراسة. ويُظهر نمط توزيع العناصر الأرضية النادرة للجزء العلوي من تكوين بالامبو في الغالب خصائص أصلية وتم تغير بعضها بسبب وجود التزويد الفتاتي. وفقًا لنسب $(La / Yb)_N$ ، كان معدل الترسيب متباين أثناء ترسيب تكوين بلامبو على حافة قارية.

Introduction

Very warm climatic conditions characterize the Cretaceous period, especially the Albian, the minor temperature gradient between the equator and the poles, lack of ice, rise in sea level, and abundance of volcanic and tectonic activities [1, 2].

The Balambo Formation is one of the widely spread Cretaceous sequences in northeastern Iraq and represents the bathyal facies deposited in a basin extending northwest-southeast in the northeastern part of Iraq [3].

The rare earth elements (REEs) are a group of elements, ranging from (57La) to (71Lu), that show similar chemical behavior and which are less affected by diagenesis processes than major and trace elements [4]. The concentration of REEs has concerned many geologists due to their unique properties [5].

Previous studies have shown that chemical sedimentary rocks such as carbonates or banded iron formations are valuable proxies for recording the REE patterns of sedimentation water [6]. The concentrations of REE in carbonate rocks are generally low. However, they help identify marine and non-marine sources of carbonates [7].

The REEs also are useful to unravel the conditions of the sedimentation, such as the lack or abundance of marine oxygen, distance from a source area, the lithology and diagenesis of the source rocks, and palaeogeography and depositional setting. The distribution of REEs in carbonate rocks also is sensitive to water depth, salinity, oxygen level, and terrestrial input sources [6]. Oceanic input sources, seawater chemistry, and oceanic oxygenation state could be determined from the signatures of REEs in ancient sediments [8]. Seawater-like REE+Y patterns are well identified in marine chemical sediments [6] that commonly show depletion in light REEs (LREEs) accompanied by enrichment in La, depletion in Ce, enrichment in Gd, and positive Y anomaly in normalized shale diagrams [9, 10]. However, the seawater signatures are commonly affected by the contribution of terrigenous materials that contain relatively high, non-seawater-related REE signatures [8, 6].

In the current study, the REEs in the successions of the upper part of the Balambo Formation (late Albian) [11] were analyzed to determine the sedimentation conditions and the nature of the REEs source.

Geological setting

The Balambo Formation is a part of the Arabian Plate Megasequence (AP8) which was deposited in a period covering the late Jurassic - late Cretaceous (149 - 92Ma) [12]. It has been reported that the Balambo Formation was deposited in an open basinal environment in an intrashelf basin along a passive margin [13].

The study focuses on the upper part of the Balambo Formation located in the Azmer anticline (near Bosheen village; east Sulaimaniya city, northeastern Iraq; Figure 1). The area lies in the High-Folded and Thrusted Tectonic Zones. The thickness of the Balambo Formation in this anticline is about 610 m. It consists in its lower part of well-bedded hard limestones including chert nodules and marly limestones alternating with layers of gray, brown, and black shale, while the upper part is composed of limestones containing ammonite, belemnite, and marly limestones alternating with layers of marl, dark gray and black shale. Reddish-brown shale alternating with layers of limestone and marl also appears in this part of the formation.

The present study focuses on an about 17 m thick succession (which were deposited in anoxic conditions [11]) from the upper part of the formation and consists of dark grey to black shale, marl, platy limestone, and clastic mudstone (Figure 2).

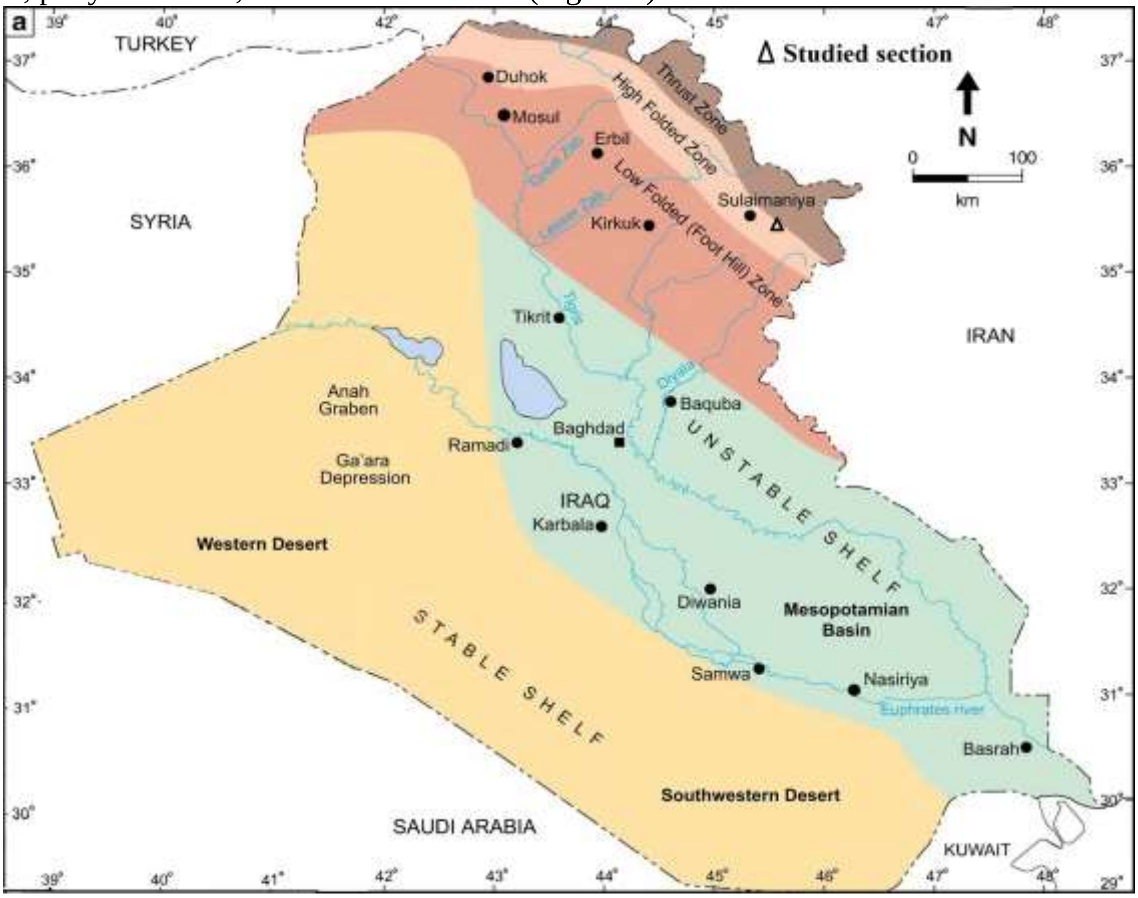

Figure 1 -Tectonic map of Iraq shows the location of the studied area after [14].

Methods and materials

Twenty-one samples (13 limestones, 1 marly limestone, and 7 calcareous shales) from the upper part of the Balambo Formation at Bosheen section (Figure 2) were collected and analyzed for REEs at laboratories of the Catholic University of Louvain (KU Leuven), Belgium using a Varian 720-ES ICP-OES device. Furthermore, some major and trace elements used in this study were added to investigate the diagenetic alteration effect or contribution of terrigenous source material, which were also analyzed at the same laboratory.

Results

REE concentrations ratios are presented in Tables 1 and 2. Post-Archaean Australian Shale (PAAS) values [15] were used for creating REE-normalized patterns of Bosheen section samples according to [10]. These patterns are given in Figure 3. The studied samples show a seawater-like REE+Y pattern with negative Ce anomalies and positive Eu anomalies.

These carbonates exhibit seawater-like REEs pattern with LREEs depletion, average $(Nd/Yb)_N$ ($_N$=shale normalized) = 0.71, and consistent negative Ce_N (Average = 0.75) and positive La_N anomalies (Average = 1.31).
The REE anomalies are expressed;

- Cerium $Ce/Ce^* = Ce_N / (0.5La_N + 0.5Pr_N)$ [10]
- Europium $Eu/Eu^* = Eu_N / (Sm_N * Gd_N)$^0.5 [15]
- Praseodymium $Pr/Pr^* = Pr_N/(0.5Ce_N + 0.5Nd_N)$ [10]

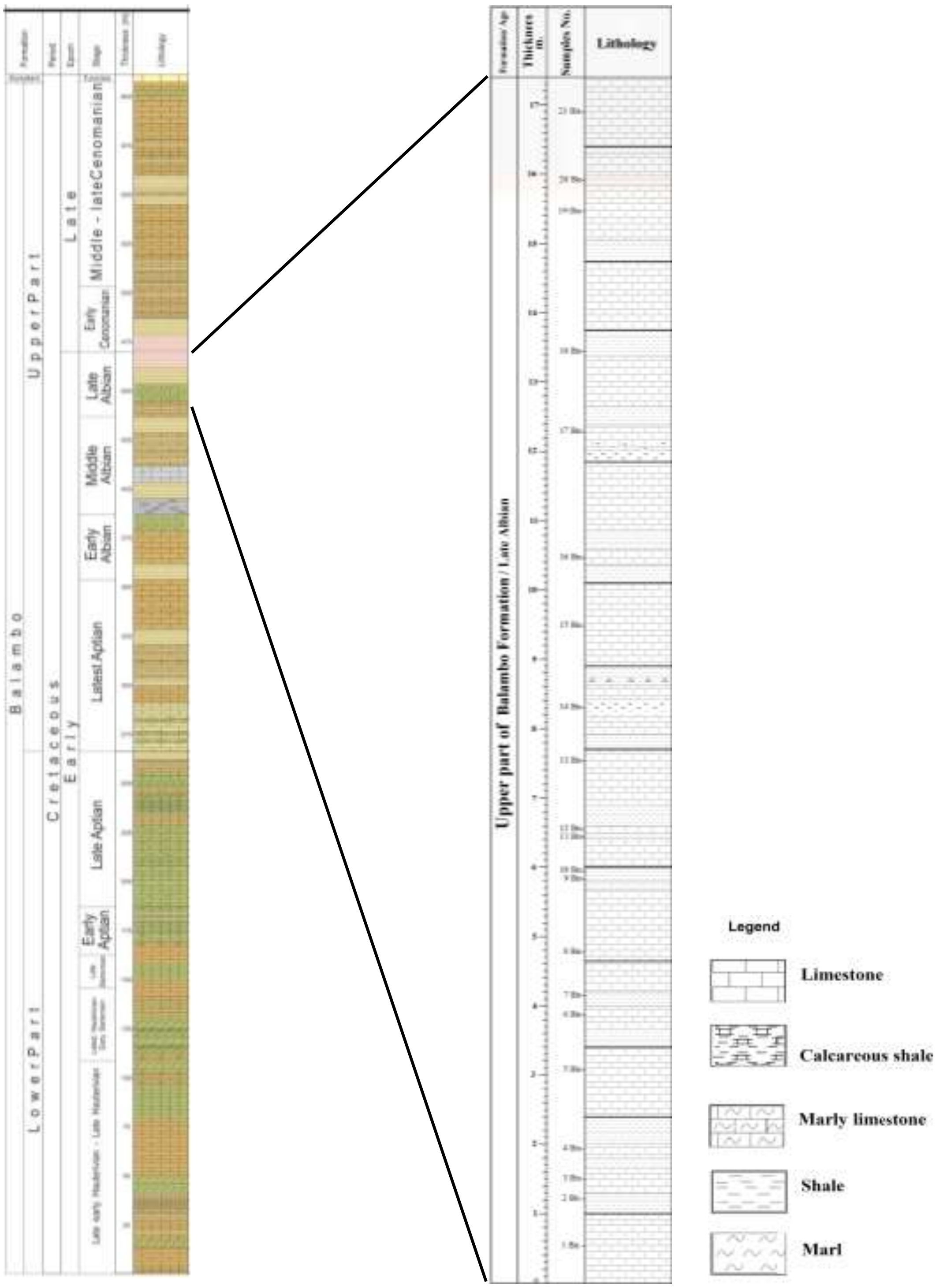

Figure 2-Stratigraphic column of the Balambo Formation in the Azmer anticline (left column) after [16] and studied sequence from the upper part of the formation near Bosheen village (right column), including samples position.

The higher contents of REEs than the typical marine carbonate value (~28 ppm) [17] in certain samples (Bn 2, Bn 7, and Bn 14; Table 1) of the Bosheen section are mainly due to the presence of high silt and clay fractions, since these samples represent marl and shale intervals, while it is content in Bn 21 is low due to carbonate dilution (see Figure 2) because REEs are readily accommodated in clay structures [18]. The total light to total heavy REEs (∑LREEs/∑HREEs) varies from 7.2 to 10.8, averaging 9.36 (Table 2).

The concentrations of some of these elements may be affected by diagenesis. Furthermore, the correlation between Mn and Sr, in general, is important to understand the diagenetic alterations in the limestones [19]. In this study, Mn and Sr have no correlation, suggesting that these limestones have not been diagenetically altered (Figur 4).

- *Ce anomaly*

The present study revealed negative Ce/Ce* anomalies ranging from 0.61 to 0.84 (average 0.75) for the Bosheen section (Table 2). Concerning the relationship between La and Ce anomalies, all studied samples (n = 21) cluster tightly in the field of negative Ce and positive La anomalies in agreement with modern open oceanic surface water. In the PAAS-normalized Pr/Pr* vs Ce/Ce* plot (Figure 5), the existence of a true Ce anomaly should lead to Pr/Pr* ≥1. Studied samples show Pr/Pr indeed* >1, which suggests that the $(Ce/Ce^*)_N$ ratios mainly result from the real Ce anomaly [10,20].

- *Europium Anomaly*

The studied section samples of the Balambo Formation display a large variation in Eu anomaly (Eu/Eu*), which ranges from 1.12 to 7.12 (average 2.31) (Table 2) and display positive Eu anomalies.

- *Y/Ho ratios*

The Y/Ho ratios for Bosheen section samples range from 30.9 to 41.9 with an average of 37.55 ppm (Table 2). Most samples show Y/Ho ratios more significant than the chondritic value (~28) but less than the seawater super chondritic Y/Ho value, which ranges from 44 to74 [8]. The low Y/Ho ratio, with a positive correlation between Y/Ho and Y/Dy (Figure 6), indicates that these limestones became contaminated with terrigenous materials, i.e. that terrigenous constituents have a control on the REE contents.

- *Er/Nd ratio*

The Er/Nd ratio for Bosheen section samples ranges between 0.11 and 0.19, with an average of 0.12 (Table 2). These values are considered high compared with the Er/Nd values reported from average shale varying around 0.085 or black shales with values between 0.076 to 0.079 of the Bonarelli Level [21].

Discussion

Higher Y/Ho ratios are typically observed due to different surface complex stabilities between Yttrium (Y) and its geochemical twin Holmium (Ho). Therefore, Yttrium (Y) usually is not removed from seawater as compared to Holmium (Ho) [9]. Higher Y/Ho (44–74) was registered in seawater compared to terrigenous materials and volcanic ash. The latter commonly have constant chondritic Y/Ho ratios of ~28. Marine carbonates also have higher Y/Ho ratios than freshwater carbonates [8].

Most of the Bosheen section samples show Y/Ho ratios lower than 40 (30.9 to 41.9 with an average of 37.5, Table-2), whereas a few samples show higher Y/Ho ratios (>40; n=3). This observed variation in the Y/Ho ratio is supported by the positive correlation between Y/Ho and Y/Dy (Figure 6), suggesting that the studied rocks of the Balambo Formation preserved the seawater signature, though contaminated by the contribution of terrigenous materials. The wind may have carried the latter from sources that have probably been affected by hydrothermal activity.

Table 1 -REEs concentrations of the Balambo Formation, Bosheen section.

Sample No.	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Sum ppm	LREE ppm	HREE ppm
1 Bn	1.49	2.02	0.28	1.13	0.23	0.13	0.24	0.04	0.23	0.05	0.14	0.02	0.11	0.02	6.13	5.52	0.61
2 Bn	8.04	10.49	1.46	5.97	1.14	1.89	1.38	0.20	1.15	0.25	0.75	0.10	0.64	0.10	33.55	30.37	3.18
3 Bn	3.37	4.02	0.59	2.20	0.38	0.15	0.40	0.06	0.37	0.08	0.27	0.05	0.32	0.05	12.31	11.11	1.20
4 Bn	3.17	4.41	0.61	2.40	0.49	0.17	0.52	0.08	0.44	0.10	0.30	0.04	0.28	0.04	13.06	11.77	1.29
5 Bn	1.61	2.38	0.32	1.35	0.25	0.17	0.26	0.04	0.24	0.05	0.16	0.02	0.15	0.02	7.02	6.34	0.68
6 Bn	4.72	7.28	0.99	4.00	0.80	0.26	0.92	0.13	0.77	0.16	0.47	0.06	0.38	0.06	21.00	18.97	2.03
7 Bn	10.79	16.42	2.29	9.26	1.85	0.49	1.96	0.31	1.81	0.36	1.08	0.15	0.86	0.13	47.74	43.04	4.69
8 Bn	2.85	4.14	0.45	1.69	0.30	0.11	0.30	0.05	0.26	0.06	0.22	0.04	0.28	0.05	10.81	9.85	0.97
9 Bn	3.05	3.74	0.57	2.38	0.49	0.16	0.54	0.08	0.48	0.11	0.29	0.04	0.22	0.03	12.19	10.94	1.25
10 Bn	7.07	9.90	1.37	5.52	1.12	0.31	1.18	0.18	1.07	0.22	0.70	0.10	0.56	0.09	29.37	26.45	2.91
11 Bn	5.24	8.35	1.03	3.99	0.75	0.24	0.80	0.12	0.70	0.14	0.49	0.07	0.43	0.07	22.43	20.41	2.03
12 Bn	1.28	2.13	0.27	1.05	0.22	0.15	0.21	0.03	0.17	0.04	0.11	0.02	0.11	0.02	5.79	5.30	0.49
13 Bn	1.79	2.82	0.36	1.40	0.28	0.26	0.29	0.04	0.26	0.05	0.16	0.02	0.17	0.03	7.93	7.19	0.74
14 Bn	8.23	12.91	1.74	7.01	1.41	0.34	1.43	0.20	1.20	0.25	0.76	0.11	0.76	0.12	36.49	33.07	3.41
15 Bn	1.28	1.89	0.25	0.95	0.16	0.09	0.20	0.03	0.17	0.04	0.11	0.02	0.12	0.02	5.32	4.82	0.50
16 Bn	4.50	6.37	0.90	3.66	0.67	0.22	0.75	0.12	0.70	0.15	0.44	0.06	0.41	0.07	19.03	17.09	1.94
17 Bn	3.43	4.33	0.62	2.47	0.44	0.17	0.56	0.08	0.54	0.11	0.34	0.05	0.29	0.05	13.47	12.01	1.46
18 Bn	3.02	4.08	0.42	1.52	0.23	0.12	0.25	0.04	0.23	0.06	0.20	0.04	0.28	0.05	10.54	9.65	0.89
19 Bn	1.50	2.11	0.30	1.16	0.21	0.12	0.24	0.03	0.23	0.05	0.14	0.02	0.11	0.02	6.23	5.65	0.59
20 Bn	2.99	4.20	0.46	1.68	0.29	0.12	0.28	0.05	0.30	0.07	0.25	0.04	0.32	0.05	11.10	10.01	1.09
21 Bn	1.24	1.31	0.19	0.68	0.13	0.08	0.13	0.02	0.14	0.04	0.13	0.02	0.15	0.02	4.29	3.77	0.52
Av.	3.84	5.49	0.74	2.93	0.56	0.27	0.61	0.09	0.55	0.12	0.36	0.05	0.33	0.05	15.99	14.44	1.55
Max.	10.79	16.42	2.29	9.26	1.85	1.89	1.96	0.31	1.81	0.36	1.08	0.15	0.86	0.13	47.74	43.04	4.69
Min.	1.24	1.31	0.19	0.68	0.13	0.08	0.13	0.02	0.14	0.04	0.11	0.02	0.11	0.02	4.29	3.77	0.49
PAAS	38.20	79.60	8.83	33.90	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.40	2.82	0.43	184.77	171.61	12.77
NASC	32	73	7.9	33	5.7	1.24	5.2	0.85	5.8	1.04	3.4	0.5	3.1	0.48	173.21	158.04	15.17

Table -2 Concentrations of some major and trace elements and REEs ratios of the studied samples.

Sample No.	Ca %	Al %	Ti %	Mn ppm	Sr ppm	Y ppm	$\frac{\Sigma LREE}{\Sigma HREE}$	Ce/Ce*	Eu/Eu*	Pr/Pr*	$(La/Yb)_N$ To PAAS	$(La/Yb)_N$ To NASC	Er/Nd	Y/Ho	Y/Dy
1 Bn	34.5	0.27	0.01	54	1303	1.90	9.07	0.72	2.52	1.07	0.96	1.26	0.12	39.22	8.27
2 Bn	25.7	2.34	0.11	37	1047	9.29	9.54	0.70	7.12	1.07	0.92	1.21	0.13	37.19	8.11
3 Bn	25.3	1.04	0.04	46	1000	2.82	9.27	0.65	1.78	1.16	0.77	1.02	0.12	34.77	7.71
4 Bn	28.2	0.59	0.03	40	1040	3.69	9.13	0.73	1.60	1.09	0.85	1.11	0.13	36.95	8.33
5 Bn	31.9	0.36	0.02	47	1256	1.89	9.33	0.76	3.23	1.05	0.79	1.03	0.12	36.65	8.03
6 Bn	26.1	0.65	0.03	35	1084	6.08	9.33	0.78	1.41	1.07	0.92	1.21	0.12	38.16	7.89

7 Bn	26.2	1.66	0.06	31	1006	13.86	9.17	0.76	1.21	1.08	0.92	1.21	0.12	38.67	7.67
8 Bn	25.2	1.18	0.05	33	1026	2.45	10.20	0.83	1.79	1.01	0.74	0.97	0.13	39.27	9.31
9 Bn	33.4	0.29	0.01	50	1333	4.37	8.75	0.65	1.47	1.10	1.03	1.35	0.12	40.14	9.19
10 Bn	25.5	1.54	0.06	46	848	8.75	9.08	0.73	1.26	1.08	0.94	1.23	0.13	39.32	8.19
11 Bn	24.4	1.98	0.08	34	884	5.62	10.07	0.83	1.42	1.05	0.89	1.17	0.12	38.88	8.00
12 Bn	33.3	0.39	0.02	42	1189	1.21	10.75	0.84	3.24	1.05	0.86	1.13	0.11	30.90	7.12
13 Bn	31.6	0.49	0.02	33	1263	1.91	9.76	0.81	4.28	1.05	0.76	1.00	0.11	36.78	7.31
14 Bn	28.1	1.00	0.04	28	1060	8.53	9.69	0.79	1.12	1.07	0.80	1.05	0.11	33.95	7.10
15 Bn	32.2	0.27	0.01	32	1235	1.42	9.69	0.78	2.42	1.07	0.81	1.06	0.12	39.40	8.21
16 Bn	28.9	0.84	0.04	46	1051	5.51	8.80	0.73	1.46	1.09	0.81	1.06	0.12	36.54	7.90
17 Bn	30.5	0.49	0.02	34	1124	4.44	8.24	0.68	1.60	1.10	0.86	1.13	0.14	40.81	8.21
18 Bn	27.4	1.51	0.07	31	969	2.00	10.80	0.81	2.24	1.00	0.80	1.05	0.13	32.25	8.72
19 Bn	33.3	0.21	0.01	31	1336	1.81	9.60	0.73	2.42	1.11	1.03	1.35	0.12	38.71	7.96
20 Bn	24.8	2.43	0.10	35	868	2.76	9.20	0.81	1.99	1.02	0.69	0.91	0.15	38.20	9.17
21 Bn	35.1	0.22	0.01	31	1446	1.50	7.20	0.61	2.88	1.17	0.60	0.79	0.19	41.86	10.40

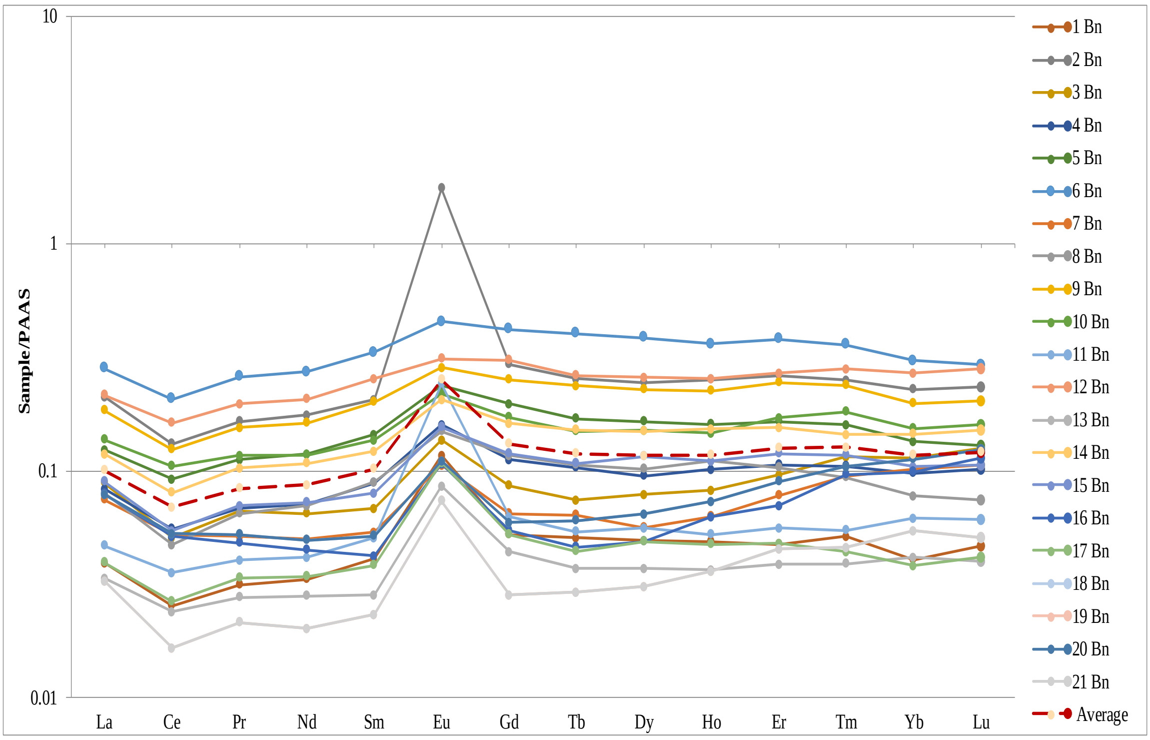

Figure 3-REEs concentrations of studied samples normalized against (PAAS).

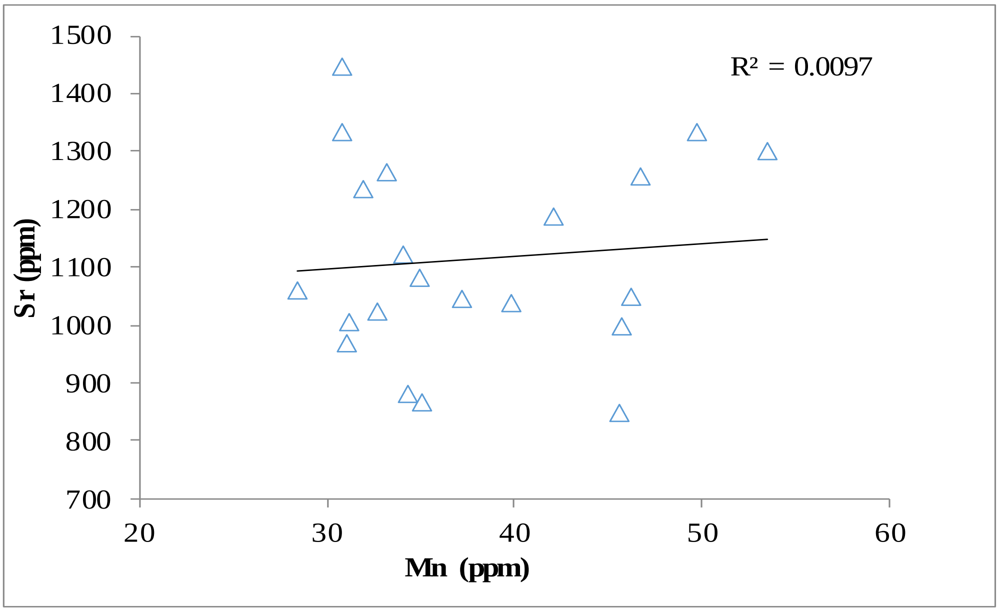

Figure 4-Relationship between Mn and Sr for the studied samples.

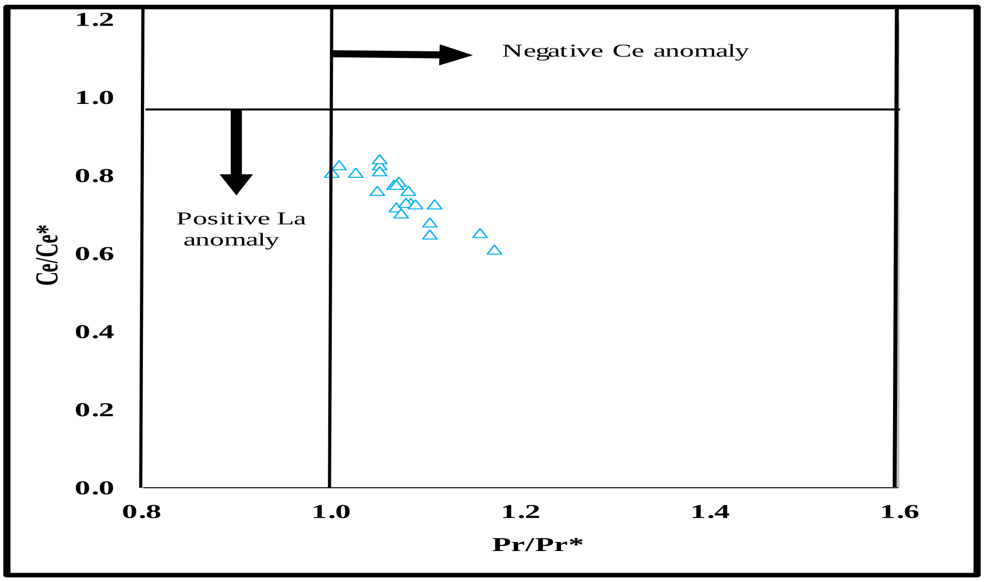

Figure 5-Plot of PAAS normalized (Pr/Pr*) versus (Ce/Ce*) modified after [10].

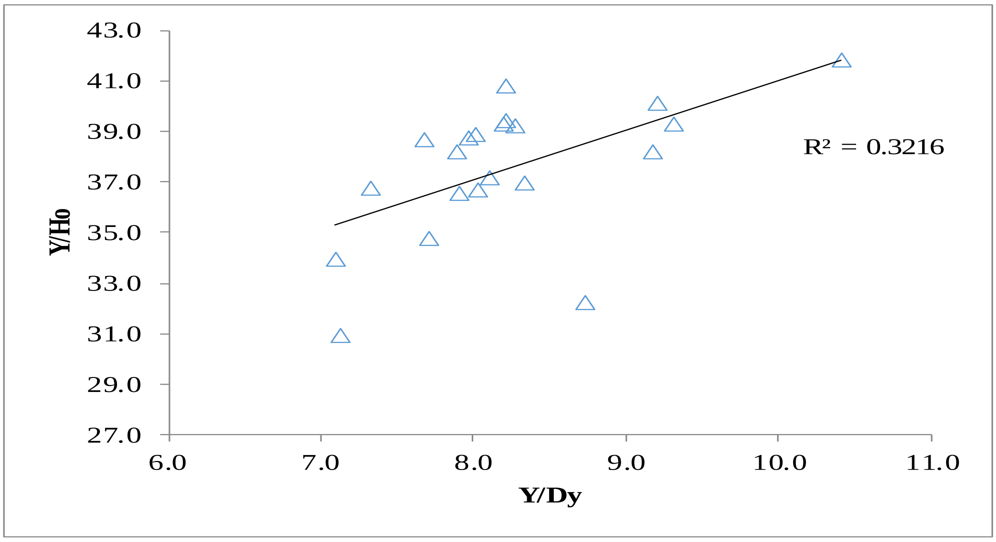

Figure 6-Relationship between (Y/Ho) and (Y/Dy) in the studied samples.

- *Cerium Anomaly and Paleo-redox Conditions*

The Bosheen section exhibits obvious negative Ce anomalies, which often is interpreted in terms of ocean waters that existed during periods of climatic warming and transgressive conditions [22], It is consistent with the values of some elements that indicate those conditions [11].

The Ce anomalies (Ce/Ce*) in marine carbonates have been considered valuable indicators for understanding paleo-redox conditions [23]. Negative Ce anomalies were formed in reducing marine environments during transgression events with minor or no influence of the influx of continental water [24]. This is supported by the geochemical evidence such as V/Ni, V/V+Ni, and Cu/Zn ratios and the presence of black laminated, platy limestone and black calcareous shale in the studied succession [11].

Ce anomalies in anoxic shales could be linked to eustatic sea level changes [22]. Depletion in Ce in anoxic sediments relates to its mobilization, while Mn^{2+} and Ce^{4+} are less soluble under oxic conditions. A negative Ce anomaly would be the result.

- *Europium Anomaly and Hydrothermal activity potential?*

Hydrothermal activity is an important sedimentation activity affecting the paleo-environmental conditions and organic matter enrichment in shale formations [25].

Positive Eu anomalies have been extensively well documented for hydrothermal fluids and sediment particulates in active ridge systems and increased oceanic input of hydrothermally originated fluids at mid-oceanic ridges [26].

The shale normalized positive Eu anomalies (Eu/Eu*) are found either in waters affected by eolian input via river or hydrothermal solutions or in the sediments resulting from high T-basalt alteration along mid-ocean ridges, back-arc spreading center, and diagenesis [4] or variations in plagioclase content [27]. It is noteworthy that at the time of the deposition of the Balambo Formation, volcanic activity was represented by the boninite volcanoes and infant-arc affinity [28].

Therefore, the positive Eu anomalies may result from input from hydrothermal discharges and hydrothermal activity along mid-ocean ridges, which is uncommon in seawater.

- *Sedimentary rate analysis*

Sedimentation rate has a role in fractionation between light and heavy REEs [29]. A high rate of sedimentation can shorten the retention time of sediments within the ocean water column leading to limited fractionation, whereas, at a low sedimentation rate, the REEs will have sufficient time to be absorbed by clays and organic matters, resulting in strong fractionation between light and heavy REEs [29]. Additionally, the normalized ratio of $(La/Yb)_N$ can also reflect the fractionation degree of the REEs and sedimentation rate [30, 31]. A $(La/Yb)_N$ ratio close to 1 is an indication of weak REEs fractionation and possible high sedimentation rate, while $(La/Yb)_N < 1$ or $(La/Yb)_N > 1$ represents enhanced REE fractionation with relatively low sedimentation rate.

The $(La/Yb)_N$ ratios of the Balambo Formation range from 0.6 to 1.03 with an average value of 0.85 (Table-2), indicating variation in sedimentation rate during the deposition of the Balambo Formation.

- *Tectonic Setting*

The $(La/Yb)_N$ ratio of La and Yb normalized by the North American shale of the continental margin region (NASC) ranges from 1.1 to 1.4, with an average value of $(La/Yb)_N$ of areas near ocean ridges varying around 0.3, and the $(La/Yb)_N$ ratio in the abyssal plain ranges between the $(La/Yb)_N$ ratios of the continental margin and ocean ridge regions [32].

The $(La/Yb)_N$ ratio (normalized to the NASC) for the Balambo Formation in the Bosheen section varied between 0.79 to 1.35 with an average of 1.11, which is relatively high (Table-2) and may refer to the continental margin source setting of Balambo Formation.

- *Possible sources of REEs in marine limestone*

The limestones of the Balambo Formation at the Bosheen section show significant variations in ΣREEs content (Table 1). The ∑REEs concentrations of the studied samples from 2 Bn, 7 Bn, and 14 Bn (33.55, 47.74, and 36.49) respectively are higher than the other samples. This result may relate to terrigenous contribution as a dominant contaminant for REEs in carbonate rocks [18].

- *REEs pattern*

As shown in Table-1 and Figure 3, REEs contents are low within the studied samples because marine carbonate phases generally contain significantly fewer REEs than detrital clays and heavy minerals [33]. The low REE concentrations of the Balambo Formation indicate that the contribution of terrigenous components to the biogenic calcite was an important factor controlling the ∑REEs. It is supported by the negative correlation between ∑REEs and CaO in the Bosheen samples (r = -0.34) and the positive correlation of ΣREEs with Al (r = 0.34) as well as with TiO_2 (r = 0.33) and with Y (r = 0.97) (Figure 7). This implies the presence of terrigenous fractions (detrital input), which may be the possible source for REEs in the studied samples.

The effects of LREEs/HREEs fractionation in modern and ancient marine systems can be represented by examining the Er/Nd ratios, whereby the Er/Nd ratio in normal seawater is about 0.27 [21]. The High Er/Nd ratio in limestone effectively reveals the seawater signature retained by the marine carbonate. Additionally, detrital material or diagenesis may reduce the Er/Nd ratio to less than 0.1 due to the preferential concentration of Nd relative to Er [17, 21]. However, the Er/Nd ratio (0.04- 0.12), which is similar to the ratio detected in the studied samples, may indicate a detrital influence on the REE signature [33].

Conclusions

The studied carbonate rocks of the Balambo Formation revealed very low REEs contents compared to recent marine sediments. Depletion of LREEs and enrichment of HREEs and $(La/Yb)_N$ ratio suggest retention of the seawater REEs pattern. The negative Ce anomaly likely reflects the precipitation of REEs directly from seawater or pore water under anoxic conditions. Terrigenous clay (detrital) contribution also reflects a mixing of two-component systems in the deposition of the studied carbonates.

Variations in the Y/Ho ratio, a positive correlation of ∑REEs with Al, TiO_2, and Y, and a negative correlation of ∑REEs with CaO implies the contribution of terrigenous fractions, a possible main source for REEs in the Bosheen section.

The sedimentary rate varied during the deposition of the Balambo Formation based on $(La/Yb)_N$ ratios which may refer that sedimentation occurs mainly on the continental margin.

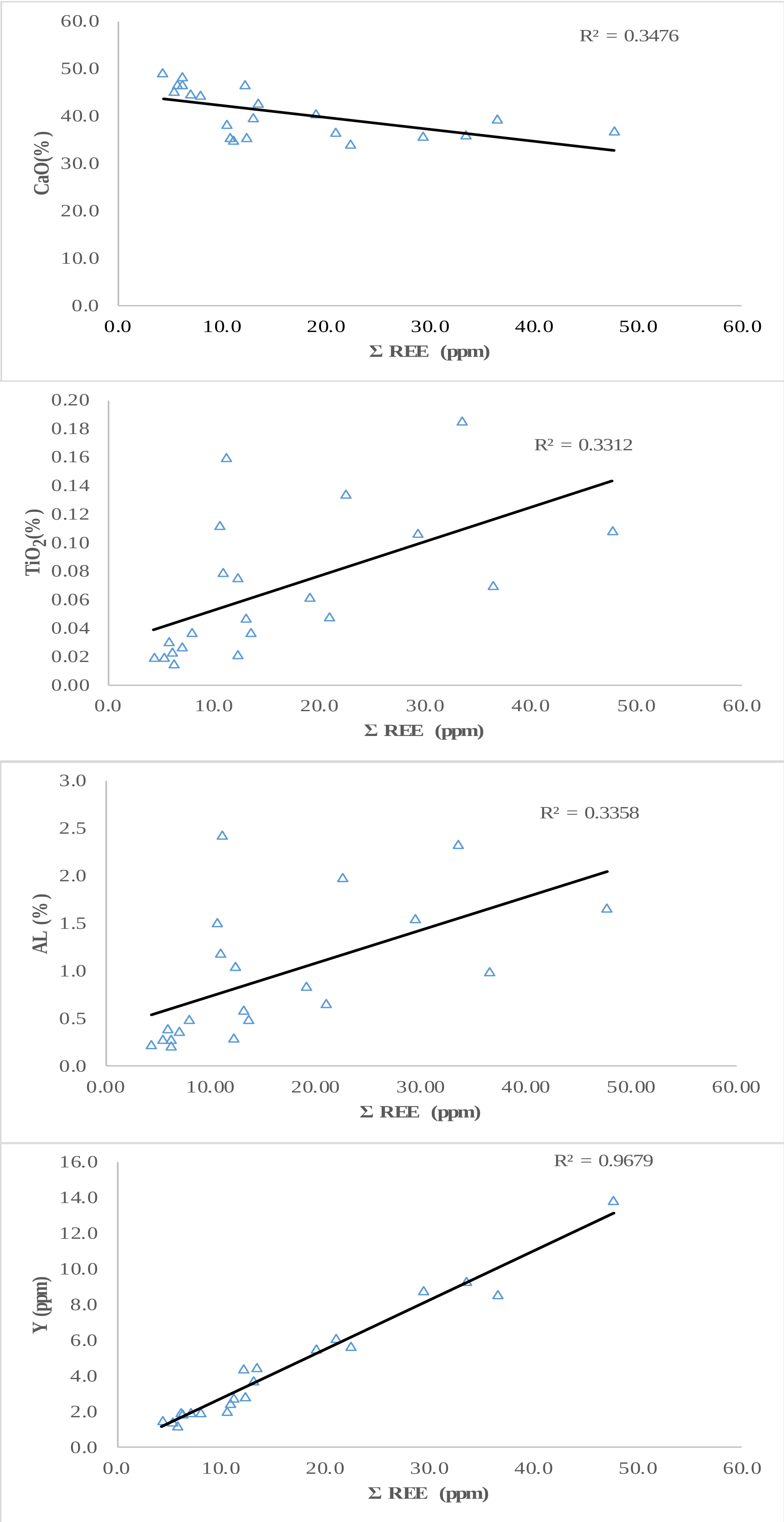

Figure 7-Relationships between ΣREEs with CaO, TiO_2, Al (%), and Y (ppm) in present samples of the Balambo Formation.

References

[1] R. M. Leckie, T. Bralower, and R. Cashman, "Oceanic anoxic events and plankton evolution: biotic response to tectonic forcing the mid-Cretaceous," *Paleoceanography*, vol.17, pp.1–29, 2002.

[2] Z. Khalifa, H. Affouria, A. Riganea, and J. Jacob, "The Albian oceanic anoxic events record in central and northern Tunisia: Geochemical data and paleotectonic controls," *Marine and Petroleum Geology*, vol.93, pp.145-165, 2018.

[3] S. Z. Jassim, and J. C. Goff, *Geology of Iraq: Dolin, Prague and Moravian Museum*, Brno, Czech Republic, 2006, 352 p.

[4] R. W. Murray, M.R., Buchholtz ten Brink, D.C., Gerlach, G.P. Ruth III, and D.L. Jones, "Rare earth, major, and trace elements in chert from the Franciscan Complex and Monterey Group, California: assessing REE sources to fine-grained marine sediments," *Geochim. Cosmochim. Acta*, vol. 55, pp.1875–1895, 1991.

[5] P. Henderson, *Rare earth element geochemistry.: Developments in Geochemistry*, vol. 2. Elsevier, Amsterdam, 1984, 510 p.

[6] L. D. Northdurft, G. E. Webb, and B. S. Kamber, "Rare-earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: Confirmation of seawater REE proxy in ancient limestones," *Geochim. Cosmochim. Acta*. vol.68, pp.263–283, 2004.

[7] J. Madhavaraju, H. Loser, Y. I. Lee, R. Lozano Santacruz, and T. Pi-Puig, "Geochemistry of Lower Cretaceous limestones of the Alisitos Formation, Baja California, Mexico: Implications for REE source and paleo-redox conditions," *Jour. South Amer. Earth Sci.*, 2015, DOI: 10.1016/j.jsames.

[8] G. E. Webb, and B. S. Kamber, "Rare earth elements in Holocene reefal microbialites: A new shallow seawater proxy," *Geochim. Cosmochim. Acta.*, vol.64, pp.1557–1565, 2000.

[9] M. Bau, "Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect," *Contributions to Mineralogy and Petrology*, vol.123, pp323-333, 1996.

[10] M. Bau, and P. Dulski, "Distribution of yttrium and rare earth elements in the Penge and Kuruman iron formation, Transvaal Supergroup, South Africa," *Precam. Res*. vol. 79, pp.37–55, 1996.

[11] F. A. Al-Miamary, *study of some oceanic anoxic events (OAE1) in the Early Cretaceous Balambo Formation using sedimentological and geochemical data at selected sections from northern Iraq. Unpublished Ph.D. thesis, Science collage, Mosul University, (In Arabic)*, 2021, 179 p.

[12] P. R. Sharland, R. Archer, D. M. Casey, S. H. Hall, A. P. Heward, A. D. Horbury and M. D. Simmons, *Arabian Plate sequence stratigraphy, GeoArabia, special publication 2, Gulf Petrolink, Bahrain*, 2001, 371 p.

[13] J. M. English, G. A. Lunn, L. Ferreira, and G. Yacu, "Geologic evolution of the Iraqi Zagros, and its influence on the distribution of hydrocarbons in the Kurdistan region," *American Association of Petroleum Geologists Bulletin*, vol. 99, pp. 231–272, 2015.

[14] R. T. Buday, and S. Z. Jassim, *The regional geology of Iraq, 2, tectonism, magmatism & metamorphism, Geology Survey and Mining Investigation, Baghdad*, 1987, 352 p.

[15] S. R. Taylor, and S. McLennan, *The Continental Crust: Its Composition and Evolution. Blackwell, Oxford*, 1985, 312 p.

[16] I. H. Al-Khafaf, *Biostratigraphy and Depositional Environment of Balambo Formation (Lower-Upper Cretaceous) in Azmer Anticline Northeastern Iraq. Unpublished Ph.D. thesis, Science collage, Mosul University, (In Arabic)*, 2018, 246 p.

[17] A. Bellanca, D. Masetti, and R. Neri, "Rare earth elements in limestone/marlstone couplets from the Albian-Cenomanian Cismon section (Venetian region, northern Italy): assessing REE sensitivity to environmental changes," *Chemical Geology*, vol.141, pp.141-152, 1997.

[18] S. M. McLennan, "Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes," *Rev Mineral Geochem*, vol 21, pp.169–200, 1989.

[19] U. Brand and J. Veizer, "Chemical diagenesis of a multicomponent carbonate system. 1. Trace element," *J. Sediment Res*., vol. 50, pp.1219–1236, 1980.

[20] R. Nagarajan, J. Madhavaraju, J. S. Armstrong-Altrin, and R. Nagendra, "Geochemistry of Neoproterozoic limestones of Shahabad Formation, Bhima basin, Karnataka, Southern India," *Geoscience. J*., vol.15, pp.9–25, 2011.

[21] C.R. German, and H. Elderfield, "Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin," *Geochimica et Cosmochimica Acta*, vol. 53, pp.2561-2571, 1989.

[22] P. Wilde, M.S. Quinby-Hunt, and B. Erdtmann, "The whole-rock cerium anomaly: a potential indicator of eustatic sea-level changes in shales of the anoxic facies," *Sedimentary Geology*, vol.101, pp.43–53, 1996.

[23] C. R. German, and H. Elderfield, "Application of the Ce anomaly as a paleoredox indicator: the ground rules," *Paleoceanography*, vol.5, pp. 823-833, 1990.

[24] M. V. N. Silva, A. N. Sial, J. A. Barbosa, V.P. Ferreira, V. H. Neumann, L. D. De Lacerda, "Carbon isotopes, rare-earth elements and mercury geochemistry across the K-T transition of the Paraíba Basin, northeastern Brazil," *Geol. Soc. London Spec. Publ.*, vol.382, pp.85–104, 2013.

[25] C. He, L. Ji, Y. Wu, A. Su, and M. Zhang, "Characteristics of hydrothermal sedimentation process in the Yanchang Formation, south Ordos Basin, China: evidence from element geochemistry," *Sedimentary Geology*. vol. 345, pp, 33–41, 2016.

[26] A. Danielson, P. Moller and P. Dulski, "The europium anomalies in banded iron formations and the thermal history of the oceanic-crust," *Chemical Geology*, vol.97, pp.89-100, 1992.

[27] J. Madhavaraju and Y. I. Lee, "Geochemistry of the Dalmiapuram formation of the Uttatur group (Early Cretaceous), Cauvery basin, southeastern India: implications on provenance and paleo-redox conditions," *Revista Mexicana de Ciencias Geolo´gicas*, vol.26, pp.380–394, 2009.

[28] K. J. Aswad, N. R. Aziz, and H. A. Koyi, "Cr-spinel compositions in serpentinites and their implications for the petrotectonic history of the Zagros Suture Zone, Kurdistan Region, Iraq," *Geological magazine*, vol.148, pp. 802-818, 2011.

[29] S. Liu, C. Wu, T. Li and H. Wang, "Multiple geochemical proxies controlling the organic matter accumulation of the marine-continental transitional shale: a case study of the Upper Permian Longtan Formation, western Guizhou, China," *J. Nat. Gas Sci. Eng*. vol.56, pp.152–165, 2018.

[30] S. Zeng, J. Wang, X. Fu, W. Chen, X. Feng, D. Wang, C. Song and Z. Wang, "Geochemical characteristics, redox conditions, and organic matter accumulation of marine oil shale from the changliang Mountain area, northern Tibet," China. *Mar. Petrol. Geol.*, vol.64, pp.203–221, 2015.

[31] Z. Wang, J. Wang, X. Fu, W. Zhan, F. Yu, X. Feng, C. Song, W. Chen, and S. Zeng, "Organic material accumulation of Carnian mudstones in the North Qiangtang Depression, eastern Tethys: controlled by the paleoclimate, paleoenvironment, and provenance" *Mar. Petrol. Geol.* vol.88, pp.440–457, 2017.

[32] N. Zheng, T. D. Li, and M. W. Cheng, "Middle-Upper Ordovician radiolarians in Hunan and Jiangxi Provinces, South China: Implications for the sedimentary environment and nature of the Nanhua basin" *Journal of Asian Earth Sciences*. vol.179, pp.261–275, 2019.

[33] I. M. Akaegbobi and G. O. Ogungbesan, "Geochemistry of the paleocene limestone of Ewekoro Formation, Eastern Dahomey Basin, Southwestern Nigeria: Implication on provenance and depositional conditions," *Ife Journal of Science*, vol.18, pp.669-684, 2016.