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Geochemistry of trace elements and their relations with organic matter in Kuh-e-Sefid phosphorite mineralization, Zagros Mountain, Iran

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ABSTRACT

The Kuh-e-sefid phosphorite is located in Zagros fold-thrust belt, in the Ramhormoz area, northeast of Khuzestan province. Phosphorite mineralization occurred as phosphorite lenses of Eocene age hosted by the Pabdeh Formation. The aim of this study is to investigate the role of organic matter in trace metal portioning during phosphorite mineralization in the Kuh-e-Sefid deposit. Field observations and petrographic studies indicate that the host-rock of mineralization is mainly consists of shale, marl, and limestone with textures varying from wackestone to packestone. Phosphoritic components, such as authigenic apatite, pellets, intraclasts, fish skeletal fragments, and micro-fossils are present. Moreover, non-phosphorite minerals including calcite, glauconite, pyrite, iron-oxide and to a lesser extend montmorillonite with microcrystalline quartz occurred in phosphorite lenses. NASC-normalized patterns of REEs showed the enrichment of Heavy Rare Earth elements (HREE) and negative Ce anomaly with co-existence of slightly negative and positive Eu anomalies represent a transitional change from oxic to anoxic sedimentation conditions during mineralization. Importantly, Ni/Co versus V/Cr ratios and V/(V + Ni) diagrams confirmed dysoxic to anoxic conditions for the hydrocarbon-bearing phosphorite and hosted shales, while non-hydrocarbon-bearing phosphorites exhibit oxic conditions. The FTIR studies revealed qualitative information about the component bonds and nature of the organic matter and mineral-organic bonds like OH, carboxylic OH, carboxylic acid C=O, C≡C alkaline, group CH₂, C=C aromatic, CH aliphatic, and aromatic stretching associated with phosphate mineralization. It seems that there is a link between a relatively high concentration of trace metals (i.e., REEs, U, Co, Zn, Ni, V, Sr and Mo) and phosphorites enriched in organic matter especially those of aromatic hydrocarbon groups.

1. Introduction

Phosphorites as marine sediments of biogenic origin are enriched in some trace elements such as uranium (U), and rare earth elements (REEs) compared with other marine sediments (Jarvis et al., 1994; Soudry et al., 2002). The chemical compositions of phosphorites are mostly linked to stratigraphy, lithology, genesis conditions, and the geographical provenance (Bech et al., 2010; Tzifas et al., 2014). Phosphogenesis occurs in sedimentary sequences that formed under quiescent conditions and low sedimentation rates (Slansky, 1979). This condition is associated with pH between 7 and 9 and Eh ranges from -0.1 to 3.0, which indicates reduced environment during phosphorite precipitation (Slansky, 1979). Taken as a whole, phosphorites are characterized by 15–20 wt% P₂O₅ and between 50 and 120 ppm U (Li

and Schoonmaker, 2003; Boggs, 2009; Tzifas et al., 2014; Pufahl and Groat, 2017). Francolite as an authigenic carbonate-rich fluorapatite [Ca10_{-a-b}Na_aMg_b(PO₄)_{6-x}(CO₃)_{x-y-z}(CO₃·F)_{x-y-z}(SO₄)_zF₂] is the main ore mineral in sedimentary phosphate deposits (Jarvis et al., 1994; Pufahl and Groat, 2017). Primary phosphogenesis in some phosphoritic deposits, especially authigenic precipitation of francolite is related to decay of organic matter by microbial activity in the sediment (Glenn et al., 1994; Emsbo et al., 2015). Predominantly, apatite appears to be present as a common product of organic matter diagenesis (Soudry et al., 2002). In general, francolite deposits occur in the suboxic-anoxic sediments especially when phosphorus and carbon are released during the decomposition of organic matter by microorganism or dissolution of bone debris and ferric oxy-hydroxides reduction (Feroelich et al., 1988; Jarvis, 1992). Importantly, marine phosphorites may contain economic

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concentration of elements, such as REE, U, Th, and Sc (Altschuler, 1980; Donnelly et al., 1990). The REEs enrichment in francolite by REE substitutes for Ca in the francolite crystal lattice has been known for more than a century (Jarvis et al., 1994; Piper, 1999; Emsbo et al., 2015). Variations in the contents of REE in the different types of phosphorites have been attributed to the change in depositional conditions, and the variation in composition and amount of associated detritus, redox, pH, age, and water depth cause variable REE patterns (Picard et al., 2002; Baioumy, 2011; Khan et al., 2012).

Organic matter as phosphorus source and an energy source to change in oxidation-reduction condition proved to be necessary for phosphogenesis (Jarvis, 1992). Microbial degradation of organic matter is attributed to the mobility and bio-availability of trace metals through a series of microbial-mediated redox reactions owing to the decreasing energy production and provides a mechanism for immobilizing the metals (Feng et al., 2011; Pufahl and Groat, 2017). Overall, bacteria are important factors for providing an important mechanism for release of phosphorus from phospholipids and other phosphorus compounds by decomposition of organic phosphate and organic carbon oxidation (Jarvis, 1992). For example studies of fossilized bacteria in several occurrences of phosphates of Japan and India showed that the role of bacteria is important to absorption of phosphorus in seawater and deposition of phosphate minerals, such as apatite (Rao and Lamboy, 1996; Ogihara, 1999). Also, as highlighted in Tzifas et al. (2014) phosphorites from NW Greece with high U concentrations occurred in organicbearing phosphorite mostly associated with aromatics.

The presence of phosphorite in the South West of Iran has been reported in 1954 during drilling of oil exploration projects. The Geological Survey of Iran began phosphorite exploration in 1963. The results identified probable reserves around 630 million tonnes at an average grade of $8.5\% P_2O_5$ in formations of both sedimentary and igneous types (Saberi, 2010).

Phosphoritic deposits in different geological sequences within the Zagros orogen, formed in Triassic to the late Pliocene (Kamaee, 2009). Totally, over than seven horizons with an extent of ~400 to 100 km have been delineated in the Zagros Mountains (Namadmalian et al., 1998). The average thickness of theses phosphorite horizons is 2.1 m and the P_2O_5 grade reaches to 9.6 (wt%) (Namadmalian et al., 1998). Although there is a widespread occurrence of phosphoritic lenses along the Zagros mountain belt, but genesis and trace metal content of these deposits are poorly understood. Accordingly, the present work tried to focus on the Kuh-e-Sefid phosphorites. The data is used to characterize the role of organic matter in concentration of trace metals in Kuh-e-Sefid deposit.

2. Geological setting

Spatially and temporally phosphorites in Iran can be divided into four age-groups: 1) Proterozoic-Cambrian in north-northwestern Iran, 2) Ordovician-Silurian in central Iran, 3) Upper Devonian in north Iran and 4) Cretaceous-Tertiary in the Zagros Fold-Thrust Belt (ZFTB; Halalat and Bolourchi, 1994; Zarasvandi et al., 2010). Nevertheless, small igneous phosphorites of Proterozoic have also been reported in central Iran (Halalat and Bolourchi, 1994). Phosphorites of the Cretaceous– Eocene Tethys basin are widely distributed in the Middle East and North Africa. These deposits could be correlated with Eocene phosphorite horizons of Zagros belt located in the western Iran (Abed and Sadaqah, 2013).

The Zagros orogen as a part of the Alpine-Himalaya belt is located in the western Iran. This is formed due to the continent-continent collision between Arabian Plate and the Central Iran during the Late Miocene. The Zagros orogenic belt is characterized by three NW–SE parallel trends including the Urumieh–Dokhtar Magmatic Arc (UDMA), the Sanandaj–Sirjan metamorphic zone (SSZ), and the Zagros Fold-Thrust Belt (ZFTB; Alavi, 1994; 2007; Fig. 1A). The geodynamic evolution of this belt is strictly associated with the evolution of Neo-Tethys basin from early subduction/obduction processes to present-day collision (Alavi, 2007; Agard et al., 2011). The ZFTB extends for almost 2000 km from the East Anatolian fault in southeastern Turkey to the Oman line in eastern and southeastern Iran (Alavi, 1994). It is composed of 7–12 km heterogeneous sequences of the latest Neoproterozoic–Phanerozoic carbonates and detrital sedimentary (Alavi, 2007).

The Kuh-e-Sefid phosphorite is located in the northeast of the Kuh-e-Sefid anticline 170 km to the east of Ahvaz city and about 30 km northeast of the Ramhormoz town. The study area is located in the ZFTB between the Bangestan anticline (south) and the Kuh-e-Siah anticline (north), in the eroded part of Kuh-e-Sefid anticline (Fig. 1B). Kuh-e-Sefid phosphorite occur as phosphorite lenses with Eocene age within the Pabdeh Formation (Paleocene-Oligocene age) in the northeast of Kuh-e-Sefid anticline, with thickness up to 1.5 m and width of 15 m. The host rocks of the phosphorite lenses are mainly shale, marl, and limestone, with textures varying from wackestone to packestone with enrichment in organic matters (Fereydouni, 2016).

The Pabdeh Formation is considered as source rock for hydrocarbon exploration in Zagros (Daneshian et al., 2012). This is overlain by the Oligocene-Miocene Asmari Formation. The Miocene Gachsaran Formation is the youngest formation in the study area (Fig. 2(. The surface exposure of the Kuh-e-Sefid anticline includes the Gurpi, Pabdeh, Asmari, and Gachsaran Formations (Fig. 3A). Field observation suggests that this anticline is a simple anticline with cylindrical sections and it seems to have a nearly vertical axial plane (Damiri, 2011). The anticline has subsequently been affected by late faulting. The Pabdeh Formation is the host of phosphoritic mineralization in the region that includes a sequence of carbonate, marl, and shale (Fig. 3B and C). The Pabdeh Formation is comprised of three main mineralization sections including; 1) the upper section containing phosphorite mineralization 2) middle section dominated by oxide minerals and 3) bottom section characterized by organic matter and phosphorite mineralization. These sections are overlain by the layers of limestone and marly limestone (Fig. 2; Ferevdouni, 2016).

3. Methodology

Totally, ten samples were taken from phosphorite mineralization (Ks-1, Ks-2, Ks-3, Ks-6, Ks-7, Ks-10), host shale (from the Pabdeh Formation; Ks-4, Ks-5, Ks-11) and the oxide zone (Ks-12; Fig. 1B and 4A–C; Table 1). Mineralogical and geochemical studies were carried out using XRD, SEM, ICP-MS, FTIR, and Rock-Eval analyses. Ten polished-thin sections were prepared. Mineralogy and petrography of the samples was determined by polarizing-reflected light optical microscopy in Shahid Chamran University of Ahvaz, Iran, and powder X-ray diffraction (XRD) using Philips 3040 PW X-ray diffractometer at Kansaran Binaloud Company in Pardis Science and Technology Park, Tehran, Iran. Scanning electron microscopy (SEM) was used to examine the structure and determination of phosphoric minerals in polished sections at the central laboratory of Shahid Chamran University of Ahvaz (LEO 1455 VP).

Geochemical studies on mineralized and host rocks were performed by inductively coupled plasma-mass spectrometry (ICP-MS) after lithium metaborate (LiBO₂/LiB₄O₇) fusion and nitric (HNO₃) digestion of 0.2 g of sample in order to determine the major, trace, and rare earth elements at Kansaran Binaloud Company in Pardis Science and Technology Park, Tehran. The minimum detection limit for major and trace elements is 0.1 ppm and 0.02 ppm for rare earth elements. Rock-Eval analysis was used to determine the quantity and quality of the respective organic matter using a Vinci Rock–Eval (6) pyrolyzer at the petroleum geology and geochemistry research center of Shahid Chamran University of Ahvaz. The analysis was conducted by heating the 70 mg of each sample (n: 10) in an open pyrolysis system under non-isothermal conditions. Fourier-transform infrared spectroscopy (FT-IR) was carried out on phosphorite samples. This technique used in order to determine the qualitative information about the bonding



Fig. 1. A: Three tectonic trends in western Iran (modified after Alavi, 2004; Zarasvandi et al., 2008), B: Geographical and geological map of the study area showing sampling locality (modified after Damiri, 2011).



Fig. 2. Geological cross section and stratigraphy column of the Kuh-e-Sefid phosphorite horizon (modified after Damiri, 2011).



Fig. 3. Field photographs showing A: General view of the studied area, B: phosphorite lenses and C: interlayers of phosphorites in the Pabdeh Formation.

pattern and nature of components of the organic matters beside sample's mineral-organic bounds using KBr pellets (2 mg/300 mg KBr) on a spectrometer (Model Bomem MB-Series 1998) at Department of Chemistry in Shahid Chamran University of Ahvaz.

4. Results

4.1. Petrography

According to the petrography, phosphorite components include authigenic apatite, pellets, intraclasts, fish skeletal fragments, and microfossils. In additions to phosphorite and biogenic components, nonphosphorite minerals, such as calcite, glauconite, pyrite, iron oxide, minor montmorillonite, and microcrystalline quartz are present. The major textures vary from wackestone to packestone. Importantly, the most of high-grade phosphorites have packestone texture.

Microscopic observation showed that pellets are the most abundant phosphorite grains in the study area (Fig. 4D and E). In general phosphatized pellets are derived from authigenic phosphate materials. Organic matter occurs as bond form in the phosphorite matrix. The dark parts of the matrix reflect the presence of organic matter and iron oxides (Fig. 4F and G). Studied glauconites like in other deposits formed as non-phosphorite particles in shallow environments (Fig. 4D, E, H, and I).

In addition, the pellets may contain different forms of biogenic and inorganic residues. Bone fragments and shells of foraminifera as biogenic inclusion occur as phosphate intraclasts (Fig. 4I). Framboidal pyrite, filling the pores of the phosphorite grains and/or calcitic microfossils was found (Fig. 4D, E, G, and H). Calcite seems to be present both as sparite and as bio-micrite in the samples. In addition to calcite, microcrystalline quartz occurs as internal cement in some of the foraminiferal tests (Fig. 4F, G, H, and I).

Many of the phosphorite grains of the Kuh-e-Sefid mineralization are dominated by an outer rim of concentric phosphorite layers coated by former phosphate peloids. Also, the results of XRD analysis showed fluorapatite and calcite are the main phosphorite mineral. However, montmorillonite and microcrystalline quartz occur as the main non-phosphorite mineral in Kuh-e-sefid phosphorite (Fig. 5).

SEM analysis showed that cryptocrystalline apatite fills the cores and rims of pelloids, foraminifera, bone fractures, and other phosphatic components that accompanied with organic matter (Fig. 6A and B). In addition, euhedral crystals of apatite and spheroidal forms of framboidal pyrite occur in the matrix (Fig. 6A and B). Phosphatized foraminiferal grains approach the alga has been observed that filled with apatite crystals (Fig. 6C and D)

4.2. Geochemistry

The phosphorites and their host rock samples were analyzed by ICP-MS for measuring the major, trace, and rare earth elements. The major, trace, and rare earth element concentrations are presented in Table 1. The positive correlation between P, Ca ($R^2 = 0.19$; Fig. 7A), and U) $R^2 = 0.99$; Fig. 7B) indicates a genetic relation between uranium and phosphate. According to Table 1, SREE vary from 68.9 ppm to 289.9 ppm, averaging 155.4 ppm. The highest concentration of these elements was found in a phosphorite samples. NASC-normalized pattern of REEs display a negative Ce anomaly in all the samples, as well as a slightly negative Eu anomaly among phosphorite, hydrocarbon shale, and phosphorite-bearing hydrocarbon shale samples. Also, there are slight positive Eu anomalies in other samples (Fig. 8). The most typical features of REE patterns are depletion of LREE relative to HREE. Also, NASC-normalized pattern of REEs indicate negative anomalies for Tm and Lu (Fig. 8). Thulium and lutetium are the least abundant REEs in the Kuh-e-Sefid samples, especially in the shale samples (Table 1; Fig. 8). In this study cerium anomalies were calculated from Ce/ $Ce^* = 3Ce_n/(2La_n + Nd_n)$, Pr anomalies from $Pr/Pr^* = 2Pr_n/$ $\left(\text{Ce}_n\times \text{Nd}_n\right)^{1/2}$ and also the Eu anomaly was calculated using the equation of $Eu/Eu^* = Eu_n/(Sm_n \times Gd_n)^{1/2}$ (Wright et al., 1987; Bau and Dulski, 1996; Chen et al., 2006; Table 1). The Ce/Ce*, Pr/Pr* and Eu/Eu* anomalies are vary between 0.57-0.76, 1.20-1.30 and



Fig. 4. Different samples taken from Kuh-e-Sefid phosphorite deposit including A: phosphorite with hydrocarbon contamination, B: the host shale sample associated with organic matter and C: oxide zone. Photomicrographs of D: phosphorite components with packestone texture (XPL), E: phosphatic pellet (Fig D in PPL), F: Organic material in shale matrix, pyrite and iron oxide, G: Thin layers of organic materials in the field of phosphorite and pyrite veins that it has been found with dashed line, H: phosphorite biozone with abundant microfossils of foraminifera in some part, their tests filled by calcite (bright white) or apatite (dark) and pyrite, and I: sphere shows the intraclasts with biogenic inclusions. (P = pellet, Gl = Glauconite, Py = pyrite, Bf = bone fragments, OM = Organic material, I = intraclasts, Cc: calcite).

0.900-1.149, respectively; Table 1).

The variation of Ce_{an} between 0.57 and 0.76 represent negative anomalies for Kuh-e-Sefid phosphorite samples. Cerium anomalies may be overestimated due to the enrichment of La (Bau and Dulski, 1996; Abedini and Calagari, 2017). Thus, in order to determine the effect of La enrichment, discrimination diagram of Ce/Ce^{*} versus Pr/Pr^{*} was plotted (Bau and Dulski, 1996). As shown in Fig. 9, all samples fall in the IIIb field suggesting that the negative Ce anomalies are real in all samples. The Kuh-e-Sefid Phosphorite samples clearly indicate high ratios of Pr/Pr^{*} and low Ce/Ce^{*}. It is also possible to use for interpreting of paleo-redox conditional parameters including redox states, pH of the pore water and seawater (Bau and Dulski, 1996; Ounis et al., 2008; Joosu et al., 2016).

The discrimination diagram of Th/Sc vs. Zr/Sc is useful to characterize the primary conditions prevailed during the formation of deposits (Rollinson, 1996; Tzifas et al., 2014; Fig. 10A). Most of the samples show sediments of pelagic origin with some close to the average shale field (Tzifas et al., 2014). In addition, the Ni/Co were obtained as an indicator for the determining of redox condition (Jones and Manning, 1994). Ni/Co < 5 determines the oxic zone, while ratios above 5 are related to the suboxic-anoxic zone (Jones and Manning, 1994). In the studied samples, Ni/Co ratios reach the highest in hydrocarbon-bearing phosphorite and shale-hosted samples (> 5; Table 1). Whereas non-hydrocarbon phosphorite samples are characterize by a relatively lower Ni/Co ratios (< 5; Table 1). Binary diagram of V/(V + Ni) versus Ni/Co confirmed suboxic-anoxic conditions for hydrocarbon-bearing phosphorite and shale-hosted samples and also oxic conditions for non-hydrocarbon phosphorite samples of Kuh-e-Sefid deposit (Fig. 10B).

4.3. Organic matter

The Fourier Transform Infrared (FT-IR) spectra have been used to evaluate function groups of the specimens in Kuh-e-sefid phosphorites. Thus, infrared spectra were recorded in the range of 4000–400 cm⁻¹ in order to characterizing the functional groups in the studied samples (Fig. 11).

The results of this analysis and interpretation of the spectral pattern for Kuh-e-sefid samples are presented in Table 2. In general, the broad absorption band at 3000–3600 cm⁻¹ is assigned to hydroxyl (–OH) groups and water appearing in various organic and inorganic matter (Ellerbrock and Gerke, 2004; Gerzabek et al., 2006; Tzifas et al., 2014). Major bands with strong intensity at ~1600 cm⁻¹ correspond to an increase of the carbonyl oxygen and hydroxyl. Absorption band at ~700 to 900 cm⁻¹ is related to non-simple Bands of C–H in Aromatic units that gives valuable information about the patterns of aromatic groups' substitution (Gezici et al., 2012). The organic component is indicated by the bands of the CH₃– and CH₂–groups (2862, 2870, 2922

Table 1

Major, trace, and rare earth elements in the studied rocks.

Sample Rock Type ppm	Ks-1 Phosphate horizon	Ks-2 Phosphate horizon	Ks-3 Phosphate horizon	Ks-4 Interlayer shale	Ks-5 Interlayer shale	Ks-6 Phosphate	Ks-7 Phosphate horizon	Ks-10 Phosphate horizon	Ks-11 Interlayer shale	Ks-12 Iron oxide layer
Al Ca Cr Fe K Ma	135 329943.2 143 13862.4 4798 292	128 425164.8 158 14360.7 5032 205	132 533488.3 368 14237.8 6422 2400	860 288388.2 134 7631.1 3060 247	2120 14752.64 69 11391.7 5748 271	112 53,781 503 13344.8 4.92 220	163 475150.4 389 16,140 6812 227	110 440350.7 188 9842.9 4362 275	530 52,181 331 28745.3 14,272 762	912 565988.3 269 60849.7 447 177
Mn	292	293	129	109	131	53	86	273 89	96	22
Na P	277 15,991	239 20,606	268 27309.98	195 13,977	161 715	233 52544.13	236 23028.6	179 21,342	257 2529	139 92244.15
Ti	487	436	319	333	911	333	524	392	2530	287
As	8.3	8.4	9	3.7	0.7	11	9.4	3.6	9.2	100.5
Ba	356	263	226	332	78	2780	469	331	428	977
ве Cd	0.8	0.9	1.4	0.7 4 9	0.7	1 34	1.5 9.8	0.9	1.4 14.2	1.2 27.6
Co	7.9	9.2	10.8	5.1	9	7.6	9.5	5.8	10	4.4
Cs	2.9	3	3.1	2.7	3.8	3.1	3.5	2.8	8.4	2.5
Cu	19	18	50	26	22	89	58	32	67	45
Ga	5.6	7.32	9.11	3.82	2.7	12.75	9.75	4.87	3.09	6.28
HI Mo	0.3	0.5	0.4	0.6	1.45	0.58	0.76	0.63	2.86	0.5
Nb	1.3	1	0.9	1	2.9	1.1	1.6	1	10.2	0.9
Ni	33	36	103	60	91	158	15.4	61	195	109
Pb	15	20	32	78	123	172	35	26	18	27
Rb	20	22	29	16	28	21	32	20	71	15
Sb	< 0.5	< 0.5	0.6	1.1	1.2	2.1	1.5	< 0.5	4.6	9.2
SC	3.8	4.4	5.9	3.7	4.1	8.9	6.9 0.51	3.9	10	2.1
Sn	1.7	1.7	1.7	1.6	3.3	1.9	2.3	1.8	3.2	1.5
Sr	841.5	904.3	1273.3	1130.4	1004.6	1513.1	1300	1241.4	417.8	1425.4
Та	0.09	0.1	0.01	0.05	0.06	0.06	0.1	0.01	0.32	0.05
Th	4.03	4.54	5.08	3.41	5.05	5.14	5.89	4.19	8.1	2.61
Ti	487	436	319	333	911	333	524	392	2530	287
11	1.21	1.43	4.9	3.08	1.73	5.07	6.48 25 5	2.53	3.66	6.09 142.2
v	62	68	111	80	87	293	141	126	357	328
Zn	20	21	88	125	34	505	149	145	269	804
Zr	14	12	9	11	27	20	21	14	79	13
La	17	20	24	12	10	34	28	15	14	25
Ce	29	35	39	20	20	49	43	25	27	34
Pr Nd	5.31 23.7	0.33 27 9	7.74	3.97 17	3.77	10.55 45 5	8.52 36.8	4.8 20.6	4.82	0.34 26 5
Sm	4.31	5.39	6.67	2.84	2.38	9.62	7.36	3.8	2.98	4.79
Eu	1.09	1.42	1.79	0.73	0.52	2.9	2.04	1	0.71	1.36
Gd	5.6	7.32	9.11	3.82	2.7	12.75	9.75	4.87	3.09	6.28
Dy	4.88	6.68	8.35	3.31	2	12.25	9.22	4.32	2.49	5.76
Er	3.34	4.4	5.82	2.47	1.25	8.95	6.6 0.75	3.27	1.77	4.38
Yb	3.2	4.4	5.9	2.6	1.3	9.6	6.8	3.4	2.3	4.7
Lu	0.51	0.64	0.81	0.45	0.28	1.22	0.92	0.53	0.39	0.68
Y	32.7	43.8	61.7	23.3	8.2	90.7	64.6	29.3	11	42.8
ΣREE	131.95	165.11	206.73	93.43	68.93	289.91	225.79	117.05	90.53	164.08
Ce/Ce*	0.66	0.68	0.63	0.64	0.74	0.57	0.61	0.65	0.761	0.590
Eu/Eu [~] Dr/Dr*	0.97	0.99	1.008	0.97	0.900	1.149	1.057	1.020	1.02	1.088
Ni/Co	4.18	3.91	9.54	11.76	10.11	20.8	1.62	10.52	19.5	24.77

Ce/Ce* anomaly from Wright et al. (1987), Pr/Pr* anomaly from Bau and Dulski, (1996) and Eu/Eu* anomaly from Chen et al. (2006).

and 2851 cm^{-1}). The spectrum is dominated by a characteristic band around at ~3000 cm⁻¹, which originates from aliphatic and aromatic hydrocarbons. Position and intensity of absorption bands of moderate to strong at 1400 cm⁻¹ along with 877–879 cm⁻¹ are attributed to vibrations in the carbonate radical. The band at ~873 cm⁻¹ is particular to calcium carbonate, which is used to determine the presence of calcite in phosphorite minerals (Fleet, 2009; Tzifas et al., 2014). The intensity of the absorption bands in the range of 1040-1027-1042 cm⁻¹ and also lower band strength at ~1092 cm⁻¹ are assigned an asymmetric stretching bands of phosphorus-oxygen, while several low absorption bands at ~962 cm⁻¹ indicate symmetric stretching band of phosphorus compounds. These vibrations are characteristic of the PO₄ groups indicating the presence of apatite group (Liou et al., 2004).

4.4. Rock-Eval pyrolysis

Rock-Eval pyrolysis determines the quality and thermal maturation of organic matter in samples. The range of TOC content of Kuh-e-Sefid phosphorite samples is between 0.14 and 8.81 wt% (Table 3). According to the values of total organic carbon, almost all the studied samples are classified in the range of poor rocks, except for Ks-5 sample that have been allocated to the fair category. Also Ks-11 sample is placed in the range of excellent that shows organic rich feature of sample. According to the S₂ (the power of sample hydro carbonization)



Fig. 5. Spectra of XRD analysis of Kuh-e-Sefid samples. A: XRD analysis spectrum of phosphorite sample, B: Spectrum related to hydrocarbon-bearing phosphatic shale, C: XRD analysis spectrum of phosphorite horizon with hydrocarbon shale and D: Spectrum of phosphorite horizon.



Fig. 6. A: Scanning electron microscope image of carbonate-rich fluorapatite (francolite) hexagonal crystals, B: image A using a $750 \times$ magnification, Scale bar = $20 \,\mu$ m, C: SEM image of a typical microorganism in shale-hosted sample, D: photomicrograph C using a $220 \times$ magnification, Scale bar = $100 \,\mu$ m.

versus TOC (total organic carbon) diagram the amount of organic matter in the all studied samples are extended between the poor to appropriate fields; only one sample is placed in the range of good (Fig. 12). Combining the uranium concentration, samples plotted in the field of poor to appropriate (Fig. 12) have uranium concentration (average, 48.55 ppm), while Ks-11 sample in the field of good (Fig. 12) contains 10.28 ppm uranium value (Table 1).

The $(S_1 + S_2)$ versus TOC diagram determines the potential of samples for generation of hydrocarbon (Huang et al., 2003). In this

diagram, Ks-1, Ks-2, Ks-3, Ks-7, and Ks-10 samples with low hydrocarbon-generating potential (lean filed) have uranium contents of 19.9, 27, 42.1, 35.5, 32.9 ppm; respectively. Also, the phosphorus of these samples is 15991, 20606, 27309.98, 23028.6 and 21342 ppm (respectively, Table 1). In addition, Ks-6 and Ks-12 samples are plotted in the field of poor potential. The U content of these samples is 81, 142.2 ppm, respectively. These samples have P values of 52544.13, 92244.15 ppm, respectively (Table 1). The Ks-4 and Ks-5 samples with uranium concentration of 20.3 and 7.8 ppm are plotted in the field fair. Also, P



Fig. 7. A: Correlation between Ca and P, B: Correlation between the U and P. Phosphorite samples in purple, shale samples in blue and iron oxide sample in violet.

content of these samples is 13,977 and 715 ppm, respectively (Table 1). Ks-11 sample represents the highest potential of hydrocarbon generation. The uranium and phosphorus content of this sample are 10.28 and 2529 ppm, respectively (Fig. 13).

5. Discussion

In the studied samples, the lack of phosphorite cement and concentric structures as well as the presence of intraclasts suggest that a part of phosphatic grains have been remobilized from the original depositional environment (Tarawneh, 2005; Fig. 4I). Apatite was seen autigenically in the phosphorite. In general, apatite precipitation could be affected by biological processes like bacterial activity (Soudry et al., 2002). Also, apatite acts mainly as the filler of biogenic materials (Stamatakis, 2004; Fig. 4I). In the studied samples, the presence of pellets and phosphate intraclasts seem to be related to the collection of different processes. In other words, pellets and phosphate intraclasts are created in an open sea and when the concentration of soluble phosphate in sea water is high (Varol, 1989). Phosphoric pellets in the Kuh-e-Sefid show high-energy and shallow environment (Awadalla, 2010; Fig. 4D, E). As common indication, the phosphate mineralization is poor in detrital materials, composed particularly of apatite group minerals and traces of microcrystalline quartz as clastic minerals and clays (Stamatakis, 2004; Fig. 5). Glauconite is an indicator of sub-oxidizing, shallow and energetic environment (Feroelich et al., 1988; Fig. 4D, E, H and I). The presence of framboidal pyrite shows reducing conditions of

diagenesis during the formation of the phosphorite (Awadalla, 2010). The widespread occurrence of framboidal pyrite is reported from organic matter bearing-pelagic sediments from anoxic pore water where bacterial Fe and sulfate reduction create Fe^{2+} and sulfide (Fazio et al., 2007; Pufahl and Groat, 2017; Fig. 4D, E, G and H). The apatite group minerals fill foraminifers' skeletons and other biological compounds (Fig. 4I). In the study area, foraminifera cavities seem to be one of the main centers of phosphorite mineralization. They were caused by the destruction and decay of organic matter, transfer and reworking processes, and deposition of apatite in the cavities (Stamatakis, 2004; Fig. 4I).

The geochemistry of phosphorites is mainly used to evaluate the paleo-marine chemistry. Importantly, marine phosphorites are considered as an economic potential for elements such as REE, Sc, U and Th (Altschuler, 1980; Donnelly et al., 1990; Emsbo et al., 2015; Tzifas et al., 2016). Kuh-e-Sefid samples are characterized by positive correlation between U and P ($R^2 = 0.99$; Fig. 7B), analogous to those reported previously for other marine phosphorites (e.g., Soudry et al., 2002; Tzifas et al., 2014). This is attributed to contribution of P and U in the carbonate-rich fluorapatite (francolite) crystal structure (Tzifas et al., 2014; Emsbo et al., 2015). Rare earth elements derived either directly or indirectly from seawater by remobilization of clastic, ferromanganese oxides, biogenic remain and combination of these sources, in phosphorites (Khan et al., 2012). The REE patterns of authigenic apatite are mainly used to infer the ancient ocean redox chemistry. Also, REE composition of apatite may record the ambient water



Fig. 8. NASC-normalized REE patterns of the samples in the study area (Gromet et al., 1984). Phosphorite samples in purple, shale samples in blue and iron oxide sample in violet.



Fig. 9. Binary diagram of Ce/Ce^{*} versus Pr/Pr^{*} diagram to determine the no or uncertain Ce anomaly (Bau and Dulski, 1996). Field I: no anomaly; Field IIa: positive La-anomaly causes apparently no Ce anomaly; Field IIb: negative La-anomaly causes an apparently no Ce anomaly; Field IIIa: positive Ce anomaly; Field IIIb: negative Ce anomaly; Field IV: positive La-anomaly disguises positive Ce anomaly. Phosphorite samples in purple, shale samples in blue and iron oxide sample in violet.

conditions during precipitation (Wright et al., 1987; Joosu et al., 2016). It should be noted that concentration of REEs and the NASC-normalized REE pattern with Ce and Eu anomalies are key indicators for the interpretation of geochemical feature of sedimentary environment, and sedimentation of initial seas (Jiang et al., 2007; Fig. 8). Sea water generally shows enrichment in HREE with negative Ce anomalies. This negative anomaly indicates that REEs were originated from sea water during phosphogenesis (Bonnot-Courtois and Fleoteaux, 1989). The cerium anomaly in is controlled mainly by redox conditions in sea water (Jiang et al., 2007). The observed negative Ce anomaly in the samples could indicate an oxide and anoxic environment (Jiang et al., 2007; Fig. 8). In general, HREE enrichment is a common characteristic of old marine phosphorites, particularly those located in the Tethytian belt (Altschuler, 1980; Tlig and Sassi, 1985; Bonnot-Courtois and Fleoteaux, 1989). In the studied samples, depletion of LREE than HREE may indicate the effects of sea water in enrichment of HREE (Leybourne and Johannesson, 2008; Fig. 8; Table 1). In addition, depletion of LREE than HREE may also provide insight into the REE absorption by iron oxides or organic complexes (Wigley and Compton, 2007). Positive Eu anomalies reflect deposition under reducing conditions (Ogihara, 1999; Kidder et al., 2003; Jiang et al., 2007). The positive Eu anomaly has been seen in some phosphorite samples especially in phosphorites enrich organic matter and host shale (Fig. 8). The degradation of organic matter quickly consume the oxygen in reducing condition and developed favorable conditions to reduce Eu^{+3} to Eu^{+2} and thus Eu^{+2} could easily contribute in the Ca site of apatite structure. The variation of Eu anomalies (Eu/Eu^{*} = 0.900–1.149) indicate fluctuating conditions from oxic to anoxic (Jiang et al., 2007; Table 1). In the Kuh-e-Sefid thulium has lowest concentration amongst rare earth elements, analogous to other deposites (Tzifas et al., 2014). The behavior of Tm is similar to Lu and Tb. Consistently, Kuh-e-Sefid phosphorite samples show same depletion in Tm and Tb values (Fig. 8; Table 1).

Several elements that substitute Ca including rare earth elements and trace elements such as monovalent (Na⁺, K⁺), divalent (Sr²⁺, Pb²⁺, Ba²⁺, Mn²⁺, Cd²⁺), trivalent (REE³⁺), tetravalent (Th⁴⁺, U⁴⁺), and hexavalent cations (U⁶⁺), are suitable for contribute in the carbonate-rich fluorapatite/francolite ([Ca₅(PO₄,CO₃)₃(F,OH)]) structure. Hence some oxo-anions such as VO₄, As₂O₄, SO₂, SO₄ and CO₃ can be substituted into PO₄ structure in apatite group lattices (Rakovan and Hughes, 2000; Rakovan et al., 2002; Pan and Fleet, 2002; Luo et al., 2009; Tzifas et al., 2014; Tzifas et al., 2016). A wide range of trace elements, such as Sr, Ba, Se, Mo, Ag, Pb, Zn, V, Cr, Ni, Cu, Cd, and U are observed in the phosphorites (Tzifas et al., 2014). Consistently, Kuh-e-Sefid exhibit different concentration of elements such as REE, Ni, Ba, Pb, V, Mo, Cr, Cd, Se and U (Table 1).

Studies and observations have shown that micro-organisms can carry some elements release by the dissolution of apatite and moreover the deposition of secondary phosphates provide a mechanism for immobile of metals (Feng et al., 2011). The surface of bacterial cells has generally negative charge and mainly include the carboxyl, phosphate and nitrogen groups. Hence some anions (e.g. carbonate, phosphate and sulfate) can react with the adsorbed metal ions and form sediments which act as nucleation sites (Greenwood et al., 2013). The concomitance of organic matter and mineralization of phosphate showed that the oxidation of organic matter is due to the oxidation processes synchronized with the early diagenesis and phosphogenesis (Benalioulhaj and Trichet, 1990). Organic matter seems to be necessary for phosphogenesis owing to the providing phosphate source and energy for oxidation-reduction changes (Jarvis, 1992). Organic compounds react with various types of elements via changing the conditions of oxidation-reduction. These compounds also may be effective on the physical and chemical properties of mineralization (e.g., pH, mineral solubilities, depositional temperature, rock porosity and permeability; Greenwood et al., 2013). Degradation of sedimentary organic components is attributed particularly to the aerobic bacteria and bacterial sulfate reduction, respectively (Ingall and Cappellen, 1990). Thus this process seems to be essential for releasing the phosphorus and carbon from organic matter (Ingall and Cappellen, 1990).



Uranium-bearing phosphorite samples of Kuh-e-Sefid phosphorite

Fig. 10. A: Discrimination diagram of Log Th/Sc versus Log Zr/Sc (Rollinson, 1996; Tzifas et al., 2014) B: V/(V + Ni) vs. Ni/Co diagram (Rimmer, 2004). Phosphorite samples in purple, shale samples in blue and iron oxide sample in violet.



Fig. 11. FTIR Spectra of Kuh-e-Sefid samples: A: FTIR analysis Spectrum of phosphorite sample, B: Spectrum related to hydrocarbon-bearing phosphorite shale, C: FTIR Spectrum of phosphorite horizon with hydrocarbon shale and D: Spectrum of phosphorite horizon.

are presented in the form of a comparison between the average value of phosphorite for the East Mediterranean and other phosphorite in the world (Baturin and Kochenov, 2001; Li and Schoonmaker, 2003; Bech et al., 2010; Tzifas et al., 2014; Fig. 14). Trace element distribution patterns in the study area are similar to phosphorite worldwide; especially in terms of concentration of U, Se, and Cd that can be related apatite group minerals crystal lattice (Baturin and Kochenov, 2001; Li and Schoonmaker, 2003; Bech et al., 2010; Tzifas et al., 2014). As mentioned in the petrographic analysis, the main mineral is carbonaterich fluorapatite (francolite) in these samples, which is able to absorb more trace elements due the having a relatively open structure compared with apatite (Tzifas et al., 2014). In addition to uranium, Mo anomaly is observed due to its presence in phosphorite (Jarvis, 1992; Tzifas et al., 2014). Also there is some weak negative anomaly of trace elements, such as Co, Sn, As, Th, and Tl. Concentrations of Se in the phosphorite is high like all the phosphorite in the world (Tzifas et al., 2014). Also some elements, such as Tl and As, have the lowest content (Table 1).

Furthermore, trace elements spider diagram were drawn for samples of the Kuh-e-Sefid phosphorite normalized with UCC (Fig. 15). All samples show a positive U anomaly, especially in samples of Ks-12 and Ks-6, which are associated with hydrocarbons. The phosphorite samples show depletion and negative anomalies of LILE (Large Ion Lithophile Elements; Rb, K) like other phosphorites (Tzifas et al., 2014; Abed and Sadaqah, 2013). In addition to uranium some elements, like Ni, Sr, Cr, and Pb, are present in high content in the Kuh-e-Sefid phosphorite (Fig. 15; Table 1). The concentration of elements such as Cr, Zn, V, Ni, Mo, As, Cu, Se, and Cd are mainly related to the process of replacing these elements with PO_4^{3-} or Ca^{2+} ions in the structure of apatite group lattices (Provet and Lucas, 1980; Ilyin 1998). Uranium and some elements, such as V, Ni, Cr, Mo, Cd, have relatively high concentration (enrichment), due the role of organic matter in deposition and concentration of the elements in phosphorite (Veeh et al, 1974; Jiang et al., 2007). The concentration of elements, such as Ba, Sr, and REE especially Y in fluorapatite of marine sediments is high due the substitution of these elements into Ca site in the apatite crystal structure (Bonnot-Courtois and Fleoteaux, 1989). Apatite and iron hydroxides are the main factors in transporting and concentration of Zn, Cd and Pb than organic matter as well (Stamatakis, 2004).

Thorium replaces Ca site which due to the presence of close ionic

radius 1.00 Å and 1.12 Å (respectively) in the apatite group structures. Since Th is detrital within the dominant chemical precipitate thus the element is low in the phosphorite (Abed and Sadaqah, 2013). The geochemical behavior of Zr and Ti are similar to Th in sediments (Bonnot-Courtois and Fleoteaux, 1989; Abed and Sadaqah, 2013). It accommodates Zr, Ti, and Th, are both in the detrital phase. All of which represent the association of these elements with entered alluvium phase into the basin. Hence Zr, Ti, and Th are low content in Kuhe-Sefid phosphorite (Bonnot-Courtois and Fleoteaux, 1989; Abed and Sadaqah, 2013; Fig. 15; Table 1).

Based on FTIR data, vibration bands can be correlated to single bonds or functional groups of a molecule that is used for the detection of unknown compounds (Schmitt and Flemming, 1998). Hydroxyl (-OH) groups are the most active function group on the decay of uranium and organo-metals (Nakashima et al., 1984). The functional groups in organic material are the controlling factors of migration of PO₄³⁻ from surface sediments (Cooke et al., 1986). Aliphatic CH contributes to the strong and medium intensity of the bands at $2800-3000 \text{ cm}^{-1}$ and absorption in these bands suggests that the ratio of aromatic hydrogen than aliphatic hydrogen is very low. Absorption low band at 3030 and 3050 cm⁻¹ is associated C–H aliphatic as well as surface absorption intensity of single aliphatic CH bonds is always stronger than aromatic CH bonds (Cooke et al., 1986). FTIR studies identified mineral-organic bounds especially CH aliphatic and aromatic stretching associated with mineralization. The highest content of uranium is associated with carbon atoms of aromatic compounds in the rocks (Leventhal and Daws, 1986; Tzifas et al., 2014). The Kuh-e-Sefid phosphorites hosted by the Pabdeh Formation can be considered as a source rock for hydrocarbon deposits, because of the enrichment in organic matter (Daneshian et al., 2012).

Maintenance of organic matter is controlled by factors including environmental oxygen, sedimentation rate, rate of biodegradation and the composition of the organic matter in sedimentary environment (Stein, 1991). Content of total organic carbon (TOC) can generally be considered as an indicator of kerogen amount in the source rock (Peters et al., 2005). The range of TOC content of Kuh-e-Sefid phosphorite samples represents the loss of necessary conditions for the protection of organic matter or reducing the amount of organic components (Stein, 1991). The values showed the quality of hydrocarbon-bearing source rocks (Stein, 1991). Based on the results of Rock-Eval pyrolysis, it can

Table 2

niormanon from F115	analysis spectra of Kun-e-Send phosp	pnorite sampies.			
Bounds type	Bounds location of Ks-2 sample in FR [cm ⁻¹] Phosphate horizon	Bounds location of Ks-4 sample in FTIR [cm ⁻¹] Interlayer shale	Bounds location of Ks-6 sample in FTIR [cm ⁻¹] Phosphate	Bounds location of Ks-10 sample in FTIR [cm ⁻¹] Phosphate horizon	Refrence Spectrum wavelengths
Apatite Calcite	711	470		467	477 (Tzifas et al., 2014) 710 (Tzifas et al., 2014)
Calcite	877	873	879	873	873 (Tzifas et al., 2014)
Apatite	1042	1042		1040-1042	1049 (Tzifas et al., 2014)
Group CH ₂	1461	1424	1440	1430	1440–1458 (Cooke et al., 1986)
C=C group Aromatic	1598	1598	1600	1594-1600	1600 (Ellerbrock and Gerke, 2004)
Carboxylic asid C=0			1700	1725	1700–1725 (Pavia et al., 1987)
Quartz	1799	1799			1700–2000 (Calderon et al., 2011)
C≡C Alkaline			2198	2509	2100–2300 (Pavia et al., 1987)
Carboxylic OH	2516	2516	2509	2800	2400–3400 (Pavia et al., 1987)
Aliphatic CH group	2870	2834	2851	3315	2850–3000 (Pavia et al., 1987)
OH bound	3305	3333			3000–3600 (Ellerbrock and Gerke,
					2004)
Clay minerals	3611	3607	3605		3620 (Mukherjee and Srivastava, 2006)

be concluded that the highest uranium values in phosphorite mineralization are associated with the sample containing low hydro-carbonization generating potential (Poor). Most of the Kuh-e-Sefid organic matter-bearing phosphorite samples have continental carbon. The organic carbon can be of continental origin (i.e., shallow marine environmental, continental shelf, inter-tidal zone, even rivers and swamps), whereas marine organic matter has originated in the deep sea (Jones and Manning, 1994; Peters et al., 2005). No doubt both types of organic matter can be deposited in deep marine environments (Jones and Manning, 1994; Peters et al., 2005).

It seems that frequency of uranium and phosphorite mineralization associated with organic components is the result of the matter entry from the continent to the sea and also redox processes during deposition in the marine environment (Soudry et al., 2002).

Sediments rich in organic matter and their diagenetic mineral products are an important sink for oceanic U in marine systems (Soudry et al., 2002). Marine phosphorites generally contain 20-500 ppm uranium. Stable form and highly soluble uranium (U⁶⁺) is present as uranyl carbonate complex $UO_2 (CO_3)^{4-}$ in sea water (Gabar et al., 2002; Tzifas et al., 2014). Tetravalent and hexavalent forms of uranium are both present in phosphorites. The main factor controlling U concentration is ionic substitutions of Ca²⁺ by U⁴⁺ due to close ionic radius (0.97 and 0.99 Å, respectively) in the apatite structure (Gabar et al., 2002). Baturin and Dubinchuk (1979) reported that uranium usually concentrates in bubbles of organic matter and phosphate grains or as filler mineral of intergranular pore spaces in phosphorites. Levels of uranium are dependent on redox conditions in sedimentary rocks. The high concentrations of uranium occur in organic matter rich facies and low-oxygen environment in phosphorites. Two main processes occur as complexion and reduction when U reacts with organic matter (Landais, 1996). In lithogenic environments, uranium is closely related to redox-sensitive elements like Cu, Se, As, V, and Mo (Kyser, 2014).

The average concentration of U is 41.9 ppm in Kuh-e-Sefid samples, this is much higher than NASC (2.6 ppm), but lower compared to the global average for phosphorites (120 ppm; Altschuler, 1980). In general, as a result of the reduction processes, environment acidification is occurring. This favors the deposition of uranium by destabilizing a variety of complexes with both organic and inorganic ligands in marine solutions (Nakashima et al., 1984). Low amounts of actinide elements such as uranium are associated with hydroxyl functional groups and aliphatic and aromatic carbon formations in sedimentary rocks. In general, higher uranium content is correlated to the existence of carbon atoms of aromatic compounds in the rocks (Leventhal and Daws, 1986). Carboxyl functional groups of humic acids and kerogen may play a prominent role for formation of uranium complex with organic components during complex formation by ion exchange processes (Munier-Lamy et al., 1986; Tzifas et al., 2014).

The phosphorites containing a high concentration of autogenic uranium (about 50%) are closely related to organic matter in the region of British Columbia, Canada (Kolodny and Kaplan, 1970). High uranium content (648 ppm) is also linked to organic matter in Greek phosphate deposits (Tzifas et al., 2014). In addition, Langmuir (1978) suggested that the primary inorganic processes are due to sulfate microbiological reduction.

According to Rouzaud et al. (1980) regarding the reaction of uranium and organic matter, it can be said that the organic compounds are being dehydrogenated and lose two protons. Hence reduction of U^{6+} in the form of soluble to insoluble U^{4+} may also take place, which is finally precipitated during the reaction. Primary concentration of uranium is due to the presence of organic matter in the phosphites. (Tzifas et al., 2014). Many materials contain microcrystals of uraninite, while some other materials, including of uraniferous organo-metallic complexes (Rouzaud et al., 1980). Thus, organo-metallic compounds of UO_2^{2+} were formed with carboxylate groups (most likely of humic acids), as well as reduced U in the form of uraninite (Parnell and Eakin, 1987; Tzifas et al., 2014).

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Table 3

Sample Rock Type	Ks-1 Phosphate horizon	Ks-2 Phosphate horizon	Ks-3 Phosphate horizon	Ks-4 Interlayer shale	Ks-5 Interlayer shale	Ks-6 Phosphate	Ks-7 Phosphate horizon	Ks-10 Phosphate horizon	Ks-11 Interlayer shale	Ks-12 Iron oxide layer
S_1 (mgHC/g)	0.01	0.02	0.01	0.06	0.1	0.03	0.03	0.01	0.82	0
S_2 (mgHC/g)	0.22	0.22	0.55	2.76	4.38	0.46	0.61	0.48	58.46	0.2
HI	1.1	1.57	1.45	4.67	4.81	1.15	1.69	1.65	6.64	0.47
OI	3.1	4.93	3.82	1.54	0.77	4.67	4.61	4.34	0.26	8.47
PI	0.04	0.08	0.02	0.021	0.022	0.061	0.05	0.020	0.013	0
TOC (%)	0.2	0.14	0.38	0.59	0.91	0.4	0.36	0.29	8.81	0.42
$S_1 + S_2$	0.23	0.24	0.56	2.82	4.48	0.49	0.64	0.49	59.28	0.2
(mgHC/g)										



Fig. 12. S₂ vs. TOC diagram in order to determine the content of organic matter. S₂: The power of sample hydro carbonization, TOC: total organic carbon present in the sample (modified after Shaaban et al., 2001).



Fig. 13. $S_1 + S_2$ vs. TOC diagram in order to determine the genetic potential of the studied samples. $S_1 + S_2$: Rock eval values for potential of the source rocks (modified after Huang et al., 2003).



Fig. 14. Scatter diagram of trace elements in the Kuh-e-Sefid samples compared with East Mediterranean and other phosphoites of the world (data from: Soudry et al., 2002; Imamoglu et al., 2009; Bech et al., 2010; Baioumy, 2011; Tzifas et al., 2014).

Soudry et al. (2002) elucidates three major mechanisms for the transfer of seawater U into sediments: (1) bioaccumulation of U by phytoplankton (Degens et al., 1977) or bottom-dwelling macrophytes (2) diffusion of dissolved U^{6+} from seawater into bottom sediments followed by its reduction to insoluble U^{4+} in the anoxic zone of the

sediment layer (Anderson, 1987; Kolodny and Luz, 1992), and (3) adsorption or organic complexation of dissolved U^{6+} by settling particulate OM or uranyl adsorption on Fe oxyhydroxides (Hsi and Langmuir, 1985).

Furthermore, the role of organic matter is important in the



Fig. 15. UCC-normalized trace elements diagram of Kuh-e-Sefid samples (Rudnick and Gao, 2003). Normalization based on data from (Taylor and McLennan, 1985). Phosphorite samples in purple, shale samples in blue and iron oxide sample in violet.

accumulation and concentration of elements with economic value such as U and REE. So that the distribution of uranium is controlled by organic matter in surface layers of the sea, close to pelagic sediments. Study of the Kuh-e-Sefid phosphorite shows that the most important deposition and mineralization mechanisms for the study area are: (1) the complex formation and chelating, reduction of uranium by organic matter in the deposit, (2) element carriage with organic ligands accruing surface adsorption of U^{6+} due to large ionic radius from its coarse molecular physical surfaces, and (3) the reduction of the anoxic zone as a result of the decomposition of organic compounds thereby reducing uranium and substituting it into Ca sites in the carbonate-rich fluorapatite structure. Part of phosphorus derived from the consumption of organic matter by microorganisms as energy sources. However, rest of presented data implies that at least a part of phosphorus originated from continental source via entrance of detrital components to the basin. The results indicate that the abundance of organo-metals and rare earth elements could be related to the detrital phosphatic materials (continental origin) and microorganisms activity during precipitation. Organic matter seems to have important role in the deposition and/or transportation of elements, such as uranium and rare earth elements during phosphorite mineralization.

6. Conclusions

- 1. Field observation and microscopic studies indicate that phosphorite mainly consists of shale, marl, and limestone with textures varying from wackestone to packestone form. Also phosphorite components occur as authigenic apatite, pellets, intraclasts, and fish skeletal fragments and microfossils. In additions to phosphorite and biogenic components, non-phosphorite minerals such as calcite, glauconite, pyrite, iron oxide, and minor montmorillonite, microcrystalline quartz are present.
- The combination of FTIR and XRD studies have proved the carbonate-rich fluorapatite with calcite and organic material are mostly associated with phosphorite mineralization in the study area.
- 3. Shales as the phosphorite host-rock are the main factors for transmission of phosphorus and some trace metals. Also most mineralization occurs in phosphorite enriched in organic matter. It can be concluded that the shales, as the host rock of the Kuh-e-sefid phosphorite, are considered the main factor for phosphate transportation. Therefore, the highest grade mineralization occurred in zones rich in organic matter.
- 4. The NASC-normalized REE distribution pattern shows HREE enrichment, negative Ce anomalies and the coexistence of slightly negative and positive Eu anomalies. This provides evidence for transitional fluctuation from oxic to anoxic sedimentation conditions.
- 5. The Ce/Ce^{*} vs. Pr/Pr^{*} diagram indicates that the all of the Kuh-esefid phosphorite samples have anegative Ce anomaly. The Kuh-e-Sefid Phosphorite samples clearly indicate high ratios of Pr/Pr^{*} and low Ce/Ce^{*}.
- 6. According to Th/Sc versus. Zr/Sc discrimination diagrams, some samples exhibit a pelagic sediment trend, in contrast to the rest of the studied samples showing a signature closer to average shale.
- Ni/Co ratios and Ni/Co versus V/(V + Ni) reveals dysoxic to anoxic conditions for the hydrocarbon-bearing phosphorite and host shale, while is indicating oxic conditions for phosphorite –free hydrocarbons samples.
- 8. FTIR studies reveal and identified mineral-organic bonds such as OH, Carboxylic OH, Carboxylic acid C=O, C≡C Alkaline, group CH₂, C=C aromatic, CH aliphatic and aromatic stretching associated with phosphorite mineralization and associated with its elements. Moreover, the highest content of uranium is correlated to carbon atoms of aromatic compounds in the rocks.
- 9. Rock-Eval results showed that associated carbon with phosphorite mineralization have both continental origin and also phosphorus

originated from the bio-degradation of organic matter by microorganisms.

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