

The Geochemistry of Rare Earth Elements (REE), Yttrium (Y) and Scandium (Sc) in Some Upper Cretaceous Jordanian Phosphorites

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ABSTRACT

The importance of Rare Earth Elements (REE) in phosphorites had attracted attention in the last few years, since these enriched elements could be subtracted as by product in the fertilizer industry. In addition, their role in depositional environment is well established.

Therefore, thirty seven phosphorite samples from all over Jordan; twelve from SE, fourteen from central and eleven from NW were analyzed for REE and other elements.

The results show that REE are depleted relative to worldwide phosphorites (35.64- 85.23ppm) and have seawater pattern indicating the incorporation from seawater. The depletion increases southwards due to (i) less time for incorporation of the REE at the sea floor, (ii) source rock of REE which is sandstone, (iii) very shallow burial, (iv) slight weathering of phosphorites. Ce shows a negative anomaly increasing northwards indicating more oxic environment.

Y and Sc also are analyzed and treated in this manuscript since Y has similar behavior to REE and Sc lies in the same column at the periodic table.

Other major, minor and trace elements are also studied and will be treated in another article.

KEYWORDS: Jordan, Upper Cretaceous, Phosphorites, REE, Yttrium, Scandium.

1. INTRODUCTION

The importance of Rare Earth Elements (REE) in phosphorites had attracted attention in the last few years since these enriched elements could be subtracted as a by-product in the fertilizers industry. In addition to enrichment factor, another factor is encouraging the extraction, which is the cost factor since mining, beneficiation, processing and completely solubilizing of the REE in phosphorites are already paid.

REE also help in understanding the depositional environment such as depth of deposition, the oxidizing state and the application of geochemistry to problems of ore and mineral genesis and to demonstrate the economic utility of geochemical studies .

REE include the element Lanthanum (La) and the

fourteen elements that follow La in the periodic table (the lanthanides). They form a coherent group, except Ce and Eu that are slightly different in their geochemistry due to their response to oxidation-reduction state of the environment which is reflected in their anomalous behaviour in rock forming processes (De Baar et al., 1985).

Yttrium (Y) has a similar behavior to REE. That is why it is generally treated together with the REE.

Sc, which lies in the same column of the periodic table (III B) but has a lack of similarity in the geochemical behavior is treated within this article but separated from Y and REE.

The ionic radii of the REE³⁺ which range from 1.15 Å (La) to 0.93 Å (Lu) are very close to Ca²⁺ (0.99) Å (Sargent – Welsh, 1968), therefore REE substitute for Ca in the apatite structure (McClellan, 1980; Nathan, 1984) and favors solid solution in carbonates (De Baar et al., 1985).

REE were studied in picked grains of Jordanian phosphorites from central and SE Jordan by Abu Murry (1993) and Abed and Abu Murry (1997). This study deals with REE as host rock throughout the Jordanian phosphorites in SE, central and the NW in attempt to find

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out their abundances, economic value as a by-product from the fertilizer industry and to relate the abundances and distributions to depositional environment at the time of phosphogenesis.

2. Sampling and Technique

For chemical analysis, 37 phosphorite samples regardless of their P₂O₅% were chosen from all localities from Jordan. Around 25 grams of each sample were grinded at the Geology Department- University of Jordan by Timma mill for 15-20 minutes to produce particles of 40 ± 20 µm suitable for chemical analysis. The mill was cleaned, using water and glass and dried after the grinding of each sample.

The chemical analysis was done at Vancouver - British Columbia - Canada by ACME analytical laboratories using whole rock ICP-MS technique with very low detection limit.

The rock sample was crushed and pulverized to -100 mesh ASTM (-150 microns), then split to 0.2g and placed in a graphite crucible and a LiBO₂ flux is added. Duplicate splits were used to define homogeneity. Crucibles were placed in an oven and heated to 1025°C for 25 minutes, the molten sample was dissolved in 5% HNO₃ (ACS grade nitric acid diluted in demineralised water). Calibration standards, verification standards and reagent blanks were added to the sample sequence.

The sample solutions were aspirated into an ICP-mass spectrometer (Perkin-Elmer Elan 6000) for the determination of the basic package consisting of the following 34 elements: Ba, Bi, Co, Cs, Ga, Hf, Mo, Nb, Rb, Sb, Sn, Sr, Ta, Th, Tl, U, V, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. A second sample split was used to determine the concentrations of As, Cd, Cu, Ni, Pb, Sc and Zn.

3. Geological Setting

The Phosphorite Formation (PF) in Jordan, forms part of the main Tethyan giant phosphorite belt extending from the Caribbean in the west through North Africa and the Middle East extending to Iran in the east (Notholt *et al.*, 1989; Lucas and Prevot-Lucas, 1995). It lies in the Upper Cretaceous – Maastrichtian (Burdon, 1959; Karam 1967; Bender, 1974; Hamam, 1977; Cappetta *et al.*, 1996) (Table 1) and outcrop along a belt east of the highlands bordering the Dead Sea- Jordan Valley and extending from the NW of the country (Irbed area) through Central Jordan (El-Hasa and El-Abiad) to the SE

of the country (Eshidiya) (Fig. 1).

The thickness of the formation in SE and NW Jordan is 10-15m, while it is around 60m in the center of the country due to the presence of Oyster buildups in the middle of the formation. The thickness of these oyster buildups may exceed 40m (Abed and Sadaqah, 1998).

In NW Jordan, the PF is composed of friable phosphate particles of different sizes, vertebrate bones and teeth. It is highly fossiliferous and detrital quartz is not seen. Intercalations of chert, phosphatic chert limestone and laminated marl are present. As compared to Central and SE Jordan, it is more rich in foraminifera and no bioherm oyster buildups are present here which is a distinct difference, Fig. (2).

In Central Jordan, the PF is composed of marl, phosphatic marl, chalk, chert, limestone, individual phosphate beds that have the same components as NW Jordan and oyster coquina grainstone, boundstone and buildups. Oyster buildups and coquinas are forming 10-40m thick at the middle of the section. The marl is like that in the NW. It is laminated with phosphate lamina which is present as particles of authigenic pristine phosphate and forming the factory of phosphate before reworking and transportation took place to produce individual phosphate beds. Although foraminifera is present, but not as much as NW Jordan.

In SE Jordan, the PF is slightly different from NW and Central Jordan since it is very proximal to Nubian sandstone facies – shorlines. Therefore, quartz sand domain the base of the formation which is 10-15m thick and composed of phosphate particles like those in central and NW Jordan, limestone, dolomite, chert and quartz sand. Oyster buildups and coquinas are present to the north, while stratigraphically equivalent marl is present to the south towards the shorlines. No any type of foraminifera is present in the PF or younger formation which may indicate superhaline in restricted basins during the Maastrichtian (Sadaqah, 2000).

4. Scandium (Sc)

Scandium shows fundamental similarities in its chemistry to REE elements though less than Y (Frondel, 1970) and it is naturally associated with them. Its ionic radius is 0.81 Å which is not far from Ca²⁺ 0.99 Å; therefore it replaces Ca²⁺ in the apatite structure (McClellan, 1980; Nathan, 1984). In inorganic compounds, it is related to Fe³⁺ and Al³⁺ rather than lanthanides. Wagh and Pinnock (1987), argued that Sc

tends to concentrate with REE in secondary aluminum phosphates which may be a significant host for Sc.

In sedimentary rocks, Sc is found in clays and shales and low in carbonates and sandstones. It is high in phosphorites, bauxites and residual deposits together with Nb, Zr, Ga and Ti (Fron del, 1970). It is adsorbed by clays and hydrous Fe³⁺ and Al minerals.

Table (2) shows the concentration of Sc in the Jordanian phosphorites compared with worldwide phosphorites. It is clear that the average of Sc in the Jordanian phosphorites is lower but close to that of worldwide phosphorite. The sample with the maximum Sc (5ppm) at Eshidiya came from a residual layer of phosphatic marl.

The correlation coefficient shows that in NW Jordan Sc is strongly correlated to Fe³⁺, Cr, Ba, Cs, Cu and REE in agreement with the deposition in deeper environment. In central Jordan, it is correlated with Zr ($r=0.61$) indicating its presence as a detrital element. While in SE Jordan, it is very strongly correlated with Al, Fe, Mg, Ti, Cr, Cs, Ga, Hf, Nb, Rb, Zr, and REE where the correlation coefficient exceeds 0.9 for the most of these elements which indicate its presence within the residual phases of clays and other residual minerals in a slightly weathered formation (Huchriede and Wiesmann, 1968; Frondal, 1970; Abed and Abdalla, 1998).

5. REE and Yttrium

5.1 Results

The average concentration of REE and Y are shown in table (3) compared to some other phosphorites along with the range, and standard deviation.

It is clear from table (3) that SE Jordan has the lowest content within a wide range and a coefficient of variation around 1, which indicates relatively a wide dispersion, NW Jordan on the other hand has the intermediate concentration while central Jordan has the highest. The Jordanian phosphorites have remarkably lower abundance of worldwide occurrences (Bone Valley in Florida and Nile Valley), but show similar concentrations to Akashat of Iraq. This is unfortunately discouraging for extracting REE as a by-product from the fertilizer industry particularly from Eshidiya, which is becoming soon the main producing mine.

The correlation coefficients with other elements, illustrate that REE and Y are present in completely different phases in NW, central and SE Jordanian phosphorites. In the NW, REE and Y are significantly

positively correlated with Fe₂O₃, Cr, Ba, Cs, Sn, Th, U, Cu, Ni and definitely with Sc, therefore REE are present with Fe and organic matter since it is excellent with Fe and the elements that have the affinity to organic matter (Elderfield et al., 1981; De Baar et al., 1985), meanwhile REE are weakly but still positive correlated with S and very weak with P₂O₅ in agreement with the interpretation above.

In central Jordan, REE and Y are different in their correlation from NW Jordan, they are significantly positively correlated with Sc, P₂O₅, Na₂O, Sr, Th and U, and weakly correlated with Fe₂O₃ and S and negatively correlated with LOI and C; this confirms REE presence in the apatite phase.

In SE Jordan, REE, Y and Sc are different in their correlation from both NW and central Jordan, and in particular the light REE (LREE) and Intermediate REE (IREE) are strongly significant correlated with Al₂O₃, Fe₂O₃, MgO, and elements in the detrital phase (TiO₂, Cr, Cs, Ca, Hf, Nb, Rb, W, Zr) and with Th, U, Cu, Zn, Ni, negative with S, Na₂O and around zero with P₂O₅. This confirms the presence of REE, Y and Sc with the residual detrital clays and it is proven by the decreasing of REE downwards as mentioned above.

To conclude, REE, Y and Sc in NW Jordan are related to elements which have the affinity to organic matter in a deeper environment. In central Jordan, they are related to the apatite phase in a shallower environment which is interpreted by incorporation to apatite during higher reworking and oxidation of organic matter. In southeast Jordan, where reworking is more intensive, with slight weathering, they are incorporated in detritals.

Table (4) shows the averages of REE, Y and Sc and the total average of REE of the three localities of Jordan under study compared with concentrations of marine phosphorite (Altschuler, 1980), shale of the average of North America, Europe and Russia (Sholkovitz, 1988) and seawater (Hogdahl et al., 1968).

The REE in the three localities in the Jordanian phosphorites follow the well established fact of Oddo-Harkins rule (Odd-even variation) which means that in nature, the concentration of even numbered elements are greater than their odd-numbered neighbors, and the even number decreases when the atomic number increases, the odd-numbered shows the same trend, therefore La is the more abundant and Lu is the rarest (Piper, 1974).

From table (4), it is clear that the higher concentrations are Y>La>Ce and the lowest are Tm~Lu<Tb<Eu. The

Jordanian phosphorites concentrations are confined between the seawater line, which is the lowest, and shale line, which is near the top while worldwide phosphorites, which is the richest, are situated at the top.

The REE abundances for the three studied localities of the Jordanian phosphorite normalized to shale as shown in table (4) are 0.34, 0.42 and 0.17 for NW, central and SE Jordan, respectively. Comparing these figures with those of Abu Murry (1993) and Abed and Abu Murry (1997), it is clear that values in this work are much lower. Their study shows that they are 1.13 for Eshidiya and 2.3 for central Jordan normalized to shale. It is worth mentioning that their analysis was for picked phosphate grains, whereas the analysis in this study is for whole rock samples. However, both works are in agreement in the trend that it is lower at Eshidiya and higher at central Jordan.

McArthur and Walsh (1984) concluded (table 5) that the offshore phosphorites have a normalized relation less than 1 compared to more than 1 for onshore phosphorites. The normalized ratios in this work are < 1 in all the three locations. This puts the Jordanian phosphorites of this work in an offshore environment. It is worth mentioning that Abed and Abu Murry (1997) ratios are all > 1 which classifies the Jordanian phosphorites onshore. A conclusion in contradiction with McArthur and Walsh (1984) is actually because Jordanian phosphorites are deposited in the epeiric southern shelf of the Tethys (Abed, 1989; 1994; Abed and Sadaqah, 1998; Steinitz, 1977; Bandel and Mikbel, 1985; Soudry et al., 1985).

The very low abundance at Eshidiya is easily interpreted by the high influx of detrital quartz from the proximal Arabian-Nubian sandstone near the southern shorelines of the Tethys. Haskin et al. (1966) and El-Kammar et al. (1979) interpreted the low content of REE in phosphorites as due to initial source rocks, where sandstones which are low in REE content are the pre-existing REE bearing rocks. The low ratios in central and NW Jordan may be due to low concentration of REE elements in this part of the Tethys who supported the REE by upwelling since there is a complete agreement with the low abundance of Iraqi peloids and bioclasts phosphorites which are less than 1 for each element (AbaHussain et al., 1987). Even the age seems to be not a controlling factor for the concentration of REE disagreeing with McArthur and Walsh (1984).

5.2. Normalizing and Data Show

Shales are the most abundant sediments in the earth

crust, therefore they are commonly used as standards for normalization to reflect enrichment, depletion average marine relationship in phosphorites. Shales, which are used in this study, are those used by Sholkovitz (1988), which are the average of North America, Europe and Russia shales.

Normalizing of REE in phosphorite sample means the division of the concentration of each element in the sample by the same element in the reference shale (Table 4). The results are plotted graphically as the logarithm of the normalized abundance versus atomic number of REE.

Fig 3 to 5 illustrate the REE shale-normalized pattern of NW, central and SE Jordan phosphorites, respectively. Fig. (6) illustrates the REE shale-normalized pattern of the whole Jordan phosphorites compared with worldwide phosphorites (Altschuler, 1980) and seawater (Hogdahl et al., 1968). The normalized pattern shows that:

- 1- REE of the Jordanian phosphorite plot between seawater and worldwide phosphorites.
- 2- The pattern exactly mimics the seawater pattern indicating the seawater signatures.
- 3- The heavy REE (HREE) are enriched relative to light REE (LREE) in NW and central Jordan. $\Sigma\text{LREE} / \Sigma\text{HREE}$ in NW Jordan phosphorites is 2.88, in central Jordan 4.18 and in the SE it is 4.86. In the worldwide phosphorites it is 4.83 (Altschuler, 1980).
- 4- The trend of enrichment of HREE northwards may indicate the trend of depth of deposition since HREE are enriched in deeper seawater.
- 5- A negative Ce anomaly that means the deficiency of Ce due to oxidation and partial precipitation state in the three localities. It is the highest in NW Jordan (deeper environment).
- 6- It is clear from Fig. (3) for NW Jordan, that the abundances of REE in the three sections increase upwards (the samples are labeled ascending upwards) indicating increase of depth. At the same time the negative Ce anomaly also increases. The Ziglab sample which represents the deepest occurrence in NW Jordan as indicated from the lithology and microfacies, shows higher abundance and higher negative Ce anomaly. The variation of abundances between the sections is due to local depth of basins.
- 7- In central Jordan as seen from Fig. (4), the abundances of REE increase upwards when the transgression of lower Maastrichtian took place and the seawater became deeper. Later on when the progradation of oyster buildups grew up, the sea

became shallower and the REE abundances decrease at the top of the section in the Phosphorite Unit. Sample W19 in Wadi El-Hasa represents approximately the middle Campanian and has higher abundances. Sample W52 represents the contact of the Phosphorite Unit with the Chalk-marl Unit which is deposited when the transgression of Upper Maastrichtian – Lower Paleocene took place, therefore, it has higher REE abundance and higher negative Ce anomaly. Otherwise, the section shows no difference from those of Sultani and Hafira.

- 8- SE Jordan Phosphorites (Fig. 5), show the lower abundance of REE in Jordan as well as depletion of HREE relative to LREE and lower negative Ce anomaly compared with NW and central Jordan. This could be due to the very shallow depositional environment which was proximal to the Nubian sandstones and/or to the slight weathering (Abed and Abdalla, 1998). The two samples that came from the north of Eshidiya (deeper environment) show higher negative Ce anomaly.
- 9- According to McArthur and Walsh (1984), and as clear from Fig. (6) all the Jordanian phosphorites are of the type of seawater with a negative Ce anomaly gained their REE under oxic conditions, since they are mostly of carbonate, pelletal and onshore origin and where incorporation of REE happened directly from seawater or pore water after early burial diagenesis from REE carriers. The carriers are Fe oxihydroxides (Elderfield et al., 1981), biogenic silica and biogenic carbonates, where REE are very strong correlated to Fe (See above) in NW Jordan.

No Eu anomaly is present in the Jordanian phosphorites, confirming the none reducing environment of deposition because Eu^{3+} is reduced in strong reducing environment to Eu^{2+} and is incorporated with Ba in barite since they have similar ionic radius (Shannon, 1976 ; De Baar et al., 1985).

5.3. Cerium Anomaly

Ce and Eu may fractionate from other REE by oxidation of Ce^{3+} to Ce^{4+} and reduction of Eu^{3+} to Eu^{2+} in suitable environment (De Baar et al., 1985). Due to this oxidation - reduction state Ce becomes fractionated and makes complexation with CO_3 and coatings around biological tests such as foraminifera and Fe, Mn or both and is partially removed from seawater (Sholkovitz et al., 1994). Therefore phosphorites with negative Ce anomaly

form under oxic conditions (Goldberg, 1961; Piper, 1974; Elderfield and Greeves, 1982; McArthur and Walsh, 1984), while phosphorites formed under reducing environment should show no or positive Ce anomaly (McArthur and Walsh, 1984).

Shales and shale patterns do not show any Ce anomaly if fractionation happens under reducing conditions (Goldberg, 1961; piper, 1974; Elderfield and Greeves, 1982).

In seawater, Ce is more depleted at greater depth. The depletion in the Pacific Ocean is from about two folds at 200m to 25 folds at 3250m relative to shale; at the Atlantic the depletion of Ce is doubled due to oxidation state (De Baar et al., 1985). In other words, Ce is removed from seawater rapidly rather than other REE due to oxidation to a tetravalent state, that is less soluble in seawater than other trivalent REE (Elderfield and Greeves, 1982; De Baar et al., 1985). Thus, deep seawater shows a negative Ce anomaly. Consequently, phosphorites which gain their REE from seawater, show the same anomaly of Ce.

McArthur and Walsh (1984) had developed an equation to find out the magnitude of Ce anomaly, which may reflect the depositional environment. This equation is

$$Ce\ anomaly = \left[\log \frac{Ce_n}{(La_n + Nd_n)} \right]$$

Where n = shale normalized concentration.

By application of this equation, Ce anomaly was calculated for the three localities in Jordan. The results are presented with previous studies and other localities in table 6. The table illustrates that the Ce anomaly in the Jordanian phosphorites is less than -0.1, which means that these phosphorites were formed under oxidizing environment during their phosphogenesis.

The Ce anomaly is -0.21, -0.33 and -0.55 for SE, central and NW Jordanian phosphorites, respectively, which means that Ce anomaly is increasing northwards which in turn means that the depth is increasing in the same direction (McArthur and Walsh, 1984; Abed and Abu Murry, 1997). The oxidizing conditions seem to be more pronounced northwards. This is also confirmed by the presence of shale intercalations with phosphorite at El Hasa and north of Eshidiya mine and the lack of any type of fauna above the phosphorite layers at Eshidiya Mine. This trend of increasing Ce anomaly is in agreement with the results obtained by Abed and Abu Murry (1997)

though less pronounced.

This interpretation agrees with the major factor that played a main role in the phosphogenesis of the Tethys province in the Upper Cretaceous. It is the upwelling where deep cold water blew from ENE to the epeiric sea in WSW (Sheldon, 1987; Kolodny and Garrison, 1994). Consequently, a stronger negative Ce anomaly is found in the north compared to the south (De Baar et al., 1985; Abed and Abu Murry, 1997).

6. Discussion and Conclusion of REE

REE are fractionated in seawater and this is reflected on seafloor sediments. Fractionation is the relative change of in solution or particle composition for a group of trace elements due to geochemical reaction. The relative affinity of REE for complexations and adsorption is a fundamental feature of their chemistry and is responsible for their main chemistry. Fractionation of REE in seawater leads to positive anomaly and enrichment of LREE/HREE below 150m (Sholkovitz et al., 1994). This is interpreted as being controlled by biogeochemical cycle (Elderfield and Greeves, 1982; De Baar et al., 1985; Elderfield, 1988; Bertran and Elderfield, 1993).

The role of the biogeochemical cycle of skeletal material comes from two mechanisms. Firstly, the incorporation of REE cations within the crystal lattice of CaCO_3 or opal. Secondly, adsorption on surface or surface coatings of settling shells. In the two mechanisms, shells and skeletons work as REE carriers, then the REE are released and adsorbed on exposed surfaces mainly ferromanganese and phosphate debris and at the end they became enriched with REE (De Baar et al., 1985).

The removal of REE from the ocean is dominated by adsorption on settling particles, LREE are more rapidly scavenged by these particles than HREE and adsorbed at authigenic sediments (De Baar et al., 1985). Post depositional diagenesis would lead to further REE fractionation and redistribution, probably in favor of phases rich in iron or phosphorites (Elderfield et al., 1981).

McArthur and Walsh (1984) had reached to a conclusion that, at the beginning of formation of francolites, the abundance of REE is very low and it is increased and incorporated post depositional during diagenesis and catagenesis by sources from:

(1) Pore water; (2) migrating formation water; and (3) groundwater. Therefore, the abundance of REE is controlled by:

- (1) Location where onshore francolites have more concentration than offshore francolites.
- (2) Type of particles, where peloids, which have the higher surface, is more enriched in REE than other grains.
- (3) Age, where REE increase with age (Slansky, 1986).
- (4) Condensation: It is believed that the longer time that the sediments stay at the seafloor with very limited amount of terrigenous supply, the more REE become incorporated in francolite or associated clays, iron oxides or organic matter.

McArthur and Walsh (1984) had argued that, weathering, burial diagenesis and metamorphism may affect the abundances and patterns of REE, and weathering removes REE with LREE more than HREE. Balashov and Khitrov (1967) had confirmed a preferential removal of HREE by Volga river water. Ronov et al. (1967), had found that weathering products depend on mineralogical and chemical composition of primary rocks and physiochemical conditions of weathering environment and had used the ratio:

$$\frac{\sum \text{ppm La} - \text{Eu}}{\sum \text{ppm Gd} - \text{Lu}, Y}$$

to show the effect of weathering and the REE patterns and reach a conclusion that there is an increase of HREE from continent to near shore marine water.

Using the simple ratio $\Sigma\text{LREE}/\Sigma\text{HREE}$ in the Jordanian phosphorites, the results are 4.86, 4.18 and 2.88 for SE, central and NW Jordan, respectively, indicating the depletion of HREE at Eshidiya which means that they are leached either from phosphorites or associated detrital materials, and increase of these HREE in NW Jordan which means the environment of deposition is deeper (De Baar et al., 1985; Sholkovitz, 1988; Sholkovitz et al., 1994). To support this conclusion, the analysis of clean phosphate grains is recommended, which will be a future programme for this investigation.

Panczer et al. (1989) concluded that the low content of REE in some early Maastrichtian phosphorite nodules at the contact between Mishash and Ghareb formation in Negev are due to weathering and found that the REE of phosphorites are related to clay phase in spite of the low content of these clays.

In summary, regarding REE abundances in the Jordanian phosphorites the following conclusions can be drawn:

- 1- The concentration of REE in the Jordanian

phosphorites are not so high; 69.37 ppm for NW, 85.23 ppm for central and 35.64 ppm for SE Jordan, which is not so far from their concentration in the Iraqi picked grains phosphorites.

- 2- Consequently, the shale - normalized abundances are 0.34 for NW, 0.42 for central and 0.17 for SE Jordan which are also not so far from the iraqi picked phosphorites. This may put them in offshore depositional environment, but this is not the case and the depletion is postulated to be due to their depletion in this part of the Tethys which supported the epeiric shelf by upwelling and before that to the initial source rocks of sandstones and granitic rocks (Haskin et al., 1966; El-Kammar et al., 1979).
- 3- The depletion of REE at Eshidiya is due to the following factors, since it is situated very proximal to the southern shorelines of the Tethys and the bordering of Nubian Sandstones to the south. Less time for incorporation of the REE at the seafloor due to sea level fluctuations; the source rocks of REE, which are sandstones; very shallow burial; slight weathering of phosphorites.
- 4- The Jordanian phosphorites have a negative Ce anomaly like that of seawater pattern of REE, this shows that they are deposited under oxidizing conditions deepening northwards and increase

oxidizing in the same direction.

- 5- The less negative Ce anomaly at Eshidiya (-0.21) and central Jordan (-0.33) indicate a less oxidizing depositional conditions, which is proved by the intercalations of shale at El-Hasa and north of Eshidiya which supported the local basins of phosphate accumulations.
- 6- Higher negative Ce anomaly in NW Jordan is also related to proximity of the Tethys to the north where intense upwelling occurred.
- 7- The higher depletion of HREE at Eshidiya indicate shallower environment of deposition and/or weathering.
- 8- REE and Y in the Jordanian phosphorites are correlated to and present in different phases in the three localities:
In NW Jordan, they are present mainly with oxyhydroxides and organic matter, in central Jordan with apatite and in SE Jordan with associated detrital clay.
- 9- The low concentration of REE is not promising for their extraction as a by-product.

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Table (1): The stratigraphical position of the Jordanian phosphorites.

Series Epoch	Stage	Formation-Member <i>El-Hiyari (1985), Powell (1989)</i>		Unit - Member <i>Bender(1974)</i>	Group - Formation <i>Burdon (1959), Masri (1963)</i>			
Early Paleogene	Paleocene	Muwaqqar Chalk-Marl		Chalk-Marl		Muwaqqar	B3	
Upper Cretaceous	Maastrichtian	Al-Hisa Phosphorite	Qatrana Phosphorite	Phosphorite	Belqa Group	Amman	B2b	
			Bahiyah Coquina					
			Sultani Phosphorite					
	Campanian	Amman silicified limestone	Mutarammil Coquina					Silicified Limestone
	Coniacian	Ghudran	Dhiban Chalk	Massive		Ghudran	B1	
			Tafila					
			Mujib Chalk					
Turonian	Wadi Sir		Limestone	Ajlun Group	Wadi Sir	A7		
Cenomanian	Shuaib		Echinoidal Limestone		Shueib	A5-A6		
	Hummar		Limestone		Hummar	A4		
	Fuhais		Nodular Limestone		Fuhais	A3		
	Naur		Limestone		Naur	A1-A2		
Lower Cretaceous	Kurnub (Hathira) Sandstone Group							

Table 2: Sc content in the Jordanian phosphorites compared to worldwide phosphorites and Florida (ppm).

Locality	Range	Mean	St.Dev.	Reference
NW Jordan	1-4	1.73	1.01	This study
Central Jordan	1-2	1.50	0.52	This study
SE Jordan	1-5	1.67	1.15	This study
Whole Jordan	1-5	1.62	0.89	This study
Average Phosphorites	0.3-5.8	2.0		Altschuler (1980)
Bone Valley (Florida)	2-6	3		Altschuler et al. (1967)

Table 3: REE and Y content in the Jordanian phosphorites compared to some other phosphorite in ppm.

Location	REE			Y			Reference
	Range	Mean	St.Dev.	Range	Mean	St.Dev.	
NW Jordan	24.51-149.91	69.37	39.65	21.8-122	57.25	33.55	This study
Central Jordan	30.21-160.31	85.23	39.89	15.4-84.8	47.41	21.97	This study
SE Jordan	9.37-122.65	35.64	32.98	2.9-45.2	16.53	11.54	This study
Whole Jordan	9.37-160.31	64.43	42.38	2.9-122	40.32	28.69	This study
Whole Jordan*	45.23-450.6	274.43	24.66	56.38-395	192		Abed and Abu Murry (1997), Abu Murry (1993)
Worldwide Phos.	77-860	461			275		Altschuler (1980)
Akashat Iraq**	66.2-162.6			31.4-114.4			AbaHussain et al. (1980)
Nile Valley	128-691				210		El-Kammar et al. (1979)
Bone Valley (Florida)	261-640	476		50-160	110		Altschuler et al. (1967)

* Without Eu, Gd, Tm and Yb.

** Without Tb and Tm.

Table 5: REE abundance in the Jordanian phosphorites and other localities normalized to shale (After McArthur and Walsh 1984).

Location	Phos.Type	Relative Abundance	Age
OFFSHORE (Mc Arthur and Walsh 1984)			
Namibia Contin. Margin	Concretion	0.02-0.03	Pliocene-Recent
Morocco contin. Margin	Nodules	0.2-0.1	L.Cretac. - Eocene
Peru Sechura Desert	Pelletal	0.1-0.9	Miocene
ONSHORE (Mc Arthur and Walsh 1984)			
South Africa, Cape province	Pelletal	2	L.Mioc. - E. Plioc.
Phosphoria Formation	Pelletal	3-6	Permian
Morocco	Pelletal	3	L.Cretac. - Eocene
JORDAN (Abed and Abu Murry 1997)			
Eshidiya	Pelletal	1.13	Maastrichtian
Central	Pelletal	2.3	Maastrichtian
Rusaifa	Pelletal	3	Maastrichtian
JORDAN/ this study			
NW	Missila.grains	0.34	Maastrichtian
Central	missila. grains	0.42	Maastrichtian
SE	Missila. grains	0.17	Maastrichtian

Table 6: Ce anomaly compared to previous studies and other localities with oxidation-reduction environment after McArthur and Walsh (1984).

Location	Ce anomaly	OX-Redu.
Agulhas Bank; Miocene	-0.2	
Chatham Rise	-0.4	Oxidizing
Morocco; continental shelf	-0.4	
Namibia; continental margin concretions	-0.2	< -0.1
Blake plateau	-0.7	
Phosphoria Formation USA	-0.9	
Peru chile continental shelf	-0.05	Reducing
Namibia continental margin pelletal	-0.03	>-0.1
South Africa Cape province	-0.03	
SE Jordan (Abed and Abu Murry 1997)	-0.82	
Central Jordan (Abed and Abu Murry 1997)	-1.10	Oxidizing
Rusaifa (Abed and Abu Murry 1997)	-0.97	
SE Jordan (This study)	-0.21	< -0.1
Central Jordan (This study)	-0.33	
NW Jordan (This study)	-0.55	

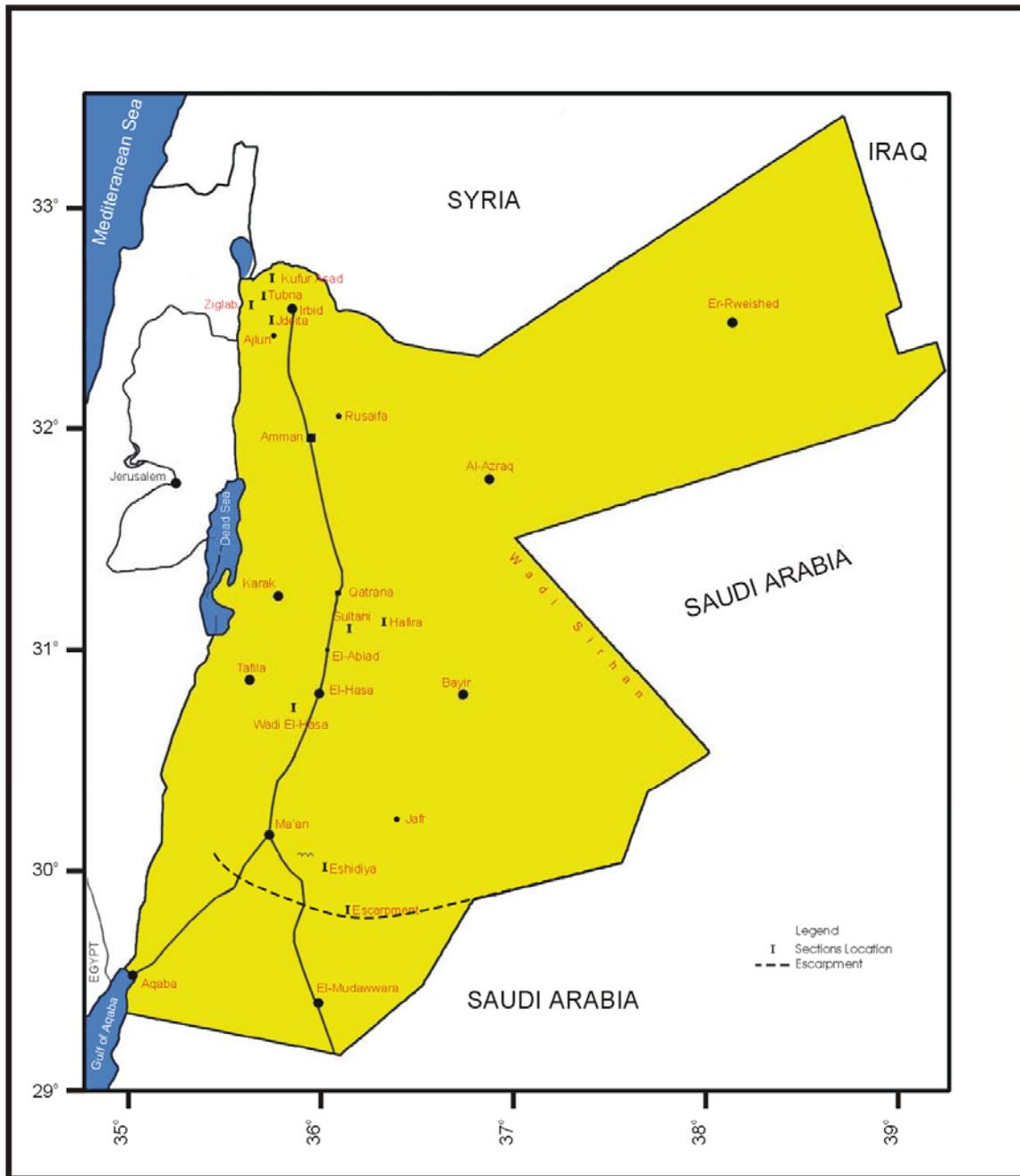


Figure (1) Location map of studied areas and sections.

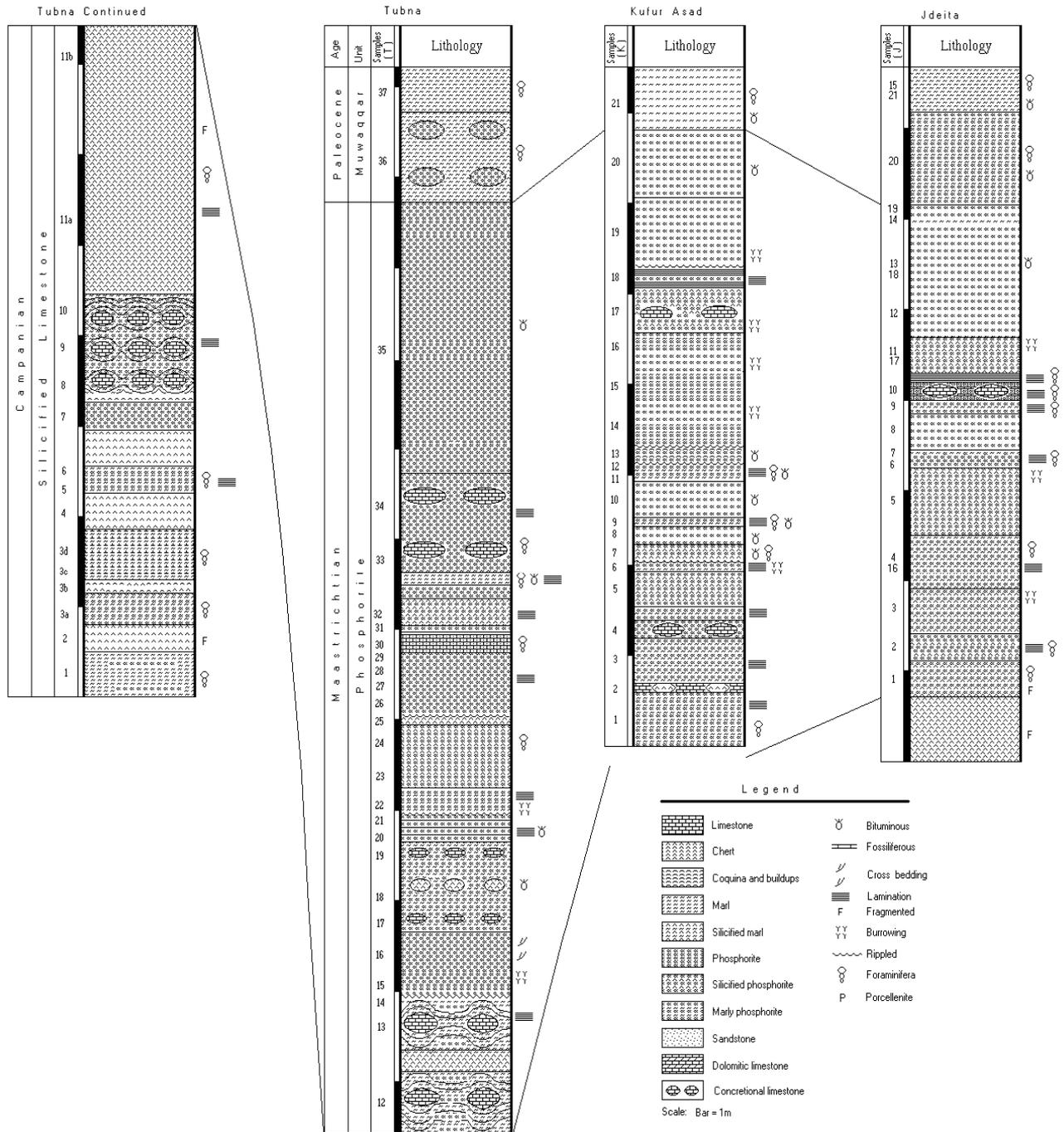


Fig (2): Columnar Sections of the Phosphorite Unit, NW Jordan.

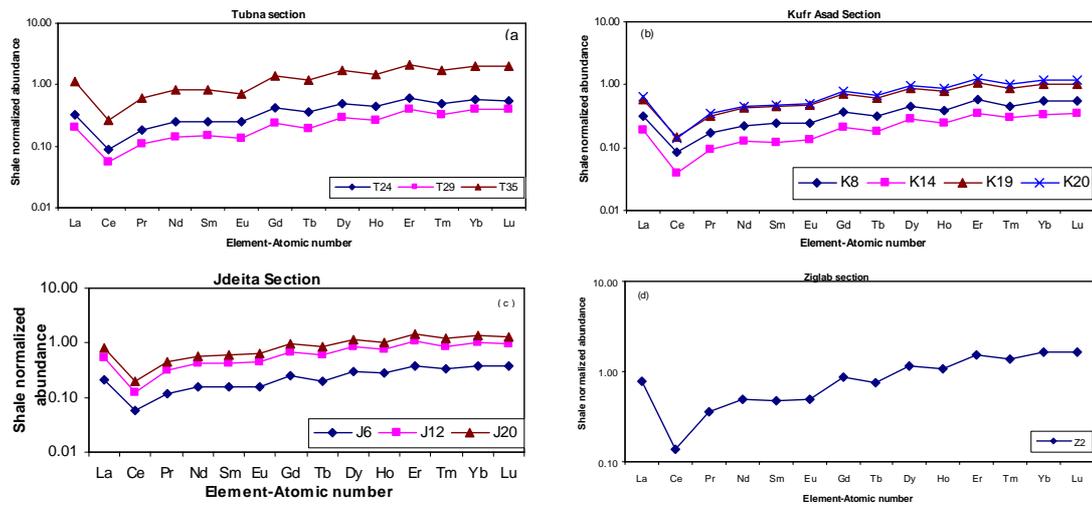


Fig (3):Shale normalized REE of NW Jordan: (a) Tubna section. (b) Kufr Asad section. (c) Jdeita section. (d) Ziglab section.

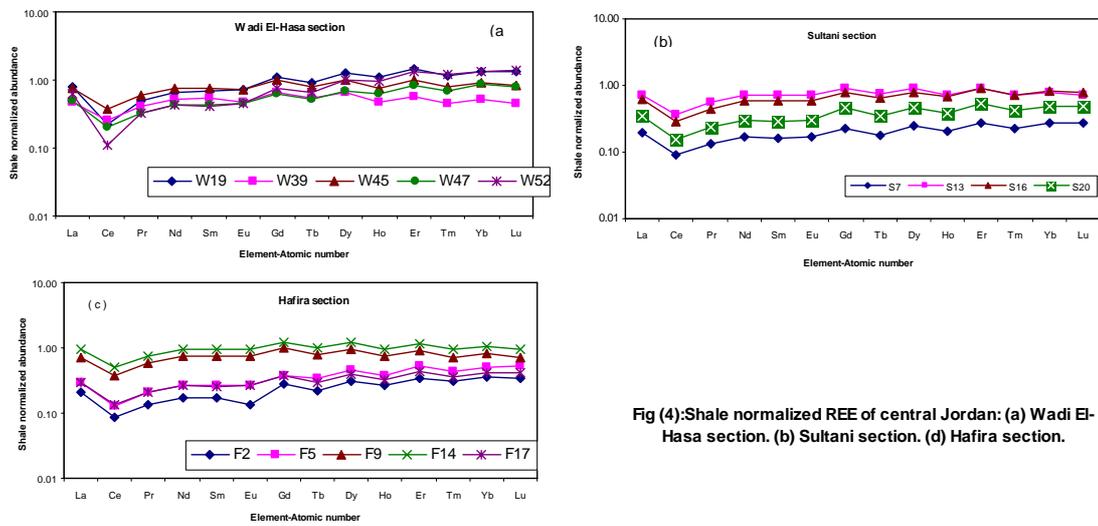


Fig (4):Shale normalized REE of central Jordan: (a) Wadi El-Hasa section. (b) Sultani section. (d) Hafira section.

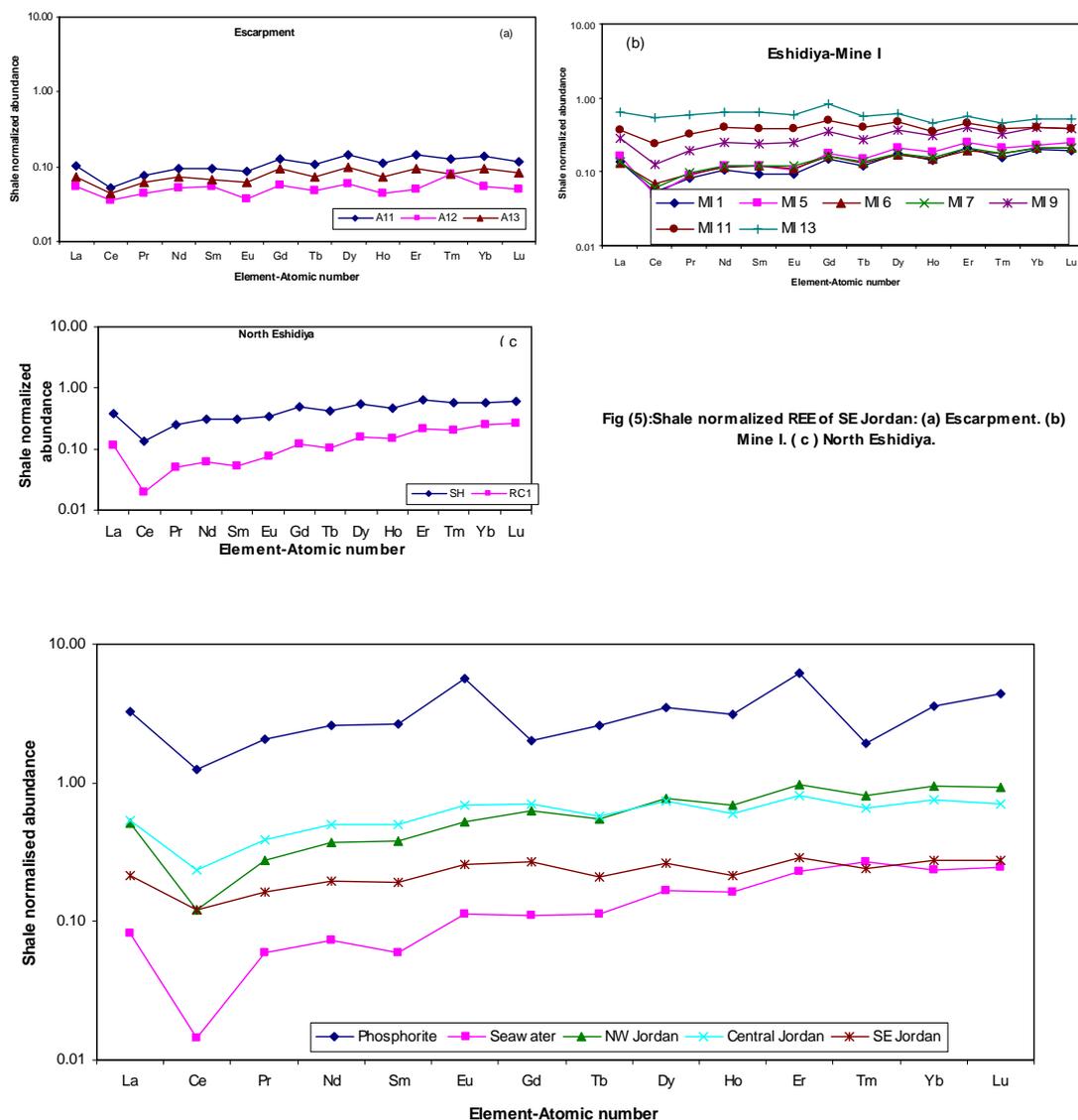


Fig (5):Shale normalized REE of SE Jordan: (a) Escarpment. (b) Mine I. (c) North Eshidiya.

Fig (6): shale normalized REE of NW, central and SE Jordan Phosphorite pattern compared to worldwide phosphorites and seawater pattern.

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