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# The Study of Phosphate Rock Forming Minerals (Francolite) of Iran through the EDX-SEM to Assessment of Compositions in Nano-Scale

F. Bolourchifard[a,b,*] , A. Memar[c]

[a] *Faculty of Earth Science, Kharazmi University, Postal code: 15719-14911, Tehran- Iran,*
[b] *Nuclear Science & Technology Research Institute (NSTRI), Nuclear fuel Cycle Research school (NFCRS), Postal code: 14155-1339, Tehran, Iran*
[c] *Nuclear Science & Technology Research Institute (NSTRI), Nuclear fuel Cycle Research school (NFCRS), Postal code: 14155-1339, Tehran, Iran*

**Abstract**

In this work, the fine grains of Phosphate rocks forming minerals (francolite-$Ca_5(PO_4,CO_3)_3F,OH$) which belong to the geological formation of phosphate rocks of Zagros mountains in IRAN were detected, analyzed and interpreted by SEM-EDX in nano-scale. Moreover, the results are compared with the results of XRD analysis and straight observations of samples through the polarized microscope. Finding the composition of elements in minerals is the best path finder and also is very important in many geological investigations. The fine grain Phosphate minerals perform as traps which attract some kinds of elements. But sometimes these minerals are very fine and it is too difficult to determine and separate them for further studies. For instance, interpretation and investigation of the composition of fine minerals in Nano-scale by using single crystal X-ray Diffraction (Single-crystal XRD) analysis is impossible. Due to variety of minerals phases in a rock sample, the interpretations of the results of total elemental analysis, for example XRF, ICP, are not so real. Therefore, the best method for determination of elements in fine grain rock forming minerals is the study of minerals by the Scanning Electron Microscopy (SEM), with Energy Dispersive X-Ray Analysis (EDX).



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*Keywords:* Fine grain Phosphate; Francolite Minerals; EDX- SEM, XRD; Nano-Scale.

* Corresponding author. Tel.: +98 21 22364314 ; fax: +98 21 88221128.
*E-mail address:* fboloorchi@aeoi.org.ir&faridbolourchifard@gmail.com


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## 1. Introduction

The methods which are employed in the investigation of concentration of materials in ultrafine grains or, Nano-scale are very important in the earth sciences. Although there are lots of methods for doing this experimentation, some are not so wise while others may be possible to do. Due to interpretation of behavior and the concentration of nano particle in some sediments that can lead to the genesis of the formation, the study of fine grain particles in geology, particularly in sedimentology and sedimentary rocks, is very important for further investigations and interpretations. Generally, the study of phosphates, especially in sedimentology and sedimentary of phosphate rocks, are very significance for human being, Ferro (2014); the other important aspects are the investigation of chemical agent and presence of important elements in chemical structure which determine the genesis of formation of phosphate deposits, Kauwenbergh (2010).

## 2. Experiments

In this study, several samples from phosphate layers of Pabdeh sedimentary formation, folded in Zagros mountains, nearby Dehdasht city (Northern Edge of Kooh-e-Lar Anticline) were selected for analysis; they were analyzed by XRD, XRF, and Scanning Electron Microscopy with Energy Dispersive X-Ray analysis (SEM-EDX).

XRD tests were done by using Philips' analytical X-Ray B.V. with PC-APD, diffraction software (Philips PW-1730) and for XRF measurements, Philips' PW-1480 was used.

These samples commonly contain fossiliferous limestone structure (Bioclastic Peloidal Packstone, consisting of Planktonic foraminiferas, Ostracod, Globorotalia, Globigerina, ...), and they belong to carbonate ramp environment of Zagros sedimentary basin (Fig. 1).

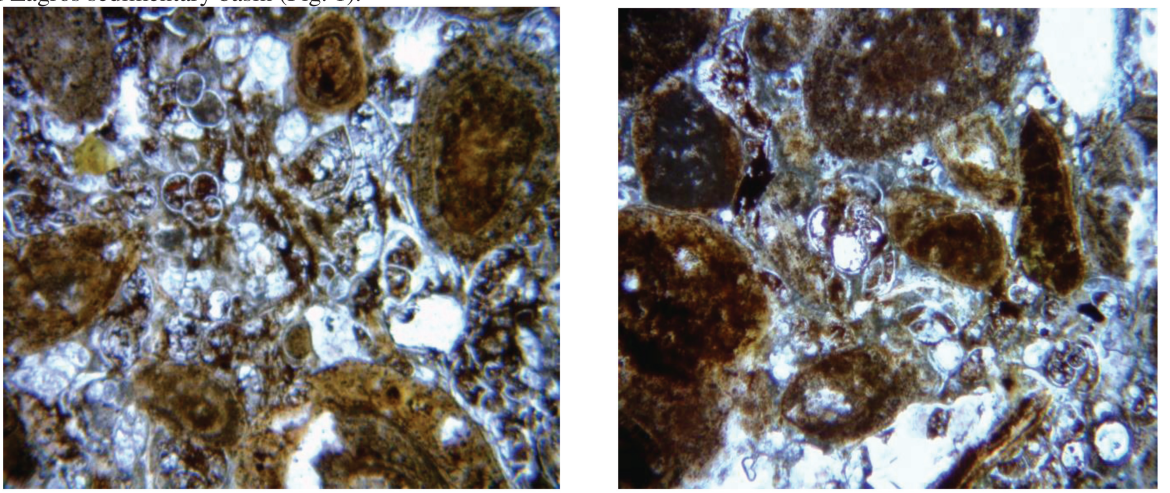

Fig.1. The optical microscopy photos of phosphate limestone (Bioclastic Peloidal packstone), containing Planktonic foraminifera (Globorotalia, globigerina, Ostracod and Gastropod), (50X, Lp).

The microscopic thin sections (Fig. 1), show the accumulation of phosphate on the crust of microfossils and pelloidal clast. The results of XRF analysis confirm that up to 30 percent of $P_2O_5$ in this sample is in agreement with Jay et al. (2007) (Table 1). Since there is no homogeneity as far as the sample is concerned, this portion of $P_2O_5$ does not belong to the whole part of the sample. The main phosphate mineral is Apatite Francolite, with the general formula of $(Th, U, Ce, Ca, Mg, Sr, Na)_{10}(PO_4, CO_3)_6F_{2-3},OH_{2-3})$.

According to the classification of Uranium deposits in the world, Dulkampt (2010), Phosphate deposits consist of phosphorite, that are formed from upwelling, nutrient-rich marine waters of continental shelf origin, containing syn-sedimentary stratiform and disseminated U in fine-grain Apatite. There are three subtypes, Burnes et al. (2013):

1. Organic Phosphate deposits.
2. Mineralochemical phosphorite deposits.
3. Continental Phosphorite deposits.

Table. 1. The result of X-Ray fluoresence analysis (XRF) of the sample is as follows:

| Sample No. | SiO2 | Al2O3 | Fe2O3 | Cao | Na2O | MgO | K2O | TiO2 |
|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % |
| 93-FB-45 | 13.212 | 1.079 | 1.911 | High* | 0.151 | 0.321 | 0.394 | 0.07 |

| Sample No. | $MnO_2$ | $P_2O_5$ | Cl | S | Ba | Ce | Co | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|
| | % | % | Ppm | ppm | ppm | ppm | ppm | Ppm | ppm |
| 93-FB-45 | 0.015 | ~30 | 97 | 1330 | 308 | 39 | N | 342 | 28 |

| Sample No. | Nb | Ni | Pb | Rb | Sr | V | Y | Zr | Zn | Mo |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ppm | ppm | Ppm | ppm | ppm | Ppm | ppm | ppm | ppm | ppm |
| 93-FB-45 | N | 80 | 19 | 15 | 1221 | 49 | 23 | 93 | 160 | 30 |

| Sample No. | U | Th | LOI |
|---|---|---|---|
| | ppm | Ppm | % |
| 93-FB-45 | 106 | 6 | 13.45 |

*Sample Contain amounts of F.*

**Carbonate* (Because of calcite matrix cement in sample even in combination of phosphate minerals)

** Phosphate Rock ($P_2O_5$>15%)

To identify the crystalline structure of minerals in this sample, X-ray diffraction analysis (XRD) was performed after proper milling. The main minerals of this sample were determined to be Calcite and Carbonate fluorapatite, with the common formula of $Ca_5 (Po_4, Co_3)_3F$, OH (So called Francolite). It is known as the apatite which is present in many different sedimentary phosphate environments. The results of XRD analysis are summarized in Fig. 2 and table 2.

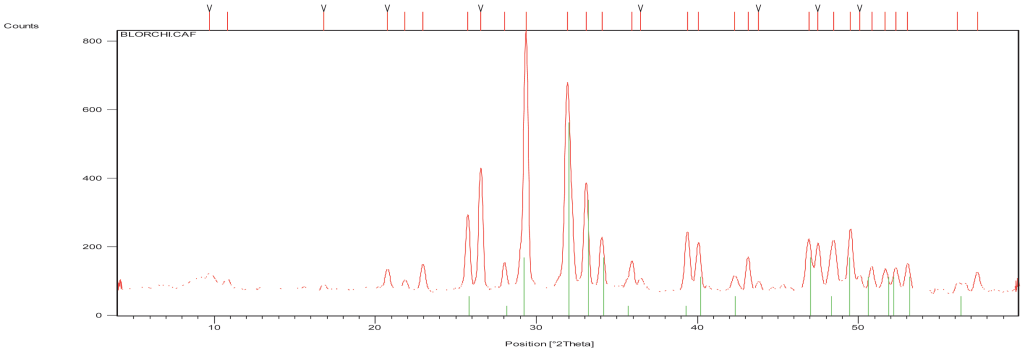


Fig. 2. XRD pattern of the sample with the details presented in table 2.

Table 2. XRD results for the sample.

| Visible | Ref. Code | Score | Compound Name | Displacement [°2Th.] | Scale Factor | Chemical Formula |
|---|---|---|---|---|---|---|
| | 00-031-0267 | 26 | Carbonate-fluorapatite | 0.013 | 0.498 | $Ca_{10}$ ( P O4 )$_5$ C $O_3$ F1.$_5$ ( O H )$_{0.5}$ |
| * | 00-002-0833 | 45 | Francolite [NR] | -0.036 | 0.631 | Ca F ( Ca , C )$_4$ [ ( P , C ) (O , O H, F )$_4$ ]$_3$ |
| | 00-021-0141 | 26 | Carbonate-fluorapatite | 0.013 | 0.498 | $Ca_{10}$ ( P O4 )$_5$ C $O_3$ F1.$_5$ ( O H )$_{0.5}$ |
| | 01-086-2343 | 38 | Calcite | 0.232 | 0.944 | Ca ( C $O_3$ ) |

## 3. Results and Discussion

Regarding the obtained data, the main phosphate crystals of this sample are Francolite. In this scale, and with these methods of analysis, finding the locations of the elements in minerals is not possible. Francolite is a common sedimentary phosphate mineral that has a lots of various cations in its formula, which may varies, depending on its location and the geological conditions (some REEs, Th, U, Ce, Ca, Mg, Sr, Na)$_{10}$($PO_4$, $CO_3$)$_6$$F_{2-3}$,$OH_{2-3}$).

Therefore, it would be important to distinguish the exact structure of the francolite crystals in the geological formations. One of the best ways to find the structure of crystals is single crystal X-ray Diffraction (Single-crystal XRD) analysis. But unfortunately, crystals are so fine (submillimeter), and it is impossible to determine the elements in the structure of crystals. Therefore, it is not wisely to have fine grains grown because of the compositional changes. Therefore, the Single-crystal XRD method should be neglected. One of the best ways for in-situ investigation of the composition of Ultra-fine grains is the Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), Sylvester (2012).

Using this method, the elemental composition of each fragment in the sedimentary rocks, particularly in microfossils, and concentration of different elements in bioclastic fragments as well as the other parts of rock could be distinguished, Fig. 3 and Fig. 4.

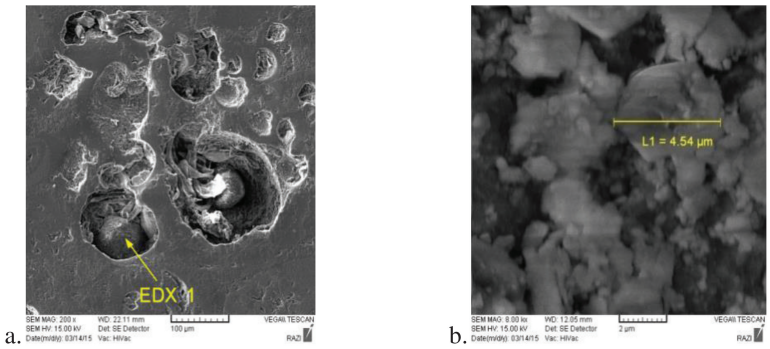


Fig. 3. (a) SEM image of a peloidal shape bioclastic phosphate in sedimentary containing different minerals; (b) cross section of Apatite crystal (Hexagonal) in higher magnifications.

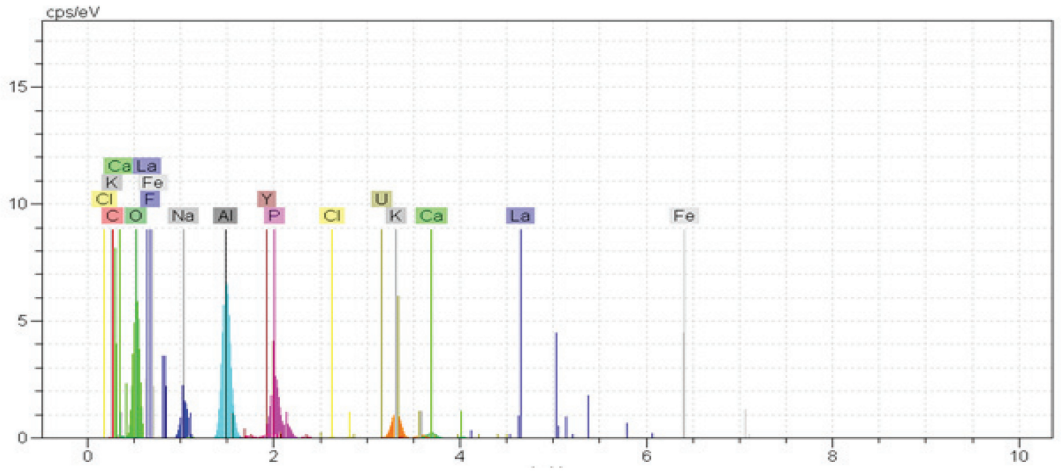


Fig. 4. SEM-EDX Spectrums corresponding to the point location marked in Fig. 3a.

Table. 3. SEM-EDX point analysis of the sample indicated in Fig. 2a.

| Element | Series | unn. C [wt.-%] | norm. C [wt.-%] | Atom. C [at.-%] | Oxide | Oxide. C [wt.-%] |
|---|---|---|---|---|---|---|
| Carbon | K series | 1.06 | 1.06 | 1.76 | $CO_2$ | 4.76 |
| Sodium | K series | 4.74 | 4.74 | 4.12 | $Na_2O$ | 7.86 |
| Aluminium | K series | 18.18 | 18.20 | 13.47 | $Al_2O_3$ | 42.29 |
| Phoshorous | K series | 10.42 | 10.43 | 6.73 | $P_2O_5$ | 29.40 |
| Potassium | K series | 7.16 | 7.16 | 3.66 | $K_2O$ | 10.61 |
| Calcium | K series | 1.66 | 1.66 | 0.83 | CaO | 2.85 |
| Iron | K series | 0.43 | 0.43 | 0.15 | $Fe_2O_3$ | 0.76 |
| Yttrium | L series | 0.68 | 0.68 | 0.15 | $Y_2O_3$ | 1.06 |
| Lanthanum | L series | 0.08 | 0.08 | 0.01 | La | 0.10 |
| Uranium | M series | 0.22 | 0.22 | 0.02 | $UO_2$ | 0.31 |
| Oxygen | K series | 55.30 | 55.34 | 69.10 | - | 23.34 |
| Total: | 99.9 % | | | | | |

As it shown in table 3, we can see the amount of REE and Yttrium in phosphate particle of sample, and it is so comparable to this kind of minerals that have been reported in our neighbor country, Iraq Asma et al. (2010).

## 4. Conclusions

If the geological and geochemical paleo-conditions (characteristic redox) are suitable, even fine grains phosphate minerals, mainly Apatite (Francolite) has the characteristic of absorbing some elements in its chemical structures. Obviously, the results of conventional analysis of samples in our study area, do not show this behavior, except using EDX-SEM. Because the samples of rocks do not have homogeneity, then different phases maybe considered together whereas, to get the best result, each part should be tested separately.

Since the quantity of REEs, such as Lanthanum, Yttrium, and Uranium is presented in the phosphate particle phase, substitution of these elements could be found in the structure of Francolit mineral (some REEs, Th, U, Ce, Mg, Sr, Na, $Ca)_{10}(PO_4, CO_3)_6F_{2-3},OH_{2-3}$). Finally, it is recommended to explore more sedimentary phosphate deposits in IRAN, reasonably by using this method and also in small scale to find new prospects.

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