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RARE EARTH ELEMENTS GEOCHEMISTRY OF SOME PALEOCENE CARBONATE FLUORAPATITES FROM IRAQ

Asma A. Aba-Hussain[*], Khaldoun S. Al-Bassam[**] and Yehya T. Al-Rawi[***]

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ABSRTACT

Marine sedimentary phosphorites of Late Cretaceous, Paleocene and Eocene age are wide spread in the Western Desert of Iraq. The Paleocene deposits (Akashat Formation) are the most extensive in thickness and distribution, and are industrially exploited. They are granular phosphorites composed mostly of ooids and peloids, with accessory amounts of coprolites and fish scales. The cementing material is calcite. The phosphate mineralogy is carbonate fluorapatite (francolite).

Rare earth elements, phosphorus and yttrium were analyzed in ten concentrated carbonate fluorapatite samples from the Paleocene phosphorite of Iraq. The concentrated apatites included coprolites, peloids – ooids, bones and teeth. The results show lower REE content relative to average world phosphorites, and the coprolites contained the highest concentrations among the three types of phosphate grains studied, whereas the bioclasts contained the lowest concentrations.

The data were normalized relative to average shale and compared to REE patterns of seawater, and average world phosphorites. The REE patterns of the Iraqi Paleocene apatites are relatively depleted in REE, but they show distribution patterns comparable to seawater and average world phosphorites. The seawater pattern with the negative Ce anomaly of the studied apatites reflects the influence of deep seawater on their origin. Variation in the REE content of the various apatite grains was related to their mode of formation, duration of contact with sea water, mass/surface ratio of the grains, as well as to probable diagenetic alterations.

جيوكيمياء العناصر الأرضية النادرة لبعض الأباتايت الكاربونيتي الفلوريدي من العراق

أسماء علي أبا حسين، خلدون صبحي البصام ويحيى توفيق الراوي

المستخلص

الفوسفوريت الرسوبي البحري من عمر الطباشيري المتأخر والباليوسين والإيوسين واسع الانتشار في الصحراء الغربية العراقية. رواسب الباليوسين (تكوين عكاشات) هي الأكبر سمكاً والأوسع انتشاراً ومستغلة صناعياً وهي فوسفوريت حبيبي يتكون غالباً من السرئيات والدمالق مع كميات قليلة من الكوبروليت وعظام الأسماك وتتكون المادة الرابطة من الكالسيت ومعدنية الفوسفات هي الأباتيت الفلوريدي الكاربونيتي (الفرنكوليت).

تم في هذا البحث تحليل العناصر الأرضية النادرة والفوسفور والإيتريوم في عشرة عينات من الأباتايت الفلوريدي الكاربونيتي من فوسفوريت عصر الباليوسين (تكوين عكاشات) في الصحراء الغربية في العراق. تم التقاط الحبيبات الفوسفاتية المختلفة يدوياً وتنقيتها كيميائياً وتضمنت كوبرولايت ودمالق وسرئيات وعظام وأسنان الأسماك وجرى التأكد من نقاوة الطور المعدني بحيود الأشعة السينية. تم تحليل العناصر الأرضية النادرة في هذه العينات بتقنية البلازما في مختبرات جامعة لندن.

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[*] Arabian Gulf University, Bahrain, e-mail:asma@agu.edu.bh

[**] State Co. of Geological Survey and Mining, P.O.Box 986, Baghdad, Iraq

[***] Gulf University, Bahrain

تمت مقارنة النتائج المستحصلة مع تركيز ونمط توزيع هذه العناصر في مياه البحر فضلاً عن مقارنتها بمعدل الصخور الفوسفاتية في العالم. كما تم معالجة النتائج بتعديلها باعتماد تحليل السجيل كمرجع وإجراء المقارنات أعلاه. بينت النتائج إن الكوبرولايت احتوت على أعلى التراكيز والعظام الفوسفاتية على أقلها وشغلت الدمالق والسرئيات الفوسفاتية مركزاً وسطياً بين الاثنين. فضلاً عن ذلك، أظهرت النتائج تماثلاً شبه متطابقاً لنمط توزيع هذه العناصر في العينات مع نمط توزيعها مع مياه البحر بظهور الشاذة السالبة لعنصر السيريوم والارتفاع التدريجي للتراكيز مع زيادة الوزن الذري للعناصر الأرضية النادرة وهو النمط المعروف للفوسفات الرسوبي البحري في العالم.

تعزى الشاذة السالبة لعنصر السيريوم إلى تأكسد Ce^{3+} السهل الذوبان إلى Ce^{4+} القليل أو عديم الذوبان وبالتالي عدم توفره لمعدن الأباتايت أثناء الترسيب. ويعود الإغناء النسبي للعناصر الأرضية النادرة الثقيلة في هذه العينات إلى نفس السبب، حيث أن هذه العناصر لها القابلية لتكوين معقدات ذائبة. تدل الشاذة السالبة للسيريوم إلى المصدر العميق للمياه البحرية المكونة للفوسفات في العراق والمتمثلة بالمياه البحرية الصاعدة من الأعماق، وهي ظاهرة سادت في محيط التيثس خلال الفترة بين الطباشيري المتأخر والإيوسين.

يعود الإغناء النسبي للعناصر الأرضية النادرة في الكوبرولايت الى أغناء هذه الحبيبات بالمواد العضوية القادرة على استيعاب تراكيز إضافية من هذه العناصر بحكم طبيعتها. في حين إن العظام الفوسفاتية ذات محتوى اقل نسبياً وذات تراكيز متغايرة من العناصر الأرضية النادرة بسبب قصر فترة التماس مع مياه البحر وتغاير الظروف الكيميائية للبيئة البينية للرواسب. وبالمقارنة يلاحظ تراكيز أعلى في الدمالق والسرئيات الفوسفاتية بسبب مساحتها السطحية الأكبر وطول فترة تعرضها لمياه البحر خلال فترة نموها وتكونها.

INTRODUCTION

The Paleocene sequence (Akashat Formation) in the area north and west of Ga'ara Depression is dominated by phosphorite, carbonate and shale facies. The phosphorite deposits are well developed in this area of Iraq; they exceed 10 m in thickness with an average grade of 22% P_2O_5 (Al-Bassam and Karim, 1992). They are granular in texture; the phosphate grains include bioclastic, coprolitic, peloidal – ooidal and intraclastic varieties. Figure (1) shows the columnar section of the Paleocene sequence in the studied area and the location from which the studied phosphate grains were chosen.

Peloids and ooids were concentrated from the main phosphorite layer in the middle part of the Paleocene sequence (Fig.1). They are rounded to spherical or ovulitic grains with light to dark brown colour. They are (0.1 – 0.2) mm in size with or without internal structure. Bone fragments were also concentrated from this layer in spite of their low presence and also from the bioclastic phosphorite layers in the lower part of the Paleocene sequence. Coprolites were taken from the coprolitic layer in the upper part of the sequence (Fig.1). They are mostly cylindrical or elongated grains that generally range from (0.5 – 30) mm in length and may reach up to 9 mm in diameter, usually rich in organic residues.

The abundance and distribution of REE in phosphorites were discussed by many workers (Semenov *et al.*, 1962; Altschuler *et al.*, 1967; Il'in and Ratnikova, 1976; Altschuler, 1980; Kolodny, 1981; Burnett *et al.*, 1983; O◌́ Brien and Veeh, 1983; Shaw and Wasserburg, 1983; McArthur and Walsh, 1985; Il’in, 1998, Mazumdar *et al.*, 1999, Shields and Stille, 2001, Chunhua and Ruizhong, 2005, Zanin and Zamirailova, 2009 among others). The international research on REE in phosphorites was concerned with two main fields: genetic; to prove the deep oceanic upwelling water role in phosphogenesis, and industrial; to investigate the potential of REE extraction as a commercial commodity. The results obtained by the previous workers support the oceanic theory of phosphorus source, except where digenesis have modified the pattern of REE distribution.

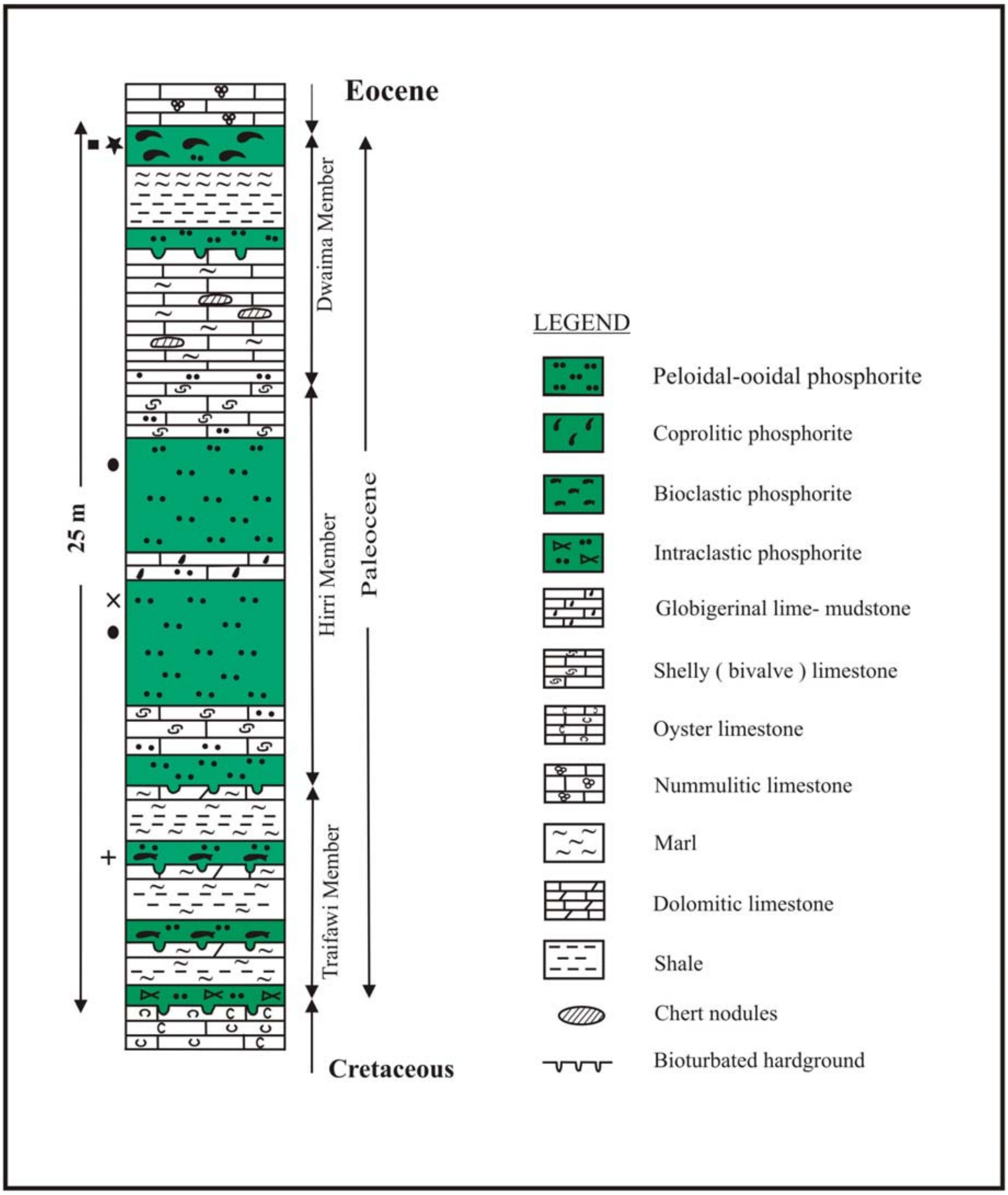

Fig.1: Columnar section of the Paleocene sequence in the studied area (Aba-Hussain, 1987), showing the location from which the studied phosphate grains were selected (★) coprolites, (●) peloids – ooids, (■) teeth, (+) bone Q1, (×) bone Q2

GEOLOGY

The Paleocene phosphorite deposits were extensively investigated by various authors, mainly because of their economic importance as a source for phosphate fertilizers and also for their scientific interesting problems. The most extensive geological investigation of these deposits was carried out by GEOSURV-Iraq during the period 1986 – 1990 (Al-Bassam *et al.*, 1990).

The Paleocene phosphorite-bearing sequence is referred to as the Akashat Formation by the official Iraqi authorities and scientific scholars (Al-Bassam and Karim, 1997). The Akashat Formation was divided into three members; from older to younger: Traifawi, Hirri and Dwaima. The phosphorite is encountered in all of them, but the main development is found in the Hirri Member.

The whole deposit is granular in texture, dominated by phosphate peloids and ooids. However, phosphate bioclasts (bones, scale, teeth) are very common in the Traifawi Member, and phosphate coprolites as well as shark teeth are common in the Dwaima Member (Al-Bassam, 1992). The cementing material is calcite.

The phosphorite beds range in thickness from 0.25 m to about 10 m interbedded with phosphatic lime mudstone and often top a bioturbated hardground. A remarkable shelly limestone cap the main phosphate bed in the Hirri Member and form the main plateau in the Akashat area.

The phosphate grains are mostly well-sorted fine sand-size peloids and ooids, but larger bioclasts and coprolites are also common, especially in Traifawi and Dwaima Members. The mineralogy of the phosphate was investigated in hundreds of samples and found to be carbonate fluorapatite (francolite) (Al-Bassam, 1974). Other, non-phosphatic minerals identified are calcite, smectite, palygorskite, opal-CT, chalcedony (as chert nodules) and traces of quartz (detrital) (Aba-Hussain, 1987).

ANALTYTICAL TECHNIQUES

The phosphatic material was concentrated and extracted to determine the abundance of their rare earth elements. Coprolites, bones and teeth were concentrated by hand-picking, whereas peloids and ooids were extracted and concentrated using 0.5 M of triammonium citrate solution at pH 8.1 following the method described by Silverman *et al.* (1952). The concentrated phosphate grains were examined by X-ray diffraction and showed that carbonate-fluorapatite is the only phosphate mineral constituent of these grains (Fig.2). Yttrium and the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, and Lu) were analysed by inductively coupled plasma (ICP) source emission spectrometry in the University College London following the procedure described in McArthur and Walsh (1985) and Jarvis and Jarvis (1985). Phosphorus was analysed by colorimetry.

RESULTS

The abundance of rare earth elements of the studied apatite grains are shown in Table (1). Table (2) shows a comparison of average REE contents of the three types of the studied samples compared to their average content in seawater (Hogdahle *et al*., 1968); shale (Piper, 1974) and marine phasphorite (Altschuler, 1980). Data in Tables (1 and 2) were normalized to average shale on an element by element basis (Tables 3 and 4, respectively), and plotted versus atomic number (Figs.3 and 4, respectively).

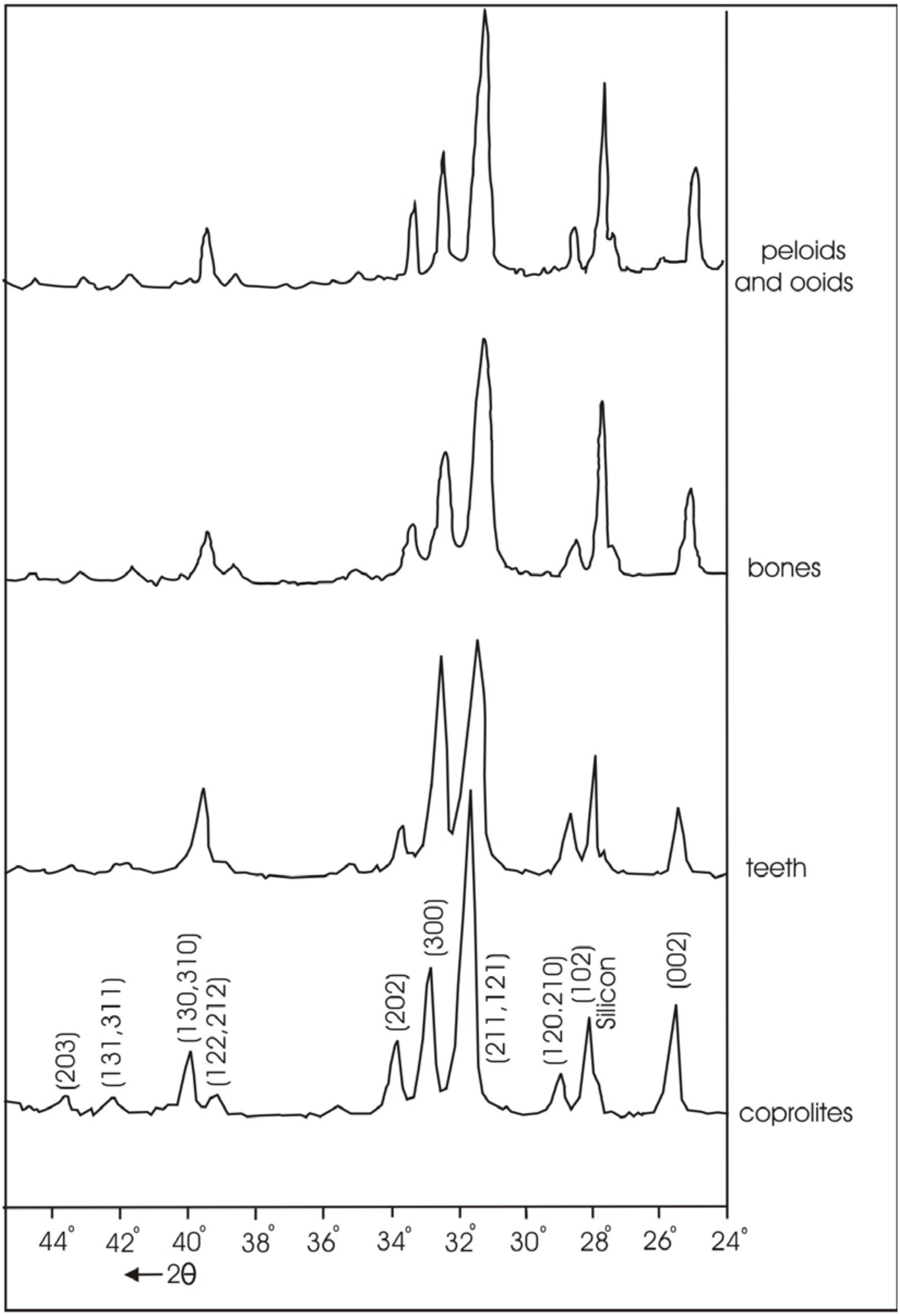

Fig.2: X-ray diffractograms of the separated phosphate grains (all hkl reflections are for carbonate fluorapatite, except silicon used as internal standard)

Table 1: Concentrations of the rare earth elements (in ppm)
of the studied concentrated phosphate grains

Samples / Elements	Coprolites			Peloids – Ooids				Bioclasts		
	X43	K	M13	D8	B20	G14	N6	Q1 (bone)	X (teeth)	Q2 (bone)
La	50.5	98.8	59.7	28.9	36.9	28.6	42.2	25.5	52.8	21.3
Ce	26.7	21.6	18.9	11.1	12.1	7.0	10.8	5.7	11.9	3.4
Pr	16.9	12.2	6.7	9.4	9.6	2.9	5.2	2.9	3.4	2.0
Nd	24.0	23.7	25.3	12.1	15.2	10.9	14.9	10.8	11.9	5.4
Sm	4.7	4.7	5.0	2.4	3.0	2.1	2.8	2.1	2.2	1.0
Eu	1.5	1.3	1.3	0.7	0.8	0.5	0.7	0.5	0.6	0.3
Gd	6.0	6.5	6.9	3.0	3.6	2.6	3.5	2.7	3.0	1.3
Dy	6.4	7.1	7.4	3.3	4.0	3.0	3.9	3.1	3.4	1.7
Ho	1.6	1.8	1.9	0.9	1.0	0.8	1.0	0.8	1.0	0.5
Er	5.3	6.2	6.4	3.1	3.4	2.5	3.3	2.7	3.2	1.6
Yb	5.5	6.3	6.4	3.0	3.3	2.2	3.2	2.8	3.5	1.9
Lu	0.9	1.1	1.1	0.5	0.5	0.4	0.5	0.5	0.6	0.3
Y	102.0	112.8	114.4	62.8	68.9	51.0	66.7	50.9	56.7	31.4
P_2O_5 (%)	31.46	29.60	31.21	32.36	28.33	28.64	31.83	33.07	33.76	33.33

Table 2: Average content of the rare earths in the studied concentrated phosphate grains, seawater (Hogdahle *et al*., 1968), marine phosphorite (Altschuler, 1980) and shale (Piper, 1974)

Element (ppm)	Coprolites	Peloids – Ooids	Bioclasts	Seawater	Average marine phosphorite	Shale
La	70	34.2	33.2	3.40	133	41
Ce	22	10.3	7.0	1.20	104	83
Pr	12	6.8	2.8	0.60	21	10.1
Nd	24	13.3	9.4	2.8	98	38
Sm	4.8	2.6	1.8	0.45	20	7.5
Eu	1.4	0.7	0.5	0.13	6.5	1.6
Gd	6.5	3.2	2.3	0.70	12.8	6.4
Dy	7	3.6	2.7	0.91	19.2	5.5
Ho	1.8	0.9	0.8	0.22	4.2	1.3
Er	6.0	3.1	2.5	0.87	23.3	3.8
Yb	6.1	2.9	2.7	0.82	12.6	3.5
Lu	1.0	0.5	0.5	0.15	2.7	0.6
Y	109.7	62.4	46.3	-----	-----	-----
P_2O_5	30.8	30.3	33.4	-----	-----	-----
TR_20_3	162.6	82.1	66.2	12.25	457.3	202.0
TR_20_3/ P_20_5	5.29	2.71	1.98	-----	-----	-----
TR_2O_3/Y	1.48	1.32	1.42	-----	-----	-----

Table 3: Normalized REE values to average shale on an element by element basis

Elements	Coprolites			Peloids – Ooids				Bioclasts		
	X43	K	M13	D8	B20	G14	N6	Q1 (bone)	X (teeth)	Q2 (bone)
La	1.23	2.41	1.46	0.70	0.90	0.70	1.03	0.62	1.29	0.52
Ce	0.32	0.26	0.23	0.13	0.15	0.08	0.13	0.07	0.14	0.04
Pr	1.67	1.21	0.66	0.93	0.95	0.29	0.51	0.29	0.34	0.20
Nd	0.63	0.62	0.67	0.32	0.40	0.29	0.39	0.28	0.31	0.14
Sm	0.63	0.63	0.67	0.32	0.40	0.28	0.37	0.28	0.29	0.13
Eu	0.94	0.81	0.81	0.44	0.50	0.31	0.44	0.31	0.38	0.19
Gd	0.94	1.02	1.08	0.47	0.56	0.41	0.55	0.42	0.47	0.20
Dy	1.16	1.29	1.35	0.60	0.73	0.55	0.71	0.56	0.62	0.31
Ho	1.23	1.38	1.46	0.69	0.77	0.62	0.77	0.62	0.77	0.38
Er	1.39	1.63	1.68	0.82	0.89	0.66	0.87	0.71	0.84	0.42
Yb	1.57	1.80	1.83	0.86	0.94	0.63	0.91	0.80	1.0	0.54
Lu	1.50	1.83	1.83	0.83	0.83	0.67	0.83	0.83	1.0	0.50

Table 4: Normalized REE values of average content of the REE in the studied phosphate grains to average shale on an element by element basis

Element	Coprolites	Peloids – Ooids	Bioclasts	Seawater	Average marine phosphorite
La	1.7	0.80	0.80	0.08	3.2
Ce	0.27	0.12	0.08	0.01	1.25
Pr	1.19	0.67	0.28	0.06	2.08
Nd	0.63	0.35	0.25	0.07	2.58
Sm	0.64	0.35	0.24	0.06	2.67
Eu	0.88	0.44	0.31	0.08	4.06
Gd	1.02	0.50	0.36	0.11	2.00
Dy	1.27	0.65	0.49	0.17	3.49
Ho	1.38	0.69	0.62	0.17	3.23
Er	1.58	0.82	0.66	0.23	6.13
Yb	1.74	0.83	0.77	0.23	3.6
Lu	1.67	0.83	0.83	0.25	4.5

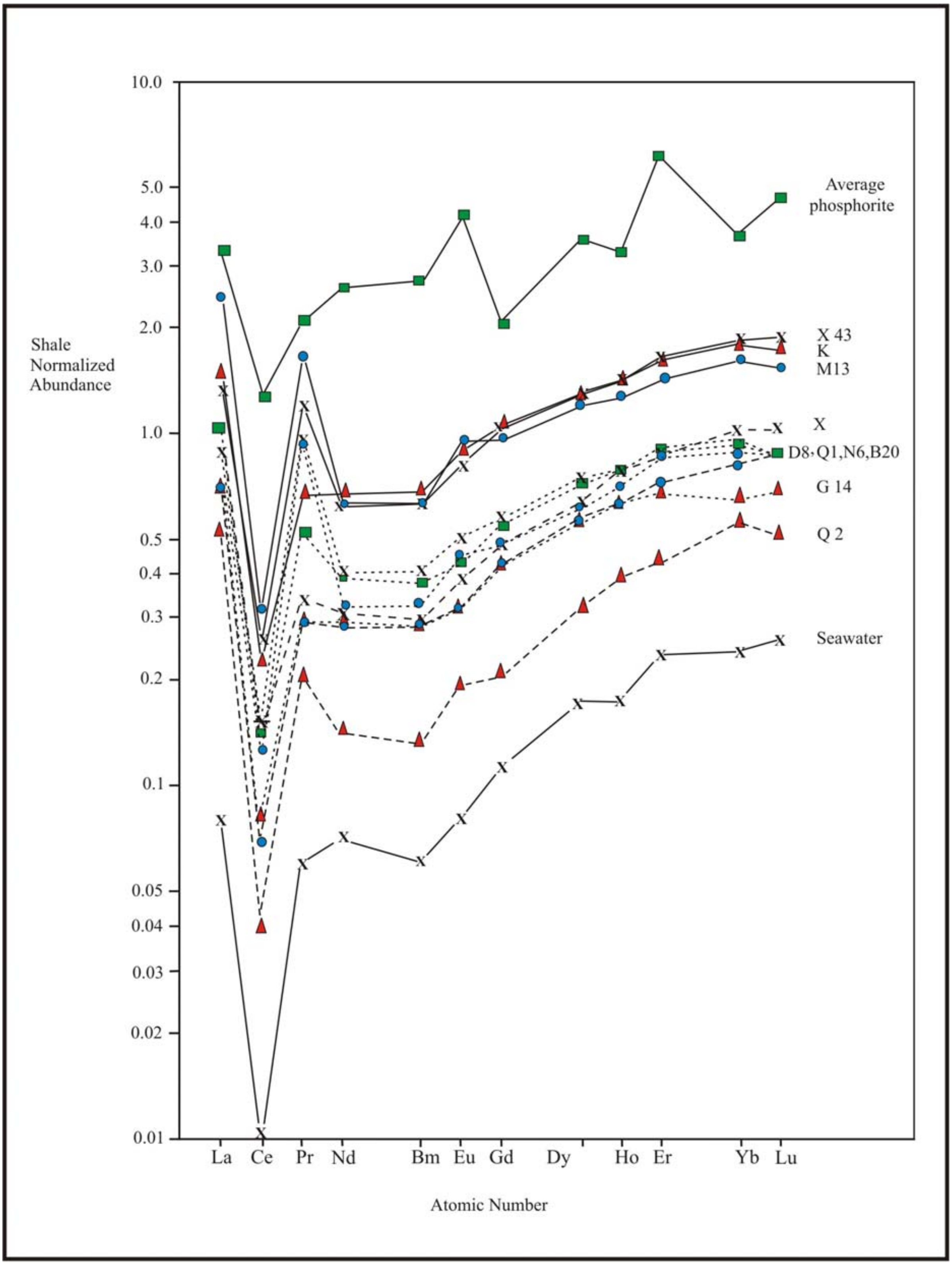

Fig.3: Shale-normalized REE patterns of the studied concentrated phosphate grains, seawater (Hogdahle *et al*., 1968) and average marine phosphate (Altschuler, 1980)

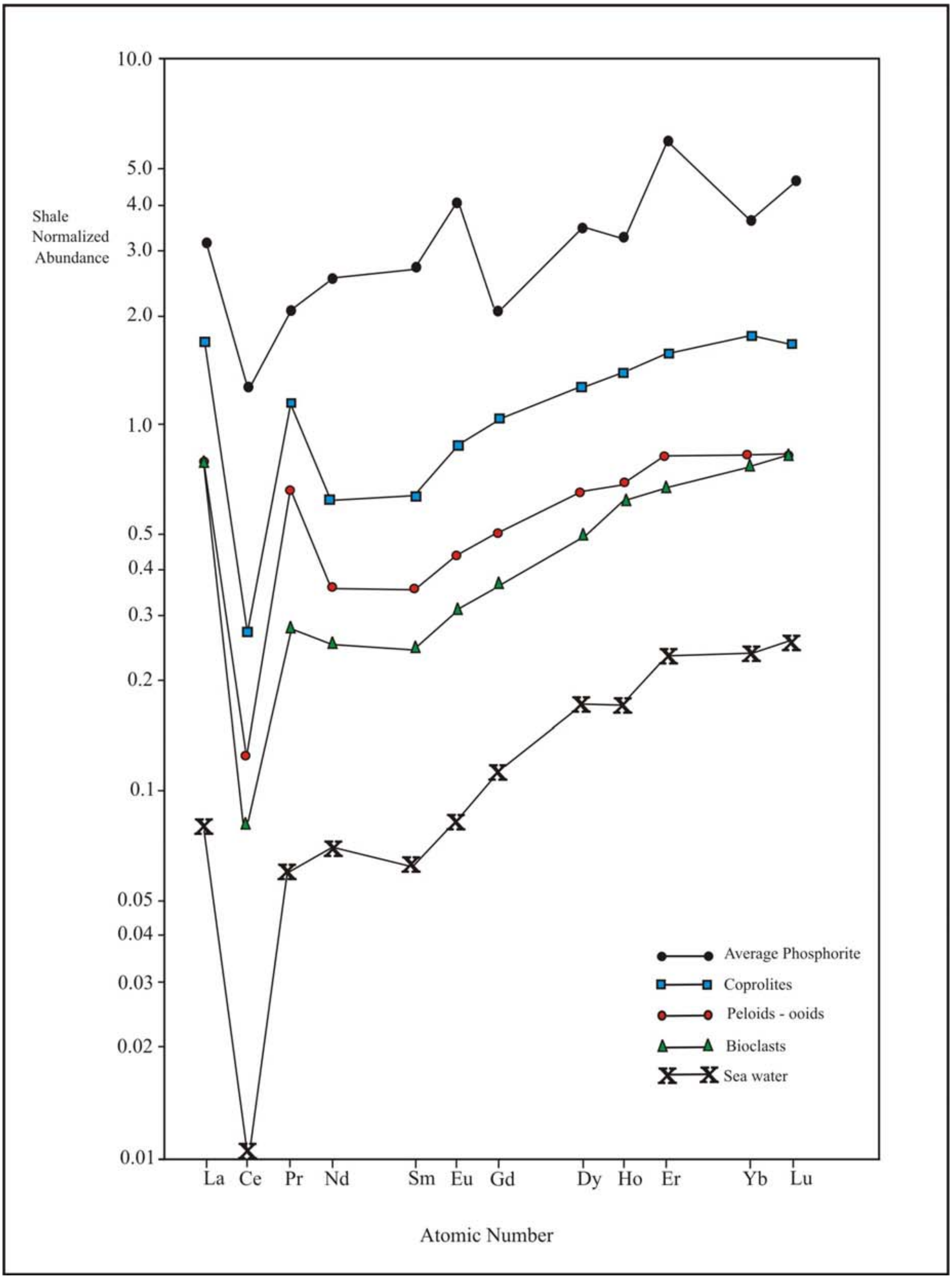

Fig.4: Shale-normalized REE patterns of the studied concentrated apatite grains, seawater (Hogdahle *et al*., 1968) and average marine phosphorite (Altschuler, 1980)

DISCUSSION

The presence of REE in apatites is generally accepted as substitution of REE^{3+} for Ca^{2+}. Such substitution is expected since the ionic radii are similar, ranging from (0.85 – 1.14) A° for REE^{3+} and 0.99A° for Ca^{2+} (Il'yin and Ratnikova, 1976; McLennan *et al*., 1979 and Elderfield *et al*., 1981). Moreover, the organic phases present in most phosphorites may represent another host for the REE in these rocks (Goldberg *et al*., 1963).

REE contents of marine phosphorites are known to vary considerably, but on average they are enriched relative to sediments. In general, there is a (2 – 6) time's enrichment of REE in marine sedimentary phosphorites relative to mean level (Il'yin and Ratinkova, 1976). It is interesting to note that the studied Paleocene phosphate grains are depleted in REE relative to average world phosphorites. However, their normalized pattern of distribution is similar to average phosphorite as well as to that of seawater (Fig.3). It is characterized by a negative Ce anomaly and enrichment of heavy REE.

Several factors may influence the concentration and pattern of REE distribution in phosphorites. These include physicochemical conditions of phosphorite formation, presence of a biogenic component in the phosphogenic system, contact duration with seawater, post depositional alterations, diagenetic modifications and texture of phosphate components (Wright *et al*., 1984; Il'yin, 1998; Shields and Stille, 2001 and Zanin and Zamirailova, 2009).

Marine phosphorites related to oceanic upwelling usually copy the REE distribution pattern of seawater, mainly being enriched in the heavy REE and show negative Ce-anomaly (Shields and Stille, 2001). The Ce anomaly (or deficiency) (Table 5 and Fig.5) is attributed to the oxidation of Ce^{3+} to the insoluble Ce^{4+} (Goldberg *et al*., 1963; Hogdahle *et al*., 1968; Elderfield and Grevaes, 1982 and Chunhua and Ruizhong, 2005). The deep oceanic waters are anoxic and the reduction of Ce^{4+} to Ce^{3+} would result in the enrichment of bottom deep waters with Ce (as Ce^{3+}). Upwelling of this anoxic bottom stratum would bring Ce-enriched waters back to the oxic marine realm, where Ce^{3+} is oxidized again to Ce^{4+} and removed from the water. Due to these oxidation reactions the shallow water environments would become rapidly depleted in Ce (Mazumdar *et al*., 1999). The variation in the stability constants of REE complexes is reflected in the relatively higher abundance of the heavy REE in seawater in contrast to the light REE, due to the ability of the heavy REE to form soluble complexes (Goldberg *et al*., 1968; Hogdahle *et al*., 1968; Piper, 1974; Fleet *et al*., 1980 and Elderfield and Grevaes, 1982). Some authors attributed the relative enrichment of the heavy REE^{3+} in marine sedimentary apatites to their relatively smaller ionic radii compared to light REE, which facilities and enhances their substitution for Ca^{2+} in the apatite structure (Elderfield *et al*., 1981).

Table 5: Ce/ La ratios and Ce anomaly in the studied concentrated phosphate grains

Sample No.	Ce/ La	Ce anomaly = Log (Ce/ La + Nd)
X43	0.53	- 0.76
K	0.22	- 1.07
N13	0.32	- 0.97
D8	0.38	-0.85
B20	0.33	- 0.94
G14	0.25	- 1.09
N6	0.26	- 1.04
Q1	0.22	-1.11
X	0.23	- 1.06
Q2	0.16	- 1.22

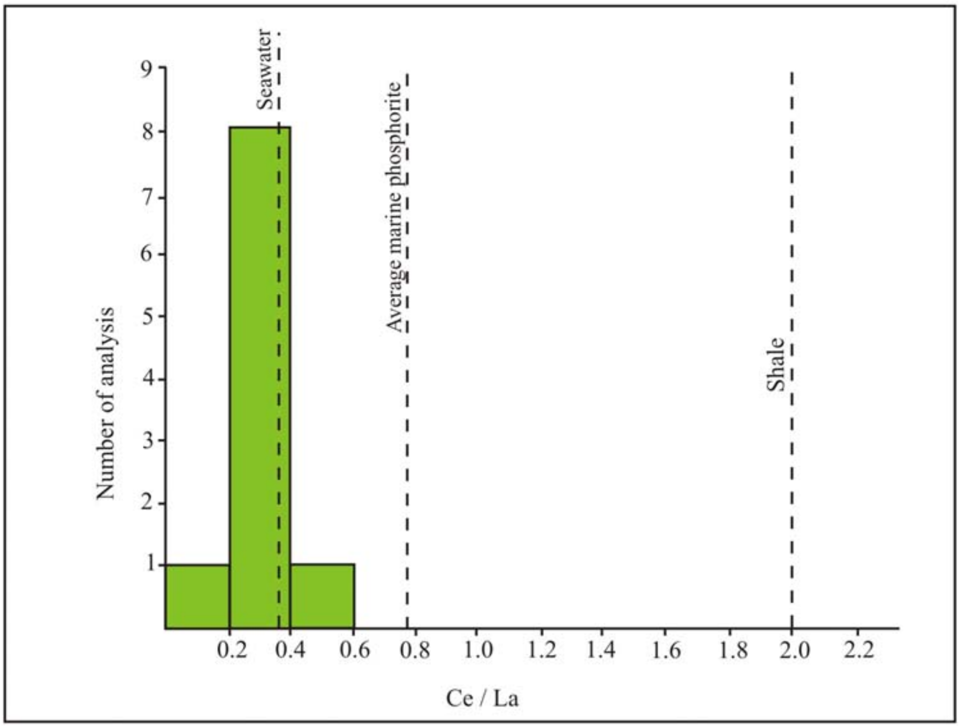

Fig.5: Histogram of Ca/ La ratios in the studied concentrated apatites, seawater (Hogdahle *et al*., 1968) average marine phosphorite (Altschuler, 1980) and shale (Piper, 1974)

The seawater pattern (Figs.3 and 4), with the negative Ce anomaly (Fig.5) reflect the influence of deep seawater on the depositional environment of the Paleocene phosphorites of Iraq, which indicates oceanic upwelling influx (Bentor, 1980); suggested by Sheldon (1980) to have occurred in the Tethys in the Late Cretaceous – Eocene time.

The P_2O_5 content of the analysed samples show some variation (28.33 – 33.76 %); the highest values are in the bioclasts. On the other hand, the REE vary considerably; Figures (3 and 4) show that among the studied phosphate grains, coprolites have the highest REE content and REE/ P_2O_5 ratio, bioclasts have the lowest REE content and REE/ P_2O_5 ratio, whereas peloids and ooids have intermediate ratios between coprolites and bioclasts.

Yttrium follows the trend of the REE in the analyzed samples; the highest concentrations are found in the coprolite and the least in the bioclasts. The REE/ Y ratio show little variation (about ≈ 1.4) in these samples. Yttrium is not a REE, but classed with them for their similar geochemical behavior. It has an atomic number of 39, but its ionic radius is similar to the elements in the middle of the lanthanides. This similarity is reflected in their common affinity for P and F. However, it is known that the REE pattern in seawater does not assimilate that of P, except they both increase with depth (Elderfield and Greaves, 1982).

The variation in the rare earth elements pattern and abundance are diagnostic of the environment and mechanism of phosphorite formation (McArthur and Walsh, 1985 and Zanin and Zamirailova, 2009). Peloids and ooids have REE content higher than that of bioclasts (Fig.3). Il'yin and Ratnikova (1976), McArthur and Walsh (1985) and Il'yin (1998) reported that peloidal phosphorites have higher REE abundance than non-peloidal ones because of the higher surface/ mass ratio of the former which promotes enrichment during the formation and diagenesis of the peloidal type. Il'yin and Ratnikova (1976) mean by peloidal phosphorite all types of phosphate grains, whereas non-peloidal phosphorite means microsphorite or phosphomud.

Granular phosphorites (peloids and ooids) seldom reveal extreme departures from the seawater norm and tend to undergo, therefore, less diagenetic alteration of REE concentration and pattern of distribution than skeletal apatite and other phosphate types (Shields and Stille, 2001). Il'yin (1998) suggested that REE are incorporated into the phosphate grains diagenetically during prolonged periods of transport and redeposition. Modern biogenic apatite on the seafloor appears to concentrate REE during early diagenesis (Wright *et al.*, 1984).

Laminations in the coated grains of the Paleocene phosphorites are suggested to be organic residues after algal mats that may represent non-depositional microbreaks in their growth history allowing for longer time of interaction with seawater (Al-Bassam, 1992). The mode of formation of these grains, their spherical shape, sorting, grain size and the internal structure (i.e. the concentric structure of the coated grains, which are common in the main phosphorite layer) suggest that they must have been in contact with seawater for relatively long periods after initial authigenic precipitation, and eventually could have picked up rare earths diagenetically, especially in agitated environments.

The high rare earths content of coprolites (Table 1) may be due to the higher abundance of organic matter in this type of grains, and consequently a post depositional enrichment of rare earth elements in the apatite (McArthur and Walsh, 1985). Al-Bassam and Al-Haba (1990) reported up to 2.14 TOC in the Paleocene phosphorites, of which 10.2 mg/l is hydrocarbon produced by cracking of Kerogene. The Eocene phosphate coprolites from Wyoming contain 0.28% Ce_2O_3 and 0.38% La_2O_3 (Bradely, 1946, in: Semenov *et al.*, 1962). The REE tend to form ionic complexes with organic ligands, especially the heavy REE (Goldberg *et al.*, 1963, in: Wildeman and Haskin, 1965).

The origin of authigenic phosphate ooids and peloids in the Paleocene phosphorites was suggested to have taken place, via a biogeneic phase, in the interstial environment near sediment – water interface, followed by variable history of submarine reworking, transportation, and accumulation within the marine environment; in contact with seawater until final burial (Al-Bassam, 1976 and Al-Bassam *et al.*, 2005). Phosphorus and the REE are among the elements enriched (in ionic state) in the deep oceanic realm and brought to the shallow parts via upwelling currents. Most of these elements are scavenged in the shallow marine environment by organisms, which represent a temporary sink for P and REE in addition to other elements. Most of these elements are released again to the marine environment under various physicochemical conditions of organic decay. Rasmussen (1996) explained the formation of authigenic REE phosphate minerals by precipitation within the sulphate reduction and methanogenesis zone of pore water, where P and the REE are released into this microenvironment, following bacterial decomposition of organic matter.

Phosphorus and part of the REE in the studied phosphorities may have been supplied from the same organic source in the interstitial environment. Later diagenetic enrichment of REE in the phosphate grains is expected to various degrees during their history of reworking and transportation in contact with seawater before final burial. The similar or nearly congruent REE patterns of the coprolites, bioclasts and the peloids – ooids samples (Figs.3 and 4), beside the geochemical characters of these types of phosphate grains and their facies reflect a geochemical condition of an open post-depositional environment and prolonged periods of contact with seawater.

CONCLUSIONS

- The shale-normalized REE pattern shown in the analyses results presented in this paper supports the upwelling marine seawater contribution to the Paleocene phosphorite origin in Iraq. This is clearly demonstrated by the negative Ce-anomaly, depicting that of seawater, and the relative enrichment of the heavy REE in these phosphates. The regional source of REE in the studied phosphate grains is the deep oceanic upwelling water.
- The relative variation in the REE content among the three types of phosphate grains (bioclasts, peloids – ooids and coprolites) is attributed to their mode of origin and contact time with sea-water during and after formation, the chemistry of interstitial water after burial as well as the organic matter contribution as a local source of REE in the depositional environment.

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