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Geochemistry of rare earth elements of magnetite and apatite in choghartiron depositand comparison with kirunairon depositand study the origin of choghart deposit (Bafq, Central Iran)

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Abstract

The Choghart iron oxide-apatite deposit is placed within felsic volcanic tuffs, rhyolite rocks and volcanic-sedimentary sections belonging to the lower Cambrian period. The major ore in the Choghart deposit includes amounts of magnetite and little amounts of hematite. These ores come with silicate albite gangues, quartz, actinolite, tremolite and apatite. Chogh artapatites are fluorapatite type with OH and CI. Choghart apatites showed enriched from LREE and depleted from EU. This distribution is similar to the rare earth elements distribution in the iron apatite Kiruna deposit. Choghart magnetite show depletion of Eu and Ce and enrichment of Gd and Pr. This depletion and enrichment are also seen in Kiruna-type apatite iron deposits. Choghart deposit is in the range of iron-apatite deposits (IOA) and a subgroup of the IOCG group and Kiruna-type deposits.Comparing the geochemistry of magnetite and apatite in the Choghart deposit with the Kiruna-type deposits shows a magmatic origin for Choghart.

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Introduction

One of the most important metallogenic periods in Iran that during which iron ore has been generated, is the Upper Precambrian-lower Cambrian metallogenesis period in the Bafq- Saghand region. One of the most important and interesting geological structure occurrences in Iran is the Orogenic movements, which is comparable with the occurrence of Katangan in Gondwana land and Baikalian in the Eurasian continent. Paleozoic vertical movements took places during the Cambrian and caused sudden change in lithology or short break in sedimentation (Eftekhar Nezhad 1975).

From tectonic point of view Iran can be divided into two marginal active fold-belts located in the NE that is Kopeh Dagh and in the SW which called Zagros Zone resting on the Hercynian terrain and the Precambrian Arabian plate respectively. Between these marginal fold belts are the Central Iran, Alborz, Zabol - Baluch and Makran units (Stocklin and Nabavi 1973).

The Iranian plateau was exposed to the tensile conditions caused by the Pan-African tectonic motion, which is characterized by alkaline magmatism and linear metasomatism. The result of this metallogenic period was the formation of deposits of iron-manganese, magnetite-apatite, rare earth elements (REEs), uranium, thorium, lead, zinc, and evaporite rocks in Central Iran and HormozSeries. The Choghartiron deposit is the largest mechanized iron mine in Iran. It is located in the southeast of Yazd city. This deposit is an apatite-iron deposit (Kiruna-type) with its major ore being magnetite. In this research, the origin and geochemical characteristics of this deposit were examined by using the results of petrographic and mineral ographic studies as well as geochemistry studies of magnetite, apatite and rocks in the deposit's whereabouts.

In this paper, we are comparing the geochemistry of magnetite and apatite of Choghart deposit with the Kiruna-type deposits and show the origin of Choghart.

Material and methods

Sampling method

During the field observations, 150 rock samples were collected from two parts of the study area. After studying the manual sample, 125 thin sections preparation and was studied with polarizing microscope. 8 samples of magnetite ores and 6 samples of apatite ores were obtained by using the ICP-MS chemical analysis and were sent to Acme Labs in Canada. Geochemical data was also analyzed by using Excel, GCDKit, Igpet, and Minpet programs.

Area under study

The mining region of Choghart and the economic reserves of iron oxide-apatite are placed within felsic volcanic tuffs, rhyolite rocks and volcanic-sedimentary sections belonging to the lower Cambrian period. This region houses significant reserves of magnetite-apatite. The mine is located 13 km northeast of Bafqcity at 55° 28' E and 31° 42' N, in the Bafq basin with more than two billion tons of iron ores. This region is of 400 km length and 200 km width and is located on the volcanic-plutonic arc of the early Cambrian period known as the Kashmar-Kerman arc.
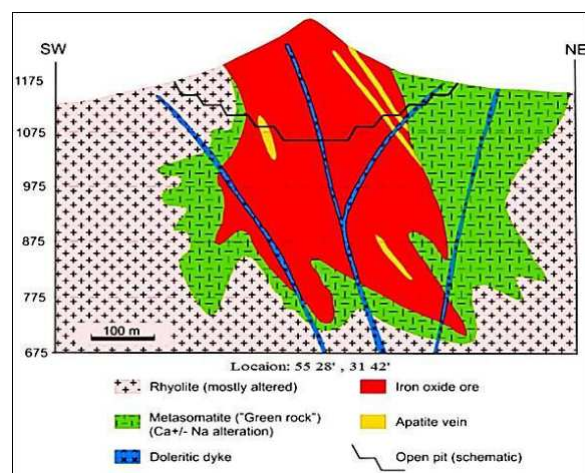

Fig. 1. Profile of the apatite-magnetite deposit in Choghart mine (adapted from Forester & Jafarzadeh, 1994).

According to geologists, rocks in the Choghart mine are of the Rizu series (Haghipour *et al.*, 1975). The Rizu series contain tuffs, tectonic lava of the middle composition (trachyandesite), acid lava (rhyolite), and porphyritic textures. The rhyolite rocks in the region demonstrate traces of iron ore genesis. The enclosing rocks in the Choghart mine have two completely different faces; a) rocks with a high content of quartz and feldspar (i.e. quartz albitophyres), b) rocks with a high content of amphibole of the actinolite- tremolite type. The latter type of rocks is known as amphibolites (Fig. 1 and 2).

Fig. 2. A view of Chogart mine rocks, view towards north.

Result and discussions

Choghart Deposit Mineralogy

The main ore in the Choghart deposit is magnetite, associated with little amounts of hematite and pyrite. Gangue minerals arealbite, quartz, tremolite-actinolite, and apatite. Magnetite ore genesis follows a substitutionary scattered and mass pattern. The crystals are euhedral to subhedral (Fig. 3). Those parts of minerals that located at depth are only slightly influenced by weathering. However, on the surfaces (especially at the site of fractures and crunches), oxidation starts from the margins of magnetite grains and fractures, and advances into crystals, resulting to the formation of secondary hematite. Moreover, apatites cross magnetites in the form of veins or veinlets.
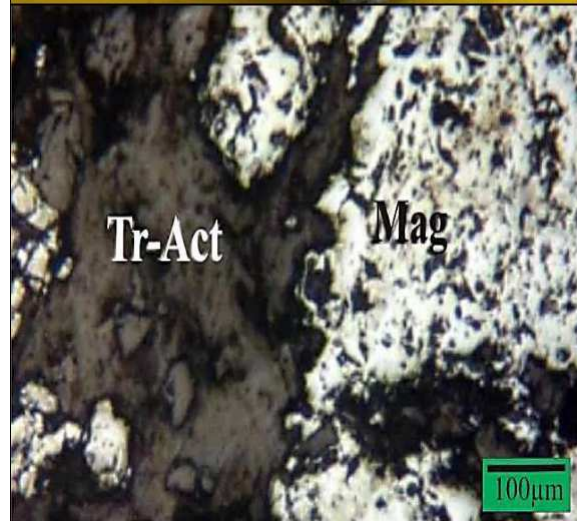

Fig. 3. Choghart magnetite in a manual sample and under reflected light..

Apatite is found in different colors and sizes (very small to very large sizes) with maximum lengths of 15 to 20 cm in iron ores and altered rocks (Fig. 4). The bulk density of apatites is high due to the presence of numerous rare earth elements in their composition. These ores contain high amounts of tin, copper, and titan (Daliran*et al.*, 2009). In the Choghart mine, apatites are considered to be wastes and are collected in the tailings storage.

The amount of hematite is lower than magnetite in this deposit. Hematite is mainly seen on surfaces and regions with outcrops of minerals. It is present in two forms in this mineral: primary hematite is in the form of a string filling the gaps between magnetite cracks,

while secondary hematite is the result of magnetite oxidation and is more frequently than string hematite. Secondary hematite is deformed wherever the mineral is exposed to tectonic forces (Fig. 5).

In this research, the geochemistry of magnetite and apatite ores of Choghart was examined. A comparison was also made between the aforementioned deposits and Kiruna-type magnetite-apatite deposits.
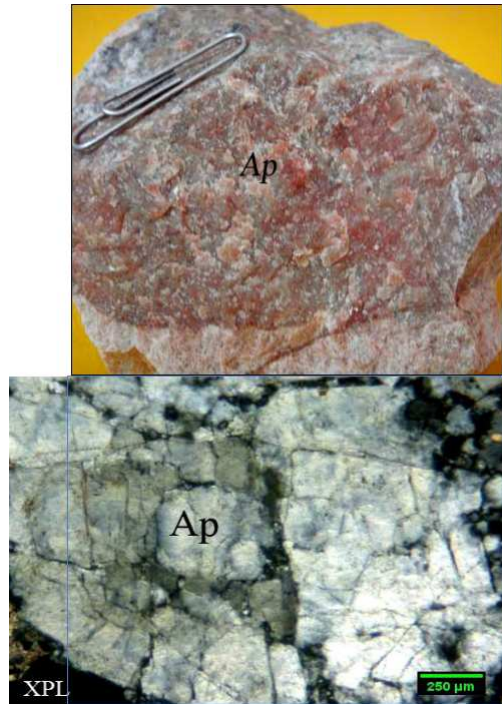

Fig. 4. Choghart apatite in the manual sample and thin section under XPL light..

Fig. 5. Primary hematite is in the form of strings while secondary hematite is the result of magnetite oxidations under PPL light..

Table 1. Results of chemical analysis of 8 magnetite samples from the Choghart mine using the ICP-MS method.

Element	1	2	3	4	5	6	7	8
Major Oxids(wt%)								
SiO_2	0.12	0.09	0.13	0.06	0.09	0.14	0.12	0.11
Al_2O_3	0.08	0.11	0.16	0.16	0.11	0.15	0.24	0.14
Fe_2O_3	65.45	66.58	66.44	65.8	65.33	66.39	64.89	66.09
FeO	28.81	28.46	28.39	28.95	28.65	27.45	29.78	28.35
CaO	2.44	2.42	1.95	2.07	2.16	2.63	1.85	2.51
MgO	1.22	1.19	0.76	0.85	1.10	1.38	1.55	0.63
P_2O_5	0.02	0.01	0.03	0.02	0.04	0.05	0.03	0.01
MnO	0.27	0.37	0.18	0.15	0.39	0.25	0.46	0.25
TiO_2	0.9	0.05	1.12	1	1.11	0.12	0.07	1
V_2O_5	0.52	0.29	0.56	0.45	0.39	0.59	0.82	0.28
Total	99.83	99.57	99.72	99.51	99.37	99.15	99.81	99.37
Trace elements(ppm)								
Ag	0.06	0.06	0.02	0.05	0.11	0.05	0.08	0.02
As	2.18	2.11	2.17	2.2	3.45	3.2	3	2.4
Ni	136	130	111	118	119	130	83	124
Ti	5395.5	299.75	6714.4	5995	6654.45	719.4	419.65	5995
V	290	320	200	450	390	420	340	220
Cd	0.45	0.27	0.46	0.37	0.39	0.27	0.26	5.5
Cu	8.43	5	9.80	11.66	15.91	5	10.06	8.56
Li	2.96	3.46	3.30	2.17	3.11	4.37	2.91	2.33
Cr	5	15	25	13	16	18	9	20
Mo	0.0	0.2	0.3	0.5	0.7	0.0	0.6	1.4
Nb	0.50	1.15	0.95	0.10	0.65	0.87	0.95	0.00
Pb	1	0.65	1.2	0	0	1.2	1	1.02

Rb	1.00	1.56	1.45	0.80	1.65	1.20	2.45	0.80
Sr	3.50	5.85	4.52	6.50	5.60	4.50	5.85	4.50
U	0.02	0.00	0.05	0.04	0.03	0.05	0.09	0.03
Zn	40	16	4	3	1	3	2	9.37
Zr	1.8	3.64	2.33	2.97	3.13	3.2	3.53	2.5
Co	170	144	117	110	89	121	104	134
Sc	1	1.3	3	0	0	3	5.5	1
Be	0.2	0.8	0.4	1.1	0.9	0.2	0.4	0.3
W	0.3	0.7	0.2	0.5	1.3	0.5	0.2	0.8
Rare earth elements(ppm)								
La	9	19	16	15	11	8	12	17
Ce	15	26	20	21	16	13	17	29
Pr	37	50	32	40	28	44	35	51
Nd	17	36	20	23	18	25	26	32
Gd	56	44	73	69	75	51	62	45
Sm	2	5	6	12	15	3	6	4
Eu	0.5	0.4	0.6	0.4	0.5	0.3	0.4	0.3
Dy	1	2	2	2	2	2	2	1
Tm	0.61	0.59	0.44	0.55	0.23	0.32	0.41	0.68
Yb	0.8	0.7	1.0	1.3	0.9	0.6	0.7	0.8
Tb	0.8	0.5	0.6	1	0.6	0.7	1	0.5
Lu	0.13	0.2	0.16	0.14	0.18	0.2	0.15	0.13
Total REE	139.84	184.39	157.8	185.4	167.4	148.1	162.7	181.4

A) Geochemistry of Magnetite

Geochemical properties of Kiruna-type magnetite-apatite deposits include the following: richness in immobile elements (V, Ni, Co), richness in elements with high crystal field energy (Th, REE, Ta, Nb, Zr), and low amounts of mobile cations (Mg, K, Ca, Rb, Cs) (Naslund, 2000). According to the existing diagrams, the amount of iron reduces with an increase in silica content, and the amount of titan increases partly with an increase in iron content (Fig. 6). The average amount of vanadium within Choghart iron minerals increases with an increase in iron. This growth is one of the characteristics of iron depositswith magma origin (Nyströmand Henriquez, 1994) (Fig. 7). The comparison of rare earth elements in the Choghartmagnetites revealed that all magnetites have a uniform distribution of REEs. The average value of $(Gd/Yb)_N$ is equal to 57 while the value of $(La/Yb)_N$ in the LREE section is equal to 10.8. The higher depletion of heavy rare earth elements (HREEs) compared to that of light rare earth elements (LREEs) is ascribed to magma differentiation (Moore and Modabberi, 2003) (Table 1). The diagrams show depletion of Eu and Ce and enrichment of Gd and Pr. Such depletion and enrichment are also seen in Kiruna-type apatite iron deposits (Naslund, 2000) (Fig. 8).
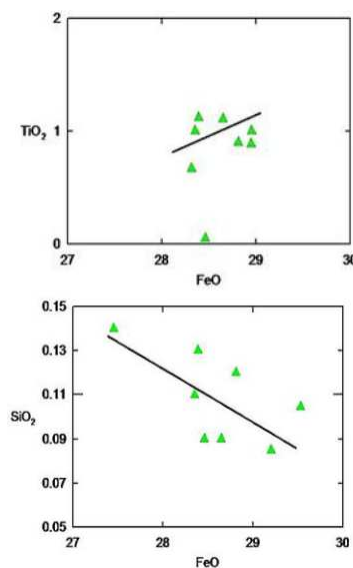

Fig. 6. Variations of SiO_2 and TiO_2 versus total FeO of magnetites in Choghart.
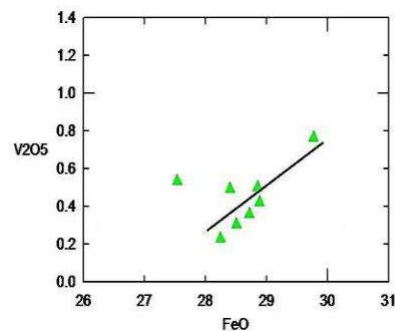

Fig. 7. Variations of V_2O_5 versus total FeO of magnetites in Choghart.
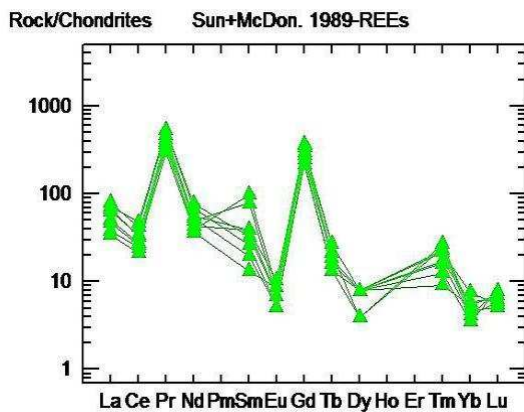
Fig. 8. Comparison of distribution of REEs in Choghartmagnetites.

B) Geochemistry of Apatites

Crystallization of phosphate phases in natural systems, as the place for storage of important rare elements such as Sr, Yb, REE and U, is a process occurring with the phosphate melt-mineral balance(Frietsch, 1995). As a result, apatite contains high contents of whole rock REE, Sr, Yb, and U (Bonyadi*et al*,2011). In fact, apatite records the chemistry of rare earth elements. Variations of concentration of earth elements in apatite depend on whole rock parameters including levels of SiO_2, fugacity of oxygen, total alkalinity, and aluminum saturation index (ASI) (Taghipour*et al*, 2013). There is a direct relationship between the plentitude of apatite and magmatic phosphor content while there is an inverse relationship between plentitude of apatite and an increase in SiO_2 content (Frietsch&Perdahl, 1984).

Results of chemical analyses of 6 apatite samples obtained from Choghart deposit suggested that Choghartapatites are fluorapatites (Fig. 9) containing OH and CI. They demonstrate slight substitution of OH and CI for F and substitution of Fe, Mg, and Mn for Ca. Some elements are of similar amounts. Elements such as Zr (526-882 ppm) and as (212-351 ppm) are of considerable amounts while U, W and Pb are of slight amounts that are close to the detection threshold. The amounts of Zn, Th, Ba and V vary from 50 to 100 ppm while the amounts of Co, Cr and Rb

vary between 10 to 50 ppm (Table 2). The mean value of $(Gd/Yb)_N$ is equal to 2.97 while the mean value of $(La/Yb)_N$ equals 19.66. Comparison of the ratio of $(La/Yb)_N$ in apatites (19.66) and magnetites (10.82) indicated that the process of differentiation in apatites is more intense than in magnetites. This differentiation process can be related to the source composition and inclusions composition of the enclosing rock. It can also be closely related to the composition of magnetites (Harlov*et al*, 2008). Total amount of REEs in apatites varies between 11962 and 13460 ppm while the total amount of REEs in magnetites varies from 148.1 to 185.4 ppm. That is to say, the highest concentration of rare earth elements is seen in apatites.

Table 2. Results of chemical analysis of 6 apatite samples from the Choghart mine using the ICP-MS method.

Samples No	AP-Z1	AP-Z2	AP-Z3	AP-Z4	AP-M5	AP-Z6
Major oxides(Wt%)						
SiO_2	0	0	0	0	0	0
Al_2O_3	0.1	0.15	0.09	0.14	0.24	0.19
FeO	0.11	0.16	0.27	0.15	0.19	0.21
MgO	0.33	0.29	0.22	0.17	0.13	0.16
CaO	53	52.57	53.6	53.3	53.05	52.87
Na_2O	0.18	0.18	0.22	0.24	0.19	0.16
K_2O	0.05	0.02	0.05	0.04	0.06	0.05
TiO_2	0.1	0.1	0.03	0.03	0.08	0.07
MnO	0.01	0.02	0.02	0.02	0.04	0.05
P_2O_5	42.14	43.3	42	42.79	42.33	42.31
F	3.41	3.23	3.15	3.1	3.17	3.18
CL	0.04	0.06	0.09	0.1	0.09	0.06
H_2O	0.06	0.09	0.13	0.15	0.11	0.12
Total	99.53	100.17	99.87	99.91	99.68	99.43
Trace elements(ppm)						
Cr	32	15	11	12	51	36
Sc	0.08	0.28	0.35	0.22	0.4	0.07
Co	12	14	15	13	15	19
Rb	9	18	19	17	16	13
Th	76	59	63	69	71	66
U	4	7	5	3	5.3	5
V	62	54	65	66	55	59
W	7.1	6.2	7	6.3	7	6
Zr	812	617	725	692	526	882
Zn	61	92	86	72	78	75
Sb	1.2	0.7	1.1	1.2	0.9	0.7
As	212	351	268	220	312	279
Ba	62	55	68	59	64	65
Pb	3	6	5	2	4	3
Sr	800	900	850	920	800	930
Rare earth elements(ppm)						
La	2750	2100	2300	2555	2600	2350
Ce	5250	4250	4700	4500	4400	4200
Pr	780	763	768	770	755	760
Nd	2200	2600	3400	3200	3000	2500
Sm	265	273	276	275	246	250
Eu	45	42	44	45	46	46
Gd	385	279	272	260	290	366

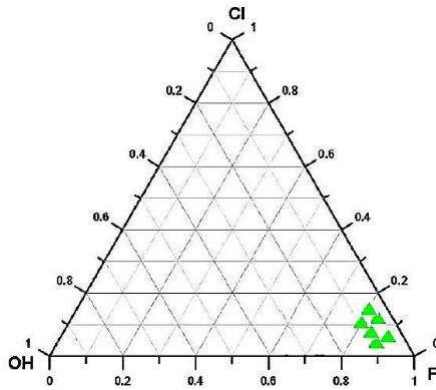|						
Tb	37	31	35	33	38	35
Dy	153	162	169	166	157	182
Y	1145	1565	1230	1300	1860	1200
Yb	68	53	59	66	61	66
Lu	7.6	7.7	7	6.9	7.3	6.7
Total REE	13086	12126	13260	13177	13460	11962

Fig. 9. Choghart apatite of fluorapatite type.

The distribution pattern of REEs in the apatite samples obtained from the Kiruna deposits is such that Ce, La, and Nd show the highest degree of anomaly while Eu shows the lowest degree of anomaly (Moore&Modabberi, 2003). Analysis of Choghartapatites also showed that minerals are enriched in LREE and depleted of EU (Fig. 10). This pattern is similar to the distribution pattern of REEs in the apatites of Kiruna iron deposit and other Kiruna-type deposits in different parts of the world (Mokhtari, 2003). In general, the overall trends of transmittal of REEs in the Kirunairon deposit and Choghart mines were similar. However, cerium in Kiruna mine showed more depletion (Fig. 11).
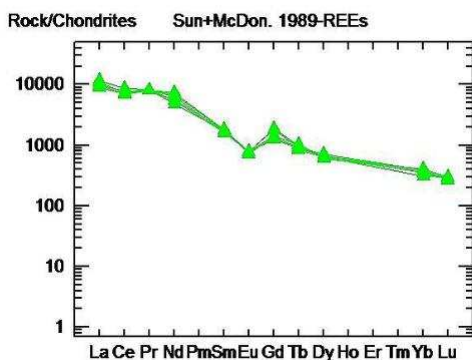

Fig. 10. Comparison of distribution of REEs in Choghartapatites.
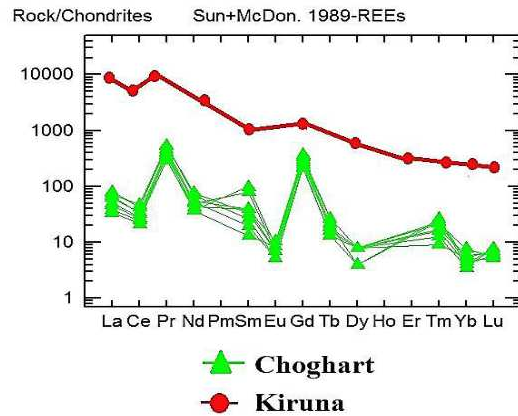

Fig. 11. Distribution of REEs in apatites obtained from the Choghart mine and comparison with Kiruna mines (adapted from data on the Kiruna mine, Lyons1988).

C) Petrogenesis of the Magnetite-Apatite Deposition
Lyons (1988) proposed the following two models for the formation of iron deposits: 1) Crystallization of iron oxide minerals from an iron-enriched oxide melt (magmatic model); 2) sedimentation of iron oxide ores from an iron-enriched hydrothermal fluid (hydrothermal model).

The most important characteristic of magmatic iron deposits is that their enclosing rocks are acid volcanic rocks enriched from alkaline substances. Their minerals are younger than their enclosing rocks and are in the form of veins and dykes. Formation of Skarnic ores (amphiboles, rarely pyroxene, and garnet) is related to ore genesis while local silicification and *sericitization* occur at the last stage of deposit formation. In these deposits, minerals enriched with apatite are always younger and penetrate into poor types of apatite.

Kiruna-type iron-apatite deposits have formed in the world near igneous rocks with basic to acidic composite ranges. The enclosing rocks in this mineral are alkaline rhyolite rocks and trachytes. The minerals in these deposits include magnetites containing low amounts of titanium and hematite. Actinolite and diopside are the major silicate minerals coming with the mineral (Nyström&Henriquez, 1994). The main characteristic of hydrothermal iron

deposits is their vast alkaline heterology and the low amounts of Ti in the magnetite and hematite minerals.

In the Choghart mine, in the early Cambrian period (533 million years ago) rhyolite rocks were formed as a result of the rift in Central Iran. This finding complies with the magmatism theory which holds the enclosing rock shall be an acidic volcanic rock enriched with alkaline materials. The mineral in the Choghart mine is younger than the enclosing rock and is formed as a network of veins in the enclosing rock. This finding complies with the magmatic theory. The sodic (the prominent albite mineral on the grid) and calcic (tremolite-actinolite) alterations take place and finally the mineral is silicated and sericiticed. These findings comply also with the magmatism theory. The apatites existing in the Choghart deposit are fluorapatites and possess lower amounts of Cl and OH. These compounds are seen in magmatic and hydrothermal apatites. The Choghart mine has not experienced base metals sulfide ore genesis due to the low amounts of sulfur and base metals in the fluid as well as in the enclosing rock. This finding complies also with the magmatism theory.

Fig. 12. Choghart,Kiruna and El Loco magnetites in the diagrams for elements Ti, V, and Ni (Loberg & Horndahl, 1983).

In addition, based on the variations of V/Ti versus Ni/Ti, iron deposits are divided into the following three categories: apatite iron deposits, banded iron formations and titanium-bearing iron deposits. Iron was also used as a measure for classifying iron deposits (Loberg&Horndahl, 1983). According to the proportions of Choghartmagnetites, the Choghart deposit is situated on apatite iron deposits. This deposit has also the same origin as the Kiruna (Seweden) and El Loco (Chile) apatite-magnetite deposits (Fig. 12).

Conclusions

Magnetite is the major mineral in the Choghart deposit. It is also accompanied with little amounts of hematite and pyrite. The gangue minerals are associated with minerals including albite, quartz, tremolie-actinolite, and apatite. Choghartapatites are fluorapatites and apatites host the highest concentration of rare earth elements. High ratios of LREE/HREE in the apatites and magnetites of the Choghart mine reflect a progressive magmatic differentiation. These values also indicate that these elements are placed within the magnetite crystalline network by post-magmatic solutions. This pattern is similar to the pattern of distribution of rare earth elements in the apatites of Kiruna iron deposit and other Kiruna-type deposits in the world (Mokhtari, 2003).

Choghartmagnetites demonstrate depletion of Eu and Ce and enrichment of Gd and Pd. This trend is also seen in Kiruna apatite iron deposit. The geochemistry of the rare earth elements of magnetite and apatitein the Choghart deposit is similar to those of Kiruna (Sweden) and El Loco (Chile) deposits. According to research results, Choghartdeposit is in the range of iron-apatite deposits (IOA) and Kiruna-type deposits. It is, therefore, a subgroup of the IOCG group (Mohammad Torab, 2009). After comparing the geochemistry of rare earth elements of magnetite and apatite in the Choghart deposit with that of other Kiruna-type deposits, it was found that Choghart has a magmatic origin.
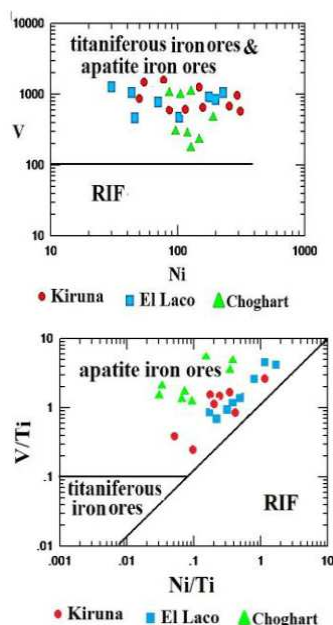
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