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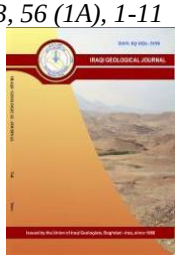

Discrimination Reef and Non-Reef Environments, Using REE Geochemistry

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Abstract

This research aims to distinguish the reef environment from the non-reef environment. The Oligocene-Miocene-succussion in western Iraq was selected as a case study, represented by the reefal limestone facies of the Anah Formation (Late Oligocene) deposited in reef-back reef environments, dolomitic limestone of the Euphrates Formation (Early Miocene) deposited in open sea environments, and gypsiferous marly limestone of the Fatha Formation (Middle Miocene) deposited in a lagoonal environment. The content of the rare earth elements (REEs) (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, Yb, Lu, and Y) in reef facies appear to be much lower than of those in the non-reef facies. The open sea facies have a low content of REEs due to being a transitional phase. The facies investigated have ΣREEs lower than the PAAS. The lagoonal facies shows an average ΣREEs higher than the Global Standard of Carbonate Rocks (GSCR), whereas reefal and open sea facies contain lower. The Y/Ho, Y/Dy, and Er/Nd were used as distinctive indicators of facies diagnosis; reefal facies have a high value of Y/Ho, Y/Dy, and Er/Nd as compared to PAAS are higher than1. In contrast, non-reef facies (lagoonal) have a lower value of Y/Ho, and Y/Dy as compared to PAAS is lower than 1, but Er/Nd is higher than 1. While in open sea facies the Y/Ho and Y/Dy have moderate values as compared to PAAS are close to 1, but a high value of Er/Nd as compared to PAAS higher than 1.

Keywords: REEs; Reef facies; Open sea facies; Non-reef facies

1. Introduction

Rare earth elements (REEs) are a useful tool for providing independent information on water depth, oceanic circulation and stratification, paleogeography, depositional models, and diagenetic processes (Murray et al., 1990; Nothdurft et al., 2004; Awadh and Hussien, 2015a). The REEs pattern in carbonate rocks is mainly influenced by the depositional environment. Several authors have attempted to distinguish geochemically between different facies (Chester, 1965; Till, 1971; Al-Bassam and Saeed, 1980; Bilings and Ragland, 1968 and Awadh, 2014). The concentration of REEs has worried many geologists due to their special properties (Henderson, 1984). REEs are used to examine ambient water from which carbonates precipitate (Bolhar and Van Kranendonk, 2007). REEs are used to understand the origin and depositional environments and used to describe different depositional environments and clarify the effect of the diagenetic processes (Boschetti et al., 2020; Awadh and Hussien, 2015a; Eker et al., 2012). They were also used to investigate the source rock potential of the Akkas Formation (Al-Juboury et al., 2021). This research examines the variance in REEs in the Oligocene-Miocene succession represented by Anah, Euphrates, and Fatha formations in western Iraq. The reef (Anah Formation) formed during the Oligocene consisted of distinct sedimentary cycles, each of which included a back-

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reef, fore-reef, and basinal facies (Al-Bassam and Saeed, 1980). On the other hand, two subcycles formed in the Miocene, which involved reef and lagoonal facies, where a basin was shallow and relatively littoral at the beginning, clastic and calcareous like the Euphrates Formation (Awadh and Al-Owaidi, 2021), and then the marine transgression forming shallow basins, with carbonate deposits, whereas in closed lagoons evaporates were Fatha Formation deposited (Sissakian and Mohammed, 2007). The research aims to use the REEs as a tool guide for discriminating the reef and non-reef facies.

2. Geological Setting

The study area is located on the western side of the Euphrates River in the Al-Anbar, within the Stable Shelf (Fig. 1). The stratigraphic succession of the area could be described from oldest to youngest as Anah, Euphrates, and Fatha formations as well as Quaternary sediments. The Anah Formation (Late Oligocene) is composed of chalky limestone, coral reef, and breccia (Al-Ali and Al-Dabbas, 2022; Awadh, 2018) deposited in a reef-backreef environment. It is covered by an unconformity surface by the Euphrates Formation represented by a thick basal conglomerate (Al-Obaidy, 2015). The Euphrates Formation (Early Miocene) is composed of dolomitic, fossiliferous, and oolitic limestones, marl and dolomitic limestone (Awadh and Hussien, 2015b; Al-Dabbas et al., 2013) deposited in an open sea environment and affected by dolomitization (Al-Dabbas et al., 2014; Awadh and Hussien, 2015a).

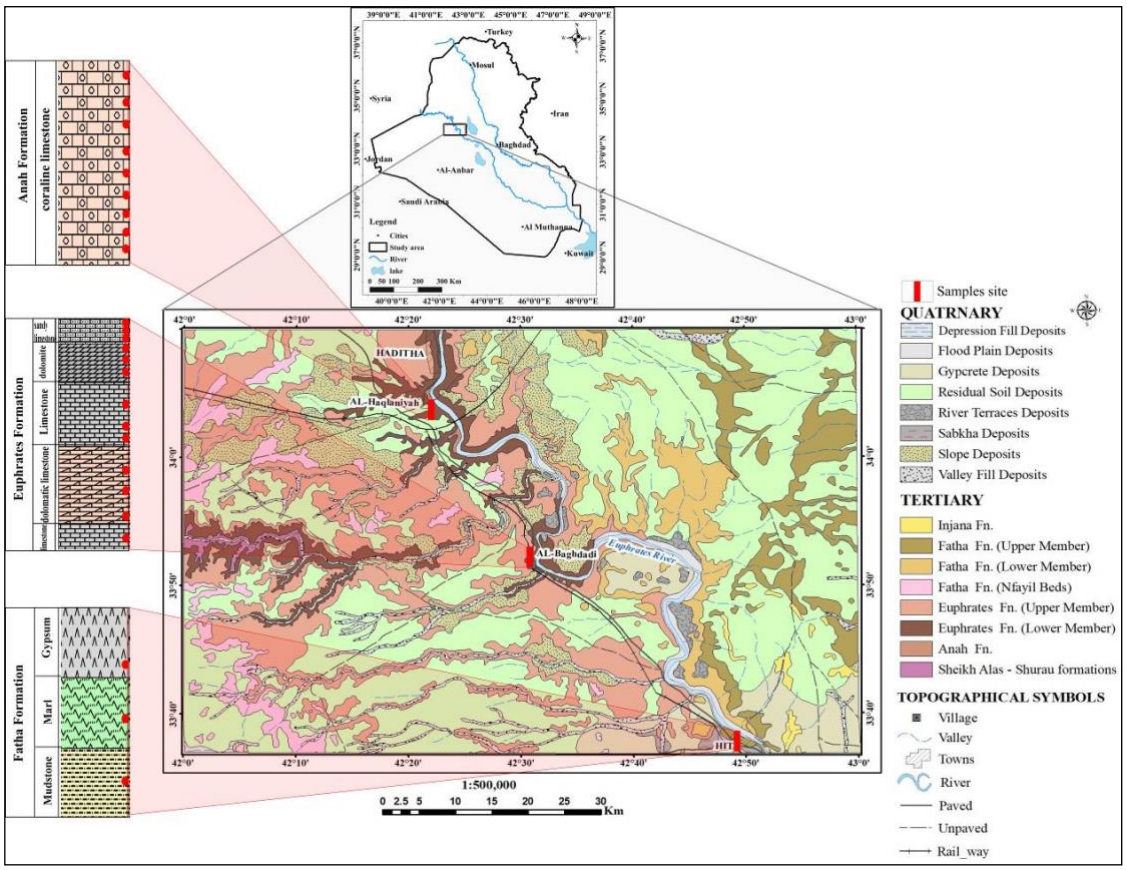

Fig. 1. Geological map of the study area (GEOSURV, 2013)

The Fatha Formation (Middle Miocene) comprises marl, limestone, gypsum, bituminous gypsum, and claystone (Al-Ali and Al-Dabbas, 2022). It was deposited in shallow marine with normal to high saline water with clear oscillation in the sea level (Awadh and Al-Ankaz, 2016). Pleistocene river terrace (sandy gravel) deposits are also present in the Quaternary. Slope sediments, floodplain sediments, valley

and depression fill sediments, and Sabkha's sediments, which include salt crust mixed with silt and clay, are examples of Pleistocene-Holocene deposits (Awadh and Al-Ghani, 2014; Khorshid et al., 2020).

3. Materials and Methods

The Oligocene-Miocene succession (Anah, unconformity zone, Euphrates, and Fatha formations) in Wadi Haqlan, Al-Baghdadi, and Hit in western Iraq was investigated (Table 1). Thirteen carbonate samples were collected from Wadi Haqlan (1AWH, 2AWH, 3UWH, 4AWH, 5AWH, 6AWH, 7AWH, 8AWH, 9AWH, 10AWH, 11EWH, 12EWH, and13EWH) with fourteen samples from Al-Baghdadi town (1UB, 2UB, 3UB, 4UB, 5EB, 6EB, 7EB, 8EB, 9EB, 10EB, 11EB, 12EB, 13EB, and 14EB) and three samples (1FH, 2FH, and 3FH) of gypsiferous marly limestone from Hit area. They are crushed, sieved to <2mm, and homogenized (Tucker, 1988). Seventeen samples (1AWH, 9AWH, 10AWH, 2UB, 4UB, 3UWH, 5EB, 7EB, 8EB, 9EB, 11EB, 12EB, 14EB, 13EWH, 1FH, 2FH, and 3FH) (Fig. 2) were analyzed for REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, Yb, Lu, and Y) using inductively coupled plasma-mass spectrometry (ICP-MS) in the Analytical Chemistry and Testing Services, Mineral Division-ALS Chemex at Sevilla, Spain. The reliability of the analytical results was accurate.

Table 1. The coordinates of the study area

Area	Easting	Northing
Wadi Haqlan	42˚ 22′ 01.00″	34˚ 05′ 25.50″
Al-Baghdadi	42˚ 31′ 48.60″	33˚ 51′ 36.35″
Hit	42˚ 48′ 41.05″	33˚ 38′ 13.93″

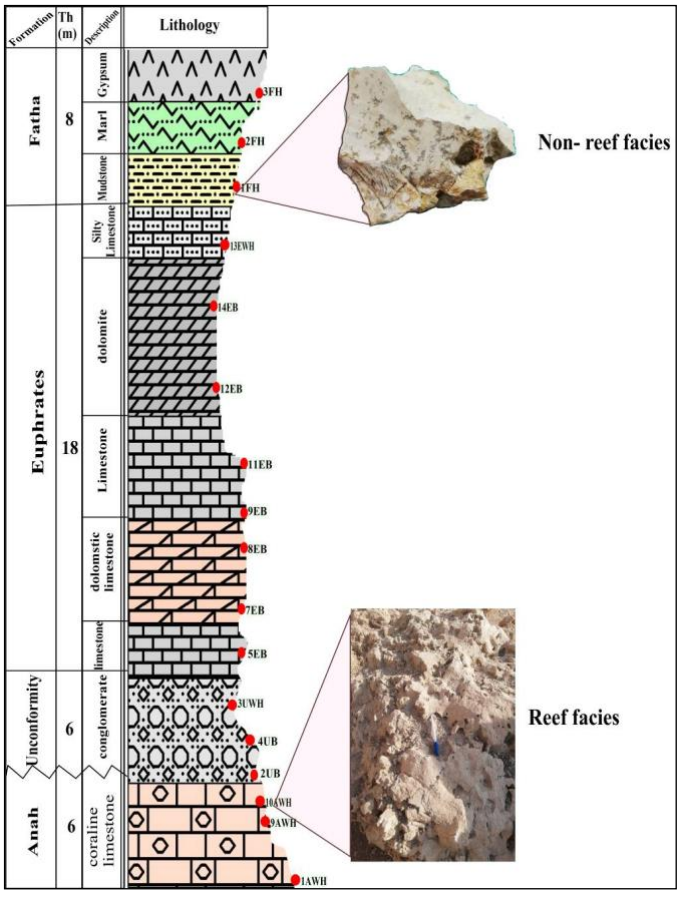

Fig. 2. Representative stratigraphic section of the formations in the study area

4. Results and Discussion

The geochemical results are compared to the Post Archaean Australian Shales (PAAS) (Taylor and McLennan, 1985) and the Global standard of carbonate rocks (GSCR) (Turekian and Wedepohl, 1961), and they are presented in Table 2.

Table 2. Rare earth elements (ppm) results of the formations studied compared to PAAS and GSCR

S. No.		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREEs	ΣLREEs	ΣHREEs
		Ppm																
1AWH	Anah Formation	0.80	1.00	0.15	0.90	0.09	0.07	0.26	0.02	0.16	0.04	0.11	0.01	0.09	0.009	3.709	3.270	0.439
9AWH		0.40	0.80	0.09	0.40	0.07	0.019	0.09	0.01	0.11	0.02	0.029	0.01	0.05	0.009	2.107	1.869	0.238
10AWH		0.80	1.20	0.22	0.90	0.31	0.05	0.25	0.04	0.24	0.05	0.10	0.03	0.09	0.010	4.290	3.730	0.560
Ave.		0.67	1.00	0.15	0.73	0.15	0.05	0.20	0.02	0.17	0.036	0.079	0.016	0.076	0.009	3.369	2.956	0.412
2UB	Unconformity	2.90	5.60	0.62	2.40	0.70	0.19	0.52	0.07	1.19	0.13	0.18	0.03	0.17	0.02	14.72	12.93	1.790
4UB		3.30	4.10	0.64	2.90	0.55	0.17	0.65	0.09	0.19	0.09	0.32	0.03	0.25	0.01	13.29	12.31	0.980
3UWH		1.10	1.60	0.20	1.10	0.22	0.11	0.47	0.05	0.35	0.08	0.25	0.03	0.27	0.04	5.870	4.800	1.070
Ave.		2.43	3.76	0.48	2.13	0.49	0.16	0.546	0.07	0.57	0.10	0.25	0.03	0.23	0.023	11.29	10.01	1.280
5EB	Euphrates Formation	1.30	2.20	0.28	1.00	0.15	0.03	0.31	0.04	0.18	0.07	0.07	0.01	0.11	0.009	5.759	5.270	0.489
7EB		1.10	1.80	0.27	1.00	0.15	0.06	0.13	0.02	0.21	0.04	0.08	0.01	0.06	0.010	4.940	4.510	0.430
8EB		0.70	1.40	0.12	0.90	0.21	0.03	0.15	0.02	0.16	0.02	0.07	0.02	0.08	0.009	3.889	3.510	0.379
9EB		0.60	1.40	0.13	0.60	0.21	0.06	0.11	0.009	0.14	0.02	0.06	0.009	0.07	0.009	3.427	3.110	0.317
11EB		0.60	1.10	0.07	0.30	0.029	0.04	0.1	0.03	0.11	0.01	0.03	0.01	0.03	0.009	2.468	2.239	0.229
12EB		0.70	1.10	0.11	0.80	0.029	0.04	0.14	0.01	0.12	0.03	0.09	0.02	0.06	0.009	3.258	2.919	0.339
14EB		0.80	1.30	0.21	0.60	0.06	0.019	0.11	0.02	0.13	0.03	0.12	0.01	0.04	0.009	3.458	3.099	0.359
13EWH		0.50	0.90	0.09	0.40	0.08	0.019	0.07	0.009	0.16	0.02	0.06	0.009	0.07	0.009	2.396	2.059	0.337
Ave.		0.78	1.40	0.16	0.70	0.11	0.037	0.14	0.019	0.151	0.03	0.072	0.012	0.065	0.009	3.699	3.339	0.345
1FH	Fatha Formation	14.0	27.4	3.43	14.6	3.08	0.81	2.76	0.45	2.58	0.58	1.71	0.25	1.58	0.2	73.43	66.08	7.350
2FH		6.70	12.2	1.63	7.10	1.10	0.32	1.21	0.22	1.26	0.26	0.79	0.1	0.69	0.12	33.70	30.26	3.440
3FH		0.40	0.60	0.05	0.20	0.08	0.019	0.11	0.01	0.049	0.02	0.03	0.01	0.029	0.01	1.617	1.459	0.158
Ave.		7.03	13.4	1.70	7.30	1.42	0.383	1.36	0.226	1.296	0.286	0.843	0.12	0.766	0.11	36.25	32.59	3.649
PAAS*		38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.4	2.82	0.43	184.76	171.82	12.94
GSCR**		-	11.5	1.1	4.7	1.3	0.2	1.3	0.2	0.9	0.3	0.5	0.04	0.5	0.2	22.74	20.1	2.64

* PAAS; Post Archaean Australian Shales (Taylor and McLennan, 1985)

**GSCR; Global Standard of carbonate rocks (Turekian and Wedepohl, 1961)

Table 3. The concentrations of Y and REEs ratios of the studied formations

S. No.		Y ppm	ΣLREE/ΣHREE	Y/Ho	Y/Dy	Er/Nd
1AWH	Anah Formation	1.90	7.45	47.5	11.8	0.12
9AWH		0.50	7.85	25.0	4.54	0.07
10AWH		1.70	6.66	34.0	7.08	0.11
Ave.		1.36	7.17	35.5	7.83	0.10
2UB	Unconformity	2.80	7.22	21.5	2.35	0.07
4UB		3.80	12.6	42.2	20.0	0.11
3UWH		3.30	4.48	41.3	9.42	0.23
Ave.		3.30	7.82	35.0	10.5	0.14
5EB	Euphrates Formation	1.30	10.8	18.6	7.22	0.07
7EB		1.10	10.5	27.5	5.23	0.08
8EB		0.80	9.26	40.0	5.00	0.08
9EB		0.80	9.81	40.0	5.71	0.10
11EB		0.50	9.78	50.0	4.54	0.10
12EB		0.80	8.61	26.7	6.66	0.11
14EB		0.80	8.63	26.7	6.15	0.20
13EWH		0.60	6.11	30.0	3.75	0.15
Ave.		0.84	9.67	32.4	5.53	0.11
1FH	Fatha Formation	15.2	8.99	26.2	5.89	0.12
2FH		7.10	8.79	27.3	5.63	0.11
3FH		0.20	9.23	10.0	4.08	0.15
Ave.		7.50	8.93	21.2	5.20	0.13
PAAS*		27.31	13.26	27.6	5.86	0.08

*PAAS; Post Archaean Australian Shales (Taylor and McLennan, 1985)

The average of ΣREEs in the formations Anah 3.36 ppm, unconformity zone 11.29 ppm, Euphrates 3.69 ppm, and Fatha 36.25 ppm is greatly lower than PAAS 184.76 ppm. Whereas after comparing an average of ΣREEs with GSCR, the Fatha Formation displays a higher average of ΣREEs 36.25 ppm than GSCR 22.74 ppm, while the other studied formations have lower than it (Fig. 3), which could be interpreted as the REEs was adsorbed with clay minerals rather than in carbonate rocks (Awadh and Hussien, 2015a).

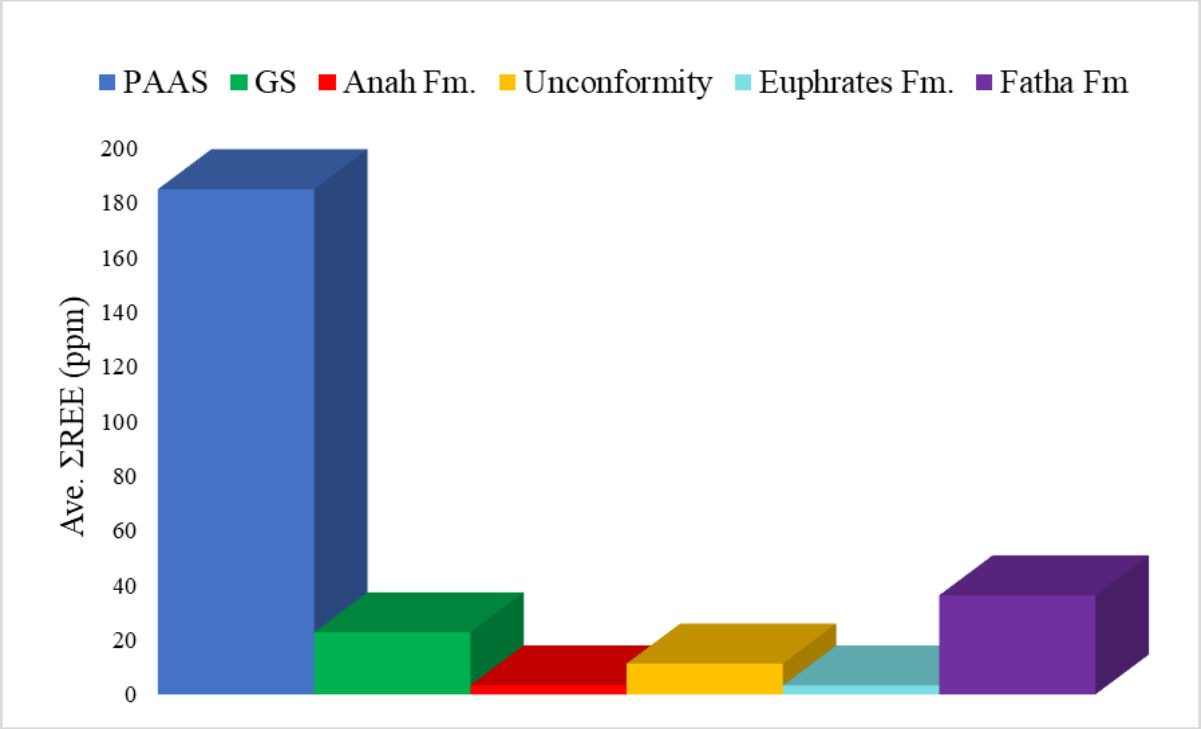

Fig. 3. Bar shape displays ΣREEs concentration in the studied formations compared to PAAS after (Taylor and McLennan, 1985) and GSCR after (Turekian and Wedepohl, 1961)

Element concentrations may be utilized to distinguish the reef from non-reef facies (Fig. 4), and the manner of their distribution may also serve as a geochemical indicator. The REEs results indicated possible discrimination between the reef and non-reef facies. The majority of variations of REEs are influenced by the diagenesis process and the contents of clay minerals. Dolomitization alters the regular pattern of REEs and may supply significant aspects of pore water solutions, when weathering and sedimentation are re-assembled in the hydrolysate minerals REEs tend to be homogenous during sedimentary processes (Awadh and Hussein, 2015a). In reefal facies, the average of LREEs 2.96 ppm was much higher than HREEs 0.41 ppm, whereas the LREE/HREE 7.17. In the unconformity zone, the average of LREEs 10.01 ppm was more than HREE 1.28 ppm; LREE/HREE is 7.82. In open sea facies, the average of LREEs 3.34 ppm was more than HREEs 0.34 ppm; LREE/HREE 9.28. Non-reef facies had high concentrations of LREEs 32.59 ppm, and HREE 3.65 ppm with LREE/HREE 8.93, due to incorporation with clays as ions exchangeable phases (Yanfei et al., 2016). REEs gave heterogeneous behavior in each facies studied (reefal, lagoonal, and open sea) as shown in Fig.5. They increased in the non-reef facies (lagoonal Facies) represented by Fatha Formation, whereas they decreased in reef facies (Anah Formation). The unconformity zone is slightly enriched in REEs due to weathering, erosion and leaching from Euphrates Formation. The intense dolomitization that converts calcite to dolomite is thought to be the cause of the Euphrates Formation's low REEs content. Therefore, lithology and sedimentary conditions influence REEs relatively (Awadh and Hussien, 2015a).

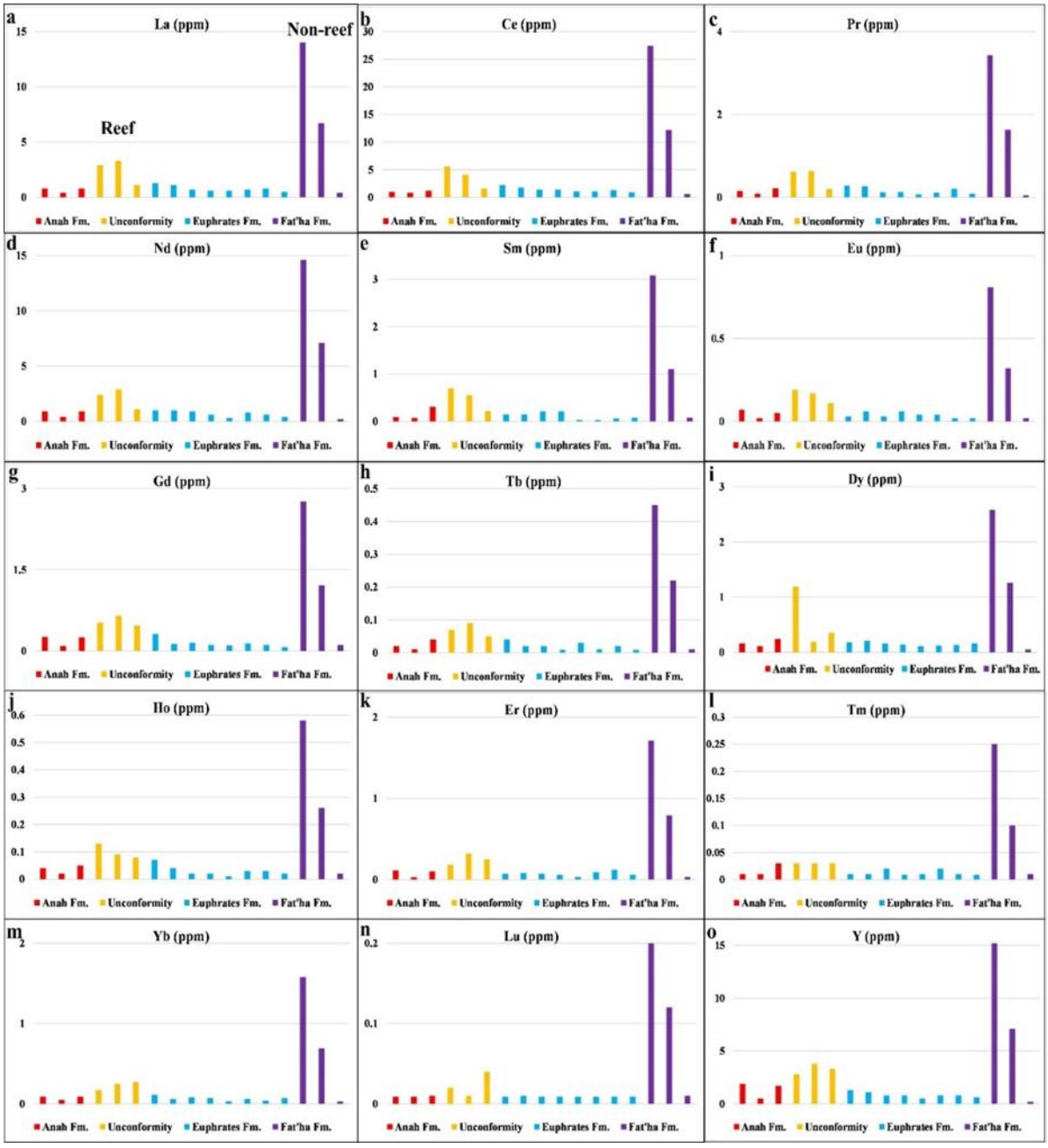

Fig. 4. Distribution of REEs in the reef and non-reef facies

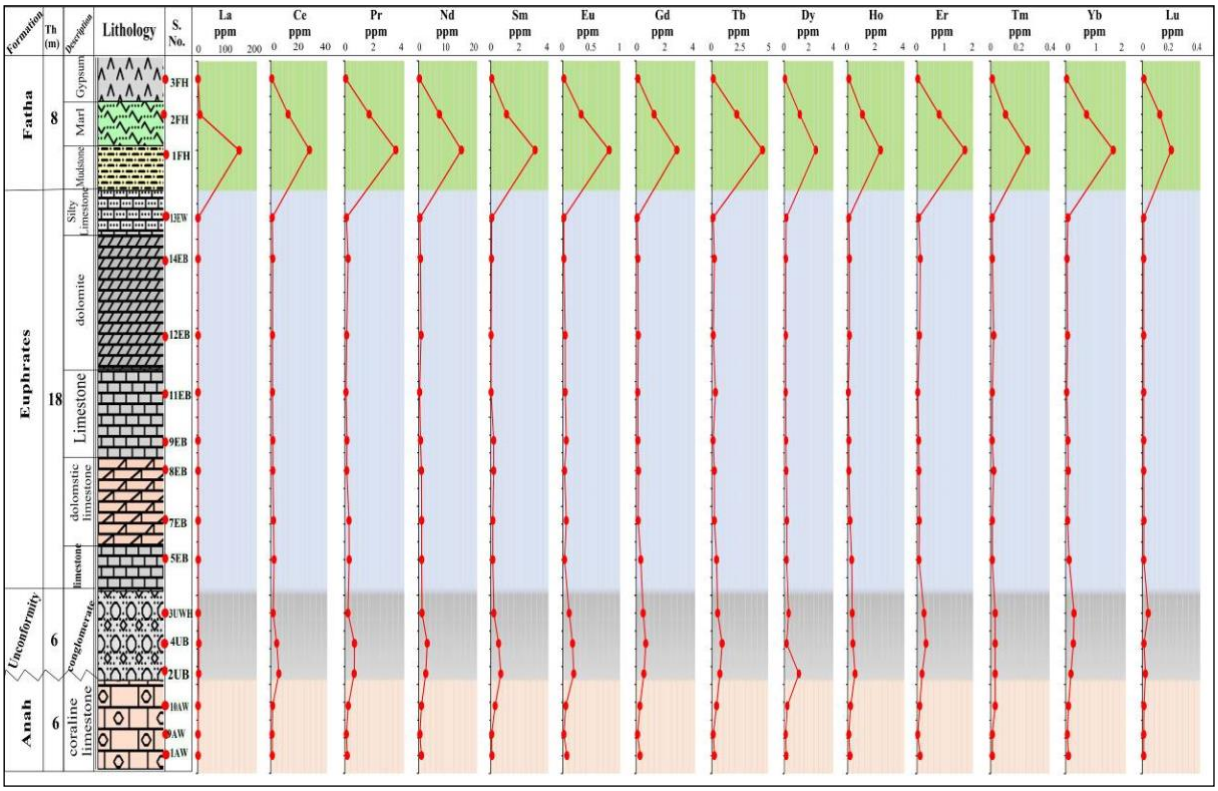

Fig.5. Chemostratigraphic variation of REEs in the formations studied

Any quantitative interpretation of geochemical data depends on correct knowledge of the basic parameters that govern the behavior of elements in geochemical systems (Bau, 1996). In the current study, the ratios Y/Ho, Y/Dy, and Er/Nd have been used as an indicator to interpret REEs pattern in different environments (Fig.6). Higher Y/Ho ratios are often noticed because Yttrium (Y) and its geochemical twin Holmium (Ho) have differing surface complex stabilities. Consequently, Y is typically not eliminated from seawater compared to Ho (Bau, 1996). The ratio Y/Ho is affected by the clastic material inputs to the sedimentary basin as it decreases with an increase in these inputs (Mahmood, 2022). Er/Nd ratios can explain the effect of detrital material or the diagenesis process (German and Elderfield, 1989).

Table 3, shows a reefal facies have a higher range of Y/Ho from 25 to 47.5, as compared to PAAS ($Y/Ho_{sample}/Y/Ho_{PAAS}$ =1.2) is higher than 1, Y/Dy ranged from 4.45 to 11.8, as compared to PAAS ($Y/Dy_{sample}/Y/Dy_{PAAS}$ =1.3) is higher than 1, and Er/Nd have a range 21.5- 42 as compared to PAAS ($Er/Nd_{sample}/Er/Nd_{PAAS}$ =1.2). In unconformity zone has an average of Y/Ho 35 as compared to PAAS >1 (1.2), Y/Dy has an average of 10.59 as compared to PAAS >1 (1.7), and the average of Er/Nd 0.14 as compared to PAAS >1 (1.7). In open sea facies, the Y/Ho has an average of 32.43 as compared to PAAS is close to it 1.1≈ 1, the average of Y/Dy (5.53) as compared to PAAS is close to it 0.9 ≈ 1, and Er/Nd has an average 0.11 as compared to PAAS > 1 (1.3). In non-reef facies, Y/Ho has a range from 10 to 27.3 as compared to PAAS < 1 (0.7), a range of Y/Dy 4.08 to 5.89 as compared to PAAS < 1 (0.8) and Er/Nd ranged from 0.111 to 0.150 as compared to PAAS > 1 (1.6). Consequently, Y/Ho and Y/Dy in reef facies > open sea facies > non-reef facies decrease toward lagoonal facies, but Er/Nd in reef facies < open sea facies < non-reef facies (Fig.7).

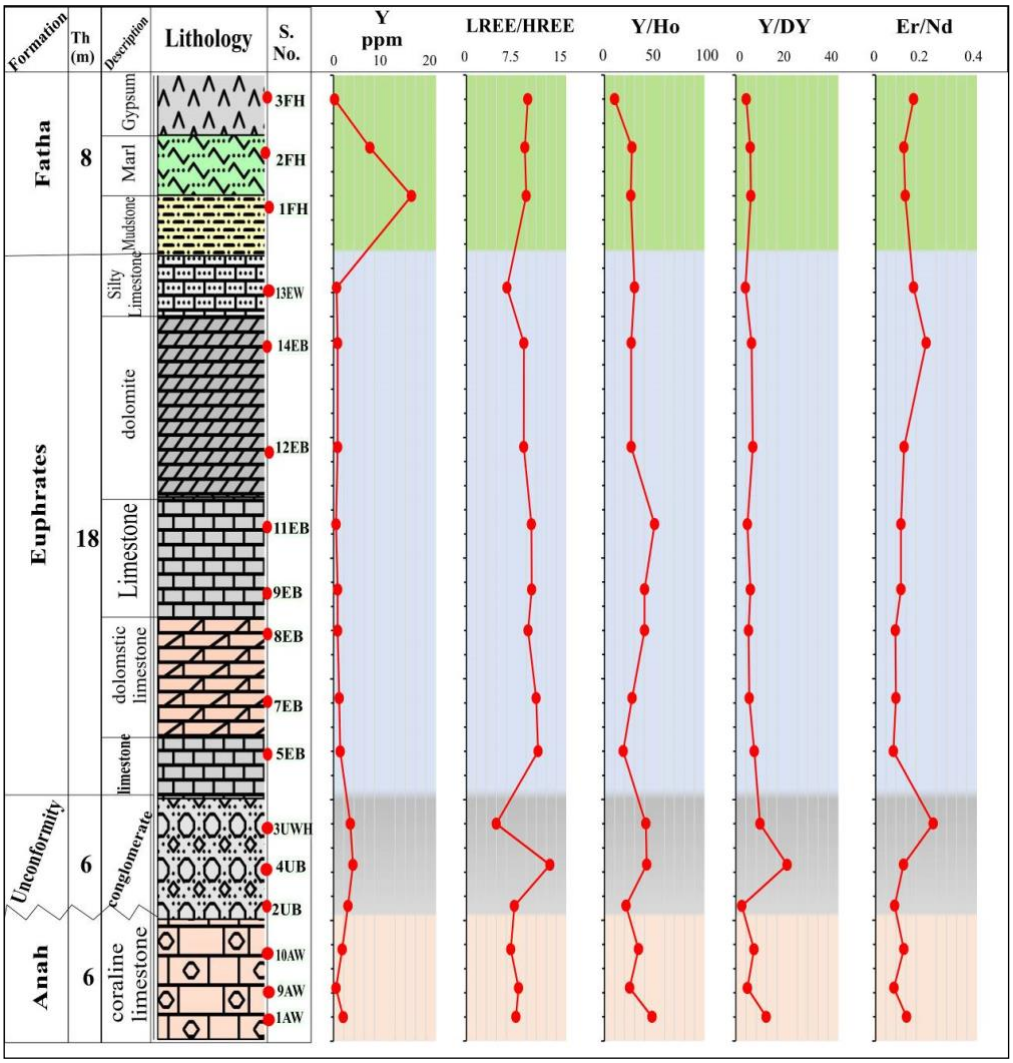

Fig.6. Chemostratigraphic variation of Y and some REEs ratios used in the present study

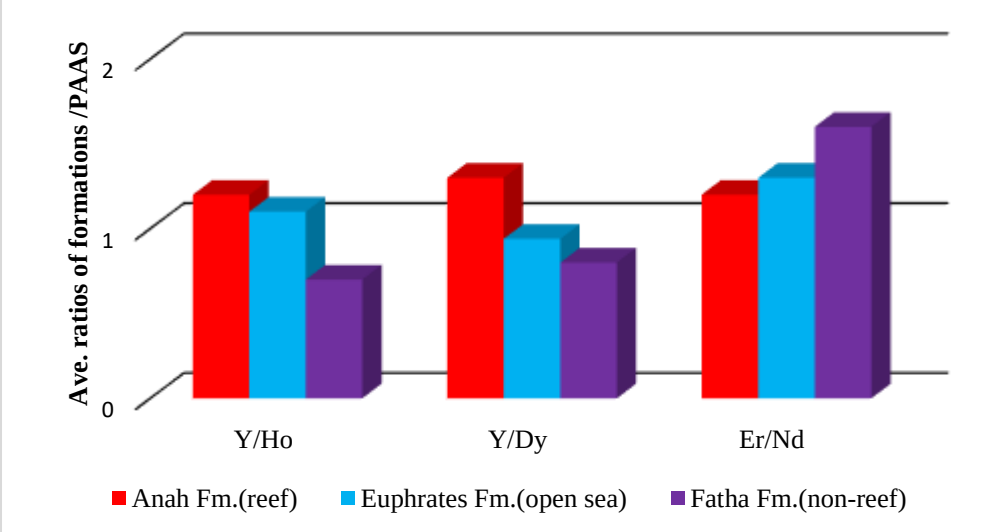

Fig.7. Geochemical parameters relative to PAAS used in the present study

5. Conclusions

This research discussed the behavior of REEs in different environments represented by the formations of Anah, Euphrates, and Fatha formations, indicating the possibility of using REEs to distinguish between different depositional environments. This research demonstrated that is possible to differentiate the reef facies (Anah Formation) from non-reef facies (Fatha Formation), in terms of the very high REEs content (36.25 ppm) in the latter due to be composed of clays and the ability of their surface to adsorb these elements, while in reef facies have the lowest content of REEs (3.36 ppm). The open sea facies (Euphrates Formation) have low REEs concentrations as a result of the dolomitization effect. All the studied facies show a lower average of ΣREEs than PAAS, while compared to GSCR, non-reef facies have a higher average of ΣREEs than it but reef and open sea facies are lower. Using geochemical parameters Y/Ho, Y/Dy, and Er/Nd can discriminate between the facies, in reef facies have a high value of Y/Ho, Y/ Dy, and Er/ Nd as compared to PAAS higher than 1, open sea facies have Y/Ho and Y/ Dy close to PAAS ≈ 1, and Er/ Nd as compared to PAAS higher than 1, in contrast, non-reef facies have a low value of Y/Ho and Y/Dy as compared to PAAS lower than 1, but Er/Nd higher than 1.

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