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Rare Earth Element Geochemistry of the Jordanian Upper Cretaceous Phosphorites

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ABSTRACT. A total of thirty-five samples of the economic grade Jordanian Upper Cretaceous phosphorites were analysed for certain major and rare earth elements (REE) with an overall objective of understanding phosphogenesis conditions. These samples represent pelletal (granular) phosphorites with traces of carbonates and marl. The deposits are of shallow subtidal environment of authigenic nature. The relative abundance of REE normalised to shale standard is indicative of proximal to onshore phosphorites. The distribution patterns of the REE show a depletion in cerium (Ce) and light REE (LREE) and enrichment in the heavy REE (HREE), indicating marine depositional environment. The highly negative Ce anomalies of these samples indicate phosphogensis under oxic marine condition which are interpreted as a signature of deep cold upwelling seawater on shallow epeiric shelf, cleanliness of these deposits from clay minerals and to the very limited diagenetic processes affecting them after deposition.

Rare earth element (REE) distribution in sea water and sediments has received an increased attention in recent years. The geochemical behavior of REE and subsequently their fractionation are governed by a number of factors including: terrigenous input, biological activities and particle-water interaction (Sholkovitz 1988, Lee and Byrne 1993, Bertram and Elderfield 1993, Sholkovitz *et al.* 1994). It has been well established that ocean water, and subsequently authigenic marine sediments, in the last 180 million years are characterised by a depletion in light REE

(LREE), a negative Ce anomaly and an enrichment in heavy REE (HREE) (Piper 1974, Wang *et al.* 1986). Also, deeper and more isolated ocean waters are higher in REE concentration relative to surface water (Elderfield and Grieves 1982, De Baar *et al.* 1985).

REE in marine phosphorites, and other authigenic sediments, were discussed by various authors (Semenov *et al.* 1962, Altschuler 1980, McArthur and Walsh 1984, Wang *et al.* 1986, Piper *et al.* 1988). It has been shown that the distribution patterns of REE in phosphorites are in general agreement with oceanic waters. However, phosphorites are relatively highly enriched in REE compared with most of other authigenic sediments. Due to this distinctive distribution pattern and because phosphorites are not subject to extensive diagenesis after deposition, their REE behavior is investigated to shed some light on the depositional environments (McArthur and Walsh 1984, Grandjean and Albarede 1989, Grandjean *et al.* 1993, Wright *et al.* 1987).

More recently, REE of biogenic apatite was the subject of detailed investigations in an attempt to use them as paleochemical indicators for ancient ocean water (Wright *et al.* 1987, Grandjean and Albarede 1989, Grandjean *et al.* 1993). The general view here is that minor or no changes have happened to these allochemes after their early phosphogenesis and thus, they can be used in this respect to predict paleooceanic chemistry. The overall objective of this paper is to evaluate the geochemical behavior of the REE in the Jordanian phosphorites in relation to environmental conditions at the time of phosphogenesis.

Geological Setting

Phosphorites are widely spread in Jordan. They form an important part of the Upper Cretaceous-Eocene Tethyan phosphorite province which includes the giant deposits of the Levant and North Africa (Sheldon 1987). High grade deposits are found at four localities (Fig. 1, Table 1). These are: northwestern Jordan, Ruseifa, central Jordan (Al-Abiad and Al-Hasa) and Esh-Shidiya in southern Jordan. Proven reserves are in excess of one billion tons.

They are of Middle Maastrichtian, topmost Upper Cretaceous. They form the upper part of the Amman Formation or the Phosphorite Unit of Bender (1974), Table 1.

A total of thirty five samples representing the economic grade phosphorites of Ruseifa (4 samples), Central Jordan (17 samples) and Esh-Shidiya (14 samples)

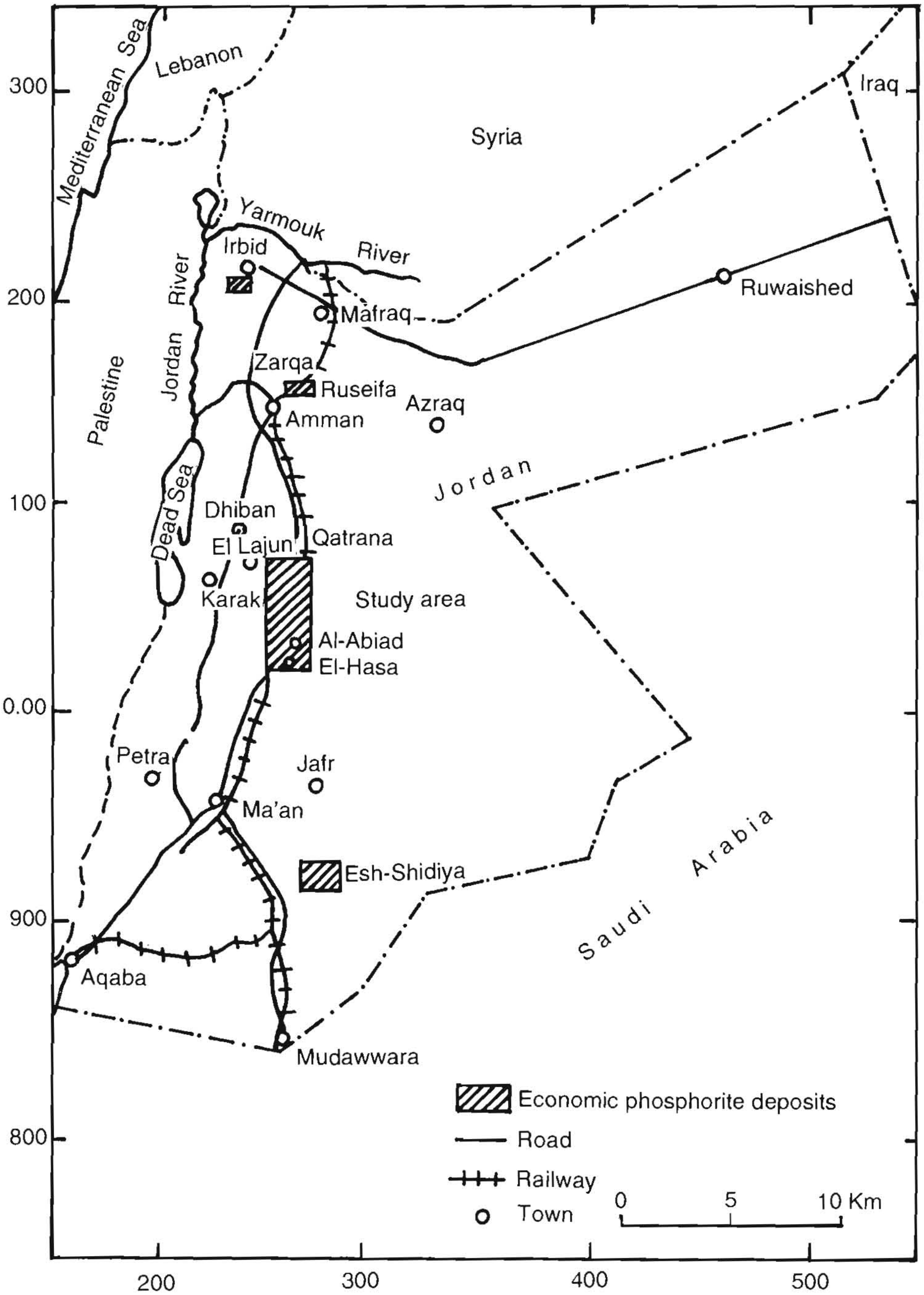

Fig. 1. Location map of the studied phosphorite deposits.

were selected for this study (Table 2 and Fig. 2). All samples are pelletal (granular) phosphorites. Allochemical particles are vertebrate skeletal fragments, intraclasts and pellets (Abed and Al-Agha 1989). The samples are all friable with virtually no cement.

Table 1. The Stratigraphical Position of the Jordanian Phosphorite and their thicknesses in East Central Jordan

Series	Stage	Members (Bender 1974)	Formations (Masri 1963)		Thickness (m)
Early Paleocene	Paleocene	Chalk-Marl	Muwaggar	B_3	300
Late Cretaceous	Maastrichtian	Phosphorite	Amman	B_{2b}	120
	Campanian				
	Santonian	Silicified Limestone		B_{2a}	
	Coniacian	Massive Limestone	Ghudran	B_1	30
			Wadi Sir	A_7	100
	Turonian	Echinoidal Limestone	Shueib	A_{5-6}	110
	Cenomanian		Hummar	A_4	
		Nodular Limestone	Fuhais	A_3	
			Naur	A_{1-2}	130
Early Cretaceous	Kurnub (Hathira) Sandstone				250

Techniques

Ten grammes of sample were treated with aqua regia and heated to complete dryness. The resultant was then dissolved with 0.1 HC1 and filtrated. For separation of REE, the filtrate was treated in a column with the ion exchanger Dowex 50 WXB, mesh 200-400 (Walsh *et al.* 1981, Crock *et al.* 1984). REE were determined using inductively coupled plasma (ICP). Certain major elements were analysed in the same sample powder by X-ray fluorescence (XRF) technique. In addition all samples were examined by X-ray diffractometry (XRD) for their mineralogical composition.

Results

Table 3 shows the mean, range and standard deviation for the major elements in the 35 analysed samples while Table 4 shows the chemical analysis of the REE. Figs. 3, 4 and 5 show the REE distribution patterns in the studied samples of Ruseifa, central Jordan and Esh-Shidiya, respectively, compared with the patterns of sea water and shale as established by other workers (Piper 1974, Sholkovitz *et al.* 1994).

Mineralogy and Geochemistry

Previous studies on the geochemistry and mineralogy of the Jordanian phosphorites were carried out in the past two decades (*c.f.*, Khaled and Abed 1982, Abed and Al-Agha 1989, Abed and Fakhouri 1996). The following is a short review of our knowledge about their mineralogy and geochemistry.

Apatite (francolite or carbonate fluorapatite) is the dominant constituent of the grade phosphorites. It is in excess of 76% (francolite = P205 x 2.75, Table 3). Calcite is around 2% on average and reaches up to 15% in Ruseifa due to the presence of some marls admixed with the phosphorites. Dolomite is not present in the studied samples and the average 0.33% MgO is mainly within the clay phase (r with $A1_2O_3 = 0.84$).

Silica makes about 10% of the studied samples which is essentially free silica or quartz. In Esh-Shidiya (the extreme SE Jordan, Fig. 1), and in particular the lowest phosphorite layer (A3) in Fig. 2, is certainly of detrital origin derived from the Arabian-Nubian sandstone continent (Khaled and Abed 1982). However, minor amounts of silica is combined in the very low clay content (mean $A1_2O_3 = 0.67\%$). The encountered clay minerals are illite/smectite mixed layers, kaolinite and small amounts of palygorskite in the Esh-Shidiya (Al-Hawari 1986, Abed *et al.* 1992).

Iron, which is an important element in the geochemistry of REE, seems to be completely incorporated (either adsorbed or within the structure) in the clay phase (r with $A1_2O_3 = 0.91$).

Table 2. The distribution of the studied samples

Location	Site	Bed No.	Sample No.	Location	Orebody	Horizon	Sample No.
Shidiya [Western Orebody]	Trial Cut No. 1 (TC1)	A0	1	El-Hasa	1	L	15
		A1-D	2		2	U	16
		A1-B	3		4	U	17
		A2	4		5	M	18
					9	U	19
	Trial Cut No. 2 (TC2)	A0	5		11	U	20
		A1-D	6		12	U	21
		A1-B	7		13N	U	22
		A2	8		13S	U	23
		A3	9		17	U	24
	Box Cut	A0	10		20	L	25
		A1-D	11		26	U	26
		A1-B	12	El-Abiad	3	U	27
		A2	13		6	U	28
		A3	14		7	U	29
Ruseifa	Zarqa-A Z-2	IV	32		10	U	30
		III	33		24	L	31
		II	34				
		I	35				

U = Upper M = Middle L = Lower

Table 3. Mean, range and standard deviation for the major elements in the studied Jordanian phosphorites

	Mean %	Range %	Std. Dev.
SiO_2	9.50	0.88 – 26.23	5.91
TiO_2	0.04	0.02 – 0.08	0.017
Al_2O_3	0.67	0.08 – 2.12	0.55
Fe_2O_3	0.25	0.07 – 0.72	0.17
MgO	0.33	0.18 – 0.61	0.12
CaO	47.50	33.90 – 53.90	4.09
Na_2O	0.51	0.03 – 1.59	0.34
K_2O	0.06	0.01 – 0.18	0.037
P_2O_5	31.09	27.09 – 34.34	2.35
SO_3	0.91	0.32 – 1.95	0.36
F	3.68	2.68 – 4.38	0.41
CO_2	4.57	2.39 – 11.14	1.58

Table 4. Rare earth element content (ppm) in the studied phosphorites

	La	Ce	Pr	Nd	Sm	Tb	Dy	Ho	Er	Lu	Total
1	79	40	3.2	60.7	13.6	2.0	9.1	2.4	12.0	0.8	222.7
2	54	35	2.9	41.0	9.5		8.9	2.4	17.6	0.9	172.1
3	51	35	1.5	27.5	5.6	0.6	5.0	1.5	10.2	0.4	138.3
4	97	35	1.4	31.9	5.7	0.7	7.2	1.9	11.6	0.8	193.1
5	88	98	1.7	25.7	6.5		5.2	1.6	10.0	0.8	237.5
6	46	36	6.3	36.5	8.4		7.7	2.2	11.8	1.1	155.9
7	53	37		23.1	5.3		3.7	1.2	11.2		134.5
8	121	41		20.0	5.9		1.8	1.1	70.0	0.4	261.3
9	245	38		18.4	3.2	1.0	4.2	1.1	8.3	0.3	319.4
10	115	39	6.7	61.8	13.0	2.8	12.1	2.4	10.5		263.2
11	77	35	4.5	42.4	8.8	0.7	10.2	2.4	11.1	2.2	194.2
12	67	36	1.8	21.3	5.1	0.3	3.7	1.1	5.9	0.2	142.4
13	85	36	3.0	27.4	6.0	2.0	7.1	1.7	8.3	0.8	177.3
14			2.9	22.2	4.5	1.4	4.2	1.4	8.5		45.23
15	94	36	3.1	31.4	5.7	2.0	7.6	2.0	9.2	0.3	191.4
16	94	37	25.9	119.8	22.8	4.2	25.6	5.5	20.1	0.8	355.6
17	100	36	18.9	91.6	17.6	1.7	1.3	4.2	18.0	0.7	290
18	131	38	29.9	124.9	26.7	2.2	25.7	5.7	20.4	0.8	405.2
19	104	35	17.9	144.0	2.3	1.4	23.0	5.7	20.0	1.3	354.5
20	183	42	4.0	67.7	15.1	6.5	14.5	3.3	12.9	1.2	350.1
21	173	41	3.4	49.5	14.3	1.5	10.2	2.3	12.1	0.6	307.8
22	118	40	17.9	93.2	19.7	2.2	19.5	4.3	17.9	1.5	334.1
23			18.9	103.0	20.1	1.7	19.3	4.4	19.0		186.3
24	115	37	18.6	90.2	21.3	5.9	16.2	3.7	14.2	0.9	323
25	89	36	35.5	173.0	35.8	4.1	29.6	6.3	23.7		432.9
26	88	36	11.6	97.6	12.3	0.8	22.0	5.1	20.9		294.2
27	153	38	7.7	75.1	14.3	1.0	12.2	3.4	11.7		316.2
28	89	36	17.9	165.3	20.2	1.8	30.0	6.9	25.1	0.9	393
29	104	37	36.3	159.1	40.0		32.2	7.0	26.7	2.7	445
30	105	37	33.0	147.0	34.8	2.5	29.4	6.7	27.1	2.4	425.1
31	77	36	16.4	72.9	16.7	1.7	15.1	3.0	16.8	1.6	257.1
32	56	35	6.6	58.0	14.3	2.4	22.3	5.8	26.8	2.6	229.9
33	43	36	21.3	94.3	23.7	3.7	32.3	7.2	31.8		293.3
34	86	37	16.2	82.9	20.4	2.3	24.1	5.7	34.4		309
35	86	36	29.9	147.4	36.4	6.1	51.3	11.5	46.1		450.6

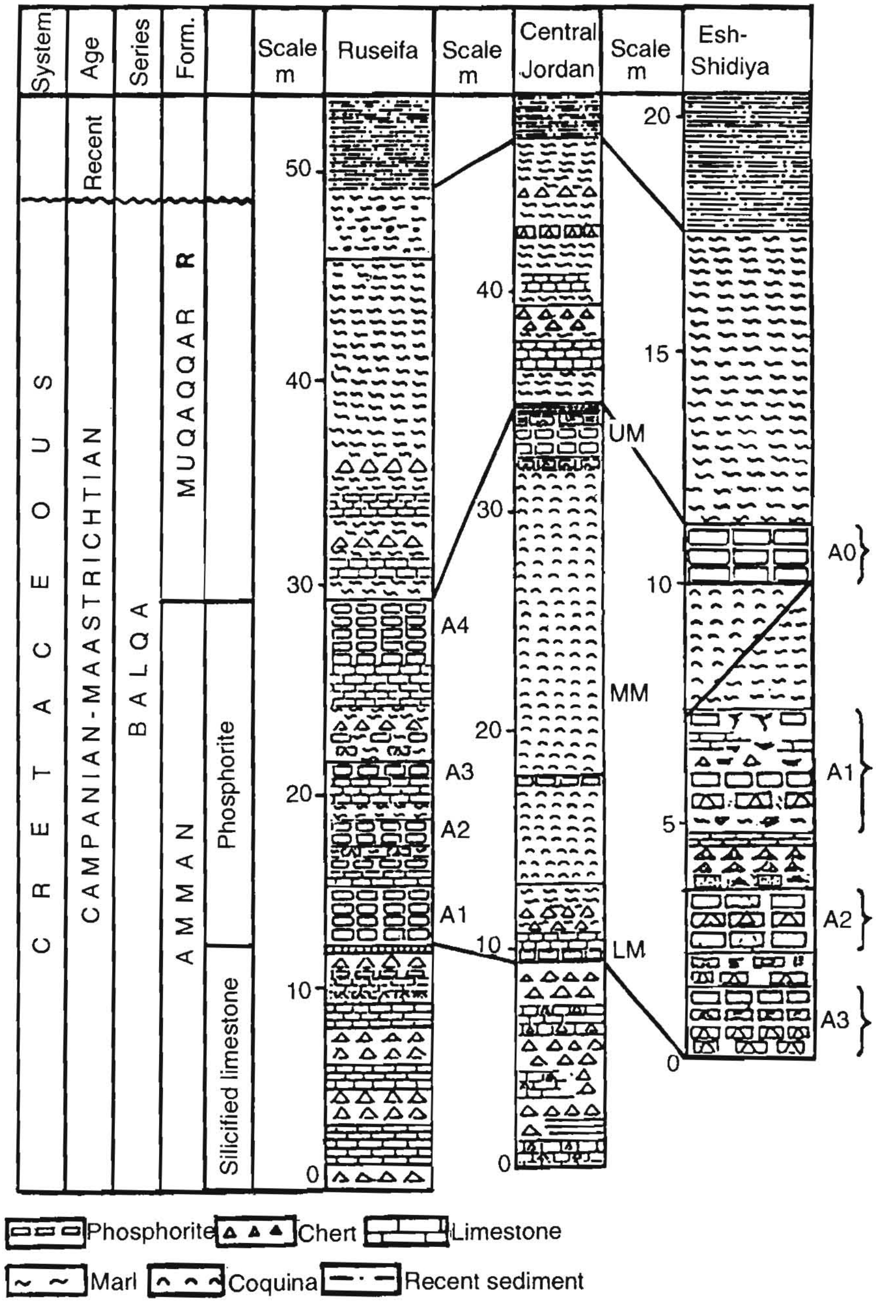

Fig. 2. Columnar sections of the three studied localities. A1, A2, ... are grade phosphorite horizons. LM, MM and UM are lower, middle and upper members in central Jordan.

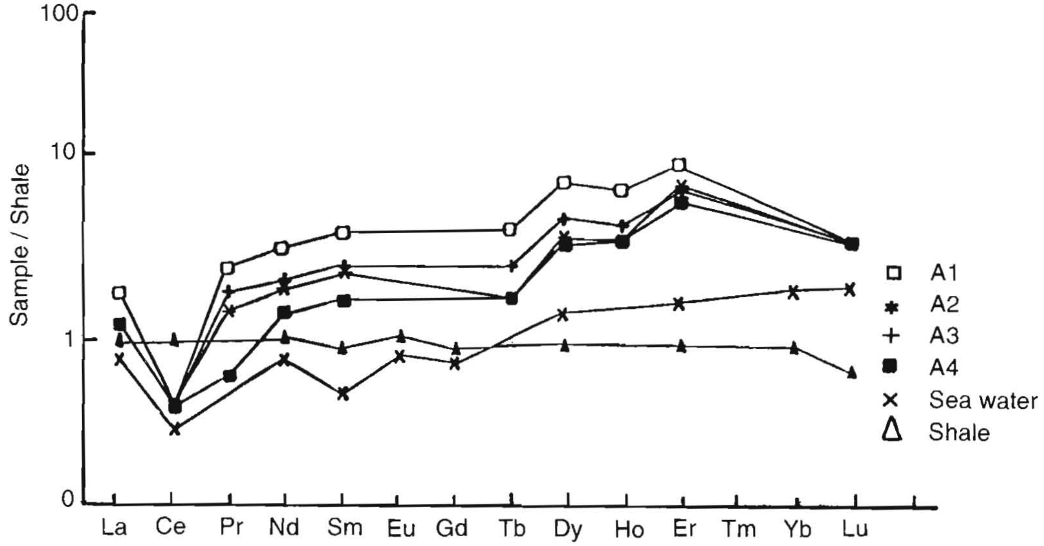

Fig. 3. REE distribution patterns of the four phosphorite horizons in Ruseifa from bottom A1, A2, A3 and A4, samples, 35, 34, 33 and 32 respectively compared with seawater (Elderfield and Grieves 1982, average 600-2500 m) and laminated shale from the Amazon delta 10 m deep (Sholkovitz 1988, sample 56A).

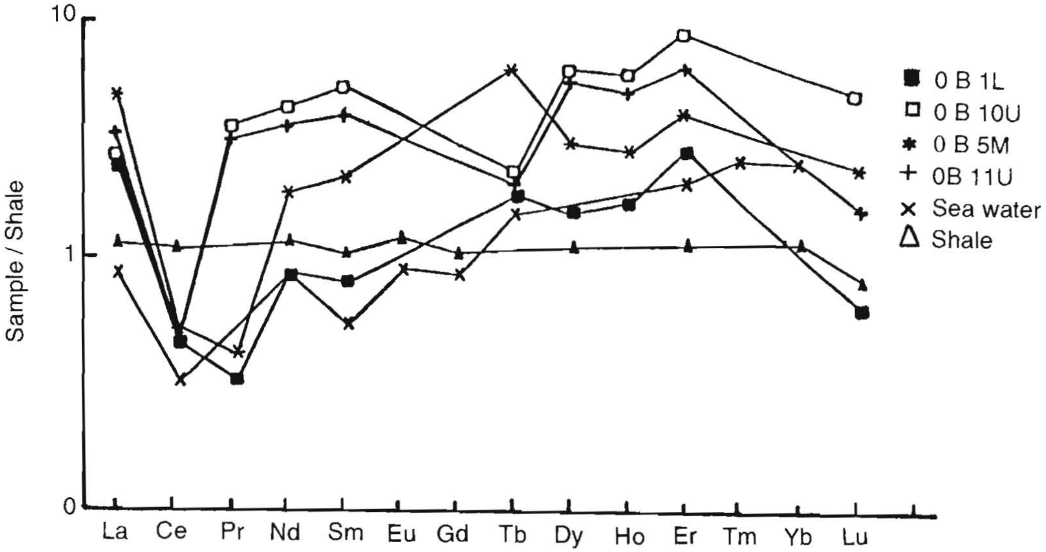

Fig. 4. REE distribution patterns for four ore bodies in central Jordan phosphorites; 0 B1, 5, 10 and 11 samples, 15, 18, 30 and 20 respectively compared with seawater and shale as in Fig. 3.

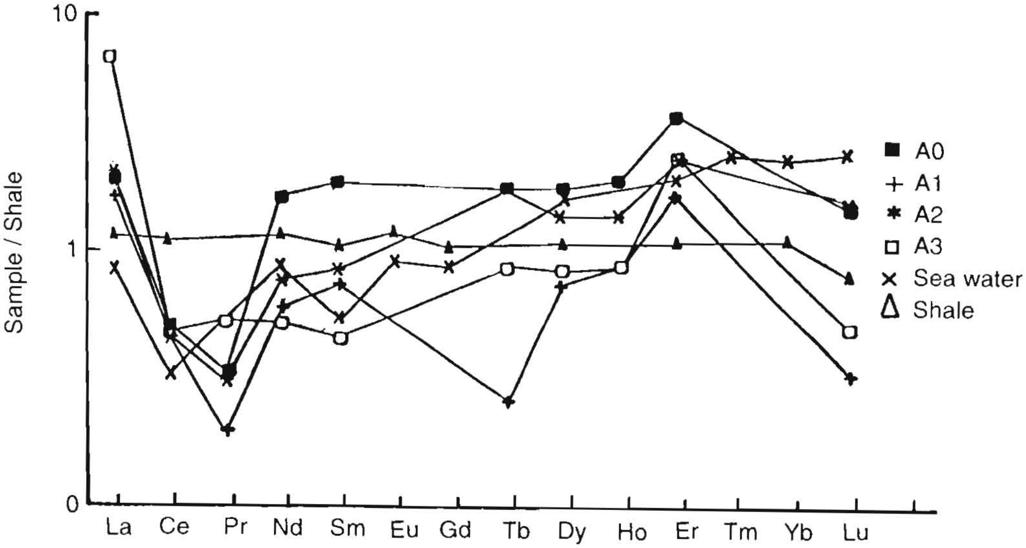

Fig. 5. REE distribution patterns for the four phosphorite horizons in Esh-Shidiya from bottom A3, A2, A1 and A0, samples 9, 13, 11 and 1 respectively compared to seawater and shale as in Fig. 3.

Discussion

Sources of REE may be sea water, marine particulate matter, terrestrial flux, Fe and Mn oxyhydroxides, complexes with carbonates and organic compounds, and pore water (Piper 1974, McArthur and Walsh 1985, Wang *et al.* 1986, Piper *et al.* 1988, Grandjean *et al.* 1993, Sholkovitz *et al.* 1994). Processes of enrichment include direct uptake from sea water or indirectly through the remobilization of REE from admixed or associated clastic material especially shale, ferromagnesian and organic coatings and pore water (Sholkovitz *et al.* 1994).

In the studied phosphorites, terrestrial materials significant as a source for REE are not present. Clays are indeed very low. (Average Al_2O_3 is 0.67%). Also, average Fe_2O_3 is 0.25% and is associated with the clay fraction (r with Al_2O_3 = 0.91). Thus, this source for REE is insignificant.

The studied deposits are authigenic, formed in the early diagenetic stage at or just below the sediment/water interface (Abed and Al-Agha 1989) via precipitation from interstitial (pore) water (Birch 1980, Southgate 1986). In a shallow environment such as the epicontinental southern shelf of the Tethyan Ocean where upwelling prevailed planktonic marine organisms would have a high rate of productivity and subsequently a high rate of death and sedimentation. Because the water column is not deep, dead organism will not be recycled in a normal deep ocean cycle (Broecker 1974). In stead, they join the bottom sediments, dissolve and liberate phosphorus and silicon. Thus, enriching pore water with P, Si and other elements (Baturin 1982) allows apatite (francolite) to precipitate directly from these pore water (authigenic phosphorite). Subsequently, this might be the probable source for enrichment in the studied phosphorites.

Abundance

Absolute elemental concentration, shale normalised abundance and the total REE content show an increase from Esh-Shidiya in the south to Ruseifa in the north. Shale normalised average in Esh-Shidiya, central Jordan and Ruseifa are 1.13, 2.3 and 3.0 respectively (Table 5).

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

Locality	Phosphorite type	Relative abundance	Age
OFFSHORE			
Namibia, Cont. Margin	Concretions	0.02 – 0.03	Pleistoc. Recent
Morocco, Cont. Margin	Nodules	0.2 – 0.1	L. Cret. Recent
Peru, Sechura Desert	Pelletal	0.1 – 0.9	Miocene
ONSHORE			
South Africa, Cape Province	Pelletal	2	L. Miocene-E. Pliocene
USA, Phosphoria Formation	Pelletal	3 – 6	Permian
Morocco	Pelletal	3	L. Cret.-Eocene
JORDAN			
Esh-Shidiya	Pelletal	1.13	L. Cretaceous
Central Jordan	Pelletal	2.3	L. Cretaceous
Ruseifa	Pelletal	3.0	L. Cretaceous
Total	Pettetal	1.9	L. Cretaceous

L = Late, E = Early.

Jordanian Upper Cretaceous phosphorites are reported to have been deposited on the flanks of small shallow basins (shallow subtidal) in the southern epicontinental shelf of the Tethys (Abed 1994). Esh-Shidiya basin, in the extreme SE Jordan, was adjacent to the southern shorelines of the Tethys and borders the Arabian-Nubian sandstone continent to the south. Ruseifa is 300 km to the north. This is reflected in the amount of detrital quartz, which could range up to 25% in the lowest A3 phosphorite bed in Esh-Shidiya. There is an enrichment factor of about 3 in Ruseifa compared with Esh-Shidiya which is likely not to be due to quartz dilution. Subsequently, the REE abundance and distribution seem to be regionally controlled where the southern locality is proximal to the continent input than Ruseifa in the north (McArthur and Walsh 1984, Sholkovitz 1988, Piper *et al.* 1988, Grandjean *et al.* 1993).

On the other hand, relative abundance normalised to shale of the studied samples are shown compared with phosphorites from other areas of the world (Table 5). McArthur and Walsh (1984) argued that offshore phosphorites have a lwoer ratio (< 1.0) compared with onshore phosphorites (> 2.0). Jordanian phosphorites have a range of 1.13 to 3.0 which puts these deposits more towards onshore environment. This conclusion is in agreement with sedimentological evidence (Abed 1989, 1994). Note that Esh-Shidiya average normalised values of 1.13 is lwoer than Ruseifa (3.0) although the former locality is closer to the continent.

REE Distribution Patterns

Figures 3, 4, and 5 show the REE distribution patterns in Ruseifa, central Jordan and Esh-Shidiya, respectively, as compared to sea water and shale. The Ce depletion, the enrichment of HREE and the non-flat patterns of these samples indicate a general agreement with patterns of marine phosphorites and other marine authigenic sediments (McArthur and Walsh 1984, Wang *et al.* 1986, Piper *et al.* 1988). These patterns look more like deep oceanic patterns. Grandjean *et al.* (1993) postulated that epicontinental phosphorites should have a pattern intermediate between sea water and shale which is not the case in these sediments. We believe cleanliness of shale (absence of significant amounts of terrestrial shale) in the studied deposits would prevent the deep water signal from being diluted by such terrestrial material.

Ce Anomaly

Ce seems to fractionate higher than other REE in sea water. It tends to be removed faster from sea water and subsequently from marine diagenetic sediments (phosphorite, opal, glauconite and the like) under oxic conditions as Ce^{4+} (Haskin *et al.* 1966, Wang *et al.* 1986, Wright *et al.* 1987, Piper *et al.* 1988). Thus, a negative

Ce anomaly relative to the other REE is preserved within these sediments. On the contrary, a positive Ce anomaly indicates deposition under reducing (anoxic) environments.

Table 6 shows the Ce anomalies for the studied samples. All anomalies are highly negative. Thus, oxidising conditions are postulated to have prevailed at the time of phosphogenesis of the Jordanian phosphorites. This is supported by the very low content (0.10%) of organic matter in these deposits, the absence of glauconite and the rare occurrence of pyrite (Jallad *et al.* 1989, Khaled and Abed 1982). It is also in agreement with the findings of other workers of a pristane/phytane ratio of more than 1.0, indicating slightly oxic conditions (Al-Arouri 1990, Belayouni *et al.* 1990).

Table 6. Ce anomalies for the studied phosphorite samples (calculated after McArthur and Walsh 1984)

Sample No.	Ce Anamoly	Mean	Sample No.	Ce Anamoly	Mean
1	−0.86		18	−1.16	
2	−0.75		19	−1.18	
3	−0.67		20	−1.09	
4	−0.88		21	−1.08	
5	−0.38		22	−1.04	−1.10
6	−0.68		23	–	
7	−0.63	−0.82	24	−1.07	
8	−0.85		25	−1.19	
9	−1.15		26	−1.04	
10	−0.97		27	−1.10	
11	−0.85		28	−1.18	
12	−0.70		29	−1.18	
13	−0.81		30	−1.16	
14	–		31	−0.84	
15	−0.86				
16	−1.09		32	−0.84	
17	−1.05		33	−0.91	
			34	−0.98	−0.97
			35	−1.14	

Samples 1-17 are from Esh-Shidiya, 18-31 from central Jordan, 32-35 from Ruseifa.

It has been shown that the magnitude of the negative Ce anomaly of the ocean water increases from surface water downwards (Elderfield and Grieves 1982, Wright *et al.* 1987, Bertram and Elderfield 1993, Sholkovitz *et al.* 1994). Also, the Antarctic ocean water has higher negative Ce anomalies than the North Atlantic water and the Pacific has the highest anomalies (De Baar *et al.* 1985). Seamount phosphorites have a very high negative Ce anomaly like those of deeper oceanic water (Burnett *et al.* 1983). It is thus, concluded by those authors and others that the deeper and more isolated the oceanic water the more negative the Ce anomaly.

Accordingly, the rather high negative Ce anomalies of the studied samples (Table 6) should indicate deep offshore deposits. This is certainly not the case in the Jordanian phosphorites which were deposited in shallow subtidal basins (less than 50 m) in the epicontinental shelf of the Tethys (Steinitz 1977, Soudry *et al.* 1985, Abed 1994).

The high negative Ce anomalies of the studied samples seem to be due to the interaction of at least three factors:

1. *Deep cold sea water:* Upwelling currents from the Tethyan ocean in the north was prevailed over those on the southern epicontinental shelf, including Jordan, during the uppermost Cretaceous (Sheldon 1987). It was the deep cold water that produced the huge phosphorite deposits of the area.

Upwelling from the Tethys Ocean in the north to the Levant during the Upper Cretaceous (Santonian-Maastrichtian) is well documented in the literature and is indicated by the presence of facies association of phosphorite, chert, porcelanite, and black bituminous marl throughout this area (Sheldon 1987, Almogi-Labin *et al.* 1993, Kolodny and Garrison 1994, Abed 1994), Fig. 6.

Thus, the high negative Ce anomalies of these deposits are the signature of this water. In fact, marine authigenic material like the phosphorites under oxic conditions should have high negative Ce anomaly regardless of depth. This is possibly the most important factor contributing to the Ce anomalies.

2. *Diagenesis:* It is now well established that phosphorites are an early diagenetic sediments that were formed just below the sediment/water interface either through the precipitation from pore water (authigenic) or from the interaction of pore water with pre-existing sediments (diagenetic) (Birch 1980, Southgate 1986, Glenn and Arthur 1988). The Jordanian phosphorites are authigenic in nature (Abed and Al-Agha 1989). The studied samples have virtually no cement. Non-phosphatic

constituents are negligible except for about 10% free silica and few percent of calcite which are not significant as REE source material. Thus, after the early authigenesis of these phosphorites, they suffered minor or no further changes (Grandjean and Albarede 1989, Grandjean *et al.* 1993).

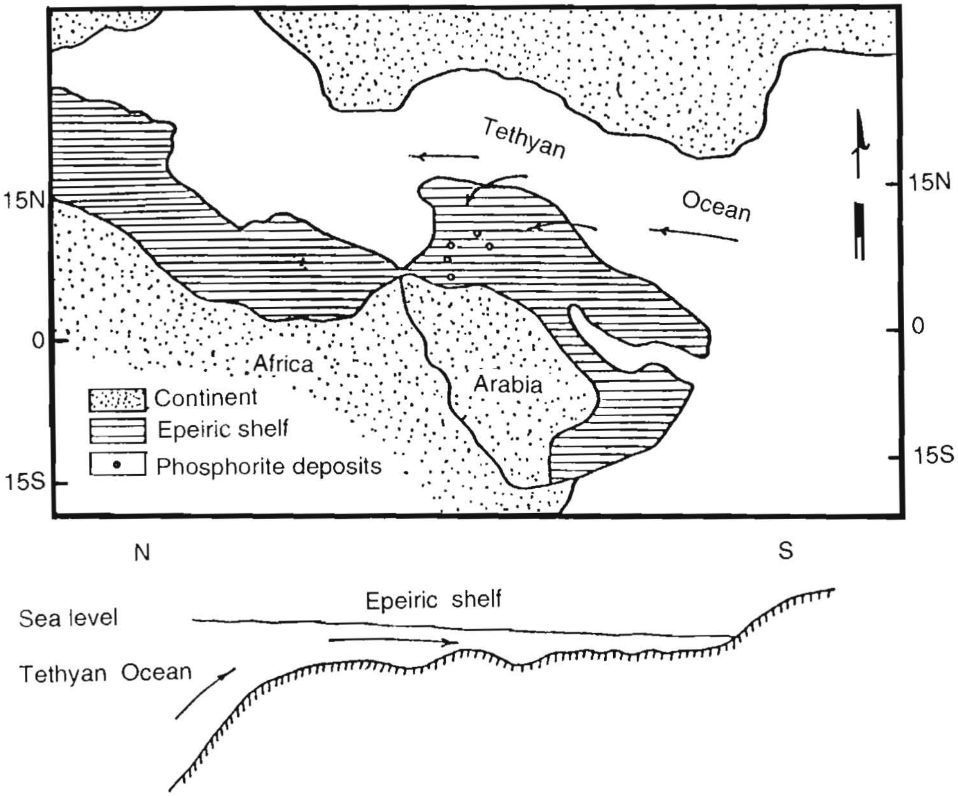

Fig. 6. A paleogeographic map showing the Tethyan Ocean proper and its southern epeiric shelf in the Cretaceous time. Note that upwelling is from east to west (Sheldon 1980, 1987). Bottom is a cross section showing the shallow epeiric shelf in the Levant.

3. *Regional control.* Table 6 shows that the Ce anomalies for Esh-Shidiya samples are less negative (–.38 to –1.09) than those of central Jordan (–.84 to –1.19) and Ruseifa deposits (–.84 to –1.14). Also, average shale-normalised abundance for the REE is 1.13 in the former locality compared with 2.5 in central Jordan and 3.0 in

Ruseifa. This clearly indicates a gradual regional control on the abundance, distribution and the Ce anomaly. Esh-Shidiya basin is proximal to the Arabian-Nubian sandstone continent. Up to 25% detrital quartz is present in the lowest, A3, phosphorite horizon with a very minor amounts of clays (average Al_2O_3 = 0.67%). Because quartz does not accommodate significant amounts of REE, most probably the regional variations, discussed above, are due to the dilution of the deep cold upwelled Tethyan water with surface water in this remote basin to the south. Subsequently, absence of clay minerals in the studied samples, as a terrigenous material, kept the negative Ce anomalies in this locality rather high although slightly lower than other localities to the north.

Conclusions

1. The studied samples are high grade pelletal phosphorites. Clays and carbonates are very low while free silica is up to 10% on average.
2. Relative abundance normalised to shale of REE in these deposits ranges from 1.13 to 3.0, which places them in proximal to onshore environments.
3. REE distribution patterns show a depletion in Ce relative to nearby elements typical for marine phosphorites and other authigenic sediments.
4. All samples have a rather high negative Ce anomaly, similar to deep water deposits indicating deposition under oxic conditions. These high negative anomalies are the signature of the upwelling of deep cold water from the Tethyan Ocean, coupled with a) a very limited diagenetic changes after the early authigenesis and b) cleanliness of terrigenous material, especially shale.
5. There is a slight regional control on the abundance and distribution of the REE, and their Ce anomalies. This is explained by the dilution of the upwelled ocean water with the surface water in the southernmost locality.

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References

Abed, A.M. (1989) On the genesis of the phosphorite-chert association in the Amman Formation in Tel es Sur area, Ruseifa, Jordan. *Sci. Geol. Bull.* Strasbourg, **42:** 141-153.

Abed, A.M. (1994) Shallow marine phosphorite-chert-palygorskite association, Late Cretaceous, Amman Formation, Jordan. *In:* **Iijima, A., Abed, A.M.** and **Garrison, R.E. (eds.).** Siliceous, *Phosphatic and Glauconitic Sediments of the Tertiary and Mesozoic.* VSP, Zeits, Netherlands, 205-225 pp.

Abed, A.M. and **Al-Agha, M.R.** (1989) Petrography, geochemistry and origin of the NW Jordan phosphorites, *J. Geol. Soc.* London, **146:** 499-506.

Abed, A.M., Hawari, Z., Sadaqa, R. and **Abu Mirri, O.** (1992) The red phosphorites of Esh-Shidiya, SE Jordan. *Geology of the Arab World.* Cairo Univ., **1:** 489-506.

Abed, A.M. and **Fakhouri, K.** (1996) On the chemical variability of phosphatic particles from the Jordanian phosphorites. *Chem. Geol.,* in Press.

Al-Arouri, K.R. (1992) *Organic geochemistry and petroleum source rock evaluation of phosphorite-oilshale association in Jordan.* Unpubl. M.Sc. thesis, University of Jordan. 216 p.

Al-Hawari, Z.Q. (1986) *Clay Minerals Associated with Jordan Phosphate and Their Possible Industrial Utilization.* M.Sc. Thesis. Univ of Jordan (Unpublished).

Almogi-Labin, A., Bein, A. and **Sass, E.** (1993) Late Cretaceous upwelling system along the southern Tethys margin (Israel): Interrelationship between productivity, bottom water environments, and organic matter preservation. *Paleooceanography,* **8:** 681-690.

Altschuler, Z.S. (1980) The geochemistry of trace elements in marine phosphorites. *In:* **Bentor, Y.E. (Ed.).** *Marine Phosphorite.* SEPM Special Publ., **29:** 19-30.

Belayouni, H., Slansky, M. and **Trichet, J.** (1990) A study of the organic geochemistry in Tunisian phosphate series: relevance to phosphogenesis in the Gafsa basin, Tunisia. *Organic Geochim.,* **15:** 47-72.

Bender, F. (1974) *Geology of Jordan.* Borntraeger, Berlin. 196 p.

Bertram, C. J. and **Elderfield, H.** (1993) The geochemical balance of the rare earth elements and neodymium isotopes in the oceans. *Geochim. Cosmochim. Acta,* **57:** 1957-1986.

Birch, G.F. (1980) A model for penecontemporaneous by diagenetic and authigenic mechanisms for the western margin of southern Africa. *In:* **Bentor, Y. (Ed.).** *Marine Phosphorite,* SEPM Special Publ., **29:** 70-101.

Broecker, W.C. (1974) *Chemical Oceanogrraphy.* Harcourt Brace, Jovanovich, New York.

Burnett, W.C., Roe, K.K. and **Piper, D.Z.** (1983) Upwelling and phosphate formation in the ocean. *In:* **Swess, E.** and **Thiede, J. (Ed.).** *Coastal Upwelling.* New York, Plenum, 377-397 pp.

Crock, J.G., Litche, F.E. and **Wideman, T.R.** (1984) The group separation of the rare earth elements and yitrium from geologic material by cation exchange chromatography. *Chem. Geol.,* **45:** 149-163.

De Baar, H.K., Bacon, M.P., Brewer, P.G. and **Bruland, K.W.** (1985) Rare earth elements in Pacific and Atlantic oceans. *Geochim. Cosmochim. Acta,* **49:** 1943-1959.

Elderfield, H. and **Greaves, M.J.** (1982) The rare earth elements in sea water. *Nature,* **297:** 214-219.

Glenn, C.R. and **Arthur, M.A.** (1983) Petrology and major element geochemistry of Peru margin phosphorites and associated diagenetic minerals: Authigenesis in modern organic-rich sediments. *Marine Geology,* **80:** 231-267.

Grandjean, P. and **Albarede, F.** (1989) Ion probe measurement of rare earth elements in biogenic phosphates. *Geochim. Cosmochim. Acta,* **53:** 3179-3183.

Grandjean, P., Feist, R. and **Albarede, F.** (1993) Rare earth elements in old biogenic apatite. *Geochim. Cosmochim. Acta,* **57:** 2507-2514.

Haskin, L.A., Wildeman, T.R., Frey, F.A., Collins, K.A., Keedy, C.R. and **Haskin, M.A.** (1966) Rare earths in sediments. *Geophys. Res.,* **71:** 6091-6105.

Jallad, I., Murry, O. and **Sadaqa, R.** (1989) Upper Cretaceous phosphorites of Jordan, *In:* **Notholt, A., Sheldon, R.** and **Davidson, D. (eds.).** *Phosphorite Deposits of the World,* **2:** 344-351.

Khaled, H. and **Abed, A.M.** (1982) Petrography and geochemistry of Esh-Shidiya phosphates. *Dirasat.,* **9:** 81-101.

Kolodny, Y. and **Garrison, R.E.** (1994) Sedimentation and diagenesis in paleo-upwelling zones of epeiric seas and basinal settings: A comparison of the Cretaceous Mishash Formation of Israel and the Miocene Monterey Formation of California. *In:* **Iijima, A., Abed, A.M.** and **Garrison, R.E. (Eds.).** *Silicecus, Phosphatic and Glauconitic Sediments of the Tartiary and Mesozoic,* VSP, The Netherlands, 133-158 pp.

Lee, J.H. and **Byrne, R.H.** (1993) Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. *Geochim. Cosmochim. Acta,* **57:** 295-302.

McArthur, J.M. and **Walsh, J.N.** (1984) Rare earth elements geochemistry in phosphorites. *Chem. Geol.,* **47:** 191-220.

Piper, D.Z. (1974) Rare earth elements in the sedimentary cycle. *Chem. Geol.,* **14:** 285-304.

Piper, D.Z., Baedecker, P.A., Crock, J.G., Burnett, W.C. and **Loebner, B.J.** (1988) Rare earth elements in phosphatic-rich sediment of the Peru shelf. *Marine Geology,* **80:** 269-285.

Semenov, E.I., Kholodov, V.N. and **Barinskii, R.L.** (1962) Rare Earth in phosphorites. *Geochemistry,* **5:** 501-507.

Sheldon, R.P. (1987) Association of phosphatic and siliceous marine deposits. *In:* **Hein, J.R. (Ed.).** *Siliceous Sedimentary Rock-Hosted Ores and Petroleum.* Nostrand Reinhold, New York, 58-79 pp.

Sholkovitz, E.R. (1988) Rare earth elements in the sediments in the north Atlantic ocean, Amazon Delta and East China Sea: Reinterpretation of terrigenous input patterns to the oceans. *Am. J. Sci.,* **288:** 236-281.

Sholkovitz, E.R., Landing, W.M. and **Lewis, B.L.** (1994) Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta,* **58:** 1567-1579.

Soudry, B., Nathan, Y. and **Roded, R.** (1985) The Ashosh-Haroz facies and their significances for the Mishash Formation paleogeography and phosphorite accumulation in the northern and central Negev, southern Israel. *Israel J. Earth Sci.,* **34:** 211-220.

Southgate, P.M. (1986) Cambrian phoscrete profiles, coated grains and microbial processes in phosphogenesis, Georgina Basin, Australia. *J. Sed. Petrol.,* **56:** 429-441.

Steinitz, G. (1977) Evaporite-chert association in Senonian bedded chert, Israel. *Israel J. Earth Sci.*, **25:** 70-75.

Walsh, J.N., Buckley, F. and **Barker, J.** (1981) Simultaneous determination of rare earth elements in rocks using inductively coupled plasma source spectrometry. *Chem. Geol.*, **33:** 141-153.

Wang, Y.L., Liu, Y.J. and **Schmitt, R.A.** (1986) Rare earth elements geochemistry of south Atlantic deep sea sediments: Ce anomaly change at the 54 MY. *Geochim. Cosmochim. Acta,* **50:** 1337-1355.

Wright, J., Schrader, H. and **Holster, W.** (1987) Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. *Geochim. Cosmochim. Acta,* **51:** 631-644.

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جيوكيميائية عناصر الأرض التادرة في صخور فوسفات الكريتاسي الأعلى في الأردن

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جرى التركيز في هذه الدراسة على خامات الفوسفات الاقتصادي في مناطق التعدين الأربعة في الرصيفة في شمال الأردن والأبيض والحسا في الوسط والشدية في أقصى الجنوب . وقد اختيرت ٣٥ عينة كل منها تمثل احدى الطبقات المعدّنة : ٤ عينات من الرصيفة و ١٤ عينة من الشدية و ١٧ عينة من الأبيض والحسا . أذيبت كميات محددة من هذه العينات بالماء الملكي وركزت عناصر الارض النادرة بمبادل أيوني وقيست بالبلازما ICP .

تمثل العينات المدروسة جميعها مستوى طبقياً واحداً هو الجزء السفلي من العصر الماسترختي الاسفل والكريتاسي الأعلى . وهي مكونة من مكورات وفتات فوسفاتي وأسنان وعظام الفقاريات غير المتماسكة . وهي من الفوسفات عالي الجودة حيث تزيد نسبة الفرانكوليت عن ٧٠٪ بينما قد تصل نسبة السيليكا إلى ١٠٪ في المعدل . وقد توصلت الدراسة إلى النتائج التالية :

١- تتراوح نسبة تركيز هذه العناصر في العينات الفوسفاتية المدروسة بالنسبة إلى تركيزها في الغضار Shale من ١,١٣ إلى ٣ . هذه النسب تصنف الفوسفات الأردني ضمن البيئات البحرية الشاطئية .

٢- تدل منحنيات توزيع هذه العناصر في العينات المدروسة على تدني تركيز عنصر السيريوم بالنسبة للعناصر المجاورة له مشابهاً بذلك رواسب الفوسفات البحرية والرواسب الأوثيجينية البحرية .

٣- ترى جميع العينات المدروسة شواذاً سالباً كبيراً لعنصر السيريوم شبيهاً بكبر الشواذ الموجود في الرواسب العميقة في البحار والمحيطات المترسبة تحت ظروف مؤكسدة . وقد فسرت هذه الشواذ السالبة على انها ناتجة عن مياه بحرية باردة عميقة ارتفعت إلى السطح بالتيارات الصاعدة Upwelling currents من محيط التيشس في الشمال .

٤- يساعد على وضوح شواذ السيريوم السالب أن الرواسب الفوسفاتية لم تتأثر فعلياً بالتغيرات اللاحقة للترسيب Diagenesis وأن هذه الرواسب خالية من المواد الطينية .

٥- تتناقص شواذ السيريوم السالب وكذلك تركيز العناصر الأرضية النادرة في اتجاه الجنوب أي من الرصيفة نحو الشدية . وقد فسّر ذلك على انه ناتج عن الموقع البعيد للشدية في الجنوب مما أدى إلى ضعف التيارات الصاعدة الباردة الآتية من الشمال وامتزاجها بمياه البحر العادية .