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Rare Earth Elements Geochemistry of the Upper Oligocene-Middle Miocene Succession in the Western Iraq

Salih Muhammad Awadh[1*], Sfoog Asi Hussien[2]
[1]Department of Geology, College of Science, University of Baghdad, Baghdad, Iraq
[2]Department of Applied Geology, College of Science, Tikrit University, Tikrit, Iraq

Abstract

Rare earth element (REE) in the Upper Oligocene-Middle Miocene succession represented by reefal carbonate rocks of Anah Formation, dolomitic limestone of the Euphrates Formation, and gypsiferous marly limeatone of Fatha Formation in the western Iraq were used as geochemical indicators. The objectives of this study are to describe the REE patterns in the different depositional environments, and clarify their response to the diagentic processes, in particular, dolomitization. The general trend of REE pattern shows similarity for Anah and Fatha Formations, with less similarity in the Euphrates Formation. The reefal limestone facies of Anah Formation was characterized by relative depletion in REE, while REEs enrichment were distinctive character of the gypsiferous marly limestone facies in Fatha Formation. The dolomitic limestone facies belonged to the Euphrates Formation was marked with an intermediate amount of REE. The normalized ΣLREEs in the Anah and Fatha Formations have a significant variation. Furthermore, they are less abundance than the normalized ΣHREEs, with the exception of the Euphrates Formation, which suffered a relatively depleted of the ΣHREEs due to dolomitization. The negative anomaly in cerium (Ce), positive anomalies of the europium (Eu) and lanthanum (La) in the PAAS-normalized REE patterns reflect well-oxygenated shallow water of Anah and Fatha Formations; and also indicate incorporation of REE into the limestone of Euphrates Formation occurred in moderately marine deep water. The vast majority of the REEs concentration was adsorped with clay minerals rather than in carbonate rocks and gypsum. Dolomitization clearly affected the real signature of the REE, particularly, in the Euphrates Formation and provided useful information on the composition of diagenetic fluids which later became relatively depleted in HREEs as it is clear in the Euphrates Formation.

Keywords: REE, Anah Formation, Fatha Formation, Euphrates Formation.

جيوكيمياء العناصر الأرضية النادرة لتتابع الأوليكوسين الأعلى–المايوسين الأوسط غرب العراق

صالح محمد عوض[1*]، صفوك عاصي حسين[2]
[1]قسم علم الأرض، كلية العلوم، جامعة بغداد، بغداد، العراق
[2]قسم علم الأرض التطبيقي، كلية العلوم، جامعة تكريت، تكريت، العراق

الخلاصة

تم استعمال العناصر الأرضية النادرة كدلائل جيوكيميائية في دراسة تتابع ألأوليكوين الأعلى–المايوسين المتوسط المتمثل بصخور الحجر الجيري الحيدي لتكوين عنه، والحجر الجيري الدولومايتي لتكوين الفرات، والحجر الجيري المارلي الجبسي لتكوين الفتحة غرب العراق. تهدف الدراسة الى وصف انماط العناصر الارضية النادرة في البيئات الرسوبية المتنوعة، وتوضيح مدى أستجابتها للعمليات التحويرية وخصوصاً عملة

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* Email:salihauad2000@yahoo.com

الدلمتة. ظهر النمط العام للعناصر الأرضية النادرة متشابهاً في تكويني عنه والفتحة وأقل تشابها مع تكوين الفرات. تميزت سحنة الحجر الجيري الحيدي لتكوين عنه بنضوب نسبي واضح للعناصر الأرضية النادرة، في حين كان الأغناء هو الطابع المميز لسحنة الحجر الجيري المارلي لتكوين الفتحة، كذلك فان سحنة الحجر الجيري الدولومايتي العائدة لتكوين الفرات تميزت بكمية متوسطة من العناصر الارضية النادرة. يُظهر مجموع العناصر الأرضية النادرة الخفيفة المعايرة في هذه التكاوين تغايراً مهماً، علاوة على ذلك، فقد كانت هي االاقل وفرة من العناصر الارضية الثقيلة المعايرة، باستنثاء تكوين الفرات الذي عانى من إستنزاف نسبي للعناصر الأرضية لثقيلة بسبب عملية الدلمتة. عكست الشذوذات السالبة للسيريوم والموجبة لليوريبيوم واللانثانيوم في نمط العناصر الأرضية المعاير مع الشيل الأسترالي بيئة المياه الضحلة المؤكسجة جيدا لتكويني عنه والفتحة، ودلت كذلك على إن إندماج العناصر الأرضة النادرة ضمن الحجر الجيري لتكوين الفرات حدث في بيئة بحرية متوسطة العمق. إن الغالبية العظمى لتراكيز العناصر الأرضية النادرة كانت ممتزة مع المعادن الطينية أكثر من إمتزازها مع صخور الحجر الجيري والجبس. أثرت عملية الدلمتة بشكل واضح على البصمة الحقيقية لنمط العناصر الأرضية النادرة، خصوصا في تكوين الفرات وزودت بمعلومات مفيدة عن تركيب المحاليل التحويرية التي اصبحت فيما بعد ناضبة نسبيا من العناصر الأرضية الثقيلة كما هو واضح في تكوين الفرات.

Introduction

Rare earth elements (REE) geochemistry is useful for paleogeographic, palaeoceanographic reconstruction, diagenetic studies and identifying geochemical processes [1] and [2]. They may provide independent information on water depth, oceanic circulation and stratification, paleogeography and depositional models [3]. Many factors control the concentration of REE in seawater, such as different input sources such as terrestrial and hydrothermal input as well as scavenging processes related to depth, salinity, and oxygen levels [4] and [5]. Limestones provide an important evidence of the water REE geochemistry in which they precipitated. Consequently, the REE geochemistry of pure limestones is confirmed as an important tool for exploring the actual state of seawater and Earth history [6]. Seawater REE patterns that are normalized to a shale standard are characterized by uniform light REE depletion, a negative Ce anomaly, and a slight positive La anomaly [7]. Skeletal carbonates exist in the reefal facies or very near to estuaries [6] has a distinct REE pattern. Many of the limestones are very well preserved, but others have been partially dolomitized allowing for the effects of some types of diagenetic processes. Dolomitization may provide important aspect of the pore water solutions, and causes change in the normal pattern of REE.

In this study, REEs were investigated in three Formations; these are Anah, Euphrates and Fatha Formations which represent the Upper Oligocene to Middle Miocene succession in the western Iraq (Figure 1). The Anah Formation is reefal facies of pure limestone which was deposited in shallow marine water [8]. The Euphrates Formation is limestone was deposited in the open sea environment and affected by dolomitization [9]. The Fatha Formation is formed mainly from gypsum as well as marly limestone reflecting lagoon facies [10] The objectives of this study are to describe the REE patterns in different depositional environments, and clarify their response to the diagentic processes, in particular, dolomitization.

Materials and methods

During many field work trips, a total of sixty one (61) samples were collected from the Oligocene-Miocene succession, which include Anah, Euphrates and Fatha Formations along the Euphrates Fault between Al-Qaim and Al-Ramadi in the Western Iraq Figure-1. Pure limestone, dolomitic limestone and gypsum to marly limestone are chosen to be a three geological material types for chemical analyses. Nine (9) Reefal carbonate samples contain skeletal organisms from Anah Formation (U. Oligocene) were considered as a pure calcic limestone. Twenty seven (27) dolomitized limestone samples from the Euphrates Formation (L. Miocene) were chosen to test the effects of dolomitization on REE distribution. Twenty five (25) samples of gypsiferous marly limestone were collected from Fatha Formation to investigate the effect of shallow depth on the REE distribution. All those samples were crushed, homogenized and managed to be representative samples according to the procedure stated in Tucker [11 and 12]. Chemical analyses were achieved in the Analytical Chemistry and Testing Services, Mineral Division-ALS Chemex at Sevilla, Spain. All samples were analyzed for some major oxides (SiO_2, Al_2O_3, CaO and MgO) and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) using the Element Package by Lithium Borate Fusion and ICP-AES for major oxides, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for REEs according to the using procedures outlined by [13].

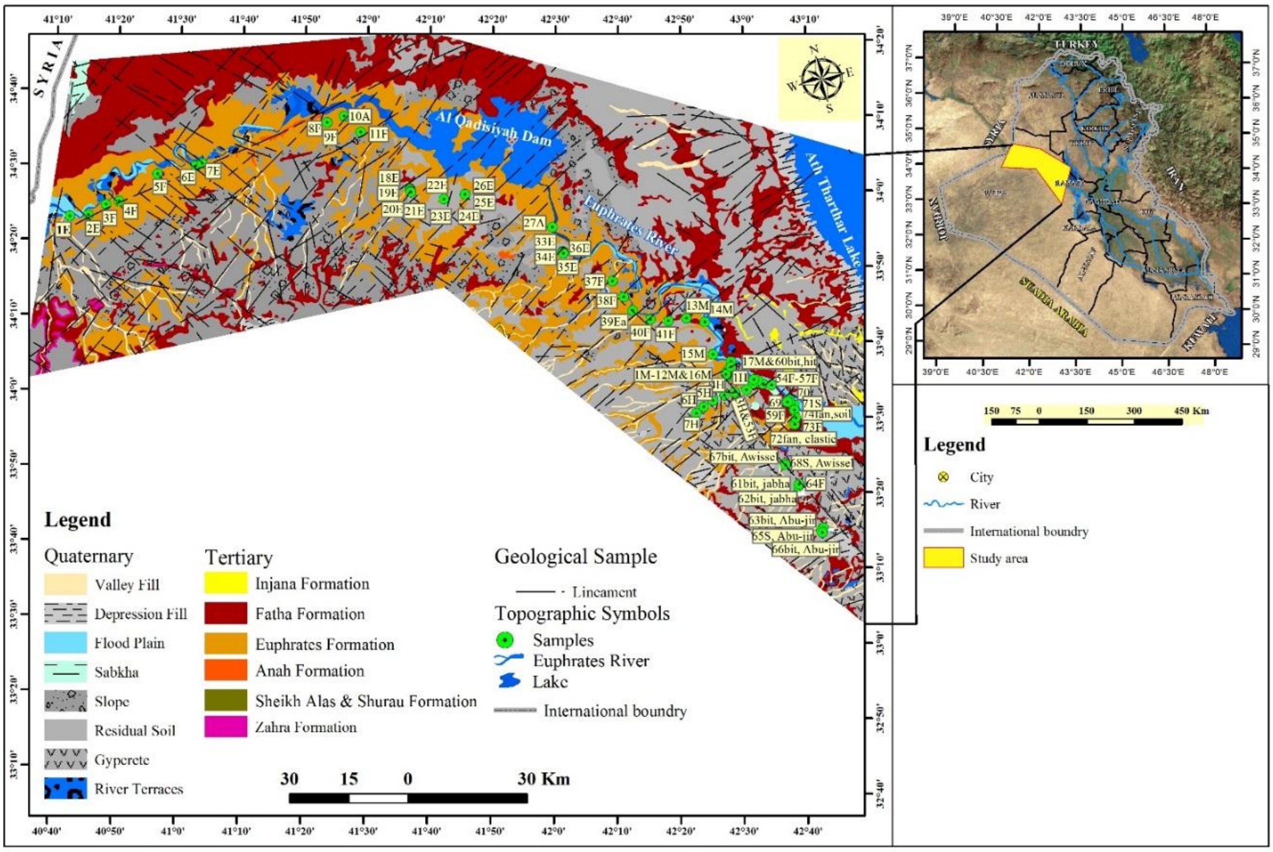

Figure 1- Geological map and sampling sites in the study area.

Results and discussion

Major oxides (SiO_2, Al_2O_3, CaO and MgO) as well as rare earth element (REE) concentrations in the tested samples are normalized to a standard shale average (Post Archaean Australian Shales - PAAS) according to [14] and listed in Tables 1, 2 and 3 respectively. The REE patterns of the Anah, Euphrates and Fatha formations are illustrated in Figures-2. The highest non-normalized and normalized mean of ΣREE is present in Fatha Formation (17.0 and 1.32), whilst the lowest is present in Anah Formation (6.32 and 0.6), where the intermediate state is marked in the Euphrates Formation to have (10.1 and 0.82) respectively. REEs tend to be homogeneous during sedimentary processes, where weathering and sedimentation are re-assembled in the hydrolysate minerals. Therefore, they may concentrated within the clay mineral in Fatha Formation. Significance variations in the mean ΣREE are detected. The REEs have a 3+ valence in most environments with exceptional of Ce that can shows 4+ state and Eu in 2+ state. This is a reason of the anomalous behavior for Ce and Eu relatively to the whole REE group [15]. In seawater, REEs remain in 3+ oxidation state, except Ce which is removed rapidly from seawater in comparison with the other REE. This is because it being precipitated from solution as CeO after oxidized to Ce^{4+}, and it can to bind with hydroxylates as a colloidal solution with pH 8 or more. The negative Ce anomalies indicate a seawater source for REE of sediments. Positive Eu anomalies were found in all studied formations, but negative Ce was characterized the Fatha and Anah Formations. Furthermore, the Euphrates Formation was characterized by depleted La. Negative anomaly of Ce was detected in the reefal facies of Anah Formation Figure-2A, and gypsiferous marly limestone of Fatha formation Figure-2C, but the dolomitic limestone facies is obviously characterized by La depletion Figure-2B. The negative anomaly in Ce refers to the preferential solution phase which removed during reoxygenation [13]. Similarly, is a reflection of Ce removed from seawater [15]. Ce is preferentially removed during reoxygenation. Actually, Ce among the REE is the only element with REDOX transformations at ambient oceanic conditions, where it increases with depth due to biologically mediated oxidation and probably light inhibited [16]. Consequently, negative Ce anomaly was noticed in Anah and Fatha Formations Figures-2A and C. The REE almost displayed similar patterns, with except of Reefal facies of Anah Formation which is displayed a relative enrichment of HREE Figure-2A. The intensive diagenetic processes, particularly dolomitization led to the depletion of HREE and La. The highest content of REE that was found in Fatha may attribute to the detrital fraction represented by clay minerals and quartz. REEs in detrital fraction mean that REE passed from weathering to deposition without lost in any chemical processes. The low ΣREE in the Euphrates Formation is attributed to the intensive dolomitization that converted calcite into dolomite. Hence, the lithology and sedimentary conditions lead relatively to a variation in ΣREE. REE in carbonates under arid conditions have similar abundances, while REE under humid conditions are varied, where they deplete under acidic to near neutral conditions [17]

Table 1- Rare earth element concentrations (ppm) of pure limestone of Anah Formation and average values of Post-Archean Australian Shale (PAAS)*.

S.No.	SiO_2	Al_2O_3	CaO	MgO	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
10 Aa	0.78	0.15	34.12	18.28	0.5	1.06	0.13	0.4	0.1	0.05	0.1	0.01	0.08	0.02	0.05	0.01	0.04	0.01	2.56
17 A	0.48	0.08	30.46	21.13	0.5	0.96	0.12	0.4	0.1	0.06	0.1	0.01	0.09	0.02	0.05	0.01	0.04	0.01	2.47
27 Aa	0.45	0.09	55.60	0.32	1.7	2.0	0.38	1.7	0.39	0.1	0.32	0.05	0.3	0.06	0.18	0.02	0.15	0.02	7.37
27 Ab	0.70	0.16	55.00	0.36	2.1	3.23	0.52	2.3	0.51	0.12	0.41	0.06	0.4	0.08	0.24	0.03	0.19	0.03	10.2
27 Ac	0.98	0.22	54.78	0.33	1.4	2.39	0.3	1.4	0.31	0.09	0.25	0.04	0.28	0.06	0.18	0.03	0.16	0.02	6.91
27 Ad	0.50	0.09	55.22	0.24	0.6	1.04	0.14	0.6	0.15	0.06	0.13	0.02	0.14	0.03	0.1	0.01	0.08	0.01	3.11
27 Ae	0.68	0.11	55.80	0.28	1.0	1.59	0.24	1.1	0.24	0.08	0.22	0.03	0.23	0.05	0.15	0.02	0.13	0.02	5.1
27 Af	0.73	0.17	54.80	0.29	1.6	2.72	0.37	1.7	0.37	0.1	0.31	0.05	0.33	0.07	0.22	0.03	0.19	0.03	8.09
27 Ag	1.34	0.28	54.20	0.34	2.2	3.73	0.5	2.3	0.53	0.13	0.48	0.07	0.47	0.1	0.31	0.04	0.25	0.04	11.1
Min	0.45	0.08	30.46	0.24	0.50	0.96	0.12	0.40	0.10	0.05	0.10	0.01	0.08	0.02	0.05	0.01	0.04	0.01	2.47
Max	1.34	0.28	55.8	21.13	2.20	3.73	0.52	2.30	0.53	0.13	0.48	0.07	0.47	0.10	0.31	0.04	0.25	0.04	11.1
Mean	0.74	0.15	50.00	4.62	1.29	2.08	0.30	1.32	0.30	0.09	0.26	0.04	0.26	0.05	0.16	0.02	0.14	0.02	6.32
St.Dev	0.28	0.07	10.09	8.58	0.67	1.01	0.15	0.75	0.16	0.03	0.14	0.02	0.14	0.03	0.09	0.01	0.07	0.01	3.22
PAAS*	---	---	---	---	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	185
Norm.	---	---	---	---	0.033	0.026	0.033	0.039	0.005	0.08	0.055	0.05	0.05	0.05	0.05	0.04	0.05	0.04	0.60

*[14]

Table 2- Rare earth element concentrations (ppm) of dolomitic limestone of the Euphrates Formation and average values of post-Archean Australian shale (PAAS)*

S.No.	SiO_2	Al_2O_3	CaO	MgO	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
1 E	1.3	0.2	53.6	0.61	0.8	1.44	0.18	0.7	0.16	0.07	0.19	0.02	0.14	0.03	0.08	0.01	0.07	0.01	3.9
2 E	0.72	0.13	35.5	18.6	0.8	1.38	0.17	0.6	0.13	0.07	0.13	0.02	0.09	0.02	0.05	0.01	0.04	0.01	3.5
6 E	1.77	0.37	28.9	18.9	0.8	1.4	0.18	0.7	0.14	0.07	0.18	0.02	0.15	0.03	0.08	0.01	0.07	0.01	7.4
12 E	1.05	0.25	29.5	20.9	1.6	2.82	0.35	1.3	0.29	0.09	0.29	0.04	0.22	0.04	0.12	0.02	0.1	0.02	7.3
13 E	1.58	0.41	30	21.2	1.9	3.36	0.43	1.6	0.34	0.11	0.35	0.05	0.29	0.06	0.16	0.02	0.14	0.02	8.8
14 E	5.56	1.54	27.8	20.1	3.2	5.84	0.82	2.9	0.7	0.2	0.68	0.09	0.52	0.1	0.28	0.04	0.22	0.03	15.6
14 E	23.3	3.91	25.3	10.9	9.7	18.6	2.6	9.3	2.03	0.48	1.87	0.25	1.47	0.28	0.78	0.1	0.6	0.09	48.1
15 E	2.08	0.58	29.8	20.8	2.0	4.2	0.53	2.0	0.47	0.14	0.46	0.06	0.37	0.07	0.2	0.03	0.15	0.02	10.7
16 E	5.81	1.37	27	19.6	2.9	5.77	0.81	2.9	0.65	0.17	0.59	0.08	0.45	0.09	0.23	0.03	0.18	0.03	14.9
18 E	1.96	0.48	30.5	21.0	1.5	4.43	0.4	1.5	0.38	0.11	0.32	0.04	0.24	0.05	0.13	0.02	0.09	0.01	9.2
19 E	4.41	1.28	28.2	20.3	3.1	5.26	0.76	2.8	0.63	0.16	0.54	0.07	0.41	0.08	0.21	0.03	0.16	0.02	14.2
19 E1	2.59	0.65	29.8	19.6	1.6	4.79	0.43	1.9	0.48	0.12	0.33	0.05	0.27	0.05	0.14	0.02	0.12	0.02	10.3
20 E	4.45	0.43	29.4	21.1	1.6	3.19	0.4	1.5	0.36	0.11	0.29	0.04	0.22	0.04	0.11	0.02	0.09	0.01	8.0
21 E	6.31	1.85	27.7	19.1	3.1	6.28	0.84	3.1	0.72	0.17	0.54	0.07	0.41	0.08	0.21	0.03	0.16	0.02	15.7
22 E	1.12	0.29	30.8	20.3	1.3	2.52	0.35	1.3	0.33	0.1	0.31	0.04	0.25	0.05	0.14	0.02	0.1	0.01	6.8
23 E	3.61	0.97	29	20.3	2.4	4.82	0.62	2.3	0.53	0.14	0.43	0.06	0.34	0.07	0.18	0.02	0.15	0.02	12.1
24 E	2.41	0.55	29.7	20.4	1.4	2.99	0.38	1.4	0.31	0.09	0.25	0.03	0.19	0.04	0.1	0.01	0.08	0.01	7.3
25 E	1.68	0.37	32	20.0	1.1	2.22	0.27	1.0	0.22	0.07	0.17	0.02	0.13	0.03	0.07	0.01	0.06	0.01	5.4
26 E	6.57	1.78	44.4	6.22	4.9	8.45	1.14	4.8	1.06	0.18	0.76	0.11	0.71	0.14	0.39	0.05	0.34	0.05	23.1
28 E	1.42	0.22	39.3	13.5	1.1	2.07	0.25	1.0	0.24	0.03	0.16	0.02	0.15	0.03	0.08	0.01	0.09	0.02	5.2
29 E	1.48	0.3	31.5	20.4	0.9	1.93	0.23	1.0	0.23	0.07	0.16	0.02	0.14	0.03	0.07	0.01	0.06	0.01	4.9
30 E	1.24	0.29	31.4	20.9	1.0	2.28	0.27	1.1	0.27	0.08	0.19	0.03	0.17	0.03	0.08	0.01	0.07	0.01	5.6
31 E	1.34	0.3	30.5	20.5	1.0	2.21	0.25	1.1	0.24	0.07	0.18	0.03	0.15	0.03	0.07	0.01	0.06	0.01	5.4
33 E	0.78	0.18	31	20.7	0.7	1.56	0.17	0.7	0.17	0.06	0.12	0.02	0.11	0.02	0.05	0.01	0.04	0.01	3.7
34 E	2.96	0.64	29.7	20.3	1.4	3.26	0.39	1.6	0.38	0.1	0.27	0.04	0.22	0.04	0.11	0.02	0.1	0.02	7.9
35 E	2.57	0.57	30.3	20.1	1.5	3.08	0.36	1.6	0.35	0.1	0.24	0.04	0.22	0.04	0.11	0.01	0.09	0.01	7.7
36 E	0.51	0.1	32	19.9	0.7	1.25	0.16	0.7	0.17	0.07	0.15	0.02	0.14	0.03	0.08	0.01	0.06	0.01	3.5
Min	0.51	0.1	25.3	0.61	0.7	1.25	0.16	0.6	0.13	0.03	0.12	0.02	0.09	0.02	0.05	0.01	0.04	0.01	3.5
Max	23.3	3.91	53.6	21.2	9.7	18.6	2.6	9.3	2.03	0.48	1.87	0.25	1.47	0.28	0.78	0.1	0.6	0.09	48.1
Mean	3.35	0.74	31.6	18.4	2.0	3.97	0.51	1.94	0.44	0.12	0.38	0.05	0.30	0.06	0.16	0.02	0.13	0.02	10.1
St Dev.	4.37	0.81	5.78	4.93	1.8	3.4	0.49	1.76	0.38	0.08	0.35	0.05	0.27	0.05	0.15	0.02	0.11	0.02	8.96
PAAS*	---	---	---	---	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	185
Norm.	---	---	---	---	0.052	0.049	0.057	0.057	0.079	0.111	0.081	0.065	0.064	0.061	0.056	0.048	0.046	0.046	0.87

* [14]

Table 3- Rare earth element concentrations (ppm) of Gypsiferous marly limestone of the Fatha Formation and average values of post-Archean Australian shale (PAAS)*.

S.No.	SiO$_2$	Al$_2$O$_3$	CaO	MgO	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
3 F	6.2	1.39	25.5	18.2	2	3.76	0.49	1.8	0.4	0.1	0.48	0.06	0.36	0.07	0.19	0.03	0.16	0.03	9.9
4 F	40.0	8.83	6.93	8.57	12.8	26.1	3.46	12.6	2.84	0.81	3.34	0.43	2.43	0.47	1.25	0.17	0.96	0.14	67.8
5 F	0.53	0.07	33.8	0.08	0.2	0.18	0.03	0.1	0.03	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	0.78
8 F	4.66	1.1	28.43	20.19	2.3	4.7	0.62	2.2	0.5	0.16	0.53	0.07	0.39	0.08	0.2	0.03	0.16	0.02	12.0
9 F	5.18	1.08	27.9	19.4	2.2	4.33	0.58	2.0	0.45	0.15	0.48	0.06	0.36	0.07	0.19	0.02	0.14	0.02	11.0
11 F	4.91	1.24	26.47	19.77	3.7	6.87	0.89	3.3	0.72	0.19	0.72	0.09	0.52	0.1	0.28	0.04	0.22	0.03	17.7
37 F	0.95	0.25	31.72	19.22	0.6	1.11	0.13	0.6	0.13	0.05	0.11	0.02	0.1	0.02	0.06	0.01	0.07	0.01	3.0
38 F	2.78	0.68	28.87	19.46	1.8	3.19	0.4	1.7	0.41	0.11	0.35	0.05	0.34	0.07	0.18	0.02	0.15	0.02	8.8
40 F	1.34	0.31	38.21	13.07	1	1.73	0.21	0.9	0.21	0.06	0.15	0.02	0.15	0.03	0.08	0.01	0.07	0.01	4.6
41 F	0.54	0.09	33.5	0.9	0.2	0.28	0.04	0.2	0.04	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	1.0
46 F	6.43	1.58	32.35	10.26	3.1	6.39	0.81	3.3	0.76	0.17	0.53	0.08	0.48	0.09	0.25	0.03	0.21	0.03	16.2
47 F	4.09	0.78	49.3	1.54	2.6	5.19	0.65	2.8	0.65	0.14	0.52	0.07	0.41	0.08	0.2	0.03	0.16	0.02	13.5
48 F	8.59	2.14	26.64	15.1	4.0	8.8	1.14	5.0	1.24	0.24	0.87	0.12	0.73	0.14	0.35	0.05	0.29	0.04	23.0
49 F	7.10	1.75	31.69	11.82	2.8	5.49	0.73	3.2	0.78	0.17	0.63	0.09	0.57	0.11	0.28	0.04	0.23	0.03	15.1
50 F	1.48	0.36	41.2	9.69	0.8	1.42	0.18	0.8	0.17	0.07	0.15	0.02	0.15	0.03	0.1	0.01	0.08	0.01	4.0
51 F	24.21	6.28	27.17	3.19	13.7	27.1	3.79	16.2	3.73	0.69	2.55	0.37	2.2	0.41	1.11	0.15	0.95	0.13	73.1
53 F	1.09	0.19	32.08	0.08	0.3	0.52	0.07	0.3	0.06	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	1.5
54 F	1.57	0.18	32.4	0.12	0.3	0.52	0.08	0.3	0.07	0.05	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	1.5
55 F	0.69	0.09	32.3	0.03	0.2	0.21	0.03	0.1	0.03	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	0.8
56 F	2.22	0.32	32.2	0.06	0.4	0.71	0.1	0.4	0.1	0.05	0.07	0.01	0.06	0.01	0.03	0.01	0.03	0.01	12.0
57 F	2.44	0.33	32.7	0.21	0.8	0.91	0.19	0.8	0.17	0.06	0.1	0.01	0.09	0.02	0.04	0.01	0.04	0.01	3.2
58 F	35.11	8.31	15.34	4.66	11.5	23.7	3.22	13.5	3.06	0.64	2.39	0.33	2.05	0.38	1.02	0.14	0.84	0.12	62.9
59 F	33.25	7.48	16.77	4.3	12.1	23.6	3.2	13.8	3.06	0.62	2.27	0.33	2	0.39	1.03	0.14	0.86	0.12	63.5
64 F	2.68	0.7	53.3	0.47	1.5	2.81	0.38	1.6	0.38	0.1	0.3	0.04	0.29	0.06	0.17	0.02	0.15	0.02	7.8
73 F	0.19	0.02	32.8	0.02	0.2	0.06	0.03	0.1	0.03	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	0.7
Min	0.19	0.02	6.93	0.02	0.2	0.06	0.03	0.1	0.03	0.04	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	0.7
Max	40.0	8.83	53.3	20.19	13.7	27.1	3.79	16.2	3.73	0.81	3.34	0.43	2.43	0.47	1.25	0.17	0.96	0.14	73.1
Mean	7.93	1.82	30.78	8.02	3.24	6.39	0.86	3.50	0.80	0.19	0.67	0.09	0.56	0.11	0.29	0.04	0.24	0.03	17.0
St. Dev	11.69	2.72	9.46	7.94	4.30	8.70	1.18	4.88	1.11	0.23	0.92	0.13	0.75	0.14	0.38	0.05	0.31	0.04	23.0
PAAS*	---	---	---	---	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	185
Norm.	---	---	----	---	0.08	0.08	0.01	0.10	0.01	0.18	0.16	0.12	0.12	0.11	0.10	0.10	0.08	0.07	1.32

* [14]

REEs are mobile in acidic solution, where LREE are less soluble than HREE. So the ΣLREEs and ΣHREEs in Anah (5.64, 0.69 ppm), Euphrates (9.36 and 0.74 ppm) and Fatha (15.65 and 1.36 ppm) respectively. Accordingly, the average ratios of LREE/HREE in these formations are 8.17, 12.6 and 11.6 respectively. The relative depletion in LREEs, suggesting preferential scavenging of LREEs during deposition by the particulate/colloid load [18]. After normalization to the PAAS, the average of LREE/HREE in Anah, Euphrates and Fatha formations are 0.81, 1.23 and 0.88 respectively. The value more than one (1.23) in the Euphrates indicates HREEs depletion. The ratio of HREEs/LREEs being elevated in suboxic and anoxic seawater [19] due to the linkage as solution ligands with humics and phosphate. On this basis, the depositional environment of these formations are oxygenated with relatively slight differences. When the Redox conditions become more reducing, the relative rate of release for the REE is LREE > MREE > HREE [19]. The average REE of the Anah and Fatha formations display a similar pattern with high REE content in Fatha; similarly of the Euphrates Formation, but with depletion in HREEs (Figure 2D). This development in REE pattern in the Euphrtes Formation support a less oxygenated, more depth depositional environment as well as the effect of dolomitization. Then the HREE depletion in The Euphrates Formation provided useful information on the composition of diagenetic solutions. The two most noted patterns that characterize the normalized REE fractionation patterns of modern seawater are the enrichments in HREEs compared to LREEs and the negative Ce anomalies [20], [4] and [21]. The reefal facies of Anah Formation of pure limestone is poor in REE, the dolomitic limestone of the Euphrates is richer, whereas the gypsiferous marly limestone of Fatha Formation is relatively enriched; this can be seen in Figure-2 which displays the average normalized REE. Water with a high pH has the lowest REE concentrations due to depletion by sorption onto particles [22]. Accordingly, Fatha Formation may be deposited in shallow environment of pH higher than the pH in which the Euphrates and Anah Formations were deposited. Limestones commonly considered as a poor in REE, but relatively higher in comparison to bio-minerals in modern skeletal carbonates; as the results of diagenetic REE enrichment [23].

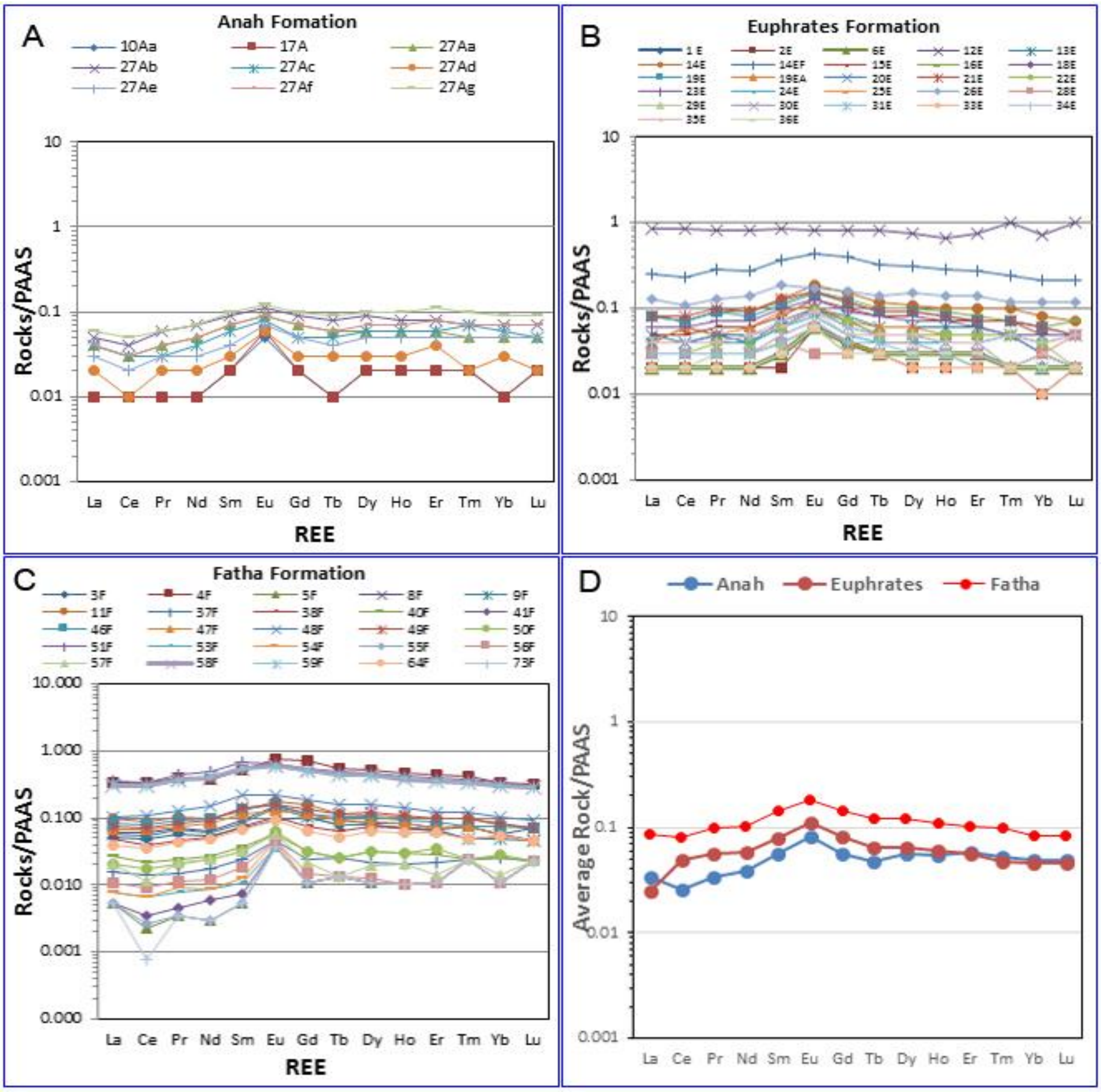

Figure 2- PAAS- normalized REE pattern of the Anah (A), Euphrates (B) and Fatha (C) Formation along with the REE averages of these formations (D); PAAS normalization values are from [14].

Plot of PAAS-normalized Pr/Pr* $[Pr/(0.5\ Ce + 0.5\ Nd]_{SN}$ versus Ce/Ce* $[Ce/(0.5\ La+0.5\ Pr]_{SN}$ stated by [7] and modified by [13] displays that the distinctive characters of Anah, Euphrates and Fatha Formations are La positive anomaly and Ce negative anomaly Figure-3.

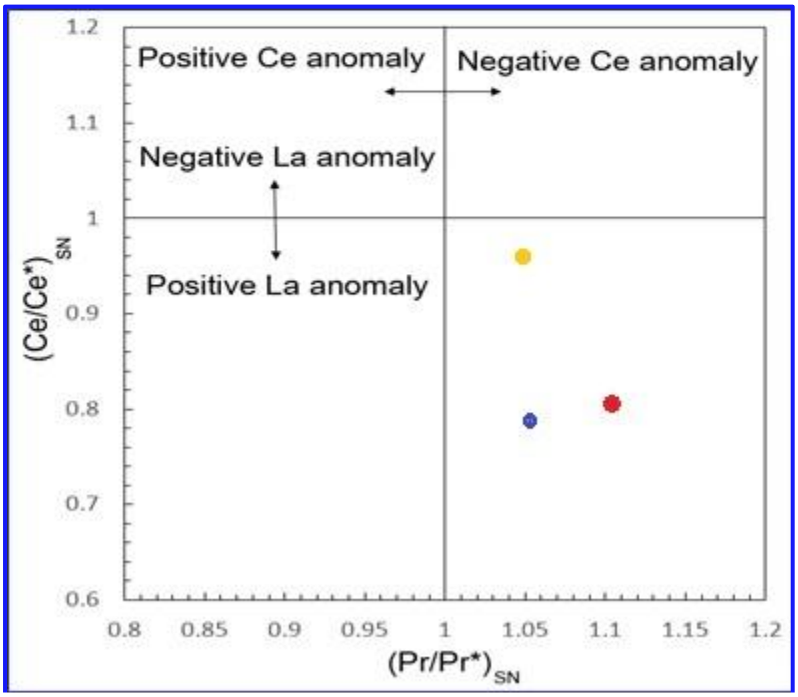

Figure 3- La against Ce anomalies using the method [7] (as modified by [13] illustrate the averages of Anah (blue circle), Euphrates (yellow circle) and Fatha (red circle) Formations tighting in the field of negative Ce and positive La anomalies in perfect agreement with modern open oceanic surface water.

In the seawater, at low temperature, the REE accumulate depending on the pH and exist dominantly as the free ion (REE^{3+}) or forming complexes [24] At low pH and low temperature, the free REE ion being more prevalent [25] and [26]. REE can form complexes by link with negative ions and radicals as F^-, OH^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}. The most REE complexes increase in stability with increasing temperature, but generally decrease in stability with increasing pressure [13]. In the reefal facies of Anah Formation, REEs appear to be in association with calcite rather than in clay minerals Figure-4A and B, while, they mostly incorporated within clay minerals rather than dolomitic limestone of the Euphrates Formation Figures-4C, D and gypsum of Fatha Formation Figures-4E and F.

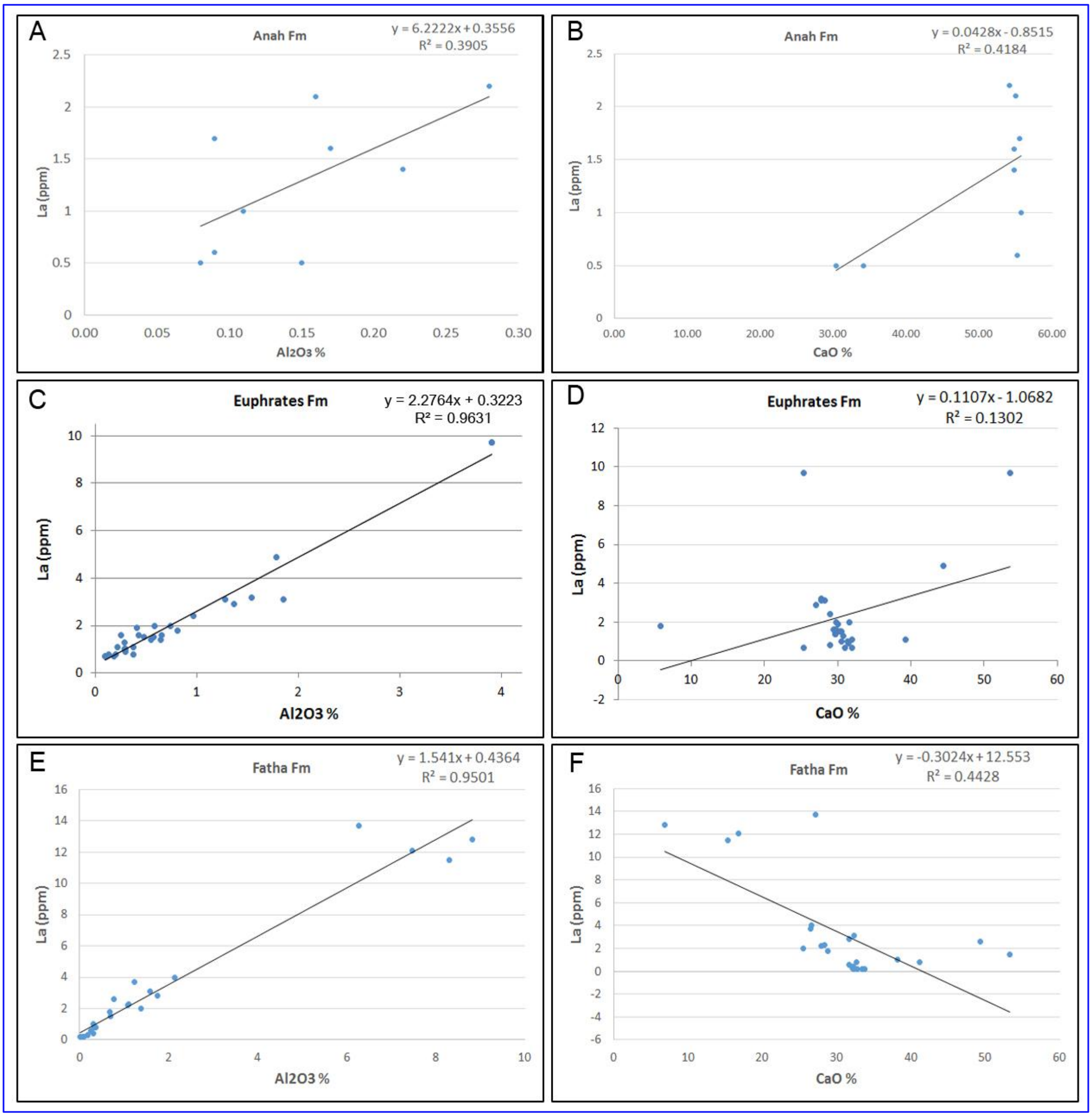

Figure 4- Relationship between La and each of Al2O3 and CaO in Anah (A and B), Euphrates (C and D) and Fatha (E and F) formations.

Conclusions

1. General trend of The REE pattern in Anah, Euphrates and Fatha Formations is almost similar. The low REE concentrations was found in the reef limestone of Anah Formation, while the highest concentrations were present in gypsiferous marly limestone of Fatha Formation, and an intermediate concentration in the dolomitic limestone of the Euphrates Formation. This may attribute to the pH value environmental deposition of each of the studied formations.
2. Significant variation in REEs concentration has been detected at different facies. The normalized ΣLREEs in Anah and Fatha are less abundant than the normalized ΣHREEs, with exceptional of the Euphrates Formation which displays relative depletion in ΣHREEs due to dolomitization process.
3. Dolomitization affected the actual REE signature and provided information on the composition of diagenetic solution, causing HREEs depletion in the dolomitic limestone facies that is frequently existed in the Euphrates Formation.

4. The distinctive character of the REE pattern in carbonates of Anah and Fatha formations reflects the uniform trivalent behavior of the elements except the Ce and Eu, which vary with oxygen levels. The well-developed negative anomaly in Ce and positive anomaly in Eu in Anah and Fatha formations is a reflection of the oxygenated depositional environment which indicates shallow water rather than deep water. The same was also notices in the Euphrates Formation, but with negative La anomaly indicating less oxygenated seawater of moderate depth.
5. REEs are incorporated with calcite in Anah Formation, while a significant concentration are mostly incorporated within the clay minerals occurred in the Euphrates and Fatha formation along with carbonates and gypsum respectively.

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