

EVALUATING GEOCHEMISTRY OF RARE EARTH ELEMENTS IN COPPER DEPOSIT OF AGHBOLAGH, NORTH OF OSHNAVIEH, WEST AZARBAIJAN PROVINCE-IRAN

AVALIAÇÃO DA GEOQUÍMICA DOS ELEMENTOS RAROS DA TERRA NO DEPÓSITO DE COBRE DE AGHBOLAGH, NORTE DE OSHNAVIEH, PROVÍNCIA DE AZARBAIJÃO OCIDENTAL-IRÃ
EVALUACIÓN DE LA GEOQUÍMICA DE ELEMENTOS DE TIERRA RAROS EN EL DEPÓSITO DE COBRE DE AGHBOLAGH, NORTE DE OSHNAVIEH, PROVINCIA OCCIDENTAL DE AZARBAIYÁN, IRÁN

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ABSTRACT

AghBolagh region is located in southwest of West Azarbaijan Province that is 10 km far from north of Oshnavieh. Most of the rocky outcrops in the region include Cambrian deposits (carbonate deposits and clastic deposits (sandstone and shale)). These deposits were later influenced and altered by granite intrusion. The intrusion is made of granite and in term of nature, it is magmatic with High-potassium calc-alkaline and peralumin. Also the penetration of intrusion and Ore maker solvent in further distances from the contact point and inside the sequences of sandstone has formed quartzite rocks and ore bearing veins of cooper. The REE pattern normalized to Chondrite for granite, skarn, and marble intrusion and vein deposits shows the fact that, although the REEs pattern is a little smooth and unified, LREEs have more enrichment compared to HREEs in different lithology. The range of normalized numbers to Chondrite in AghBolagh deposit is clearly variable (2.58 to 141.93 for La and 0.14 to 27.27 for Yb). This indicates that there have been clear differences in increase and decrease of LREEs and HREEs during the formation of AghBolagh deposit stones and rocks. The La / Y ratio shows the pH condition of the environment for formation of deposit. This ratio in AghBolagh deposit ranges from 0.09 to 2.26. The granite intrusion shows the most amount of La/Y which is equal to 2. Skarn Zone (Endoskarn and Exoskarn and Ore in Exoskarn) shows two different conditions. The first condition: the part in which $La/Y > 1$, and this can be observed in samples near the intrusion and Skarn ore is also found in this range. The second condition: the part that $La/Y < 1$, which is near to marble lithology. Also, about vein deposit, the sample is ore making in alkaline conditions, and other samples show acidic conditions. To evaluate the segregation coefficient between REEs, different ratios of REEs including $(La/Yb)_n$, $(La/Sm)_n$, and $(Gd/Yb)_n$ are used. The values of these ratios range from (0.42 to 50.56) for $(La/Yb)_n$; and from (0.25 to 80.125) for $(La/Sm)_n$; (from 0.006 to 48.8) for $(Gd/Yb)_n$. The highest segregation was between LREEs and HREEs (more than 125) and the least segregation was between MREEs and HREEs during the Skarn process.

Keywords: AghBolagh. Skarn. $(La/Yb)_n$ ratio. $(La/Sm)_n$ ratio. La/Y ratio.

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RESUMO

A região de AghBolagh está localizada no sudoeste da província de Azarbaijan Ocidental, a 10 km do norte de Oshnavieh. A maioria dos afloramentos rochosos da região inclui depósitos cambrianos (depósitos de carbonatos e depósitos clásticos (arenito e xisto)). Esses depósitos foram posteriormente influenciados e alterados pela intrusão de granito. A intrusão é feita de granito e, em termos de natureza, é magmática com cálcio alcalino e peralumina com alto potássio. Além disso, a penetração de intrusão e solvente para a produção de minério em distâncias maiores do ponto de contato e no interior das seqüências de arenito, formaram rochas de quartzito e veias de minério contendo tanoeiro. O padrão REE normalizado para Chondrite para intrusão de granito, skarn e mármore e depósitos de veias mostra o fato de que, embora o padrão REE seja um pouco suave e unificado, os LREEs têm mais enriquecimento em comparação com os HREEs em diferentes litologias. O intervalo de números normalizados para Chondrite no depósito de AghBolagh é claramente variável (2,58 a 141,93 para La e 0,14 a 27,27 para Yb). Isso indica que houve claras diferenças no aumento e diminuição de LREEs e HREEs durante a formação de pedras e rochas de depósito de AghBolagh. A relação La / Y mostra a condição de pH do ambiente para formação de depósito. Essa relação no depósito de AghBolagh varia de 0,09 a 2,26. A intrusão de granito mostra a maior quantidade de La / Y que é igual a 2. A Zona de Skarn (Endoskarn e Exoskarn e Minério em Exoskarn) mostra duas condições diferentes. A primeira condição: a parte em que $La / Y > 1$, e isso pode ser observado em amostras próximas à intrusão e ao minério de Skarn, também é encontrada nessa faixa. A segunda condição: a parte que $La / Y < 1$, que está próxima da litologia de mármore. Além disso, sobre o depósito de veias, a amostra produz minério em condições alcalinas e outras mostram condições ácidas. Para avaliar o coeficiente de segregação entre REEs, são utilizadas diferentes proporções de EREs, incluindo $(La / Yb) n'$, $(La / Sm) n$ e $(Gd / Yb) n$. Os valores dessas proporções variam de (0,42 a 50,56) para $(La / Yb) n$; e de (0,25 a 80,125) para $(La / Sm) n'$; (de 0,006 a 48,8) para $(Gd / Yb) n$. A segregação mais alta foi entre LREEs e HREEs (mais de 125) e a menor segregação foi entre MREEs e HREEs durante o processo de Skarn.

Palavras-chave: AghBolagh. Skarn. $(La / Yb) n$ razão. Relação $(La / Sm) n$. Relação La / Y .

RESUMEN

La región de AghBolagh se encuentra en el suroeste de la provincia de Azarbaijan occidental, a 10 km del norte de Oshnavieh. La mayoría de los afloramientos rocosos en la región incluyen depósitos cámbricos (depósitos de carbonato y depósitos clásticos (arenisca y lutita)). Estos depósitos fueron luego influenciados y alterados por la intrusión de granito. La intrusión está hecha de granito y, en términos de naturaleza, es magmática con calcio-alcalino y peraluminio de alto potasio. Además, la penetración de la intrusión y el disolvente del fabricante de mineral en distancias mayores desde el punto de contacto y dentro de las secuencias de arenisca ha formado rocas de cuarcita y vetas de cobre que contienen mineral. El patrón REE normalizado a Condrita para la intrusión de granito, skarn y mármol y depósitos de venas muestra el hecho de que, aunque el patrón REE es un poco suave y unificado, los LREE tienen más enriquecimiento en comparación con los HREE en diferentes litologías. El rango de números normalizados a Condrita en el depósito de AghBolagh es claramente variable (2.58 a 141.93 para La y 0.14 a 27.27 para Yb). Esto indica que ha habido diferencias claras en el aumento y la disminución de LREE y HREE durante la formación de piedras y rocas de depósito de AghBolagh. La relación La / Y muestra la condición de pH del ambiente para la formación de depósitos. Esta proporción en el depósito de AghBolagh varía de 0.09 a 2.26. La intrusión de granito muestra la mayor cantidad de La / Y que es igual a 2. La Zona de Skarn (Endoskarn y Exoskarn y Ore en Exoskarn) muestra dos condiciones diferentes. La primera condición: la parte en la que $La / Y > 1$, y esto se puede observar en muestras cercanas a la intrusión y el mineral Skarn también se encuentra en este rango. La segunda condición: la parte que $La / Y < 1$, que está cerca de la litología de mármol. Además, sobre el depósito de la vena, la muestra es mineral en condiciones alcalinas, y otras muestras muestran condiciones ácidas. Para evaluar el coeficiente de segregación entre REE, se utilizan diferentes proporciones de REE, incluidos $(La / Yb) n'$, $(La / Sm) n$ y $(Gd / Yb) n$. Los valores de estas relaciones varían de (0.42 a 50.56) para $(La / Yb) n$; y de (0.25 a 80.125) para $(La / Sm) n'$; (de 0.006 a 48.8) para $(Gd / Yb) n$. La mayor segregación fue entre LREE y HREE (más de 125) y la menor segregación fue entre MREE y HREE durante el proceso de Skarn.

Palabras clave: AghBolagh. Skarn $(La / Yb) n$ ratio. $(La / Sm) n$ ratio. La / Y ratio.

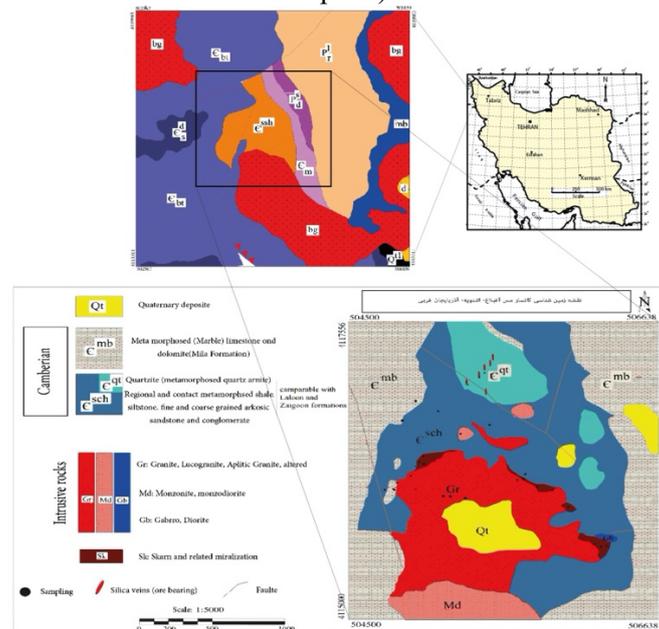
INTRODUCTION

One of the most useful methods to Petrogenic interpretation of intrusion is to utilize the Geo-Chemical data and evaluate the changes and the ratio of main and rare elements in these intrusions (Tabatabaieymanesh et al., 2011). The elements mobility in aqueous solutions happens after breakdown of initial ores during alteration and formation of secondary mineralized products. Consolidation of the Rare Earth Elements in alternated zones depends on the formation and sustainability of secondary minerals which can be a host for these elements (Terakado and Fujitani, 1998). The empirical prove of the origin of hydrothermal solutions responsible for formation Skarn deposits is one the most important stages of the studies conducted to evaluate these kinds of deposits. The condensation of rare earth elements La

(RREs) to Lu in hydrothermal solutions provides useful data on the origin of elements which form the deposit containing base elements (Kato, 1999).

The copper deposit of Aghbolagh is created in the southwest of West Azarbaijan Province, 10 km north of Oshnavieh in the east Longitude of, 45°01'to, 45°09'and, 37°09'to, 37°13'north latitude in contact of granite mass of Oshnavieh with carbonate Cambrian stones in Sirjan- Sanandaj zoon. Also the penetration of intrusion and Ore maker solvent in further distances from the contact place and inside the sequences of sandstone has led to the formation of quartzite stones and ore bearing veins of copper (Figure 1).

Figure 1 - Location and geological map of the area under the study (AghBolagh-Oshnavieh copper deposit)



The Intrusion set of Oshnavieh had been created from 3 Intrusion family including Diorite, granite and alkali Syenite-alkali granite (Ac-Ag) which is created in east-north of Sanandaj- Sirjan. The Granite Family (one of the three Intrusion set of Oshnavieh) with the highlighted feature of S type granite is the product of melting pelitic-graywacki stones. This area was previously investigated by researchers such as Naghizadeh et al. (2004) in order to prepare a geology 1:10000 map of Oshnavieh; Ghalamghash et al. (2013) evaluated it in term of the determination of the age of the isotope by potassium-argon method. Considering the formation condition of diorites in the region and the coincidence of their formation with granite rocks over 100 million years ago, the intrusion set of Oshnavieh appears to be the result of the subduction of the neotetic oceanic crust below the plate of Central Iran. The dating performed based on the K-Ar method on granitic biotite has shown the dates equal to 100 + 1.9 and 98.9 + 1.5 million years (late of early Cretaceous) (GhalamGhash et al., 2013).

METHOD

Geology

In terms of structural location, Aqbalagh copper deposit is located in the northwestern end of the Sanandaj-Sirjan zone. According to Oshwaiyeh 1:100,000 map (Naghizadeh, 2004), part of which is separated and the AghBolagh copper deposit is located in, it includes the Cambrian Geological Units (Barout Formation: Limestone and Crystallized Dolomite

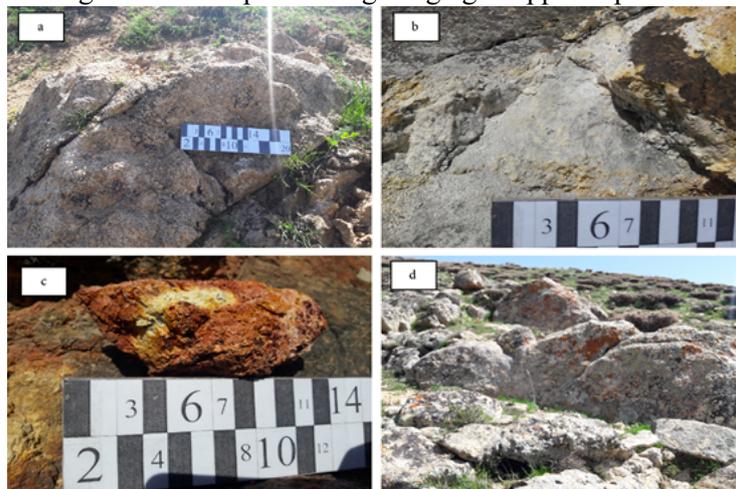
Periodicity with Gray Shale; Soltanieh Formation: Dolomite, dolomite limestone with cream color containing Chert, Marble; Mila Formation: Limestone and dolomite, locally with dark gray shale; Zagon-Lalun Formation: Shale-Siltstone and Green Sandstone With red-gray arkosic sandstone); Permian unit including (Ruteh Formation: limestone with interlaminar dolomite, shale and quartzite sandstone; Dord Formation: Red quartzite sandstone with shale and limestone interlaminae), granite Intrusion, large-grained gabbro-monzodiorite diorite. (Figure 1)

The most significant units of geology, from old to new, include Cambrian units (quartz sandstone, altered carbonate rocks (Dolomite and altered limestone), altered shale and siltstone), Permian units (quartz rocks and sandstone and dolomite), and quartz units. The most important economic geology features of this region are the presence of Cu mineralization's at the contact point of granitoid with marble rocks and towards the outside of the mineralization of copper in sandstones and quartzite veins (Figure 1).

AGHBOLAGH GRANITE INTRUSION

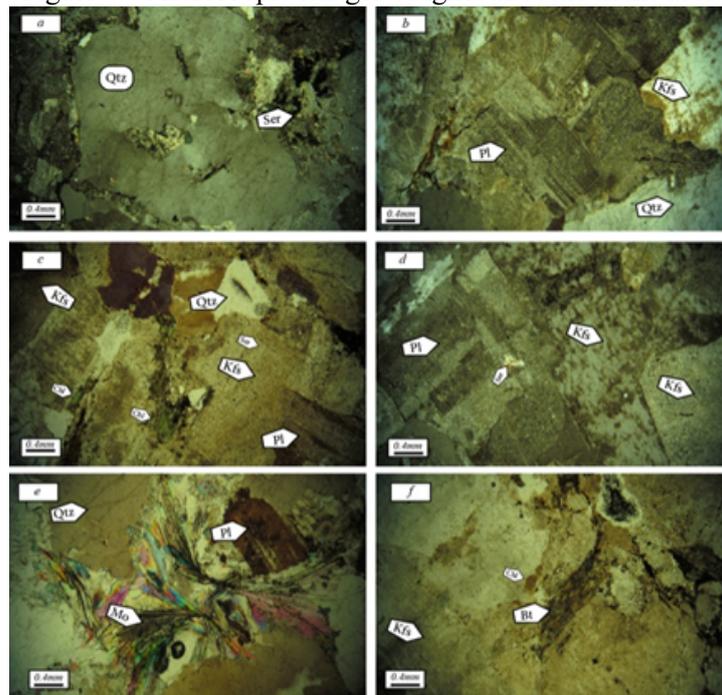
In field studies, the granite intrusion is located in the central part of the area. These granites with a modest to large crystals have transparent and white appearance (Fig. 2a and d). This intrusion is in the form of leucocratic containing the main minerals of quartz, feldspar, plagioclase and sub-minerals of biotite, muscovite, sericite and opaque minerals which are mainly Pyrite (Fig. 3). These granites are poor in term of low percentage of opaque minerals, which is a significant feature of these Granitoids, and this feature reduces their color coefficient. Based on the low percentage of mafic minerals found in these rocks, they can be called leucogranite (MoeinVaziri and Ahmadi, 2001).

Figure 2 - a: A view of granite Intrusion with light color, b: A view of a granite Intrusion with pyrite mineral, c) A view of the alteration of iron minerals and the change in their color, d: A view of the granite outcrop of the AghBoglagh copper deposit



Granite Intrusion has undergone weathering and has altered. The color of the Intrusion is mainly white with fine to medium minerals and in some cases, they have large crystal. Or those mineral can be seen in the central parts in the shape of large -grains of the crystal and near to the contact point the size of them is reduced and they change to Aplitic tissue. The opaque minerals of this intrusion are mainly pyrite (Fig. 2 (b)), and in the parts that have a greater alteration, the intrusion is red to brown (Fig. 2c). This unit is the main cause of the skarn formation and the resulting solutions from them have formed Mineralized veins.

Figure 3 - Microscopic Images of igneous rocks in the area



a) Shapeless Quartz mineral in vectors of Sericite, b): Poly-SericiteMucul in Plagioclase, which shows a slight alteration, c): Minerals forming Granite, Chlorite, Feldspar Potassium altered to Sericite, Quartz and plagioclase Intrusions, d) Plagioclase and altered potassium feldspar; e) Muscovite has birefringence with plagioclase and quartz; f) Biotite and chlorite (chloritization of biotite)
 Qtz=quartz, Pl=plagioclase, Kfs= K feldspar, Bt= biotite, Chl= chlorite, Ser= seresite, Mo= moskovite

AghBolagh intrusion has been has been evaluated in order to name, determine the type and Magmatic series and tectonic location. In this regard, two samples from different parts and one sample from the contact point were sent to Zarazma Company for 10 oxides analysis (Table 1).

Table1 - the results of analyzing 10 oxides of AghBolagh- Oshnavieh cooper deposit intrusion

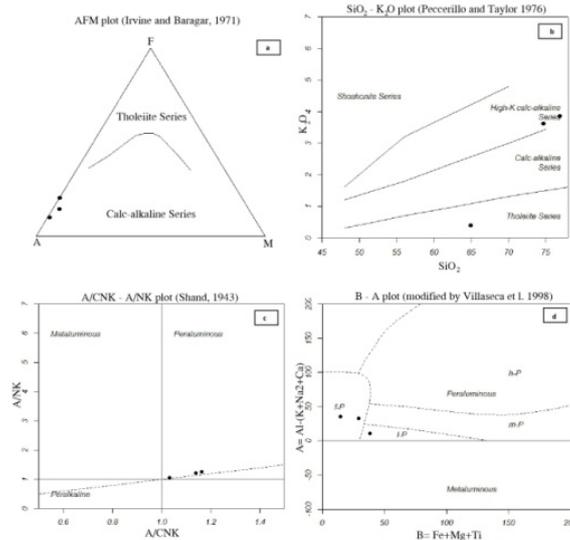
Sampl e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Ca O	Na ₂ O	K ₂ O	Mg O	TiO ₂	Mn O	P ₂ O ₅	L.O. I
Aq- GT- SH2	74.7 4	13.81	1.6	0.42	4.52	3.62	0.3	0.13	<	<	0.64
Ag- SG-2	64.8 9	17.74	2.97	0.16	10.01	0.4	<	0.09	<	<	2.03
Aq- SG-6	76.7 9	12.99	0.94	0.5	3.7	3.85	0.08	0.08	<	<	0.77

Based on the diagram designed by (Cox et al., 1979), which was generalized by Wilson for plutonic rocks in 1989, the intrusion under the study has the granitic to alkali granite composition. Based on the diagram, SiO₂ is against K₂O, which is prepared by (Peccerillo and Taylor, 1976), and the samples are in the range of calc-alkaline with high potassium (Fig. 4b). Based on the works by (Shand, 1943), the granite intrusion is in the peralumin group (Fig. 4d), and this intrusion can be classified in the S-type granites category.

The intrusion is from the type of volcanic arc granitoid (VAG) and is intercontinental that is formed at the same time with the Syn-collisional. According to the diagrams by (Schandl

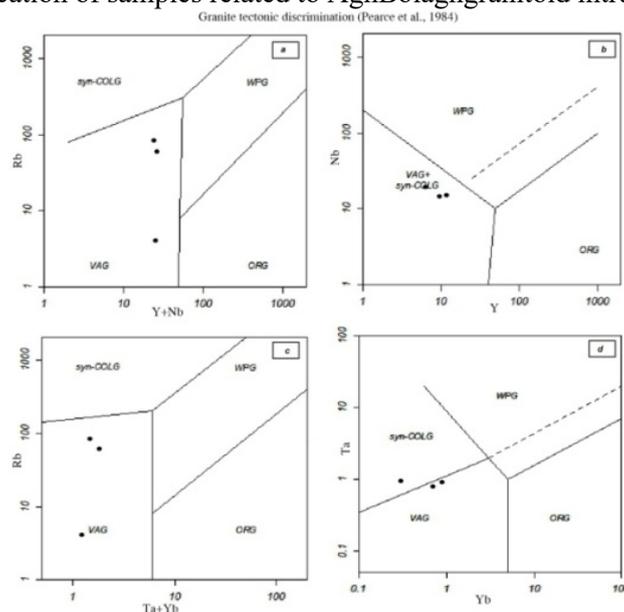
and Gorton, 2002), the granitoid under the study was related to the active continental margin, which is consistent with the nature of the Sanandaj-Sirjan zone (Fig. 5).

Figure 4 - Diagrams used to determine the magmatic series of AghBolaghgranitoid intrusion



- A. the location of intrusions samples in diagram AFM (A = (Na₂O+K₂O), F=FeO, M=MgO) (Irvine and Baragar, 1971)
 B. the location of samples in diagram, SiO₂ against L₂O (Peccerillo and Taylor, 1976)
 C. the location of samples in diagram for determination of aluminum rate A/CNK-A/NK (Shand, 1943)
 D. the location of samples in diagram B-A Plot (A=Al-(K+Na+2Ca), B=Fe+Mg+Ti (Villaseca et al, 1998).

Figure 5 - The location of samples related to AghBolaghgranitoid intrusion in Diagrams:

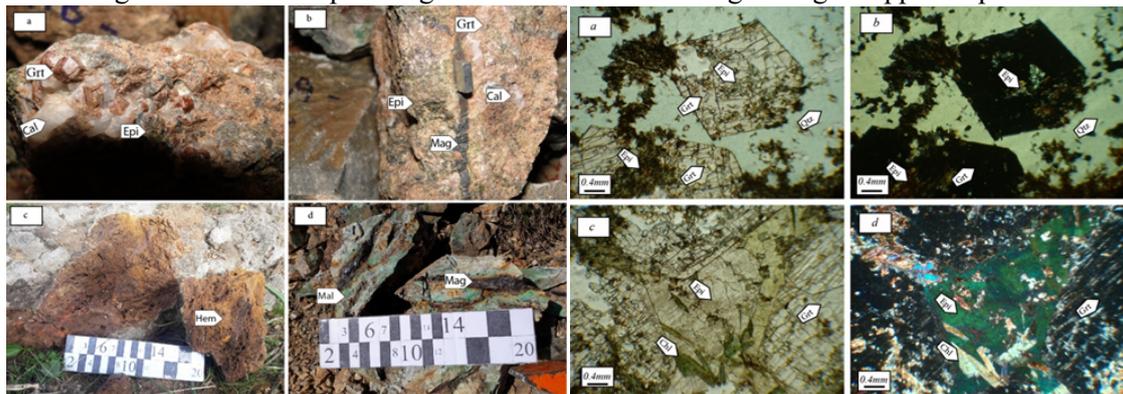


- (A) Rb against Y + Nb, (b) Nb against Y, (c) Rb against Ta + Yb, (d) Ta against Yb; to determine its tectonic position, adapted from (Pearce et al., 1984) WPG: Within Plate Granites, ORG: Expansion Zone Granites, COLG-Syn: Concurrent Granite with Continental Collision, VAG: Volcanic Belt Granite of Subduction Zone

SKARN UNIT

The skarn unit has extended discontinuously in the northern section of the intrusion and along the west to the east. This unit is fully covered and can only be detected by garnetite outcrops (Fig. 6a) and hornfels and gossans. Mineralization can be only seen in a small part of the west, but based on the fact that most of the skarn deposits are detectable, mineralization usually occurs after the garnet skarn zone (the terminal part of the garnet skarn zone). The gossans (iron hat) in this section indicates the presence of sulfide minerals in following figure (Fig. 6C). Detectable minerals in manual samples in this section include quartz, garnet, epidote, cordierite, calcite and they contain chalcopyrite, bornite, malachite, azurite and magnetite (Figures 6).

Figure 6 - Macroscopic Images of exoskarn zone of AghBolagh Copper Deposit



(a): A view of the manual sample of garnet, epidote and calcite of the exoskarn zone, (b): A view of the manual garnet sample with light brown color, epidote, calcite and magnetite vein; (c) A view of the iron hat (gossen) which represents the supergene zone, (d) a view of mineralization in the exoskarn zone along with magnetite, malachite, azurite and Chalcopyrite minerals

Grt= garnet, Mag= magnetite, Epi=epidote, Mal= malakite, Hem=hematite, Cal=calcite

Fig 7: Microscopic Images of exoskarn zone of AghBolagh Copper Deposit:

a) Garnet mineral in normal light and its alteration to epidote, b) Garnet, epidote and quartz minerals in transverse light, c) Epidotepseudomorph garnet, Chlorite in normal light, d) pseudomorphEpidote after Garnet.

Qtz=quartz, Grt=garnet, Epi= epidote, Chl=chlorite

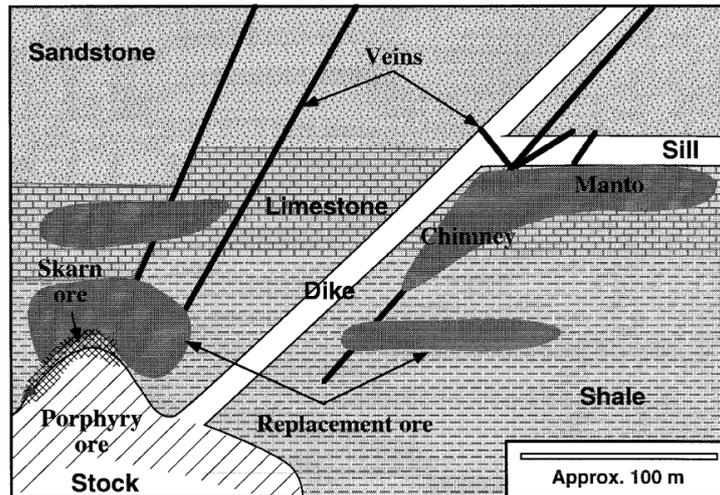
VEIN DEPOSIT

These deposits have little (10,000 tons) to very large (more than 30-40 million tons) reserves. In particular, these deposits have a host of sedimentary rocks (Dolomite, limestone, sandstone and shale) that have been affected by the influence of stokes, dikes and igneous floods, with medium to Felsic composition. The changes made to the carbonate host rock are usually from re-crystallization, dolomitization, and whitening and washed types (the process for producing lime cement in sedimentary rocks is removed). Alteration of carbonate rocks includes silica-rich jaspers and this phenomenon is common in some areas. In some regions, carbonate minerals are altered by skarn calc-silicate minerals -such as epidote, amphibole, garnet, pyroxene, and iron oxide minerals- close to intrusion contact point. Alteration of intrusion, in total, consists of quartz-sericite-pyrite and quartz-clay (argillic), which is considered as propylitic alteration (epidote, chlorite, pyrite, and carbonate) (Figure 8) (Morris, 1986; Cox, 1986).

The sandstone zone is located after the marble rocks and within 200 meters far from the intrusion. The ore bearing solutions, enter the seams and the gaps in the sandstone through

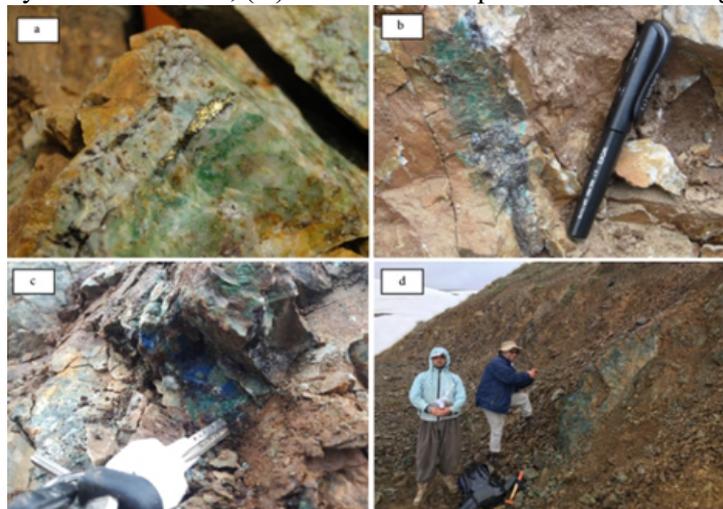
passing from marble (the gaps and seams are probably formed due to the penetration of the igneous mass), which is a good place for sediment of dissolved minerals. In this case, some veins with 2 or more centimeters up to 3 meters thickness are formed in these rocks (Fig. 9). These are quartzite veins and are based on XRD analysis and a light containing small amounts of microcline, Muscovite, sericite, hematite, goethite and copper sulfide and carbonate minerals. Structures of earth space fillers and the construction of dog teeth are abundant in this area. Chalcopyrite, Chalcocite, Azurite Malachite with quartz are the minerals found in this part of the deposit (Fig. 9).

Figure 8 - Schematic view of a substitution polymetallic deposit that shows different types and their host rocks



Source: Morris (1986); Cox (1986).

Figure 9 - a): A view of a manual quartz sample containing chalcopyrite, malachite, (b): quartzite vein containing copper mineralization (chalcopyrite, Chalcocite, malachite and azurite); (c) A view of azureite and Chrysocolla minerals, (D): A view of the quartz vein containing mineralization

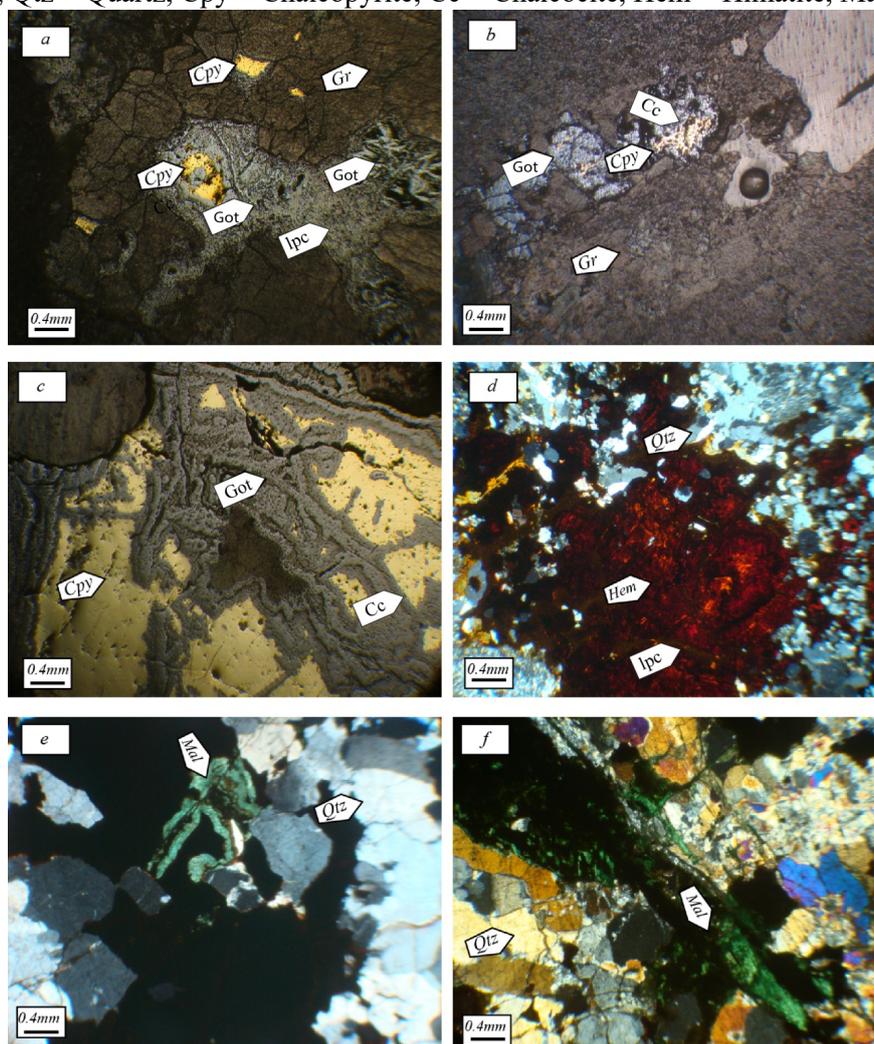


MINERALIZATION

Chalcocite is the main ore mineral both in the vein and skarn section, in the supergene zone of this deposit. Other minerals, including chalcopyrite, boronite, Covellite, boronite, malachite, azurite, gothite and magnetite, are partly found. The supergene zone has a low depth, and the amount of chalcopyrite has been reduced by digging the trench (by mining under the

supervision of industry, mining and trade organization of West Azerbaijan Province, 2011 and 2013). This mineral consists of chalcopyrite alteration and has a massive tissue (Figures 10a and c). Under the microscope, it can be seen in the isotropic state, and the presence of primary mineral of chalcopyrite in its surface and its alteration to Chalcocite and Gotaite indicates the effect of the supergene process. Chalcopyrite succession state by Chalcocite and Gotaite is clearly indicated in pictures (Figures 10 a, b, c). The mineralization in the skarn zone is done by a garnet and is formed due to retrograde alteration. Malachite, azurite is formed at the surface by oxidation of sulfide minerals (figures 10e and f). Chalcocite mineral in the skarn zone has intrusion, skeletal, and cavity tissues. The mineralization with garnet, epidote mineral (the result of garnet alteration), indicates the formation of metal ores in the process of primary retrograde alteration and the late of second progressive alteration. The Malachite mineral is green and is placed in the margin space of the minerals, and according to the formed tissue, it indicates the formation of secondary retrograde alteration (10 e and f). The process of converting chalcopyrite to Chalcocite has occurred from margins and weak areas with fractures (Fig. 10a, b and c).

Figura 10 - (a): Chalcopyrite, which has altered to Chalcocite from the margin, and gotaite (b) Chalcopyrite alteration to Chalcocite and gotaite (c): The greater the amount of chalcopyrite with increasing depth and the alteration of the mineral to the Chalcocite and gotaite from the margin, (d): Hematite resulted from iron sulfide minerals alteration (e): Malachite and quartz in the vein zone (f): Malachite placement in the final stages of alteration in the vein section with green color
Gr = Garnet, Qtz = Quartz, Cpy = Chalcopyrite, Cc = Chalcocite, Hem = Himatite, Mal = Malachite



In the vein section of AghBolagh ore deposit, mineral diversity of copper is more than skarn zone. In this zone, malachite, azurite are located between quartz minerals in surface parts in string form with green and blue colors and more often reflect the filler tissue of the empty space. This placement is in the way that malachite is located around the early minerals and does not show any filter pressing, and this issue represents the final stages of the alteration of the deposit (Fig. 10 e and f). Due to alteration of sulfide minerals such as pyrite, hematite is formed in brown color in quartz minerals (Fig. 10d).

As previously stated, in the vein part of the vein deposit, the copper mineralization has a greater diversity, and in addition to chalcopyrite, malachite and azurite, there are Covellite, Bornite, goethite and hematite minerals in very tiny amount (less than 0.2 mm to 0.4 mm).

GEOCHEMISTRY OF RARE EARTH ELEMENTS

The study of the behavior of REE rare earth elements in rocks and minerals is carried out for several reasons: First, REEs exhibit certain behaviors in different geochemical processes, which is why they are used as detectors in identifying the origin of minerals and rocks and also the processes and geological and tectonic positions. Second: in environmental issues, it is very useful for radioactive waste management and REEs are known as washable plutonium and uranium products in nuclear power plants (Brooking, 1984; Rard, 1988). Third: Economically, they have several great uses.

REEs are divided into three groups (LREE, MREE and HREE) (Rollinson, 1993). It has been cited that, one the main and important feature of them is easy replacement of REE by Calcium as one of the feature of isomorphism with calcium (Knarchenco and Pokrovsky, 1995; Pollard, 1995).

LAB EVALUATIONS

For microscopic study of samples, 21 thin and polished sections were prepared. After microscopic study of samples and identification of tissue relationships between minerals and in order to perform geochemical works, 22 samples were analyzed by XRD and ICP-MS methods and 3 samples were sent for 10 oxides analysis to Zarazma Co. (Table 2).

Table 2 - Rare earth elements of various samples in AghBoglagh copper deposit

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Er	Tm	Yb	Lu
AqSG2	1	1	0.02	0.1	0.01	0.08	0.03	0.16	0.55	0.17	0.3	0.08
AqSG6	17	28	1.46	4.1	1.5	0.48	0.51	0.28	0.86	0.21	0.7	0.14
AqGTSH2	27	46	2.76	8.3	2.22	0.68	1.17	0.35	1.07	0.24	0.9	0.16
AqSM3	2	3	0.03	0.4	0.01	0.08	0.03	0.08	0.03	0.08	0.03	0.08
AqSM17	5	13	0.23	3.3	1.38	0.26	1.05	0.28	0.42	0.12	0.1	0.08
AqSM18	2	3	0.03	0.4	0.07	0.08	0.03	0.22	0.44	0.12	0.1	0.08
AqSES7	30	58	6.54	27	6.01	1.42	5.48	0.88	3.71	0.59	5.7	0.54
AqSHS9	34	64	5.97	23.4	4.77	1.4	4.19	0.7	2.86	0.49	3	0.41
AqSES10	27	61	5.38	21.1	4.31	0.74	3.13	0.54	1.74	0.31	1.8	0.24
AqGO20	12	8	0.81	3.4	0.82	0.17	0.14	0.21	0.35	0.11	2.8	0.08
AqGA21	1	4	0.48	7.1	2.51	0.6	1.68	0.35	0.59	0.15	1.6	0.08
AqEP23	13	24	2.02	8.6	2.29	0.57	1.53	0.73	1.01	0.2	0.9	0.13
AqEPSH4	33	64	5.58	19.3	3.27	0.72	2.62	0.5	1.73	0.31	2.3	0.24

AqEXSH1	4	0.8	0.03	0.4	0.59	0.08	0.03	0.2	0.31	0.12	3.6	0.08
AqGAEP	5	18	1.43	7.4	2.62	0.63	1.88	0.34	0.44	0.12	2	0.08
AqSNS8	44	80	8.54	33.2	6.47	1.56	6.04	0.88	3.53	0.58	4.6	0.53
AqV15	15	26	1.85	6.5	1.19	0.29	0.05	0.21	0.42	0.15	0.2	0.08
AqV16	0.8	0.8	0.03	0.4	0.01	0.08	0.03	0.08	0.03	0.08	0.03	0.08
AqVT8	3	0.8	0.03	0.4	0.06	0.08	0.03	0.16	0.03	0.11	0.2	0.08
AqVT9	11	9	1.01	4.3	1.13	0.27	0.76	0.3	0.86	0.19	1.8	0.1

In this part, first, rare earth elements of all samples from all parts of the deposit (intrusion, endoscopic, exoskarn, marble, vein deposit), which were normalized to Chondrite, were drawn in a spider diagram to investigate the changes process. The REE pattern normalized to the chondrite for granite, skarn and marble intrusion and vein deposits shows that although the REEs pattern is slightly uniform and smooth, but in general, LREEs show a higher enrichment than the HREEs in different lithologies (Fig. 11). The range of normalized numbers to chondrites varies considerably in the AghBolagh deposit (from 2.88 to 141.93 for La and from 0.14 to 27.27 for Yb). This indicates that there are significant differences in the increase and decrease of LREEs and HREEs during the formation of AghBolagh deposit rocks.

To evaluate the segregation coefficient between REEs, various ratios of REEs including $(La / Yb)_n$, $(La / Sm)_n$, and $(Gd / Yb)_n$ are used (Table 3). $(La / Yb)_n$ calculates the segregation coefficient of LREEs from HREEs during geochemical processes (Aubert et al., 2001; Yusoff et al., 2013) and two other segregation coefficients between LREEs and MREEs and between MREEs and HREEs (Yusoff et al., 2013). These ratios range from (0.42 to 50.56) for $(La / Yb)_n$ and (0.25 to 80.125) for $(La / Sm)_n$ and (0.006 to 48.8) for $(Gd / Yb)_n$. The highest segregation was between LREEs and HREEs (more than 125) and the least segregation was between MREEs and HREEs during the Skarn process. The highest coefficient of these ratios and proportions is related to the marble zone and only the coefficient $(Gd / Yb)_n$ in skarn has the highest coefficient, which shows the highest segregation in the marble zone is not only due to HREE deficiency but also because of the lack of HREE and MREE in this Zone (Fig. 12a). The ratio of La / Y indicates the pH condition for deposit formation environment. The amount of $(La / Y > 1)$ represents alkaline conditions and $(La / Y < 1)$ represents acidic conditions (Crinci and Jurkovic, 1990). This ratio in AghBolagh zone ranges from (09/02 to 26/2). The intrusion shows the highest ratio (La / Y) equal to 2.26. The skarn zone (endoskarn and exoskarn and ores in exoskarn) shows two types of conditions. The granite intrusion shows the most amount of La/Y which is equal to 2. Skarn Zone (Endoskarn and Exoskarn and Ore in Exoskarn) shows two different conditions. The first condition: the part in which $LA/Y > 1$, and this can be observed in samples near the intrusion and Skarn ore is also found in this range. The second condition: the part that $La/Y < 1$, which is near to marble lithology. These divisions show Acid-Alkaline conditions of hydrothermal alteration during the process of skarn. This condition is also observed in the vein section of the AghBolagh deposit. According to the deposit diagram, from the first of the granitic intrusion to the middle of the exoskarn zone (sample of Aq-SES7), the alkaline conditions is dominant and from this point to the end of the host rock (marble) Acid conditions is dominant. In the case of vein deposits, the sample is mineralized in alkaline conditions, and other samples show acidic conditions. Therefore, we can predict that in an environment influenced by hydrothermal solutions, acidic and hot solutions containing REE are affected by interaction with dilute carbonate rocks and alkaline state (Figure 12 b).

Eu ANOMALY IS CALCULATED BY THE FOLLOWING EQUATION

$$Eu/Eu^* = (2Eu/Euchondrite) / (Sm/Smchondrite + Gd/Gdchondrite)$$

Eu / Eu * anomalies in the AghBolagh copper deposit have a range of (0.62 to 12.12) (Fig. 12c and Table 3). The value more than one is called positive anomaly and value less than one is called negative anomaly. The Eu / Eu* anomalies are positive in the intrusion, showing a negative anomaly in the skarn zone and again positive in the marble section. So in this section, we have two positive anomalies on the side of the intrusion and the host stone, and a negative anomaly is observed in the skarn zone. These anomalies can be interpreted with plagioclase on the intrusion and the presence of albite in the marble zone and the vein deposit area. In the Skarn zone, due to the absence of plagioclase, there is a negative anomaly (Zamanian and Radmard, 2016).

Table 3 - The ratio of rare earth elements of AghBolagh Deposit and Ratios of Rare Earth Elements for Investigation of deposit Formation 210

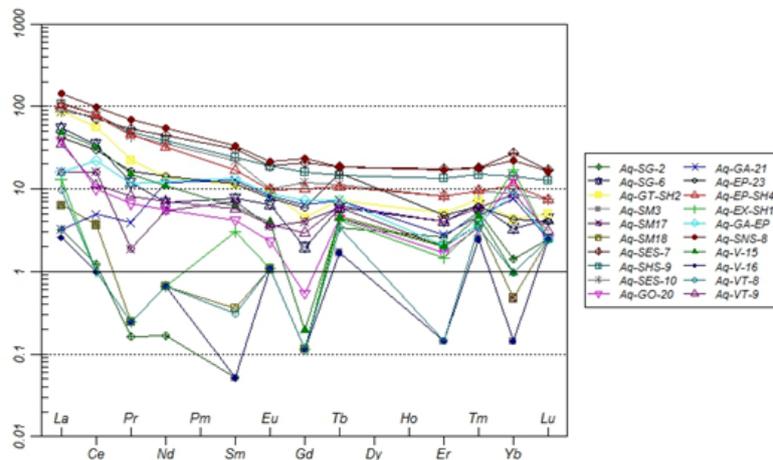
Sample	AqSG2	AqSG6	AqGTS H2	AqSNS8	AqEPSH 4	AqSESI 0	AqGO20	AqSHS9	AqEP23	AqSES7
LREE La-Nd ppm	2.12	50.56	84.06	154.74	121.88	114.48	24.21	127.37	47.62	121.54
MREE Sm-Tb ppm	0.28	2.77	4.42	14.95	7.11	8.72	1.34	11.06	5.12	13.79
HREE Er-Lu ppm	1.1	1.91	2.37	9.24	4.58	4.09	3.34	6.76	2.24	10.54
∑REE (La-Lu) ppm	3.5	55.24	90.85	189.93	133.57	127.29	28.89	145.19	54.98	145.87
(Ln/Lu)n	1.30	12.61	17.53	14.28	15.58	2.60	5.77	6.49	11.69	2.60
La/Y	0.15	1.77	2.27	1.38	1.89	1.76	1.71	1.29	1.12	0.95
Eu/Eu*	14.12	1.68	1.29	0.76	0.75	0.62	1.53	0.96	0.93	0.76
(La/Sm)n	62.90	7.13	7.65	4.28	6.35	3.94	9.21	4.48	3.57	3.14
(La/Yb)n	2.25	16.37	20.23	6.45	9.67	10.11	2.89	7.64	9.74	3.55
(Gd/Yb)n	0.08	0.59	1.05	0.92	0.04	0.24	0.78	8.48	1.40	0.81
(Pr/Yn)n	0.11	3.57	5.25	3.18	4.16	5.12	0.50	3.41	3.85	1.97
Sample	AqEXS H1	AqGAE P	AqSM3	AqSM1 7	AqSM1 8	AqV15	AqV16	AqVT8	AqVT9	
LREE La-Nd ppm	5.23	31.83	5.43	21.53	5.43	49.35	2.03	4.23	25.31	
MREE Sm-Tb ppm	0.9	5.47	0.2	2.97	0.4	1.74	0.2	0.33	2.46	
HREE Er-Lu ppm	4.11	2.64	0.22	0.72	0.74	0.85	0.22	0.42	2.95	
∑REE (La-Lu) ppm	10.24	39.94	5.85	25.22	6.57	51.94	2.45	4.98	30.72	
(Ln/Lu)n	1.30	10.39	5.19	6.49	8.62	19.48	1.04	3.90	11.42	
La/Y		0.53	0.67	0.53	0.27	2.24	0.32	0.48	0.78	
Eu/Eu*	1.84	0.87	14.12	0.66	5.34	3.64	14.12	5.77	0.89	
(La/Sm)n	4.27	1.20	125.81	2.28	17.97	7.93	50.32	31.45	6.12	
(La/Yb)n	0.75	1.69	44.95	33.71	13.48	50.57	17.98	10.11	4.12	
(Gd/Yb)n	0.85	1.37	0.01	0.76	1.06	0.20	0.81	0.12	0.34	
(Pr/Yn)n	0.01	1.22	1.71	3.94	0.51	15.85	1.71	0.26	0.96	

Eu positive anomaly shows the stages of rock changes in acidic environments (Kikawada, 2001). Also, the Eu positive anomaly and (La / Lu) n indicate acidic fluids with high temperatures (Wood, 1990). Based on the two parameters of Eu / Eu * and (Pr / Yb) n in the skarn zone, two types of hydrothermal solutions can be identified that have affected the host's stone: 1) REE solution with low concentration with Eu Positive anomaly and acidic condition

and oxidizing properties; 2) A REE rich solution with negative Eu anomaly indicates the alkaline conditions of such a solution (Fig. 12c and d).

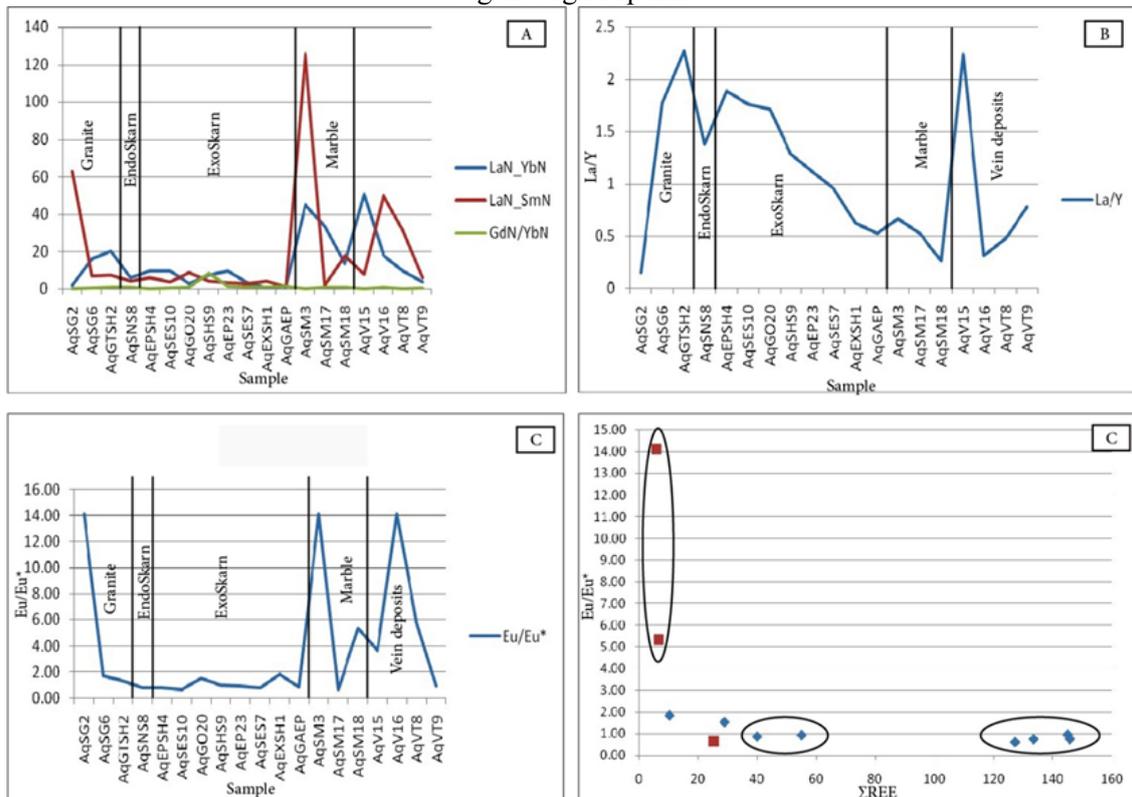
The presence of the high ratio of exoskarn to endoskarn and expansion of exoskarn zone show the low depth (less than 5 km) and sever activity of oxygen (Oxidation conditions) (Zamanian, 2003).

Figure 11 - Spider diagrams of samples in different zones of AghBolagh cooper deposit normalized to Chondrite



Source: Boynton (1984).

Figure 12 - a) the process of changes in the ratios of (La / Yb) n, (La / Sm) n and (Gd / Yb) n in different zones of AghBolagh deposit. b) process of changes in La / Y ratios in different zones of AghBolagh deposit; c) The diagram of changes of Eu / Eu * in different zones of AghBolagh deposit; d) The diagram of changes of ΣREE ratio against Eu / Eu * in the exoskarn and marble zone of AghBolagh deposit



CONCLUSION

Studies have shown that Oshnavieh (AghBolagh), copper mineralization has occurred in two states of skarn and veins in connection with the Oshnavieh granite intrusion. The intrusion is a reason for of S-type mineralization, high calcium calc-alkaline and peraluminous in the active continental margin and in the volcanic arc with syn-collisions (VAG, syn-COLG). Skarn mineralization in carbonate rocks is adjacent to the granite intrusion and the vein mineralization in farther distance (an average of 200 meters) and is formed in the sandstone of the area in the shape of quartzite veins. The main minerals in this deposit are in two parts, including the supergene and hypogene, including Chalcocite, chalcopyrite, and in partial shape, it exists in the forms of bionite, malachite, azurite and magnetite.

Different ratios of REEs including $(La / Yb)_n$, $(La / Sm)_n$ and $(Gd / Yb)_n$ were used to evaluate the segregation coefficient between REEs. Based on the obtained results, the highest segregation coefficient was between LREEs and HREEs (more than 125) and the least separation between MREEs and HREEs during the Skarn process. The highest segregation coefficient of these ratios happened in the marble zone and only the $(Gd / Yb)_n$ has the highest coefficient in in skarn, which shows that the highest separation in the marble zone is due not only to HREE deficiency but also due to the lack of HREE and MREE in this Zone.

The La / Y ratio in the AghBolagh deposit ranges from (0.09 to 0.26). The intrusion shows the highest ratio (La / Y) to 2. 26. The skarn zone (endoskarn and exoskarn and ores in exoskarn) shows two conditions. The first condition: the part in which $La/Y > 1$, and this can be observed in samples near the intrusion and Skarn ore is also found in this range. The second condition: the part that $La/Y < 1$, which is near to marble lithology. These divisions show Acid–Alkaline conditions of hydrothermal alteration during the process of skarn. This condition is also observed in the vein section of the AghBolagh deposit. According to the deposit diagram, from the first of the granitic intrusion to the middle of the exoskarn zone (sample of Aq-SES7), the alkaline conditions is dominant and from this point to the end of the host rock (marble) Acid conditions is dominant. In the case of vein deposits, the sample is mineralized in alkaline conditions, and other samples show acidic conditions. Therefore, we can predict that in an environment influenced by hydrothermal solutions, acidic and hot solutions containing REE are affected by interaction with dilute carbonate rocks and alkaline state (Figure 12 b).

The Eu / Eu* anomalies are positive in the intrusion, showing a negative anomaly in the skarn zone and again positive in the marble section. So in this section, we have two positive anomalies on the side of the intrusion and the host stone, and a negative anomaly is observed in the skarn zone. These anomalies can be interpreted with plagioclase on the intrusion and the presence of albite in the marble zone and the vein deposit area. In the Skarn zone, due to the absence of plagioclase, there is a negative anomaly

REFERENCES

AUBERT, D. STILLE, P.; PROBST, A. REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. **Geochimica et Cosmochimica Acta** 65, 387–406, 2001.

BROOKING, D.G. **Geochemical aspects of radioactive waste disposal**. Springer, New York, 1984, 374 p.

COX, D. P. Descriptive model of Zn-Pb skarn deposits. In: COX, D.P.; SINGER, D.A. (eds.). Mineral deposit models: U.S. **Geological Survey Bulletin** 1693, 1986, p. 90.

COX, K.G., BELL, J.D.; PANKHURST, R.J. **The Interpretation of Igneous Rocks**. George, Allen and Unwin: London, 1979.

CRINCI, J.; JURKOWIC, I. Rare earth elements in Triassic bauxites of Croatia Yugoslavia. **Travaux** 19, p. 239–248, 1990.

GHALAM GHASH, J., HOUSHM; MANAVI, S., VOSOUGHI ABEDINI, M. Geology, Geochemistry and Petrogenesis of the Oshnavieh Intrusion (North-West of Iran). **Journal of Earth Sciences**. Twenty-second year, No 88, p. 219-232, 2013.

IRVINE, T.N., BARAGAR, W.R.A. A guide to the chemical classification of the common volcanic rocks. **Canadian Journal of Earth Sciences**, Volume 8, p. 523-547, 1971.

KATO, Y. Rare earth elements as an indicator to origins of skarn deposits, example of the Kamioka Zn-Pb and Yoshiwara-Sannotake (Cu-Fe) deposit in Japan. **Resource Geology** 49, p. 183–198, 1999.

KIKAWADA, Y. Experimental studies on the mobility of lanthanides accompanying alteration of andesite by acidic hot spring water. **Chemical Geology** 176, p. 137-149, 2001.

KNARCHENKO, S.M.; POKROVSKY, B.G.. The tomtor al–kaline ultrabasic massif and related REE-Nb deposit, Northern Siberia. **Economic Geology** 90, p. 676-689, 1995.

MOEINVAZIRI, H.; AHMADI, A. **Petrography and Petrology of igneous age of veins**. TarbiatMoallem University, Tehran, 2001.

MORRIS, H.T. Descriptive model of polymetallic replacement deposits. In: COX, D.P.; SINGER, D.A. (eds.). Mineral deposit models: U.S. **Geological Survey Bulletin** 1693, p. 99-100, 1986.

NAQIZADEH. Geological Map 1: 100,000 Oshnavieh. **Geological Survey of Iran**, 1986, 2005.

PEARCE, J.A.; HARRIS, B.W.; TINDLE, A.G. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. **J. Petrol.**, 25, p. 956-983, 1984.

PECCERILLO, A.; TAYLOR, S. R. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area, Northern Turkey. **Contributions to Mineralogy and Petrology**, 58, p. 63-81, 1976.

POLLARD, P. J. A special issue devoted to the geology of rare metal deposits, geology of rare metal deposits: An introduction and overview. **Economic Geology** 90, 489–494, 1995.

RARD, J. A.. Aqueous solubility's of praseodymium, Europium and lutetium sulfates. **Journal of Solution Chemistry** 17, 499–517, 1988.

ROLLINSON, H., **Using Geochemical data: evolution, presentation, interpretation**. Longman: London, 1993, 652 p.

SCHANDL, E. S.; GORTON, M. P. Application of high field strength elements to discriminate tectonic settings in VMS environments. **Economic Geology**, 97, p. 629-642, 2002.

SHAND S. J. **Eruptive Rocks**. Their genesis, composition, classification and their relation to deposits. London: Thomas Murby and Co., 1943, 448p.

TABATABAIEMANESH, S. M.; MIRLOHI, A.; MOVAHEDI, M. Petrology and mineral chemistry of Ochestangranitoids (south of Mahallat, Markazi province). **Petrology** 2(7): p. 51-76 (in Persian), 2011.

TAYLOR, B. E. **Origin and significance of C-O-H fluids in the formation of Ca-Fe-Si skarn, Osgood Mountains, Humboldt County, Nevada**: Unpublished Ph.D. thesis, Stanford, CA, Stanford University, 1976, 149 p.

TERAKADO, Y.; FUJITANI, T. Behavior of the rare earth elements and other trace elements during interactions between acidic hydrothermal solutions and silicic volcanic rocks, southwestern Japan. **Geochimica et Cosmochimica Acta**, Volume 62, Issue 11, p. 1903-1917, 1998.

VILLASECA, C., BARBERO, L., ROGERS, G. Crustal origin of Hercynianperaluminous granitic batholiths of central Spain: petrological, geochemical and isotopic (Sr, Nd) constraints. **Lithos**, 43, p. 55-79, 1998.

WILSON, M. **Igneous petrogenesis**: a global tectonic approach: London, Unwin Hyman, 1989, 466 p.

WOOD, S.A. The aqueous geochemistry of the rare-earth elements and Yttrium. Theoretical predictions of speciation in hydrothermal solutions to 350°C at saturation water vapor pressure. **Chemical Geology** 88, p. 99-125, 1990.

YUSOFF, Z.M., NGWENYA, B.T.; PARSONS, I. Mobility and fractionation of REE during deep weathering of geochemically contrasting granites in a tropical setting, Malaysia. **Chemical Geology** 349-350, p. 71-86, 2013.

ZAMANIAN, H. **Iron mineralization related to the Almoughlagh and south Ghorveh batholiths with specific reference to the Baba Ali and Gelali deposits**. University of Pune, 2003, 220p.

ZAMANIAN, H., RADMARD, K. Geochemistry of rare earth elements in the Baba Ali magnetite skarn deposit, western Iran- a key to determine conditions of mineralization. **Geologos** 22, 1: p. 33-47, 2016.