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Rabah Kechiched, Rabah Laouar, Olivier Bruguier, Sihem Laouar-Salmi, Ouafi Ameur -Zaimeche, et al.. Preliminary data of REE in Algerian phosphorites: a comparative study and paleo-redox insights. Procedia Engineering, 2016, 138, pp.19-29. 10.1016/j.proeng.2016.02.048 . hal-01412572

HAL Id: hal-01412572

<https://hal.science/hal-01412572>

Submitted on 8 Dec 2016

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“SYMPHOS 2015”, 3rd International Symposium on Innovation and Technology in the Phosphate Industry

Preliminary data of REE in Algerian phosphorites: a comparative study and paleo-redox insights

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Abstract

This study deals with the preliminary data of rare earth elements (REE) obtained on northeastern Algerian phosphorites from the Tébessa region. These phosphorites are located in two different basins: the northern basin represented by Dj. El Kouif, Dj. Dyr and Tazbant showings and the southern basin with the giant Dj. Onk phosphate deposit. The host sedimentary formation is Late Paleocene to Early Eocene. Twenty-six (26) samples from the four (4) localities were collected and analyzed for their REE contents using the ICP-MS technique. Phosphates from the southern basin (Dj. Onk deposit) show Σ REE contents ranging from 174.41 and 906.39 ppm (average Σ REE = 623.01 ppm), while the northern phosphorites have lower Σ REE contents (from 125.45 to 472.44 ppm; average = 265.57 ppm). PAAS-normalized REE patterns and binary Box plot of (Sm/Pr)_N vs (Sm/Yb)_N show HREE enrichments for samples from the northern localities while most samples from the southern basin are HREE depleted. Normalized (La/Yb)_N vs (La/Sm)_N plot shows that (La/Sm)_N ratios of all samples are similar to those of modern seawater (from 0.83 to 1.55). However, the (La/Yb)_N ratios of the two basins are significantly higher (from 0.67 to 1.18), which indicates an early diagenesis. The Ce/Ce* vs Pr/Pr* diagram shows that the observed Ce anomaly was not affected by diagenesis and more likely represents a proxy for redox conditions. The obtained results substantiate that the northern phosphorites were formed in more oxic environment with more pronounced negative Ce anomalies, whereas the southern phosphorites have lower Ce anomalies. Northern phosphorites are different from those from the south probably because the northern basin was more connected to an open sea as did the Sra Ouartan basin in northern Tunisia. These results have also been confirmed by statistical method studies, such as factorial discriminate analysis.

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Peer-review under responsibility of the Scientific Committee of SYMPHOS 2015

Keywords: Phosphorites; HREE; LREE; Ce anomaly; Tébéssa.

1. Introduction

The geochemistry of rare earth elements (REE) in sedimentary phosphorites has been studied by many authors as it brings important insights in reconstructing paleo-depositional environments eg. [1-10]. Algerian phosphorites are located mainly in the Tébéssa area (600 Km southeast of Algiers) (Fig. 1), and are part of many deposits and showings that outcrop in northern Africa. These phosphorites are hosted by Paleocene to Eocene marine formation. The present study focuses on phosphorites located in two different basins: (a) The northern basin comprises Djebel el Kouif, Djebel Dyr and Djebel Tazbant showings and (b) the southern basin consists of the giant Kef Essennoun phosphorite deposit of Djebel Onk region. A comparative study of the REE behavior in phosphorites from these basins is carried out in order to highlight paleo-redox environments in which these phosphorites were deposited.

Nomenclature

REE	Rare earth elements
HREE	Heavy rare earth elements
LREE	Light rare elements
Ce _{An}	Cerium anomaly
FDA	Factorial discriminate analysis

2. Presentation of studied areas and sampled outcrops

The investigated phosphorites are hosted by Late Paleocene to Early Eocene marine formations and are a result of a large period of phosphogenesis that occurred in the Tethys Ocean from North Africa to the Middle East [11-15]. Phosphogenesis occurred during this period in northeastern Algeria as a result of upwelling currents, and phosphatic material was deposited around Kesserine Island that was formed as emerged zone during the Paleocene-Eocene period. Three major basins were individualized: (1) the Sra Ouartan basin (northern basin); (2) the Meknassy-Mezzouna basin (eastern Tunisia basins); and (3) the Gafsa-Metlaoui-Onk basin (Southern basin). The most important deposits and phosphorites showings in Algeria are located in the eastern Saharan Atlas close to the Tunisian border and are distributed in two different basins: the northern basin (Dj. El Kouif; Dj. Dyr. and Tazbant showings) and the southern basin (Dj. Onk giant deposits) (Fig. 1).

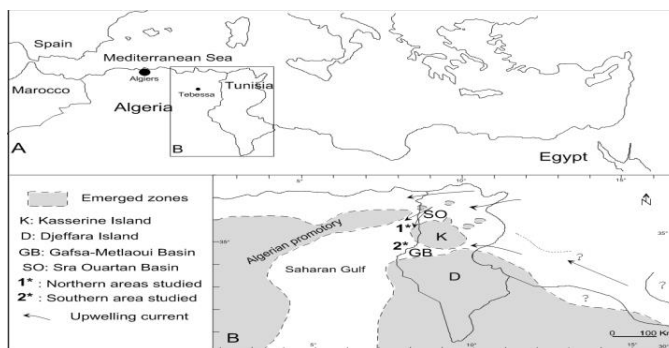


Fig. 1. (A) Geographic position of the studied areas. (B): Paleogeographic situation of the Algero-Tunisian phosphorites during the early Eocene with location of the investigated areas [16-21].

2.1. Northern basin

The sedimentary sequences of the northern basin were studied by many authors eg. [22-27]. The outcrops are represented by a series of Early Cretaceous (Albian) to Miocene formations that are partly overlain by Quaternary continental formations. NE-SW-oriented Triassic evaporitic diapirs intrude these series and are brought up to the surface under the Atlasic (Eocene) tectonic events. Phosphorites are hosted within Tertiary formations (Paleocene-Early Eocene). Carbonaceous formations are contemporaneous to phosphorite mineralization and indicate sedimentation in an open marine environment. The phosphorites are glauconite-bearing, fine-grained, hard and compact rocks, interbedded with thin layers of marls [28]. Below is a brief description of phosphorite outcrops (Fig. 2):

- Djebel Dyr consists of a perched syncline located nearby Tebessa city. It shows tabular structure that was affected by a number of E-W faults. The phosphorites occur as thin layers (from 10 cm to 50 cm thick) between marls and dolomites at the bottom and cherty limestones on top.
- Djebel El Kouif is located at about 20 km northeast of Tébéssa city. The sedimentary outcrops occur as tabular structures and range in age from Late Paleocene to Early Lutetian. The lithology is dominated by limestones and marls and shows five phosphorite interlayers [28]. Their thickness range from 10 cm to 60 cm.
- Tazbant prospect is located at 10 km southeast of Tébéssa city. The Paleocene-Eocene formation which overlays the Maastrichtian [29] consists of marls alternating with limestone and cherty limestone and shows thin (20 cm) levels of phosphorites.

2.2. Southern basin

The Gafsa-Metlaoui-Onk basin (Fig. 1) is characterized by a subsidence with a major control of NW-SE and W-E faults [31]. Many authors suggest that sedimentation involved restricted water exchanges with the eastern open sea at that period [16-17,28,30]. Dejbél Onk mining district belongs to the Gafsa-Metlaoui-Onk basin, and phosphorite mineralization is distributed into five sectors: Kef Essennoun, Djemi Djema, Bled El Hadba, Northern Djebel Onk and Oued Betita [31-35]. Kef Essennoun is taken as an example and was sampled for this study. The regional geology was studied in detail by Visse [31] and later by Prian and Cortiel [36]. The lithologies of Djebel Onk region are composed of a succession of about 500 m thick sedimentary layers that were deposited during the Upper Cretaceous (Maestrichtian) to Middle Eocene (Lutetian). The latter is partly covered by Quaternary continental clastic sediments (sandstones and clays). The Kef Essennoun deposit is characterized by a thick layer (~ 35 m) of Upper Thanetian phosphorites (Fig. 2) which is, itself, divided into 3 sub-layers known in all Djebel Onk district according to the P_2O_5 and MgO contents [36]. From the bottom to the top, these sub-layers are:

- *The basal sub-layer*: It consists of about 2 m thick alternation of marl, phosphorites and dolomite. Phosphorites show relatively low P_2O_5 content (from 13 to 15 %) and high MgO content (8 to 10 %). Heterogeneous phosphorite grains are cemented by marl and clay matrix.
- *The main sub-layer*: It has a thickness of 25 to 30 m and is mined for phosphorites. It is characterized by high P_2O_5 content (24 to 28 %) and low MgO content (less than 4 %). Homogeneous phosphorite particles are cemented by clay or carbonaceous cement.
- *The Upper sub-layer*: It is composed of a phosphatic dolomite layer with relatively low P_2O_5 content (14 to 18 %) and MgO high content (6 to 11 %). This sub-layer is also characterized by a high SiO_2 content ranging from 1 to 6 %. Phosphorites particles are heterogeneously grained.

3. Analytical techniques

Twenty-six bulk phosphorite samples were collected from four different deposits in the northern and southern basins. Three (3) localities belong to the northern basin: Dj. El Kouif (8 samples), Dj. Dyr (9 samples), Dj. Tazbant

for pellets and from 250 μm to 500 μm for coprolites. X-ray diffraction (XRD) was used to determine the phosphorite mineralogy. XRD was performed using BRUCKER-AXS type D8 ADVANCE machine at Biskra University (Algeria). XRD characteristics are: radiation source Cu K α with a wavelength λ of 1.540598 Å, acceleration voltage of 40 KV. The rare earth elements (REE) contents in whole-rocks were analyzed on untreated samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermofinnigan Element XR at Geosciences Montpellier (France). For each sample, about 50 mg of whole-rock powder was dissolved twice in a mixture of hydrofluoric acid (0.5 m HF) and nitric acid (1 ml HNO₃) on a hot plate at 110 °C for 48h. After dissolution, the solution was evaporated to dryness and diluted before analysis in HNO₃ 2%.

4. Results

4.1. Mineralogy and petrography

The examination of thin sections shows that the main phosphorites are composed of particles with different shapes and sizes. Pellets are rounded to sub-rounded with grain size ranging from 80 μm to 250 μm , whereas coprolites have cylindrical to irregular forms with grain size ranging from 250 μm to 1 mm. Bioclasts, such as teeth and bones, are usually found in phosphorites. The phosphorite particles are cemented by either argillaceous (soft phosphorites) or carbonaceous (hard phosphorites) matrix. Hand-picked phosphorite particles show mainly two colors in addition to different shapes and sizes. Indeed, pellets and coprolites are yellowish, milky to brown due to the content of organic matter and its oxidation degree. They sometimes present imprints of contact between grains which were acquired when the particles were still soft (Fig. 3. D; E; G). The XRD patterns performed on phosphorites of these localities show that Carbonate Fluor-apatite (CFA) is the main phosphatic mineral. Calcite, dolomite and quartz were found and represent the matrix of phosphorite grains (Fig. 3. F).

4.2. Rare earth elements (REE) abundances

The Dj. El Kouif phosphorites (Northern basin) show ΣREE contents ranging from 163.68 ppm to 472 ppm (average = 343.55 ppm). The Dj. Dyr and Tazbant showings (Northern basin) show a range of ΣREE from 125.45 ppm to 293.36 ppm (average = 213.59 ppm). The southern basin, represented by Kef Essennoun deposit, displays higher ΣREE contents (up to 906.39 ppm; average = 623.01 ppm) compared to those of the northern basin. High REE contents are also reported in Tunisian, Egyptian, Jordanian and Iraqi phosphorites e.g. [8-10, 37-39]. It is worth noting that the ΣREE in the southern basin are enriched compared those of the Gafsa – Metlaoui basin (Table 1 to 3).

Table 1. Descriptive statistics of REE (ppm) in whole rock - Dj. El Kouif phosphorites belongs to the northern basin.

Element	Nb. Samples	Min.	Max.	Average	Variance	Standard Dev.
La	8.00	58.19	150.90	103.05	783.67	27.99
Ce	8.00	23.96	123.75	71.45	1294.95	35.99
Pr	8.00	7.01	22.17	15.82	30.28	5.50
Nd	8.00	31.10	96.33	69.29	555.41	23.57
Sm	8.00	5.85	18.29	13.15	20.99	4.58
Eu	8.00	1.57	5.02	3.51	1.45	1.20
Gd	8.00	8.87	26.10	17.23	28.03	5.29
Tb	8.00	1.23	3.70	2.45	0.57	0.75
Dy	8.00	9.06	27.03	17.35	26.80	5.18
Ho	8.00	2.23	6.42	4.01	1.36	1.17
Er	8.00	7.17	20.46	12.63	13.29	3.65
Tm	8.00	0.98	2.86	1.75	0.26	0.51
Yb	8.00	5.41	16.20	9.91	8.51	2.92
Lu	8.00	1.08	3.23	1.94	0.33	0.58
ΣREE	8.00	163.68	472.44	343.55	12018.33	109.63
$\Sigma\text{LREE (La To Eu)}$	8.00	127.67	392.77	276.28	8575.51	92.60
$\Sigma\text{HREE (Gd to Lu)}$	8.00	36.01	106.00	67.27	391.32	19.78

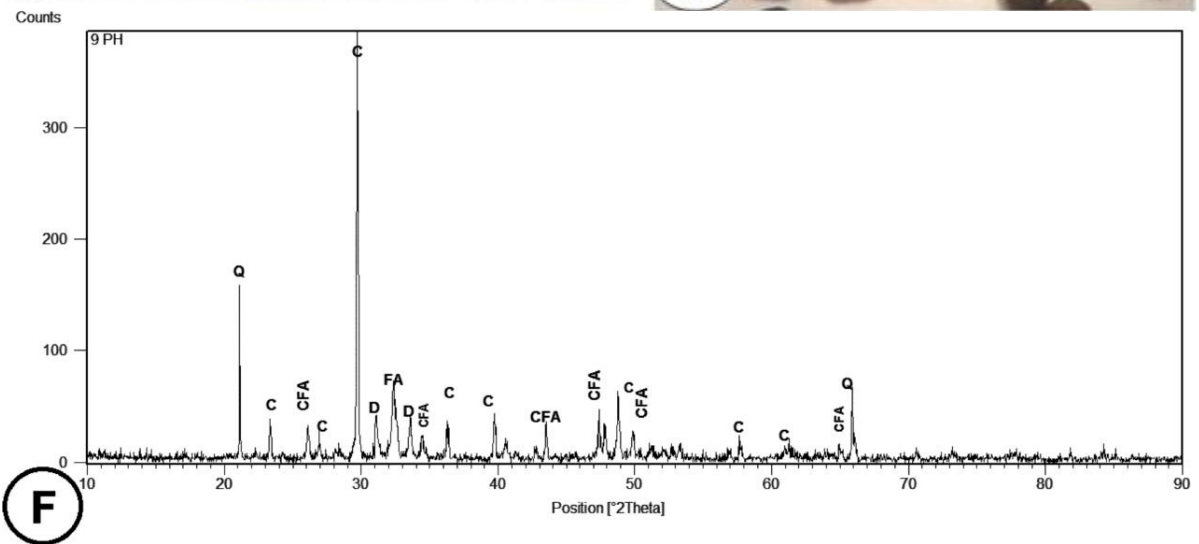
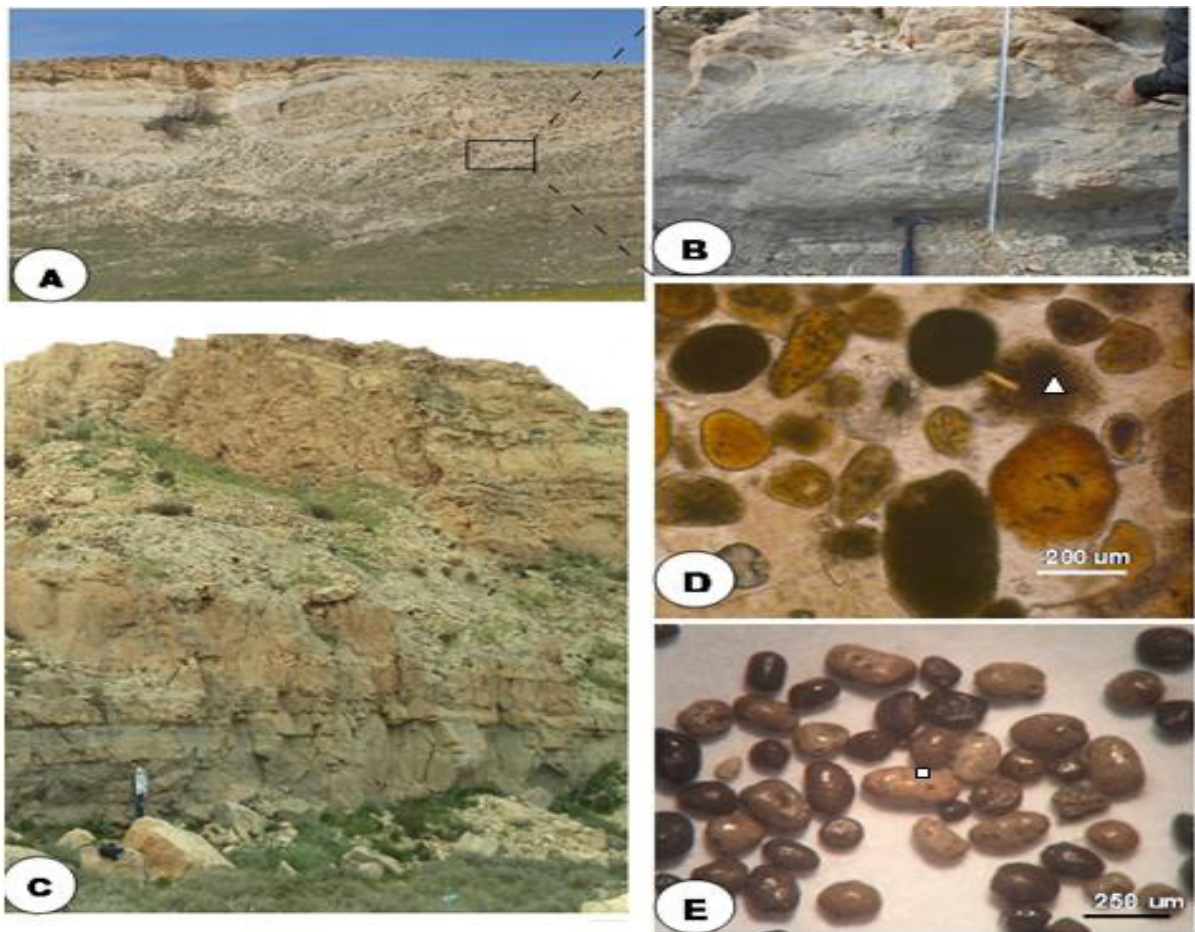




Fig. 3. (A) Photograph of Djebel Dyr outcrop (northern phosphorite basin of Tebessa). (B) Main phosphorite layer at Dj. Dyr showing fine phosphorites with marly cement. (C) Photograph of Dj. El Kouif outcrop showing many phosphorites layers: clay-bearing, soft phosphorites at the bottom and hard phosphorites hosted by dolomite and limestone at the top. (D) Thin section of phosphorite sample from Dj. El Kouif (Paleocene – Eocene) showing phosphatic grains with different sizes and shapes (60 μm to 200 μm slightly rounded pellets; 200 μm to +500 μm cylindrical coprolithes; the white triangle show pellets as cement in the rock). (E) Pellets selection separated from their matrix. Pellets have different colors white – grey to brownish – dark. Pellets are borrowed due to contact with other grains (white square). (F) Example of X-ray diffraction pattern of phosphorite sample (in Dj. Dyr locality) showing the main phosphorite mineral (Carbonate Fluor-Apatite (CFA)), the exogangue represented by calcite (C), minor quartz (Q) and dolomite (D). (G) Coprolites from Dj. El Kouif phosphorite sample showing a cylindrical morphology, generally attributed to a fecal origin [40].

Table 2. Descriptive statistics of REE (ppm) in whole rock - Dj. Dyr (9 samples) and Tazbant showing (3 samples) phosphorites belong to the northern basin.

Element	Nb. Samples	Min.	Max.	Average	Variance	Standard Dev.
La	12.00	42.07	100.75	67.17	352.39	18.77
Ce	12.00	17.18	67.13	41.55	224.16	14.97
Pr	12.00	5.48	13.72	9.67	6.33	2.52
Nd	12.00	24.22	60.32	42.65	129.95	11.40
Sm	12.00	4.37	11.71	8.08	5.13	2.26
Eu	12.00	1.20	3.15	2.16	0.40	0.63
Gd	12.00	6.31	15.90	10.87	10.97	3.31
Tb	12.00	0.89	2.25	1.53	0.22	0.47
Dy	12.00	6.13	16.35	10.87	12.01	3.47
Ho	12.00	1.41	3.80	2.52	0.69	0.83
Er	12.00	4.33	12.24	7.98	7.27	2.70
Tm	12.00	0.59	1.72	1.10	0.14	0.37
Yb	12.00	3.31	9.88	6.23	4.51	2.12
Lu	12.00	0.63	1.96	1.22	0.18	0.42
ΣREE	12.00	125.45	293.36	213.59	2981.02	54.60
$\Sigma\text{LREE (La To Eu)}$	12.00	98.60	238.63	171.28	1804.71	42.48
$\Sigma\text{HREE (Gd to Lu)}$	12.00	24.35	64.09	42.32	185.77	13.63

Table 3. Descriptive statistics of REE (ppm) in whole rock – Dj. Onk phosphorites belong to the southern basin.

Element	Nb. Samples	Min.	Max.	Average	Variance	Standard Dev.
La	6.00	64.61	199.20	144.23	1678.92	40.97
Ce	6.00	21.57	295.04	196.43	7167.12	84.66
Pr	6.00	7.53	47.87	32.65	153.99	12.41
Nd	6.00	33.28	207.25	138.66	2928.82	54.12
Sm	6.00	6.05	34.96	23.75	78.03	8.83
Eu	6.00	1.69	8.60	5.88	4.45	2.11
Gd	6.00	9.51	35.39	24.93	62.42	7.90
Tb	6.00	1.31	4.90	3.42	1.19	1.09
Dy	6.00	9.91	30.73	21.84	40.08	6.33
Ho	6.00	2.45	6.33	4.57	1.39	1.18
Er	6.00	7.93	18.24	13.42	9.97	3.16
Tm	6.00	1.09	2.43	1.78	0.17	0.41
Yb	6.00	6.24	13.07	9.67	4.46	2.11
Lu	6.00	1.24	2.39	1.79	0.13	0.36
ΣREE	6.00	174.41	906.39	623.01	50580.90	224.90

Σ LREE (La To Eu)	6.00	134.73	792.91	541.59	41061.24	202.64
Σ HREE (Gd to Lu)	6.00	39.67	113.48	81.42	504.02	22.45

4.3. PAAS - Normalized REE

REE in investigated samples were normalized to Post Archean Australian shale (PAAS) [41]. In this paper, Cerium anomalies (Ce_{an}) were calculated using the method of Wright et al., 1987 [42]. Ce/Ce^* denotes $3Ce_N/2(La_N+Nd_N)$. Ce_{An} as log Ce/Ce^* ratio while $Pr/Pr^* = 2Pr_N/(Ce_N+Nd_N)$ [43]. PAAS-normalized REE patterns show enrichment in HREE in the northern localities. However, most samples in the southern locality are HREE depleted (Fig. 4). Patterns highlight a negative cerium anomaly in all phosphorites with different extents. We note that the sample from the upper sub-layer of phosphorites displays a pattern similar to the northern samples (Fig. 4 D.).

5. Discussions

5.1. Is Ce anomaly a real paleo redox indicator of phosphorite basins?

The negative cerium anomaly (Ce_{an}) indicates a deficiency in that element due the oxidation of Ce^{3+} to an insoluble state Ce^{4+} in oxidizing environments. Ce becomes fractionated and can make a cover on biological tests so that, it is partially removed from seawater [44]. Phosphorites with negative Ce_{an} indicate that they were formed under oxic conditions [3, 45-47]. Therefore, Ce_{an} can be used as a redox parameter providing the REE content is inherited from seawater and was not affected by post depositional alteration such as diagenesis and weathering which may mask or overprint the original signature. A diagram of $(La/Sm)_N$ versus $(La/Yb)_N$ [7] is used in this study to test the investigated samples against diagenesis effects (Fig. 5. A). It shows that all samples from the four localities (both northern and southern) have $(La/Sm)_N$ ratios ranging from 0.83 to 1.55, which is comparable to modern seawater (from 0.79 to 1.66 [7]). However, the $(La/Yb)_N$ ratios range from 0.67 to 1.18, which is higher than modern seawater (from 0.2 to 0.5 [7]). Some authors interpreted these high $(La/Yb)_N$ ratios by an adsorption of the REE onto apatite during early diagenesis [7]. The diagram of Bau and Dulski (1996) [43] is used to check the Ce_{an} strength. It consists of a projection of samples into a Pr/Pr^* versus Ce/Ce^* diagram (Fig. 5. B.). In this diagram, all samples are located in the IIIB area which indicates a real Ce_{an} and consequently this parameter is taken as a real paleoredox indicator. The calculated Ce_{An} highlight a significant difference between the northern and southern phosphorites. The Northern localities yield high Ce_{An} slightly variable between the three localities (Ce_{an} from -0.19 to -0.73, $\bar{x} = -0.49$, $\sigma = 0.17$, $n = 20$). The Ce_{An} is increasing from western to eastern localities and indicates more oxidizing conditions towards Kessrine Island. In other word, we suggest that the depositional environment tend to be shallower in Dj. El Kouif deposit. We also note, that Ce_{An} increases relatively from bottom to upper layers. Samples from the southern locality show low Ce_{An} values compared to northern localities and it indicate a sub-oxic environment (Ce_{An} from -0.16 to -0.18, $\bar{x} = -0.176$, $\sigma = 0.01$, $n = 5$). One sample from the upper sub-layer in this deposit shows a high Ce_{An} (-0.73), which indicates that redox conditions have changed to a more oxidizing environment.

5.2. Factorial discriminate analysis

Factorial discriminate analysis (FDA) is a multi-variate statistical method. Unlike principal component analysis, which summarizes the information focused on factors [48], FDA method aims at finding the sub-space of the original variable space that best separates the m classes by maximizing the inter-class variance regarding to the total variance [49-50]. This method is mainly based on several statistical hypotheses such as: prior probabilities, estimations of means and variances and equal dispersions [51]. FDA performed on samples issued from the four localities represents qualitative variables and their REE values are the explicative variables. Samples were projected on factorial axes, which show the variability cumulative of 94.98% (Fig. 5. C.). This highlights that samples are discriminated according to their REE signature and it shows an opposition between the northern and southern samples against F1 factor. Northern localities are slightly similar with nearby groups.

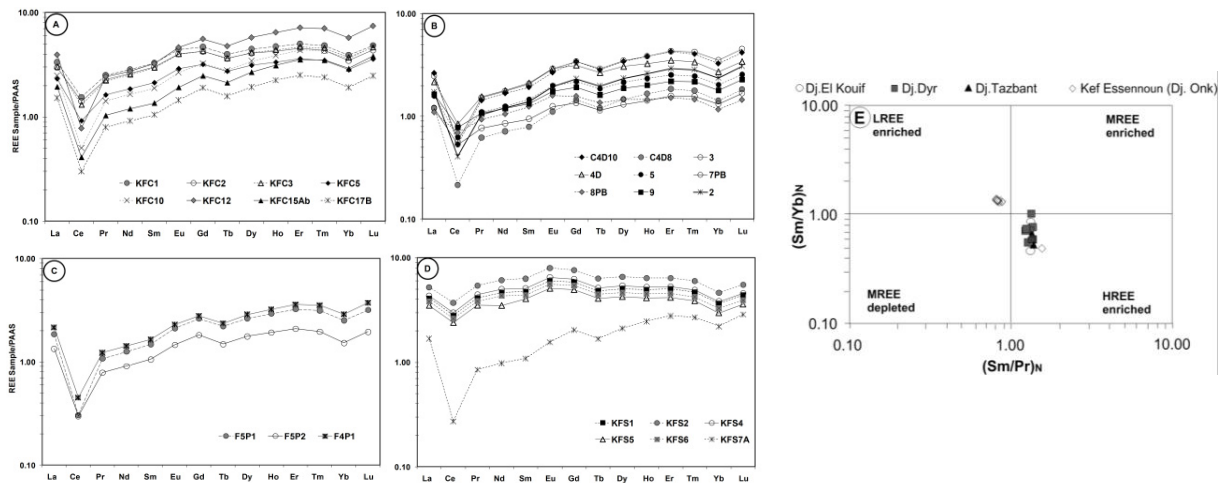


Fig. 4. PAAS - normalized REE patterns for investigated samples. Northern phosphorites show an enrichment in HREE: (A) Dj. El Kouif; (B) Dj. Dyr; (C) Dj. Tazbant showings. (D) Normalized REE patterns in southern locality (Kef Essenoun) show depletion in HREE except for one sample of the Upper sub-layer. (E) Binary Box plot of all samples show HREE enrichment in northern phosphorite samples.

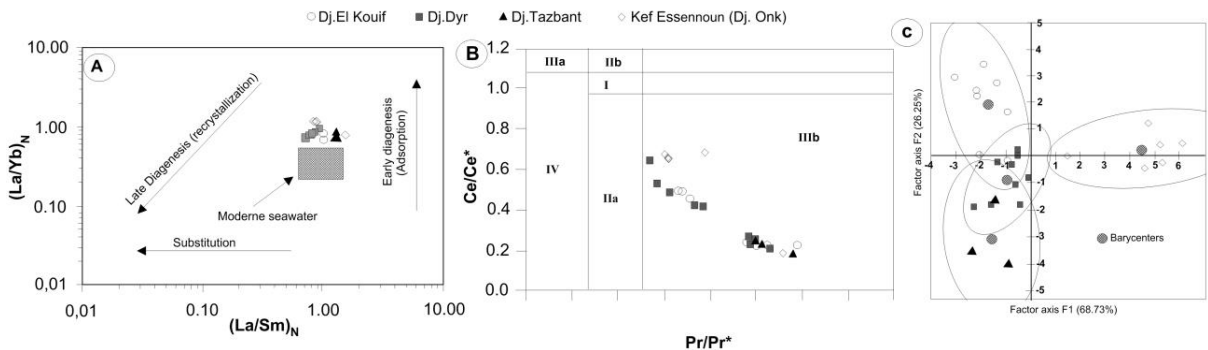


Fig. 5. (A) Binary plot of $(La/Sm)_N$ vs. $(La/Yb)_N$ ratios of studied samples reported in the diagram of Reynard et al. (1999) [7]. Samples show $(La/Sm)_N$ ratios similar to modern seawater, while their $(La/Yb)_N$ is higher indicating an early diagenetic process. (B) The Ce/Ce^* vs. Pr/Pr^* diagram [43]. Field I: no anomaly; Field IIa: positive La anomaly causes apparent negative Ce anomaly; Field IIb: negative La anomaly causes apparent positive Ce anomaly; Field IIIa: real positive Ce anomaly; Field IIIb: real negative Ce anomaly; Field IV: positive La anomaly disguises positive Ce anomaly. All samples show real negative Ce anomalies. (C) Scatter plot (F1 vs. F2) of studied samples from FDA analysis showing discriminate groups of phosphorites according to their location. The majority of Kef Essenoun (Djebel Onk) samples are grouped, except one sample from the upper sub-layer, which exhibits a similarity with northern phosphorites.

6. Conclusion

This study presents the preliminary results of REE analyses on Algerian phosphorites, located in the northeastern part of Algeria. During the course of this study, four (4) localities were investigated in the Tébessa region. These phosphorites are hosted in marine sedimentary formations of Late Paleocene to Early Eocene age. The REE analyses show a significant difference between the northern to southern phosphorites. PASS-normalized REE patterns indicate that the northern phosphorites are enriched in HREE while the majority of southern samples are HREE depleted. This study highlights that all phosphorites, while affected by early diagenetic processes, preserved the original signature inherited from paleoseawater. Cerium anomaly is used as a redox indicator. These phosphorites display real negative Ce anomalies although variable in extent. Therefore depositional environments were different in their redox conditions. The northern phosphorites show more pronounced negative Ce anomalies, which substantiates more oxygenated conditions. We suggest that the northern basin was connected to an open sea similarly to the Sra Ouartan basin in northern Tunisia [10]. Southern phosphorites show less pronounced negative cerium

anomalies, which indicate a sub-oxic environment characterized by a restricted water exchanges. These results are confirmed by factorial discriminate analysis.

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