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## Research Paper

# Geochemical Evaluation of Rare Earth Elements Using Step Factor Analysis and Fractal Modeling in Qalikouh Oil Shale in Western Iran

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**Abstract:** Qalikouh area is located 35 km southwest of Aligudarz city, Lorestan province, SW of Iran. The area is located in the central part of the Zagros Geological Zone. The oil shales of the area are located in the Upper Triassic and Lower Jurassic of Sargalu and Garau Formations. The Sargalu Formation contains a series of shale, carbonate and clays. Garau Formation includes oil shale horizons with different thicknesses, ammonite shales and black cherty layer. In order to investigate the enrichment ratio and relationship between elements and organic matter, 53 samples of oil shale from Garau and Sargalu formations were selected. The samples were analyzed by XRD, XRF, ICP-MS and Rock-Eval analyzer. Data processing was performed using factor analysis, fractal modeling, stepwise factor analysis and principal component analysis. The data show that Sargalu Formation with average TOC = 13.27% and Garau Formation with average TOC = 18.13%, have high content of organic matter in central and NW of the area. Concentration-number fractal modeling showed that the Co, Mo, Ni, Pb and U have significant anomalies. The stepwise factor analysis (SFA) method showed a significant correlation between the anomalous elements and TOC. Geochemical maps showed that the anomalies are located for Co and Pb in the center and SE, for Mo, Ni in the NW and center, for V and REE in the NW, and for U in central part of the area.

**Keywords:** Oil shale, Stepwise factor analysis, Fractal modeling, Qalikouh area, Western Iran.

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## INTRODUCTION

Oil shales are unconventional hydrocarbon resources which is composed of fine-grain sedimentary rocks [1,2]. Trace elements can be concentrate in oil shales because of they were formed in reduction condition [3-5]. According to the different researches, considerable oil shale reserves in the Qalikouh area have been formed in Garau and Sargalu formations [6]. In this research we used concentration-number fractal modelling and stepwise factor analysis method to analysis geochemistry of rare earth and trace elements (Co, Mo, Ni, Pb, U, V, and  $\Sigma$ REE) of Qalikouh oil shales. Also, related factors to mineralization and geochemical maps were determined and finally the single element maps were compared to factor rating maps.

## MATERIALS AND METHODS

53 samples were chosen from various geological sections of Qalikouh oil shales for geochemical analysis of and organic matter. After sample preparation, organic matters were analysed by Rock-Eval method, and trace and rare earth elements were analysed by ICP-MS [5]. In order to evaluate multivariate data, the principal component analysis (PCA) method was used. This method is a suitable tool for reducing the volume of geochemical data. Then, correlation and variations between these elements were investigated by using Stepwise Factor Analysis (SFA) method [1,7,8]. Finally, we used Concentration-Number fractal (C-N fractal) modelling, geochemical background and anomaly threshold values to calculate and draw concentration maps. The general formula for this model is as follows [9]:

$$N(\geq\rho) = F \rho^{(-D)} \quad (1)$$

Where:

$\rho$ : element concentration

$N(\geq\rho)$ : cumulative number of samples with values greater than or equal to  $\rho$

F: constant data

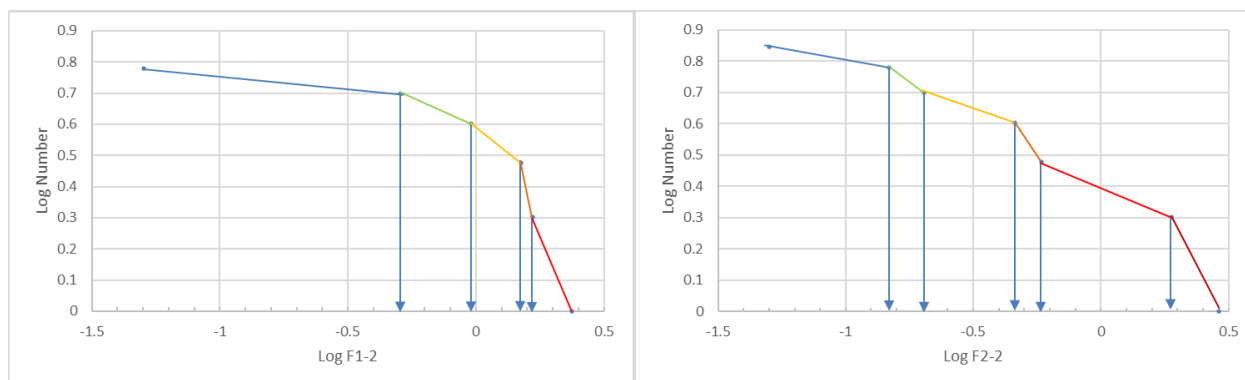
D: is fractal distribution of elements concentration.

## RESULTS AND DISCUSSIONS

The statistical show that the average of organic carbon (TOC) is 15.3%. Average for Co, Mo, Ni, Pb, and U is 16.73 ppm, 287.29 ppm, 238.85 ppm, 21.10 ppm, and 51.28 ppm, respectively. These average are high in the Garau Formation relative to Sragalu Formation. Average for V and REE is 751.53 ppm and 39.66 ppm. These average are high in the Sragalu Formation relative to Garau Formation. U, Mo, Ni, V, and partly Co show high correlation to organic matter. It can be concluded that the increase in concentration of these elements are related to the increase of organic matter.

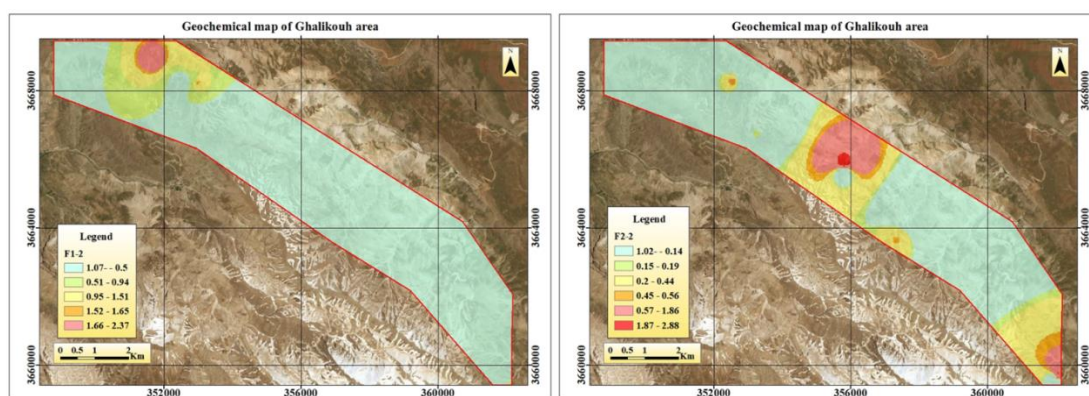
Elements concentration were classified by using Step Factor Analysis (SAF) method. In first step, the elements were classified on the basis of genesis characters. Threshold limit of 0.6 were used for separation of elements in different factors. First factor (F1-1) includes Ag, Al, Cd, Cr, Cs, Ga, K, Li, Nb, Rb, Sb, Ti V,  $\Sigma$ LREE, and  $\Sigma$ HREE. Factor II (F2-1) includes As, Co, Cu, Fe, Mo, Ni, P, Pb, S, Sr, Tl, U and TOC. Factor III (F3-1) includes Hf, Na, and Zr. Factor IV (F4-1) includes Ba and Mg. Factor V (F5-1) includes Sn and Ca, Mn, Th and Zn.

In the final stage, all elements were classified into 5 factors, and two groups including of F1-2 and F2-2. According to the stepwise factor analysis, light and heavy rare earth elements are located in F1-1. There is good correlation between Al, K, Ti and Ga in this factor which indicates these elements were originated from aluminosilicate minerals weathered [5]. The presence of the TOC parameter in F2-1 indicates that other variables in this group are controlled by organic matter. Presences of V, Ni, Mg and Cu confirm the origin of biological processes for these elements. The presence of P in this group show that concentration of P in organic matter. Also, Mo and U represent the sediments rich in organic matter which were deposited in reducing conditions. It seems that they are added to the sediments through the diffusion of porous water [5]. C-N fractal modeling were calculated based on F1-2 (including V, LREE and HREE) and F2-2 (including Co, Mo, Ni, Pb, U and TOC) data. C-N logarithmic diagram was plotted based on F1-2 and F2-2 and SFA data (Figure 1).



**Figure 1.** Concentration-number logarithmic diagram - F1-2 and F2-2

F1-2 and F2-1 anomaly maps were calculated according to C-N fractal modelling data (Figure 2). The maps show that F1-2 data has an anomaly in the NW part of the area and F2-2 show anomaly in the centre, partly in SE and NW of the area. Also, SFA data show that F1-2 anomalies are mostly related to Garau Formation and F2-2 anomalies are mainly related to Sargalu Formation.



**Figure 2.** F1-2 and F2-1 anomaly maps obtained by C-N fractal modelling

Elemental Enrichment Factor (EF) was calculated based on the average of Australian Archean shales. The results show that the enrichment ratio are as  $Mo > U > V > Ni > Pb > Co > \sum LREE > \sum HREE$  in Garau Formation. In Sargalu Formation, enrichment ratio are as  $Mo > U > V > Ni > Pb > Co > \sum LREE > \sum HREE$ .

## CONCLUSIONS

Oil shales in the Qalikouh area are mainly associated with Sargalu and Garau formations (Jurassic-Cretaceous). The average of TOC in Sargalu and Garau formations is 13.27% and 18.13%, respectively. The data show high content of organic matter in these shales. Average of Co, Mo, Ni, Pb, and U is 16.73 ppm, 287.29 ppm, 238.85 ppm, 21.10 ppm, and 51.28 ppm, respectively in Garau Formation samples. Average of V and REE is 751.53 ppm and 39.66 ppm in Sargalu Formation samples. The data show a good correlation between organic matter and Co, Mo, Ni, V, and U elements. Comparison of the main anomalies (calculated by fractal C-N method) indicates high enrichment for Co, Mo, Ni, Pb, U, and V elements, which confirm the hope to find good potential these elements in these oil shale as by-products.

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