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## A Reconnaissance Study of Rare Earth Elements Systematic in Phosphate Coprolites: Comparison between Continental Shelf and Intracontinental Basin Deposits

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### Abstract

The behavior of rare earth elements (REE) in phosphate coprolites; deposited in marine upwelling shelf system (Iraq) and a condensed section of the intracontinental basin (Czech Republic) is compared and discussed in the present study. The eight coprolite samples show that the REE incorporated in the apatite of these phosphatized faecal trace fossils have significantly different behavior in the two sedimentary regimes and hold the REE source's signature in the local sedimentary conditions. The behavior of heavy REE, light REE, Ce-anomaly and shale-normalized ratios of Ce/La, Sm/Yb and Pr/Ce can be mainly attributed to REE fractionation at the source. In contrast, middle REE enrichment may be attributed to local fractionation below the sediment-water interface. Nd/La and REE/P<sub>2</sub>O<sub>5</sub> ratios indicate local sedimentation rate and residence time in contact with seawater. Elevated La/Yb ratios indicate shallowing and submarine reworking events. Most of the REE patterns in the studied coprolites were acquired in the early stages of diagenetic phosphatization and crystallization of the apatite, and minor modifications took place later. The REE behavior in phosphate coprolites proved useful indicators of marine sedimentary environments in the present reconnaissance study and encourage further work on phosphate coprolite samples from other world deposits.

**Keywords:** REE; Upwelling currents; Condensed sections; Redox conditions; Residence time

### 1. Introduction

Coprolites are fossilized faeces (fossil excrements) found in terrestrial and marine sediments; first described in geological literature by Buckland [1] and defined by Hunt et al.[2] as fossilized faeces belonging to a group of ichnofossils called bromalites. Phosphatized coprolites are common in most marine sedimentary phosphorite deposits, associated with other granular phosphate components, such as ooids, peloids, skeletal remains and shark teeth. Their faecal origin is supported by several lines of evidence, including chemical composition (primarily calcium phosphate), external morphology and nature of the inclusions, demonstrating the diet of the producing animals [3]. Preservation of coprolites as fossils suggests early lithification, preventing the faecal matter's disintegration and facilitating transportation and introduction to the host sediments [4]. In marine sediments coprolites are usually cylindrical and coiled and may reach several cm in length and 1–2 cm in diameter; mostly attributed to sharks and other fish excrements. Rare Earths Elements (REE) in apatites

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of biological origin were first detected by Cossa in 1878; cited by [5], in spectrographic studies of fossil bones and coprolites from Nassau, Germany. The presence of REE in apatites is generally accepted as a substitution of  $\text{REE}^{3+}$  for  $\text{Ca}^{2+}$ , which has been recognized for more than a century [6]. Such substitution is possible since the ionic radii are close, ranging from 0.85 to 1.14 Å for  $\text{REE}^{3+}$  and 0.99 Å for  $\text{Ca}^{2+}$  [7, 8 and 9]. The variation in REE pattern and abundance are believed to be diagnostic of the environment and mechanism of phosphorite formation [10, 11]. Because of the presumed correlation between the trace-elements characteristics of biogenic apatite and the depositional environment, REE and other trace elements of the fossil bones have been used in a wide range of paleoenvironmental studies [12, 13 and 14]. However, to the best of the author's knowledge, marine phosphate coprolites have not been tested for that purpose yet.

The present reconnaissance study aims to explore the environmental impact on REE behavior in phosphate coprolites deposited in two different marine sedimentary realms; one is a marine inner shelf basin of upwelling currents regime, and the other is a condensed section in a semi-closed intracontinental basin. The comparison includes REE distribution pattern, source of REE, redox conditions, REE fractionation, sedimentation rate and diagenetic modifications. The study is based on eight phosphate coprolite samples; 3 of Upper Paleocene age (Iraq) and 5 of Upper Turonian age (Czech Republic). The raw chemical analyses of REE presented in this article are adopted from [15 and 16], processed, and reinterpreted here to serve the purpose of the present study. In view of the limited number of phosphate coprolite samples available with REE analysis, this study can be considered a reconnaissance study that shows significant results worth following up.

## 2. Geological Setting

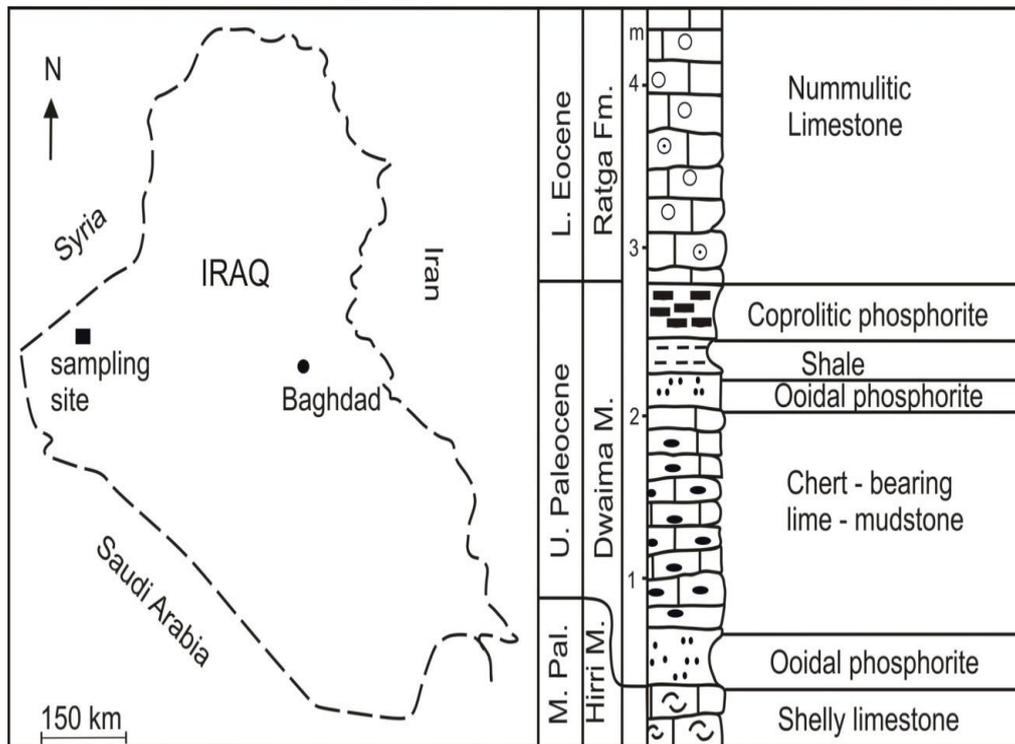
### 2.1. Upper Paleocene Coprolites from the Iraqi Western Desert

The marine sedimentary phosphorites of Iraq (Upper Cretaceous – Paleogene) are part of the Tethyan phosphorite belt extending from North Africa to the East Mediterranean, which was deposited in a marine upwelling sedimentary regime [17, 18, 19, and 20]. By the Late Cretaceous, the New Tethys Ocean was developed into an elongated narrow seaway, as a result of the continuous northward movement of the African-Arabian Plate towards Eurasia [19 and 21]. Upwelling deep oceanic cold currents were active along the southern margins of the Tethys during the Upper Cretaceous–Paleogene times, bringing P- and Si-rich waters from deeper parts of the sea to the shallow warm shelf. The phosphorus-rich bottom waters, welling up to shallow shelf basins, represented the regional controlling factor that initiated this extensive phosphogenic event (20, 22 and 23).

The Paleocene phosphorite-bearing sequence in Iraq, recognized as the Akashat Formation is divided into three members: Traifawi (Lower Paleocene), Hirri (Middle Paleocene) and Dwaima (Upper Paleocene) [24]. The main phosphorite deposits in the Hirri Member are dominated by phosphate peloids and ooids in calcareous cement. Phosphate bioclasts (scales and teeth), ooids and intraclasts, topping firmground, are common in the Traifawi Member, whereas coprolites and shark teeth are distinct phosphate components in the Dwaima Member [25].

The Dwaima Member shows a typical Tethyan phosphate-bearing cyclic sequence consisting of alternations of phosphorite, chert-bearing lime mudstone and shale. It is comprised of (2–3) m thick chert-bearing lime mudstone with quartz-geodes, bound from top and bottom by (0.2–0.5) m thick granular phosphorite (Figure 1). The upper part consists of (0.3–0.5) m thick papery shale topped by a remarkable (0.5 – 1.0) m thick bed of calcareous clayey coprolitic phosphorite, rich in a heterogeneous and poorly sorted mixture of phosphoclasts, including coprolites, shark teeth and skeletal bone remains. Based on faunal assemblages, the coprolite-bearing bed was deposited in an inner shelf basin [26] marking the

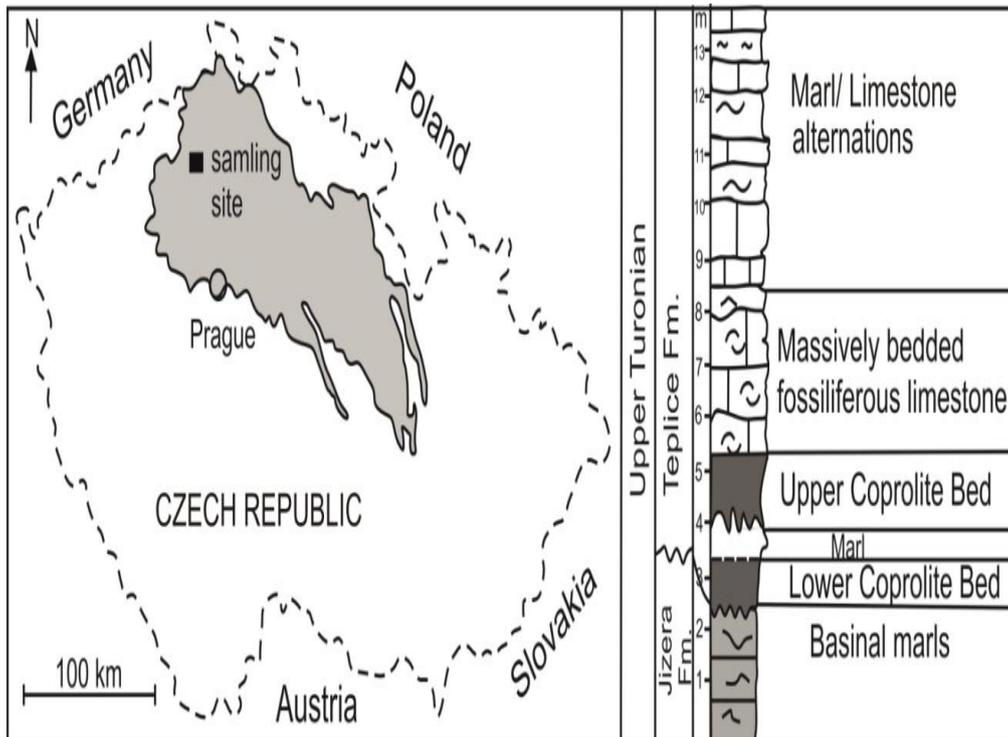
uppermost part of the Paleocene phosphorite-bearing sequence in the Western Desert of Iraq [24].



**Figure 1**-Location map and stratigraphic section of the Upper Paleocene coprolite-bearing sequence in Iraq [15].

## 2.2. Upper Turonian Coprolites from the Czech Bohemian Cretaceous Basin

The Bohemian Cretaceous Basin (BCB) is an intracontinental basin, formed in the mid-Cretaceous as a seaway between the North Sea and the Tethys Ocean [27]. Between the Late Cenomanian and Santonian, the BCB functioned as a relatively shallow seaway extending along reactivated fault zones in the basement of the Bohemian Massif [28]. The Cretaceous sequence at the BCB ranges in age from Cenomanian to Coniacian and grades from estuarine facies at the base to hemipelagic in the middle and terminates with shoreline sandstone deposits. The sequence witnessed several condensation episodes and anoxic events [28]. Within the Upper Turonian part of the BCB sequence, two coprolitic marker beds are recognized at the base of the Teplice Formation (Figure 2) [29 and 30]. The boundary between the Teplice Formations and the underlying Jizera Formation is erosional with borings and taken at the Lower Coprolite Bed (LCB) base. The LCB is (20–30) cm thick, glauconite-rich with phosphate coprolites, glauconite, quartz grains, inoceramid shells and phosphate clasts. The LCB grades upward into dark marl, terminated by another erosive surface and topped by the Upper Coprolite Bed [30 and 31] (Figure2). Both coprolite-bearing beds hold the criteria of condensed sections and slow deposition sequences with sedimentological breaks, marked by bored firmground [32].

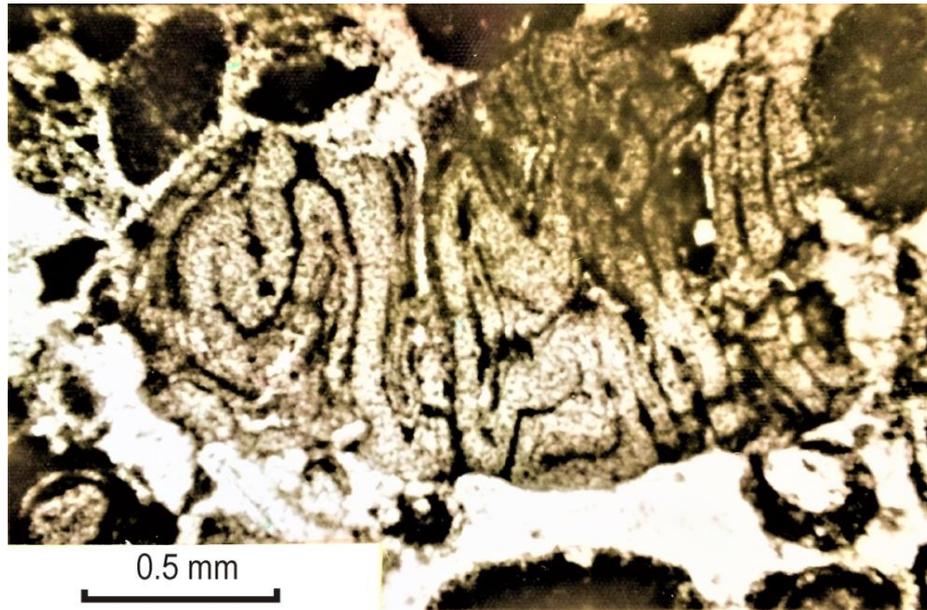


**Figure 2-**Location map and stratigraphic section of the Upper Turonian coprolite-bearing sequence in the BCB of the Czech Republic [30].

### 3. Material and Methods

The coprolite samples of Iraq (samples M13, K and X43) were collected from the upper part of the Dwaima Member, exposed in three sections in the vicinity of the Akashat region [15] (Figure 1). They are cylindrical elongated grains, occasionally coiled and twisted, generally ranging between 0.2 and 2 cm in length and up to 0.5 cm in diameter (Figure 3). The mineral composition is dominated by carbonate-fluorapatite, ranging from 90 to 95 modal % [15]. The Iraqi coprolite samples were concentrated by hand-picking and examined by optical microscopy and X-ray diffraction analysis (XRD) [15]. The rare earth elements were analysed by inductively coupled plasma (ICP) source emission spectrometry at the University College London following the procedure described by [10 and 33]. Phosphorus was analysed by colorimetry at Iraq Geological Survey [34].

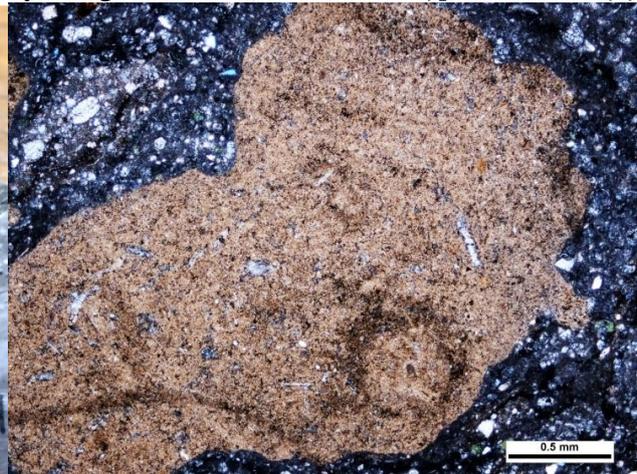
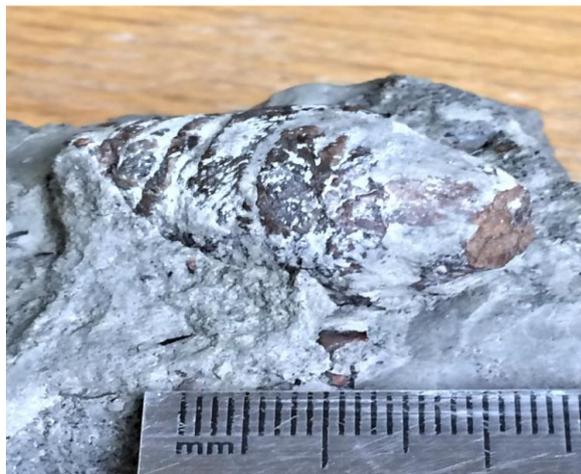
The phosphate coprolite samples of the BCB (samples 28A, 30A, 31A, 39A and 41C) were collected from the LCB, exposed at the Úpohlavy quarry (Figure 2). They are brown, cylindrical with a spindle shape and reach several cm in length and up to 1 cm in diameter (Figure 4). They are embedded in dark gray marl and limestone, rich in benthonic, planktonic and nektonic fauna. The coprolites are rich in organic matter, fish remains and pyrite (Figure 5). They are composed of carbonate-fluorapatite (72 – 90) modal %, calcite (5.3 – 18.8) modal %, glauconite (up to 7) modal % and pyrite (up to 2.6) modal % [16 and 35].



**Figure 3-**Photomicrograph of a coprolite in the Dwaima Member showing twisting and convolutions,

The Czech coprolite samples represent hand-picked individual coprolites. They were examined under a polarized microscope and analyzed by XRD [16]. The REE concentrations were measured using an Agilent 7900x ICPMS, housed at the Czech Geological Survey. Basalt BHVO-2 (USGS) and REE-rich phosphate sample IC10D [36] were used for monitoring the instrumental bias and assessing the quality control. Phosphorus was analysed by colorimetry [37]. The REE analytical data, presented in Table (1), are normalized in the present study to the average world shale reported by [38]; based on values of [39] and presented in Table (2). The normalized values are plotted in comparison to REE pattern of seawater using values of [40] and presented in Figure 6. The Ce-anomaly is calculated according to [12]; (Equation 1):

$$\text{Ce-anomaly} = \log [3 \times \text{Ce}_N / (2 \times \text{La}_N + \text{Nd}_N)] \dots\dots\dots (1)$$



**Figure 4-** Hand specimen of a coprolite in lime-fragment mudstone (sample 39A), XN.

**Figure 5-**Photomicrograph of a coprolite in fossiliferous lime mudstone (sample 31A), XN.

**Table 1**-REE (ppm) and P<sub>2</sub>O<sub>5</sub> (wt. %) concentration in the studied coprolites compared to average world shale and seawater (ppb).

Depositional environment	Inner Shelf in Marine Upwelling System, Iraq			Condensed Section in Intracontinental Basin, CZ					Comparative reference values	
	Samples	M13	K	X43	41C	39A	31A	30A	28A	Shale*
La	59.7	98.8	50.5	228	109	116	166	364	41	3.40
Ce	18.9	21.6	26.7	362	157	226	288	750	83	1.20
Pr	6.7	12.2	16.9	31.9	14.3	22.1	26.3	72.2	10.1	0.64
Nd	25.3	23.7	24.0	127	56.7	91.8	107	300	38	2.80
Sm	5.0	4.7	4.7	21.8	9.4	17.2	18.8	54.1	7.5	0.45
Eu	1.3	1.3	1.5	5.6	2.5	4.3	4.9	13.3	1.61	0.13
Gd	6.9	6.5	6.0	31.5	14.8	22.7	26.4	69.4	6.35	0.70
Tb	n.d.	n.d.	n.d.	4.2	2.0	3.1	3.6	9.1	1.23	0.14
Dy	7.4	7.1	6.4	25.6	12.8	18.6	21.3	52.3	5.5	0.91
Ho	1.9	1.8	1.6	5.6	2.9	4.0	4.7	10.8	1.34	0.22
Er	6.4	6.2	5.3	15.9	8.4	10.9	13.0	28.6	3.75	0.87
Tm	n.d.	n.d.	n.d.	1.8	0.97	1.2	1.5	3.0	0.63	0.17
Yb	6.4	6.3	5.5	11.7	6.5	7.7	9.4	18.3	3.53	0.82
Lu	1.1	1.1	0.9	1.8	1.0	1.1	1.4	2.6	0.61	0.15
REE $\Sigma$	147.2	191.3	150.0	874.2	398.9	546.6	692.3	1747.9	204.15	12.60
P <sub>2</sub> O <sub>5</sub> (wt. %)	31.21	29.60	31.46	26.3	28.4	23.4	22.9	22.8		
REE/P <sub>2</sub> O <sub>5</sub> $\Sigma$	4.57	6.46	4.77	33.24	14.05	23.36	30.23	76.66		
Nd/La	0.42	0.24	0.48	0.55	0.52	0.79	0.64	0.82		

n.d.: not determined, \* after [39], \*\*after [40]

#### 4. Discussion

The studied coprolites are phosphatized faecal materials produced by sharks and other fish, and the phosphatisation of the initial faecal material took place below sediment – water interface [15 and 16]. The process; discussed by [16] involved the release of phosphorus entrapped in organic matter of the faecal material under dysoxic conditions, followed by phosphatisation of the coprolites, crystallization of apatite later reworking at the seafloor for variable periods before final burial. Therefore, the initial REE composition of the apatite in these coprolites should bear the signature of chemical characteristics of the pore water in the depositional basin and later enhanced and/or modified by seawater at the sediment – seawater interface [13, 41 and 42]. The variation in REE behavior in the studied coprolites is discussed here in terms of REE provenance, local depositional environment and diagenetic modifications. The paleoenvironmental REE indicators found significant in this reconnaissance study in the discrimination between the two sedimentary regimes are listed in Table 3 at the end of the discussion.

##### 4.1. Distribution Patterns and Source of REE

In the marine sedimentary environment, there are two potential sources for the supply of REE to the depositional basin. One is deep marine sources, transported to the shelf by upwelling currents [21], and the other is terrestrial sources, transported by rivers from adjacent land [43 and 44]. The REE derived from terrestrial sources carries the original signature of the REE pattern of the land source with no appreciable fractionation, e.g., [38, 45 and 46]. On the other hand, the REE derived from the dissolved load to the sea suffers fractionation in oxidized seawater and copies the seawater pattern, e.g., [5 and 12].

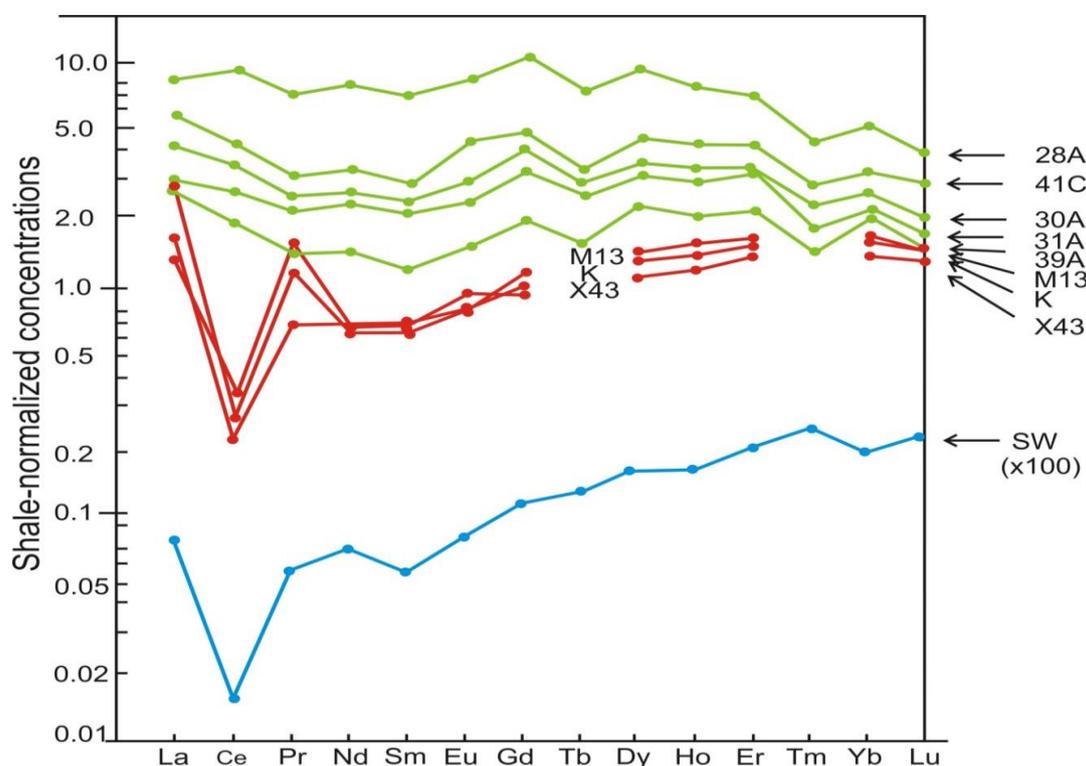
**Table 2-**Shale-normalized values and significant parameters of REE in the studied coprolites and seawater

Depositional environment		Inner Shelf in Marine Upwelling System, Iraq					Condensed Section in Intracontinental Basin, CZ		
Samples	M13	K	X43	41C	39A	31A	30A	28A	Seawater (x1000)
La	1.46	2.41	1.23	5.56	2.66	2.83	4.05	8.88	0.083
Ce	0.23	0.26	0.32	4.36	1.89	2.72	3.47	9.04	0.014
Pr	0.66	1.21	1.67	3.16	1.42	2.19	2.60	7.15	0.059
Nd	0.67	0.62	0.63	3.34	1.49	2.42	2.82	7.89	0.074
Sm	0.67	0.63	0.63	2.91	1.25	2.29	2.51	7.21	0.060
Eu	0.81	0.81	0.94	3.48	1.55	2.68	3.04	8.26	0.080
Gd	1.08	1.02	0.94	4.96	2.33	3.57	4.16	10.93	0.110
Tb				3.41	1.63	2.52	2.93	7.40	0.114
Dy	1.35	1.29	1.16	4.65	2.33	3.38	3.87	9.51	0.165
Ho	1.46	1.38	1.23	4.18	2.16	2.99	3.51	8.06	0.164
Er	1.68	1.63	1.39	4.24	2.24	3.75	3.47	7.63	0.232
Tm				2.86	1.54	1.90	2.38	4.76	0.270
Yb	1.83	1.80	1.57	3.31	1.84	2.18	2.66	5.18	0.232
Lu	1.83	1.83	1.50	2.95	1.63	1.80	2.30	4.26	0.246
(Ce/La) <sub>N</sub>	0.15	0.11	0.26	0.78	0.71	0.96	0.86	1.01	0.17
(La/Yb) <sub>N</sub>	3.24	4.73	2.41	1.68	1.46	1.30	1.52	1.72	0.36
(La/Sm) <sub>N</sub>	2.18	3.82	1.95	1.91	2.13	1.24	1.61	1.23	1.38
(Sm/Yb) <sub>N</sub>	0.37	0.35	0.40	0.88	0.68	1.05	0.94	1.39	0.26
(Pr/Ce) <sub>N</sub>	2.87	4.65	5.72	0.72	0.75	0.81	0.75	0.79	4.21
Ce-anomaly	-0.73	-0.84	-0.51	0.02	-0.02	0.01	-0.07	-0.04	-0.70
Mean LREE <sub>N</sub>	0.74	1.03	0.90	3.87	1.74	2.49	3.09	8.03	0.29
Mean MREE <sub>N</sub>	1.08	1.04	1.01	4.13	1.96	3.04	3.50	9.03	0.47
Mean HREE <sub>N</sub>	1.70	1.66	1.42	3.51	1.88	2.52	2.86	5.98	1.14

LREE: light REE (La–Sm); MREE: middle REE (Eu–Dy); HREE: heavy REE ((Ho–Lu).

The diverse shapes of REE patterns have been interpreted, in addition to provenance, as indicators of varying depositional realms [43, 44 and 47]. The LREE-enriched patterns are typical of coastal environments. The MREE-enriched patterns indicate estuarine or closed marine conditions, and the HREE-enriched patterns correspond to the open marine setting. However, after initial burial and during early diagenesis, the REE derived from pore water sources usually show patterns influenced by early diagenetic REE fractionation, controlled by local depositional parameters, such as redox potential and residence time at the sediment-water interface. All trends are believed to be subject to alteration according to local sedimentary conditions and later diagenetic modifications [10, 48, 49, 50 and 51].

The REE in the studied coprolite samples shows two main groups of distribution patterns (Figure 6). The first is the coprolite samples of marine inner shelf environment characterized by a strong negative Ce-anomaly and enrichment in HREE, depicting that of open marine water. The second group is the coprolite samples of the BCB condensed section, which lack the characteristic Ce-anomaly and are enriched in MREE (Table 2), which resemble REE patterns of estuarine or closed marine basin origin [43, 44 and 47].



**Figure 6**-Shale-normalized REE patterns of the studied coprolites compared to that of seawater [40].

The REE patterns of the Upper Paleocene coprolites of Iraq attest to the oxic deep marine upwelling source that supplied P and REE to the shelf environment. It is generally agreed that upwelling currents, rich in P, Si, and N, have initiated and controlled the deposition of the Tethyan phosphorites in favorite shelf basins during the Upper Cretaceous–Paleogene times; e.g., [18, 22 and 52]. On the other hand, the REE patterns of the Upper Turonian coprolites of the Czech Republic, deposited under slow sedimentation and condensation, support the depositional model proposed for the BCB as an intracontinental semi-closed depositional basin which received its load of sediments carrying P and REE from the adjacent land via rivers and estuaries [16, 28, 29, 30 and 35].

The REE source in the studied coprolites, illustrated in the contrasting behavior of Ce in the two sedimentological settings, can also be observed in some geochemical ratios of the

normalized REE values (Table 2). The marine shelf coprolites of Iraq have  $(\text{Ce/La})_N$  ratio ranging (0.11–0.26), which matches that in seawater of 0.17; expressive of typical Ce-depletion, compared to higher ratios ranging (0.71–1.01) in the coprolites of the BCB condensed section, resembling shale pattern with no Ce-depletion. Normalized Pr value is elevated relative to its neighbors (Ce and Nd) in some of the marine shelf coprolites of Iraq (Figure 6) with a  $(\text{Pr/Ce})_N$  ratio for the three samples ranging from 2.87 to 5.22 and resembling that of seawater of 4.21, compared to much lower values of  $(\text{Pr/Ce})_N$  ratio in the coprolite samples of the BCB condensed section ranging (0.72–0.81) (Table 2). The elevated  $(\text{Pr/Ce})_N$  values in the former are caused not only by the depletion of Ce but also by the elevation of Pr concentration in some of these samples (samples K and X43) which show  $(\text{Pr/Ce})_N$  ratios closer to that of seawater.

#### 4.2. REE Fractionation

One of the most significant fractionations in the REE takes place in the deep marine oxidizing environment, where cerium is oxidized from the soluble  $\text{Ce}^{3+}$  to the highly insoluble  $\text{Ce}^{4+}$ , which is removed from seawater and most probably adsorbed on Mn- and Fe-oxides of the deep oceanic sediments [53 and 54]. Consequently, a negative Ce abundance is created in seawater and its minerals, such as apatite and glauconite; e.g., [12 and 52]. On the other hand, the terrestrial or land-derived REE, transported to the sea as particulate matter in suspension, carries the original signature of the REE pattern of the land source with no appreciable fractionation in the REE. Consequently, the REE pattern would be somewhat similar to that of shale, showing almost flat patterns; e.g., [38, 45 and 46]

Pore-water redox conditions, however, may influence cerium behavior; high dissolved  $\text{Ce}^{3+}$  concentrations are expected in anoxic pore waters, where the redox mobilization of Ce is almost identical to its behavior in anoxic basins [55]. The removal of dissolved Ce in pore water environments is believed to occur by adsorptive scavenging and/or incorporation in rapidly settling large particles like faecal pellets [54]. Moreover, the REE in the seawater-derived sediments may be further fractionated through complexation, especially with  $\text{CO}_3^{2-}$ , which leads to higher concentrations of the HREE relative to the LREE [9, 45 and 57].

The REE of the coprolites discussed in this work show various degrees of fractionation; the marine inner shelf coprolites of Iraq show enrichment in the shale-normalized values of the HREE; ranging from 1.42 to 1.70, relative to MREE; ranging (1.01–1.08) and LREE ranging (0.74–1.03), depicting in this way the trend noticed in seawater (Table 2 and Figure 6). On the other hand, the coprolites of the BCB condensed section show relative enrichment in the MREE; ranging (1.96–9.03) relative to HREE; varying from 1.88 to 5.98 and LREE; ranging from 1.74 to 8.03, resembling in this behavior REE patterns of estuarine or closed marine basins. The fractionation of REE noticed in the studied marine coprolites of both sedimentary systems may be mainly inherited from the parent sources of the REE, i.e., the oxidized deep marine waters in the former and the fluvial-transported terrestrial sources in the latter.

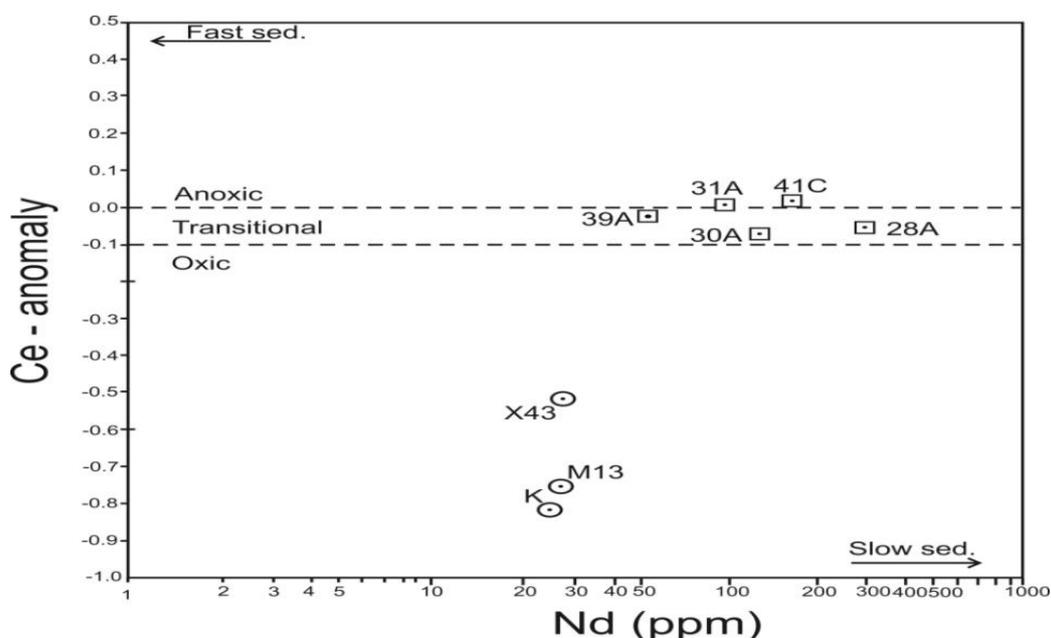
Further REE fractionation during early diagenetic phosphatisation cannot be excluded, especially with regard to the enrichment of MREE in the condensed section coprolite apatites of the BCB, which may have been enhanced by REE fractionation in the pore water environment. Haley et al. [58] suggest that MREE-enriched patterns may often reflect the composition of the diagenetic fluids. According to Herwartz et al. [59], reducing Fe-oxyhydroxides, carrying the main MREE budget in the interstitial pore environment, can produce MREE-enriched patterns. This seems to be one of the modifications on the original REE fractionation, inherited from the terrestrial source of the condensed section coprolites.

#### 4.3. Redox Conditions

The Ce-anomaly in the marine inner shelf coprolites of Iraq falls well within the oxic field of Wright et al. [12], resembling Ce behavior in most Tethyan phosphorites; e.g., [52 and 60].

The Ce-anomaly in the coprolites of the BCB condensed section ranges from slightly positive to slightly negative values. As a bulk, they fall within the transitional field between oxic and anoxic domains defined by [12] (Figure 7). The coprolites of the BCB condensed section witnessed a dysoxic environment during slow deposition [16], whereas the inner shelf basin was better oxygenated and had open access to the main Tethyan Ocean. Both sequences contain abundant benthonic fauna, reported by [28] and [26] respectively, which attest to the availability of oxygen to sustain life at the bottom waters. Redox conditions above the sediment-water interface are expected to be more oxidizing than those prevailing in the interstitial pore environment due to bacterial action [14]. Shields and Stille [49] suggest that post-depositional alteration of REE patterns may include, among other things, the reverse of Ce-depletion usually noticed in seawater REE patterns.

The behavior of REE concerning Ce-depletion in the studied coprolite samples seems to reflect early fractionation of REE in the source, less modified by local environmental conditions. However, the positive Ce anomalies in some of the condensed section (BCB) coprolites and specifically the higher (Ce) normalized value of sample 28A (Table 2 and Figure 6), may suggest that a substantial fraction of the REE was derived from the upward flux of reduced pore waters [14]. The positive Ce-anomaly and elevated (Ce) normalized values may be explained according to [49] as post-depositional alteration of REE patterns induced by pore water.



**Figure 7**-Plot of Ce-anomaly vs. Nd concentration in the studied coprolites showing redox conditions and relative residence time (scheme after [12]).

#### 4.4. Residence Time and Sedimentation Rate

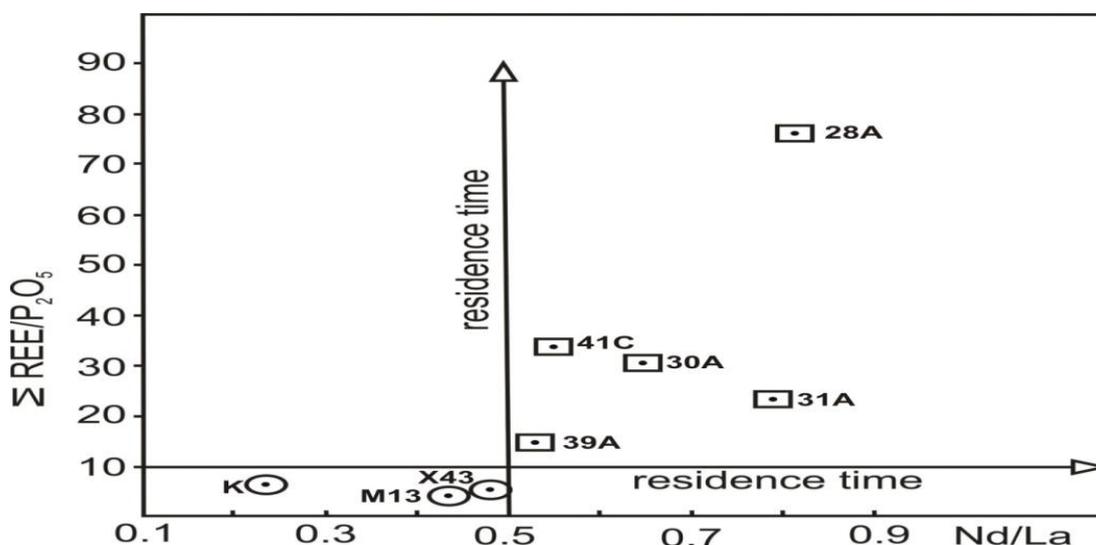
Slow sedimentation rates, typical of condensed sections, leave the biogenic phosphate components (coprolites, shark teeth and skeletal remains) exposed at or near the sediment – water interface for a long period, where incorporation of REE by these apatites continues under slow or no deposition so that the total REE build up to hundreds or thousands of ppm. In shallower water environments usually prevailing on continental shelves, the sedimentation rates are faster, and consequently, lower concentrations of REE in biogenic apatites are observed [12]. This is illustrated in the lower concentration of  $\sum$ REE than shale in the marine shelf coprolites of Iraq (Table 1). Low  $\sum$ REE concentrations are also reported in the associated phosphate peloids, ooids and bioclasts of the same deposit [15] and some Tethyan

East Mediterranean deposits; e.g. Al-Kora phosphorite province in Jordan [52], in contrast to higher REE concentrations in some North African phosphate deposits; e.g., Dj. Onk deposit of Algeria [60].

Further intake of REE is bound to happen as long as the coprolites are in contact with seawater, increasing their concentration in the coprolites apatite, before final burial. Using  $\sum\text{REE}/\text{P}_2\text{O}_5$  ratio in the apatite coprolites as an indicator of residence time is very expressive in the present study. It is ( $<10$ ) in the marine-shelf coprolites; ranging between 4.57 and 6.46, and ( $>10$ ) in the coprolite samples of the BCB condensed section, ranging between 14.05 and 76.60, which attest to a longer residence time and slower sedimentation rate associated with sequence condensation in the latter case.

Moreover, among the REE, neodymium (Nd) concentration is suggested to reflect sedimentation rate [12] due to its relatively short residence time in the marine environment, estimated at  $3 \times 10^2$  yr, compared to  $6.1 \times 10^3$  yr for Ce and  $1.1 \times 10^4$  yr for La [61]. The plot of Nd concentration versus Ce-anomaly, using the scheme of Wright et al. [12] (Figure 7), shows the condensed section coprolites have witnessed slower sedimentation rates than the marine-shelf coprolites. However, using Nd concentration alone to indicate sedimentation rate, as suggested by [12], can be misleading in the present comparison since Nd concentration would vary up and down in accordance to the overall concentration of REE. The alternative use of Nd/ $\sum\text{REE}$  ratio would also be misleading, distorted by the characteristic Ce-depletion in the open marine phosphates and, therefore, not helpful in comparing residence time in these two sedimentary systems.

The concentration of Nd relative to La, expressed as Nd/La concentration ratio may be more informative in this respect, considering the markedly different residence times of the two elements in the marine environment, as indicated by [61]. The Nd/La ratio in the studied samples is lower ( $<0.50$ ) in the marine shelf coprolites ranging (0.24–0.48) in contrast to higher values ( $> 0.50$ ) in the coprolites of the BCB condensed section (0.52–0.82) (Table 1). The higher value of Nd/La ratios in the latter is in accordance with their higher  $\sum\text{REE}/\text{P}_2\text{O}_5$  ratio and point to a longer residence time and slower sedimentation rate (Figure 8), which are typical criteria of condensed stratigraphic sections. The present results, based on REE behavior, complement previously presented evidence on condensation and slow deposition of the BCB coprolite-bearing sequence, which were based on the abundance and maturity of glauconite in the phosphate-bearing sediments [35] and the bored firmground at the base of the coprolite-bearing beds [30 and 32].

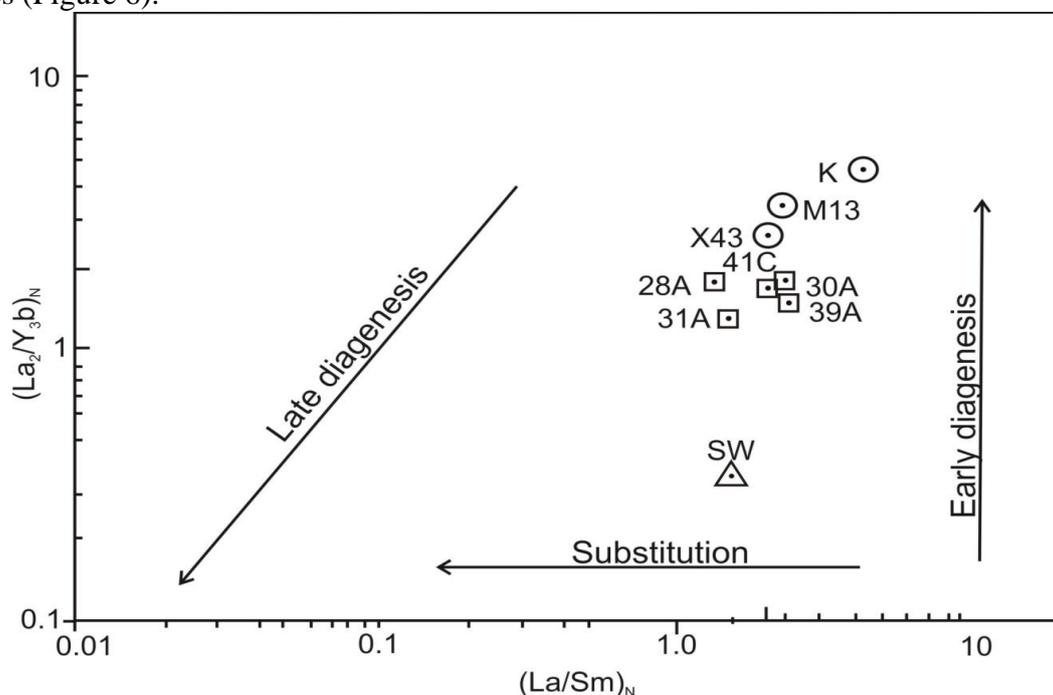


**Figure 8**-Plot of  $\sum\text{REE}/\text{P}_2\text{O}_5$  vs. Nd/La showing response to residence time (developed in the present work).

#### 4.4. Diagenetic Modifications

Wright et al. [12], Henderson et al. [41], and Shemesh [62] suggested that the enrichment of biogenic apatites in most trace elements occurs in the early stages of diagenesis and is associated with crystallographic changes of the apatite. Alternatively, Reynard et al. [63] suggested several potential multistage diagenetic alterations on the REE distribution that occur by adsorption (early diagenesis), recrystallization (late diagenesis) and preferred substitution in the apatite lattice. But, Grandjean et al. [64] and Wright et al. [12] believe that once recrystallized, fossil biogenic apatite seems to be rather insensitive to later diagenetic geochemical changes.

The plot of  $(La/Sm)_N$  vs.  $(La/Yb)_N$  ratios of the present results (Figure 9), using the framework presented by [63], shows that the REE signature in the studied coprolites was acquired in the early diagenetic stage during phosphatization of the coprolites and subsequent crystallization of the apatite. Post depositional alteration on the REE norms in the studied samples is shown in further concentration of REE and relative enrichment of Nd and the MREE. Minor post-depositional modifications on the original Ce behavior inherited from the source, are noticed in some condensed section coprolite samples as elevated Ce normalized values (Figure 6).



**Figure 9**-Plot of  $(La/Yb)_N$  vs.  $(La/Sm)_N$  showing the position of the studied coprolites relevant to various diagenetic processes (scheme after [63]).

#### 4.5 Sea-Level Fluctuation and Reworking

The  $(La/Yb)_N$  ratio was found closely related to turbulence; higher turbulence and higher  $(La/Yb)_N$  ratio mark periods of lowered wave base or higher storm, producing agitation of bottom waters and transferring pore waters upward to the bottom seawater [14]. Significant REE fractionation at the pore water is reported by [45], which may well influence their distribution pattern in the overlying bottom seawater when the sediments are disturbed, and the REE-rich pore waters are released to seawater at the sediment-water interface.

In this respect, the marine inner shelf phosphate coprolites of Iraq show higher  $(La/Yb)_N$  ratios (Table 2), ranging from 2.41 to 4.73 and pointing to the shallower and frequently disturbed environment of deposition at the uppermost part of the Akashat Formation, evidenced by the heterogeneity of the phosphate clasts and their unsorted size distribution [24]. The lower  $(La/Yb)_N$  values in the coprolites of the condensed section in the BCB,

ranging from 1.30 to 1.72, match their formation in the deeper and quieter environment at the base of the Teplice Formation [28]. Apatite and glauconite formed and matured under longer periods of undisturbed slow sedimentation, which may have induced the early diagenetic enrichment of the phosphate coprolites in MREE [35].

**Table 3-** Paleoenvironmental REE indicators in the studied phosphate coprolites

Diagnostic REE indicators	Inner Shelf in Marine Upwelling System, Iraq	Condensed Section in Intracontinental Basin, CZ	Controlling Environmental Factors
(LREE) <sub>N</sub>	0.74 – 1.03 (0.89)	1.74 – 8.03 (3.84)	Fractionation at source
(MREE) <sub>N</sub>	1.01 – 1.08 (1.04)	1.96 – 9.03 (4.33)	Local fractionation in pore water environment
(HREE) <sub>N</sub>	1.42 – 1.70 (1.59)	1.88 – 5.98 (3.35)	Fractionation at source
Ce-anomaly	-0.84 – -0.51 (-0.69)	-0.07 – 0.02 (-0.02)	Fractionation at source + Local redox conditions
(Ce/La) <sub>N</sub>	0.11 – 0.26 (0.17)	0.71 – 1.01 (0.86)	Fractionation at source
(Sm/Yb) <sub>N</sub>	0.35 – 0.40 (0.37)	0.68 – 1.39 (0.99)	Fractionation at source
(Pr/Ce) <sub>N</sub>	2.87 – 5.72 (4.41)	0.72 – 0.81 (0.76)	Fractionation at source
∑REE/P <sub>2</sub> O <sub>5</sub>	4.57 – 6.46 (5.27)	14.05 – 76.66 (35.51)	Local sedimentation rate and residence time
Nd/La	0.24 – 0.48 (0.38)	0.52 – 0.82 (0.66)	Local sedimentation rate and residence time
(La/Yb) <sub>N</sub>	2.41 – 4.73 (3.46)	1.30 – 1.72 (1.54)	Local sea-level oscillation and reworking

## 5. Conclusion

Despite the limited number of samples adopted for this preliminary survey, the results of this study show distinctly different REE behavior and geochemical indices clustered according to their sedimentary regimes that enable justified discrimination between the two. The condensed section coprolites of the intracontinental basin show distinctly higher normalized values of HREE and MREE and higher ratios of Nd/La, (Ce/La)<sub>N</sub>, (Sm/Yb)<sub>N</sub> and ∑REE/P<sub>2</sub>O<sub>5</sub>. Whereas, the upwelling marine shelf coprolites show stronger negative Ce-anomaly and higher (Pr/Ce)<sub>N</sub> and (La/Yb)<sub>N</sub> ratios. The significant variation in REE systematic in these two sedimentary regimes is controlled by the source of REE, local depositional environment and post-depositional alteration during diagenesis and reworking.

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