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Insight on the possible use of black shales for geological storage of radioactive wastes

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ABSTRACT

This study was undertaken to investigate the natural materials before and after appropriate physicochemical treatments. The samples were collected at different depths from the outcrop Lamsied located in the Tarfaya-Boujdour basin. This work concerns a mineralogical and geochemical characterization of local black shale. For instance, mineralogical and granulometric analysis showed that the local black shale is composed essentially of calcite, and the texture does not depend neither on the depth nor on the lithology. The distribution of stable elements such as rare earth elements (REE) and other trace and major elements was determined. Different techniques of analysis were used for the characterization of the samples. Enrichment or depletion of major elements was observed. NASC-normalized REE patterns revealed a heavy REE (HREE) enrichment, a light REE (LREE) depletion, a positive Eu anomaly and a negative Ce anomaly. The result indicates reduction conditions. Results of correlation analysis suggest the association of La, Ce, Dy, Ho, Er, Yb and Lu with terrigenous minerals and of Eu, Sm and Tm with carbonates and TOC (total organic carbon).

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Capsule Summary: The mineralogical and geochemical study of black shales from Tarfaya-Boujdour area was performed aims to evaluate the behavior of rare earth metals and results suggest an association of La, Ce, Dy, Ho, Er, Yb and Lu with terrigenous minerals and of Eu, Sm and Tm with carbonates and TOC.

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INTRODUCTION

The final storage of radioactive wastes from industry and radioactive installations (hospitals, research centers etc.) is a big interest nowadays. The use of black shales, collected in the vicinity of Tarfaya and Timahdit, in Morocco, for trapping chemical elements, including radioactive isotopes, has been studied by our research group since 2002 (Khouya, 2002 ; El Harti, 2014 ; Oumam et al., 2003). Moreover, other publications presented the behavior of uranium and thorium in black shales: uranium would be associated to humic acids whereas thorium is partially distributed in silicate minerals and pyrite (Galindo et al., 2006; Galindo et al., 2007).

In this work, a possible use of the mentioned geological materials to the design of matrices, for the containment and stabilization of radioactive wastes, is discussed (Ayach et al., 2017; El Aouidi et al., 2017; Ait Malek et al., 2017). The characterization of the mineralogical structure and chemical composition of these materials, and the determination of the chemical elements distribution within them, is firstly determined. Then, the concentration of trace elements in this material and its relation to major elements and mineralogical structure is presented to localize the organic and inorganic trapping sites of these elements. These results can be used to design natural matrices for the stabilization and sorption of radioactive wastes. In fact stable elements can reflect the behavior of their radioisotopes, rare earths on which was focused in the present work, has known to be analogue of minor actinide (Am, Cm etc.) (Krauskopf, 1986), which are highly radioactive (Harwood et al., 2011).

Different analysis techniques were applied to the black shale samples. Indeed, X-ray fluorescence (XRF) was applied to determine concentration of trace elements and major elements. Rare earths elements (REE) concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The particle size distribution of the samples and their mineralogical structures were determined by laser diffraction and X-ray diffraction (XRD), respectively.

Additionally, this work would be a contribution to the knowledge and applications of the trace elements geochemistry in sedimentary rocks. The main application, in our case, would be to design methods for separating these elements and for developing natural origin materials for sorption of stable and radioactive elements.

MATERIAL AND METHODS

Samples collection

The analyzed samples were collected from Lamsied (Laâyoune) area, which is located in Tarfaya-Boujdour basin (El Batal, 2014). This basin corresponds to the section of the Moroccan Atlantic margin. It is limited in the West by Central Atlantic Ocean and in the East by Zemmour fault, which separate it from anti-Atlas massif, Tindouf basin, Reguibat and Mauritanides massif (Fig. 1). This area is located just 18 km southeast of Laâyoune, on the road leading to Smara, and halfway between Laâyoune and Boujdour (El Batal, 2014).

Nature and lithology of samples

Fig. 1: Geological map of the Tarfaya-Boujdour basin (Gebhardt and Zorn, 2008).

Fig. 2a: Diffractogram of S6 (1) sample, where C: Calcite

Fig. 2b: Diffractogram of S₆ (3) sample, where C: Calcite, H: Halite, Q: Quartz

The black shales from Lamsied outcrop (Table 1) are arrayed in organic matter-rich marl layers, and clay limestone interlayers, the whole is surmounted by successive strata of chalky clay.

Physical and chemical characterization

Granulometry

The particle sizes distributions were determined in every sample using wet Laser Diffraction equipment (Malvern

Mastersizer 2000), with a dispersion unit Hydro 2000G (Mejjad et al., 2016). This equipment and its associated protocol allow obtaining the particle size from 0.02 to 2000 μm . The analysis procedure was by introducing 1g of sample in the dispersion unit containing deionized water, used as dispersant. Measurements were done after 10 seconds of ultrasound application, to disperse any agglomerates. This analysis was carried out in the National Center for Energy Sciences and Nuclear Techniques (CNESTEN- Morocco).

Analysis by x ray diffraction (XRD)

Fig. 3a: NASC-normalized major elements concentration in marl with high amounts of organic matter samples

Fig. 3b: NASC-normalized major elements concentration patterns of clay limestone samples

Figure 3c: NASC-normalized major elements concentration patterns of clay limestone samples

Fig. 4: Concentrations of REE in the analyzed samples

Fig. 5a: Concentrations of REE normalized to NASC for samples of chalky clay of superior layers

Fig. 5b: Normalized concentration of REE of marl relative to NASC for layers of high amounts of organic matter

Fig. 5c: Normalized concentration of REE of marl relative to NASC for clay limestone interlayers

Table 1: Characteristics and lithology of collected samples (El Batal, 2014)

Samples	TOC (%)	% of CaCO ₃	% of Silicates	Altitude (m)	Lithology	Age	Site
S ₆ (1)	6.00	55.93	35.07	0.5	Marl with high amount of organic matter	Upper Cretaceous	Lamsied region
S ₆ (2)	0.59	91.53	7.59	2	Clay limestone		
S ₆ (3)	3.83	47.46	46.8	4	Marl with high amount of organic matter		
S ₆ (4)	0.58	84.75	14.38	6	Clay limestone		
S ₆ (5)	3.19	38.98	56.23	8	Marl with high amount of organic matter		
S ₆ (6)	1.94	16.95	80.14	10	Chalky clay		
S ₆ (7)	5.04	27.12	65.32	12	Chalkyclay		

Table 2: Granulometry and texture of samples collected in Lamsied outcrop

Samples	Lithology	Texture	Particle size in μm		
			< 2 (Clay)	2 to 50 (Lime)	50 to 2000 (Sand)
S ₆ (7)	Chalkyclay	Loamysand	0.16	35.62	64.22
S ₆ (6)	Chalkyclay	Sand	0.02	9.94	90.04
S ₆ (5)	Marl with high amounts of organic matter	Siltyclay	30.48	53.42	16.1
S ₆ (4)	Clay Limestone	Loamysand	0.14	35.41	64.45
S ₆ (3)	Marl with high amounts of organic matter	Loamysand	0.17	29.89	69.85
S ₆ (2)	Clay Limestone	Loamysand	0.05	41.81	57.87
S ₆ (1)	Marl with high amounts of organic matter	Sandyloam	0.25	58.48	41.27

Table 3: Concentration (%) of most abundant elements (oxides) in the samples collected in Lamsied outcrop (ND means not detected)

Samples	S ₆ (7)	S ₆ (6)	S ₆ (5)	S ₆ (4)	S ₆ (3)	S ₆ (2)	S ₆ (1)
CaO	21.65	26.02	26.76	48	10.5	41.1	20.7
SiO ₂	15.2	34.7	9.7	1.77	3.89	10.1	9.03
Al ₂ O ₃	3.7	2.4	4.3	0.6	0.81	2.31	2.14
MgO	19.3	14.8	26.8	1.25	1.63	1.51	0.95
Fe ₂ O ₃	0.47	0.3	0.57	0.12	0.13	0.51	0.33
K ₂ O	ND	ND	ND	0.1	0.28	0.27	0.44
P ₂ O ₅	2.45	1.9	2.42	1.0	0.29	0.09	0.55
Na ₂ O	--	--	--	1.55	20.2	1.81	14.4
TiO ₂	0.08	0.26	0.1	--	0.13	0.09	0.06

The mineralogy was detected in the National Center of Scientific and Technical Research (CNRST), using a diffractometer of 2-circles X'Pert Pro MPD PANalytical. This equipment has a theta-theta goniometer, an autosampler and an ultra-rapid X'Celerator detector.

Analysis by x ray fluorescence (XRF)

The major oxides and trace elements other than RRE were using an X-Ray Fluorescence spectrometer, so called, "Axios System". It is low wavelength-dispersive spectrometer (1 kW), which has a cooling unit with SST tube technology that allows an excitation of 20–60 kV and 10–50 mA. This analysis was done in the National Center of Scientific and Technical Research (CNRST).

Fig. 6: Variation of rare earths concentration versus carbonate concentrations (%)

Table 4: Concentrations of trace elements (in ppm) in samples collected in Lamsied outcrop

Samples	S ₆ (7)	S ₆ (6)	S ₆ (5)	S ₆ (4)	S ₆ (3)	S ₆ (2)	S ₆ (1)
Cl	--	--	--	9700	84300	9440	45200
Rb	55.3	23	39	--	--	25.4	--
Sr	1183	1016.7	1343	551	360	330	625
I	--	--	--	231	--	--	109
Br	--	--	--	--	70.2	--	48.8
V	38.67	66	44.33	--	--	--	298
Ni	401	280	473.7	11.47	59.83	10.08	80.06
Zr	84	76.3	96	--	--	--	50.2
S	--	--	--	4900	9260	3330	14800
Cr	319.3	208.3	238.3	47.38	38.65	16.06	45.91
Co	4	2.33	5	--	--	--	--
Pb	14	<LD	12	--	--	--	--

Fig. 7: Variation of rare earths concentration versus concentration of silicates (%)

Table 5: Rare earths concentrations (ppm) in black shales collected in the outcrop of Lamsied (Laâyoune)

Samples	S ₆ (7)	S ₆ (6)	S ₆ (5)	S ₆ (4)	S ₆ (3)	S ₆ (2)	S ₆ (1)
La	28.52	23.1	27.6	2.49	3.16	0.79	3.63
Ce	10.7	42.3	10.7	1.25	1.05	0.79	1.21
Nd	74.17	99.24	82.72	38.65	10.53	0.79	6.06
Sm	28.6	23.4	750.05	658.35	639.34	217.38	838.22
Eu	28.7	23.1	27.6	38.65	44.24	148.86	99.33
Gd	28.1	23.5	30.33	1.25	321.25	107.9	31.49
Dy	37.08	25.38	24.8	1.25	1.05	6.3	8.48
Ho	28.7	23.7	27.9	1.25	1.05	0.79	1.21
Er	28.8	23.6	27.4	2.49	2.11	0.79	3.63
Tm	62.76	25.4	432.93	460.1	444.48	139.41	545.09
Yb	28.8	23.1	27.3	1.25	1.05	0.79	1.21
Lu	28.56	23.7	27.7	1.25	1.05	0.79	1.21
ΣREE	412.93	376.93	1497.01	1208.23	1470.36	625.38	1540.77

Fig. 8: Variation of rare earths concentration versus concentration of TOC (%)

Table 6: Anomaly values of Ce, Eu, Σ LREE, Σ MREE, Σ HREE and enrichment factor

Samples	Eu/Eu*(NASC)	Ce/Ce*(NASC)	La _n /Yb _n	Σ LREE	Σ MREE	Σ HREE
S ₆ (7)	4.43	0.10	0.1	113.40	122.67	176.87
S ₆ (6)	4.43	0.40	0.11	164.62	94.62	117.70
S ₆ (5)	0.81	0.09	0.13	121.00	832.78	543.23
S ₆ (4)	5.97	0.05	0.19	42.39	699.50	466.34
S ₆ (3)	0.43	0.08	0.29	14.74	1005.88	449.74
S ₆ (2)	4.31	0.44	0.09	2.37	480.44	142.57
S ₆ (1)	2.71	0.11	0.28	10.90	977.52	552.35

Fig. 9: (a) Variation of carbonates concentration (%) and (b) silicates concentration (%) versus TOC (%)

Fig. 10: (a) Variation of carbonates concentration (%) and (b) silicates concentration (%) versus TOC (%)

ICP-AES analysis

The REE concentrations were determined with an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) placed in the National Center of Scientific and Technical Research (CNRST). The samples were

preconditioned by attacking them with aqua regia (1/3 HNO_3 and 2/3 HCl).

RESULTS AND DISCUSSION

Granulometry and texture

The granulometric analysis was also performed and results thus observed are shown in (Table 2). According to these results, four textures are observed in black shales from Lamsied area a;

- (i) Loamy sand texture in the case of samples S6 (7), S6 (4), S6 (3) and S6 (2).
- (ii) Sand texture concerning the sample S6 (6)
- (iii) Silty clay texture for the sample S6 (5).
- (iv) Sandy loam texture for the sample S6 (1).

Mineralogical composition

Based on X-ray diffraction spectra, samples have proved to be essentially formed of calcite. This fact is shown in the spectrum of sample S6 (1), presented in (Fig. 2a). On the other hand, some samples like S6 (3) revealed the presence of quartz and halite (Fig. 2.b). Halite is a chemical fraction arising from the direct precipitation of ions, due to an intense evaporation of marine brine. The presence of halite gives to the sample S6 (3) an evaporitic character. Previous works have shown that black shales from Tarfaya are mainly composed of calcite (63.7 %), dolomite (3.5 %), quartz (6.5 %), pyrite (<1%) and clay (10 %) (Rahali, 1985)

Major elements (oxides)

Among the major elements, we consider as the most important, the group Si, Al, Fe, Ca, K, P; because their geochemistry. Major oxides concentrations are listed in (Table 3). Their variation was found to be independent of the lithology and depth of the samples. Indeed, the concentration of CaO ranging from 10.5 to 48 %, SiO₂ is in the range of 1.77 – 34.7 %, MgO varies from 0.95 to 26.8 %, Al₂O₃ varies from 0.6 to 4.3 %, and P₂O₅ is in the range of 0.09 – 2.45 %. The iron oxide (Fe₂O₃) and the potassium oxide (K₂O) have content lower than 1 %.

Major oxides concentrations were normalized to NASC (North American Shale Composite) (Nyakairu and Koeberl, 2001), normalized curves and are represented in (Fig. 3a, Fig. 3b and Fig. 3c). According to these curves, the samples are enriched in CaO and P₂O₅, and impoverished in other oxides such as SiO₂, Al₂O₃, Fe₂O₃, and K₂O. Otherwise chalky clay and organic matter-rich marl layers showed enrichment in MgO, which gives them a chalky dolomitic character. On the contrary, the low ratio Mg/Ca (0.02–0.13) found in the samples suggest that calcite is the most predominant phase of carbonates, which could crystallize in low depth seawater (Ries, 2010). As conclusion, black shales from Lamsied area are relatively enriched in CaO, Na₂O and P₂O₅, and impoverished in SiO₂, Al₂O₃, Fe₂O₃, and K₂O. The deficiency in Si, Fe, Al and K, which are of detrital origin, is due to the presence of quartz and clay minerals in low proportions (Brijraj, 2008).

XRD analysis spectra showed that black shales from Lamsied area, are formed, essentially of more or less dolomited calcium carbonate. Which were deposited in a

marine aquatic medium, eventually by chemical precipitation.

Trace elements

Trace elements concentrations contained in our samples are listed in (Table 4). The data analysis shows the following observation;

- (i) Sample showed the following observation;
 - (a) Halogens: The concentrations of (Cl) ranging from 9440 to 84300 ppm, (Br) is in the range of 48.8–70.2 ppm and Iodine concentration varies from 109 to 231 ppm. This can be explained by an intense evaporation of high salinity marine system, which leading to production of chalky deposits
 - (b) Strontium: its concentration in the studied samples was from 330 to 1343 ppm.
 - (c) Chrome: Here the concentrations vary from 16.06 to 319.3 ppm
 - (d) Sulfur: its concentration is in the range of 3330–14800 ppm.
 - (e) The concentration of Ni, V and Zr were in the ranges of 10.08–473.7 ppm; 38.67–298 ppm and 50.2–96 ppm, respectively.
- (ii) An impoverishment in Pb (≤14ppm) and Co (≤ 5ppm). It is important to note that high trace elements concentrations were observed in the S6(1) sample located at the base of the outcrop.

Geochemistry of REE

The REE concentrations in samples collected from Lamsied black shale outcrop are listed in (Table 5). These results are also presented in (Fig. 4), and exhibit that REE concentrations vary independently of the depth and the lithology of samples. The Ratios of La/Yb, Ce/Ce* and Eu/Eu*, as well as light REE (LREE), middle REE (MREE) and heavy REE (HREE) are presented in (Table 6).

Rare earths concentrations were normalized to NASC (North American Shale Composite) (Piper and Bau, 2013), normalized curves for the three lithologies (organic matter rich-marl layers, chalky clay layers and clay limestone interlayers), which are presented in (Fig. 5a, Fig. 5b and Fig. 5c).

- (i) A relative enrichment of heavy rare earths (HREE) compared to light rare earths (LREE), which is confirmed by (La/Yb) ratio that varies from 0.09 to 0.28.
- (ii) A negative Ce anomaly that varies from 0.05 to 0.44.
- (iii) A significant positive Eu anomaly that is ranged from 2.71 to 5.97. For the samples S6 (3) and S6 (5) which are organic matter rich-marl, the Eu/Eu* ratio was lower than the unity. This fact is explained by the high Sm and Gd concentrations in the sample S6 (3) and only the high Sm concentration in the sample S6 (5) (Fig. 5b).
- (iv) Relative to NASC, organic matter rich-marl layers, chalky clay layers and clay limestone interlayers have high concentrations of Sm, Gd, Ho, and Tm.

Fig. 11: Variation of light REE concentrations versus P2O5 content

Fig. 12: Variation of light REE concentrations versus Sr content

The negative Ce anomaly: Previous studies on the Ce anomalies in old sedimentary rocks (marine authigenic), such as the analyzed samples in the present work, shown that Ce anomaly can be considered as a potential tool to determine the paleo-redox conditions of former marine

ecosystem (Wright, 1987). The Ce anomaly could be explained by a direct Inclusion of Ce from the seawater into the sedimentary deposit under oxic conditions (Sholkovitz, 1994). In oxic environment the excess of Ce in the sedimentary rock, relative to the close rare earths is due to

two successive facts: (i) oxidation of Ce^{3+} to Ce^{4+} , (ii) the Ce^{4+} which is low soluble is included into sediments (De Baar, 1991). While in anoxic (reducing) environment, Ce is depleted and the sediments show a negative anomaly (Quinby-Hunt, 1996). Thus the negative Ce anomaly encountered in our samples confirms that these latter have been deposited under anoxic (Reducing) marine medium.

To better understand the behavior and distribution of rare earths, it is necessary to consider the very complex composition of black shales and the physical and chemical processes that are responsible of the analyzed rare earths spectra. For this, we have plotted correlation curves (Fig. 6, Fig. 7, and Fig. 8), of every rare earth element versus the main organic and inorganic phases constituting our samples, namely, total organic carbon (TOC), carbonates which is the predominant phase, and silicates that obtained (Table 1) using the formula (1) (Durand and Monin, 1980). Likewise correlation curves of these constituting phases between each other were established.

$$\text{Silicates (\%)} = 100 - 1,5 \text{ TOC (\%)} - \text{CaCO}_3 \text{ (\%)} \quad (1)$$

$Eu/Eu^* = Eu_n / (Sm_n \times Gd_n)^{0.5}$; $Ce/Ce^* = Ce_n / (La_n \times Nd_n)^{0.5}$; n: means normalized value

The data analysis (Fig. 6, Fig. 7, and Fig. 8), showed the following observations;

(i) The correlation curves between the rare earths and the organic and inorganic phases are affected by points dispersion. This fact is explained by a possible alteration of sedimentary deposits. This hypothesis is confirmed by the low concentration of some oxides (Al and K).

(ii) Eu, Sm and Tm concentrations are positively correlated with both Carbonate and TOC concentrations. On the contrary, they are negatively correlated with silicates.

(iii) La, Ce, Dy, Ho, Er, Yb, Lu concentrations are positively correlated with silicates fraction and negatively correlated with TOC.

According to the data (Fig. 9a, Fig. 9b), the carbonates are positively correlated with TOC, whereas the silicates are negatively correlated with TOC, which indicate that the organic matter is related to carbonates, predominant mineral fraction of the studied black shales. These carbonates have been chemically precipitated in an anoxic marine medium in the form of calcite. The very high concentration of Chlorine and moderately high concentration of Iodine and Bromine (Table 4) confirm the precipitation of carbonates. Indeed, previous works (Jarousse, 1981; Fakhi et al., 2003) have considered that the deposit of these halogens was due to rapid evaporations, in a marine medium, under high paleosalinity.

In this paleoenvironment, Eu, Sm and Tm, which are correlated with both carbonates and TOC, are trapped in the carbonate/organic matter interface. The negative Ce anomaly, confirms that studied samples have been deposited in a Reducing marine medium. The high concentrations of Sm and Tm could be explained by

competition between carbonate anions and organic molecules for complexing Sm, and Tm.

La, Ce, Dy, Ho, Er, Yb, Lu are characterized by a positive correlation with silicates. For that it is possible to conclude that these REE have been adsorbed from seawater by the surfaces of minerals and/or inorganic colloids such as clay of terrigenous origin.

The positive correlation between SiO_2 and Ce, confirms the deposition of the rare earths (under investigation) in the terrigenous fraction of analyzed sedimentary rocks. Elsewhere, the (Fig. 11 and Fig. 12) show how Sr and phosphates are trapped as well as Ce in the terrigenous fraction.

As a conclusion, Ce as well as La, Dy, Ho, Er, Yb, Lu, have shown a positive correlation with silicates. This correlation can be explained by the adsorption of these REE from seawater onto the surfaces of minerals and/or inorganic colloids such as clay of terrigenous origin. On the contrary, Eu, Sm and Tm, which are positively correlated with carbonates and TOC, have been complexed by both carbonates and organic matter. The negative Ce anomaly makes sure the occurrence of complexation process in a reducing marine medium.

CONCLUSIONS

The geochemical approach of major and trace elements including RRE in the Lamsied-Laâyoune outcrop located in the Tarfaya-Boujdour basin was undertaken after physicochemical characterization of sedimentary deposits. The study showed that sediments of the Lamsied outcrop, which are very rich in organic matter and contain more or less dolomitized carbonates and very low concentrations of clay, are deposited in the marine environment by chemical precipitation. The depletion of terrigenous origin oxides SiO_2 , Al_2O_3 , Fe_2O_3 , and K_2O and the enrichment of oxides formed, essentially, in marine environment CaO , Na_2O and P_2O_5 confirms this hypothesis. The distribution of the trace elements shows that, in general, their contents increase with the increase of the organic matter. It also reveals enrichment in Sr, Cr, S, Ni, V and Zr. These elements are, therefore, mainly associated with the organic matter intimately linked to the mineral part. The enrichment of halogens (Cl, Br and I) can be attributed to the high palaeo-salinity of the marine system which has undergone intense evaporation. The study of the rare earth elements distribution in blackshales showed that Ce as well as La, Dy, Ho, Er, Yb, Lu, which have shown a positive correlation with silicates, have been probably adsorbed from seawater onto the surfaces of minerals and/or inorganic colloids such as clay of terrigenous origin. On the other hand, Eu, Sm and Tm, which are positively correlated with carbonates and TOC, have been complexed by both carbonates and organic matter. The negative Ce anomaly makes sure the occurrence of complexation process in a marine reducing medium. The knowledge of behavior of trace elements and REE in the sedimentary deposits can help to obtain a geological storage of radioactive wastes.

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REFERENCES

- Ait Malek, O., Fakhi, S., El Hadi, H., El Aouidi, S., Laissaoui, A., Ayach, A., Bouih, A., Benmansour, M., Yaakoubi, H., Fait, S., 2017. Study of a Moroccan Clay Siltstone: Physicochemical Characterization and Approach of Their Sorption Properties Using Methylene Blue. *International Journal of Materials and Chemistry* 7(3), 55-62
- Ayach, A., Fakhi, S., Faiz, Z., Bouih, A., Aitmalek, O., Benkdad, A., Benmansour, M., Laissaoui, A., Adjour, M., Elbatal, Y., Vioque, I., Manjon, G., 2017. Adsorption of Methylene Blue on bituminous schists from Tarfaya-Boujdour. *Chemistry International* 3(4), 343-352
- Brijraj, K.D., Birgit-Gaye, Parkash, K., 2008. Geochemistry of Renuka Lake and wetland sediments, Lesser Himalaya (India): implications for source-area weathering, provenance, and tectonic setting. *Environmental Geology* 54, 147-163.
- De Baar, H.J.W., Schijf, J., Byrne, R.H., 1991. Solution chemistry of the rare earth elements in seawater. *European Journal of Solid State and Inorganic Chemistry* 28, 357-373.
- Durand, B., Monin, J.C., 1980. Elemental analysis of kerogens (C, H, O, N, S, Fe). In: Durand B. (Ed.), *Kerogen: insoluble organic matter from sedimentary rocks*. Edition Technip, Paris, 113-142.
- El Aouidi, S., Fakhi, S., Laissaoui, A., AitMalek, O., Benmansour, M., Ayach, A., El Batal, Y., Aadjour, M., Tahri, M., El Yahyaoui, A., Benkdad, A., 2017. Geochemical Characterization of the Black Shale from the AmaFatma Coastal Site in the Southwest of Morocco. *American Journal of Chemistry* 7(5), 153-162.
- EL batal, Y., 2014. Le potentiel pétrolier du bassin méso-cénozoïque Tarfaya-Boujdour : Caractérisation sédimentologique, lithostratigraphique, géophysique et géochimique de la roche mère d'âge Crétacé supérieur. Thèse de Doctorat en géologie, Faculté des Sciences Ben M'sik, Université hassan II de Casablanca, Maroc.
- El Harti, M., 2014. Contribution à la Valorisation des Schistes Bitumineux Marocains de Timahdit: Activation et application dans l'élimination des métaux stables, radioactifs et des bactéries. Thèse de Doctorat en chimie, Faculté des Sciences Ben M'sik, Université Hassan II de Casablanca, Maroc.
- Fakhi, S., Aadjour, M., Feddan, B., Khouya, E.H., Andres, Y., Abbe, J.C., Bandombele, M.M., 2003. Approche géochimique élémentaire des dépôts sédimentaires du bassin d'essaouira-doukkala : tentative de corrélation entre l'uranium et la présence de la matière organique. *Physical and Chemical News* 10, 52-62.
- Galindo, C., Mougin, L., Fakhi, S., Nourreddine, A., Lamghari, A., Hannache, H., 2007. Distribution of naturally occurring radionuclides (U, Th) in timahdit's black shale (morocco). *Journal of Environmental Radioactivity* 92, 41-54.
- Galindo, C., Mougin, L., Nourreddine, A., Fakhi, S., 2006. Study of the partitioning of uranium and thorium in Moroccan black shale. *Czechoslovak Journal of Physics* 56(S4), D49-D54.
- Gebhardt, H., Zorn, I., 2008. Cenomanian ostracods of the Tarfaya upwelling region (Morocco) as palaeoenvironmental indicators, *Revue de Micropaleontology* 51, 273-286.
- Jarousse, J., Moine, B., Sauvin, P., 1981. Etude pétrographique et géochimique des métasédiments évaporitiques du Trias pyrénéen. *Bulletin de la Société Géologique de France* 4, 377-386.
- Khouya, E.H., 2002. Elaboration de nouveaux adsorbants à partir des schistes bitumineux marocains: application au traitement des effluents faiblement contaminés par des radioéléments. Thèse de Doctorat en chimie, Faculté des Sciences Ben M'sik, Université Hassan II de Casablanca Maroc.
- Krauskopf, K.B., 1986. Thorium and rare-earth metals as analogs for actinide elements. *Chemical Geology* 55, 323-335.
- Lewis, F.W., Harwood, L.M., Hudson, M.J., Drew, M.G., Desreux, J.F., Vidick, G., Bouslimani, N., Modolo, G., Wilden, A., Sypula, M., 2011. Highly efficient separation of actinides from lanthanides by a phenanthroline-derived bis-triazine ligand. *Journal of the American Chemical Society* 133, 13093-13102.
- Mejjad, N., Laissaoui, A., El-Hammoumi, O., Benmansour, M., Benbrahim, S., Bounouira, H., Benkdad, A., Bouthir, F.Z., Fekri, A., Bounakhla, M., 2016. Sediment geochronology and geochemical behavior of major and rare earth elements in the Oualidia Lagoon in the western Morocco. *Journal of Radioanalytical and Nuclear Chemistry* 309, 1133-1143
- Nyakairu, G.W.A., Koeberl, C., 2001. Mineralogical and chemical composition and distribution of rare earth elements in clay-rich sediments from central Uganda. *Geochemical Journal* 35, 13-28.
- Oumam, M., Abourriche, A., Adil, A., Hannache, H., Pailler, R., Naslain, R., Birot, M., Puillot, J.P., 2003. Elaboration et caractérisation d'un nouveau matériau adsorbant à partir des schistes bitumineux du Maroc *Annales de Chimie Science des Matériaux* 28, 59-74
- Piper, D.Z., Bau, M., 2013. Normalized Rare Earth Elements in Water, Sediments, and Wine: Identifying Sources and Environmental Redox Conditions. *American Journal of Analytical Chemistry* 4, 69-83.
- Rahali, I., 1985. Notes Service, Ministère des Mines, Département Géologie, Géologie Maroc 30, 51

- Ries, J.B., 2010. Review: geological and experimental evidence for secular variation in seawater Mg/Ca (calcite- aragonite seas) and its effects on marine biological calcification. *Biogeosciences* 7, 2795-2849.
- Sholkovitz, E.R., Landing, W.M., Lewis, B.L., 1994. Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. *Geochimica et Cosmochimica Acta* 58, 1567-1579.
- Wilde, P., Quinby-Hunt, M.S., Erdtmann, B.D., 1996. The whole-rock cerium anomaly: a potential indicator of eustatic sea-level changes in shales of the anoxic facies. *Sedimentary Geology* 101, 43-53.
- Wright, J., Schrader, H., Holser, W.T., 1987. Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. *Geochimica et Cosmochimica Acta* 60, 4631-4644.

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