Geochemistry and Microthermometry of Fluid Inclusions of Cu and Fe Mineralization in North Khour Volcanic Rocks, Northwestern Birjand

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ABSTRACT

The volcanic complex of North Khour is located in southern khorasan province, in 90 km of northwest of Birjand. The study volcanic igneous rocks are including Basaltic andesite, Andesite and trachyandesite, Latite, Dacite to Rhyodacite and pyroclastic rocks are including Tuff and breccia. The majority texture of these rocks is porphyry. Magmatic series of most samples are calc alkaline but some samples have inclination to tholleiitic serie. Furthermore in diagram of magmatic arc definition, the study rocks are situating in field of continental arc and seems which magmatism of area has been result of subduction of a oceanic crust under the continental crust. Because of the area is an upper part of a cu porphyry system, this paper is a very important research to know more about this system. Iron mineralization in area is as magnetite, hematite and as lower amount of goethite and with attention to the field observations, it seems this mineralization has magmatic origin. Burnite as alone Cu ore has been formed as primary and very little. The presence of bornite and pyrite as sulfide phases as very little and absence of other Cu primary sulfide ores in area together with secondary Cu mineralization phases in very high amounts, is showing a hydrothermal solution with high oxidation degree which has passed the latest magmatic differentiation and has caused to form surface Cu ores as calcosite in supergene zone. The thermobarrometry studies of fluid inclusions has specified degree of 10 weight percent of NaCl, 50 megapascal pressure and temperature range of 200-220 centigrade degrees for this mineralization. Therefore it seems that mineralization is related to upper parts of a Cu-porphyry system which is showing a lower temperature.

Keywords: North of Khour (Birjand); Cu porphyry; Mineralization; Geochemistry; Fluid inclusion; Calc alkaline; Volcanic arc

INTRODUCTION

The area investigated in the present study is a volcanic complex located in North Khour in South Khorasan Province, 90 km to the northwest of the city of Birjand, spread over the longitude of $58^{\circ}26'36''$ to $58^{\circ}41'49''$ and the latitude of $33^{\circ}14'66''$ to $33^{\circ}02'78''$. The presence of old metal mining work in the investigated area, which is an undeniable feature in the identification of areas prone to mineralization, is an important feature pointing to the possibility of the existence of mineral resources in the area under investigation [1]. The present study aims at conducting a petrographic and geological analysis of volcanic rocks containing Cu and Fe mineralization in North

Khour area and of the origin of this mineralization and a thermometry of its fluid inclusions. To now, no detailed economical studies have yet been undertaken on the thermometry of ore deposits of study area and genesis of volcanic metal hosted rocks of area [2]. The principal aim of this paper is to fill this important gap. Because, we believe the mineralization of area is upper ore bearing veins of a Cu porphyry system. Specific objectives are to provide information on thermometry of ore mineralization of area which is upper part of a subduction arc ore bearing volcanic suite, geochemistry and determining the tectonic environment of ore bearing rocks which is important to understand and improve information about genesis of ore minerals in study area [3].

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METHODS

After gathering and studying the information, reports, and the maps related to the area, field studies and experimental studies were carried out as follow:

At first taking more than 70 samples for lithological, alteration, and mineralization analyses of semi-deep andesitic masses and dikes of the area and host mineralization rocks including tuffs and andesites. Also, taking samples of transparent siliceous veins and semi-veins at the same time as the mineralizations. Then has prepared 40 thin sections for lithological and alteration analyses. Also has prepared 12 polished sections from ores for mineral ographic analyses [4]. Furthermore has prepared 6 doubly polished sections from quartz single crystals for thermometric fluid inclusions and also, referring 13 samples of the investigated rocks to the laboratory of Binaloud Corporation for chemical analysis using an XRF method. Studying doubly polished sections using linkam stage (THMSG 600 model) in Payam-e Nour University of Tabriz Branch and drawing a variety of lithological and tectonic diagrams using computer softwares and analyzing and interpreting them. Finally, determining depth and pressure of the positioning of the mineralizing masses and dikes that have penetrated to the host rocks [5].

DISCUSSION

Geology

North Khour volcanic complex in South Khorasan Province is located 90 km to the northwest of the city of Birjand and in the 1:100000 rectangular rigging map. The geographic coordinates of the area is as follows: the longitude of 58°26'36" to 58°41'49"and the latitude of 33°14'66" to 33°02'78" and in terms of tectonic-sedimentary divisions, this area is considered as part of the Lut Block. One of the prominent features of the zone is its widespread magmatic activity in the Tertiary, which started in the Eocene and reached a peak in the Oligocene accompanied by fissures and fractures of semi-deep penetrating masses in the area which has manifested its effects mainly in the form of dikes. Tectonic and alteration activities have complexified the effects and consequences caused by volcanic activities [6].

As mentioned earlier, a vast part of the investigated area is made up of Middle Eocene to Upper Oligocene volcanic stones, which is considered an equivalent of Karaj Formation in the stratification of Iran. However, it should be noted that, according to the geological 1:100000 rectangular ragging map, volcanic rock of Karaj Formation aging middle Eocene in the area investigation is not spread widely and can be observed is only some parts of the area. However, the lithologies separated on the map in this area which are considered separately from the Karaj Formation appear to be part of the formation. In addition to the volcanic rocks mentioned above, other outcrops of volcanic rocks aging Upper Eocene-Oligocene also exist in the investigated area, which have a more basic composition in comparison with Eocene volcanic rocks [7]. Based on field and experimental analyses, the volcanic rocks in the area include basalt andesite, andesite and trachy andesite, latite, dacite to rhyodacite, and igneous rocks including tuff and breccia, with the andesites and tuffs being the host rocks. Andesite dikes have crystalized due to positioning within the above volcanic complexes and, as a results, have altered the rocks in their vicinity. This volcanic complex is identified by its greenish gray with porphyry texture and fine grains in the desert. The above-mentioned rocks are mostly affected by sericitic and argilic alterations, and, as a result, their ores have mostly changed to sericite and clay minerals. These rocks have also been affected by other alterations such as propylitic silica, and zeolite alterations, which are of secondary importance. Several old mining works and slags of metal melting furnaces exist in this volcanic complex. In fact, the spread of the area to be investigated was selected based on four mining works, which are in themselves indicators of the existence of mineralization in this area [8].

Petrography

The study area volcanic complex including basalts, andesites, latites, dacites and rhyodacites that is identified mostly by porphyry and felsophyry textures in thin sections. Petrography of these rocks are as follow:

Andesite-trachy andesite: andesite lava which hosts mineralizations in the area contain medium to coarse grain phenocrysts from plagioclase in the manual sample and are seen as green to dark brown in color. The main constituting minerals of these rocks are medium to coarse grain crystals of plagioclase, clinopyroxene, hornbelende, and metal minerals which are placed within a microlite to very granular and sometimes glassy context [9]. The phenocrysts of these rocks vary in size from 0.5 to 2 millimeter and are often identified through fine grained, porphyry, vitrophyric and orthophytic textures. Sericite, clay minerals, calcite, epidote have resulted from plagioclase alteration in andesite, and iron oxide can be seen on the surface of some of them. Sever dissolution and corrosion and reactive edges can be seen in a number of plagioclases. The evidence is taken as an indication of magmatic mixing in rocks. Instability of plagioclase crystals while moving upward is considered to be the reason for emergence of a sieve texture in them, since some parts of plagioclase is fractionally melted and the products of plagioclase melting begin to crystalize inside the crystal. Depending on whether the temperature drops rapidly or slowly, these products are crystalized in the form of glass or in the form of a new plagioclase inside the primary plagioclase and cause these texture to emerge [10].

Dark minerals compose 5 to 20 % of the volume of andesites and include hornblende and biotite. Most of these minerals are burned and have changed to iron oxides, opaque minerals in the edges and have changed to chlorite in central parts. Pyroxenes, including both clinopyroxene and orthopyroxene, are observed as phenocrysts and fine grains, and compose 10% of the volume of the rock in andesites. These crystals are in a better condition than other coarse-grained crystals and have changed to in their central parts. In addition to plagioclases, some magmatic mixing effects can also be seen. Also, magnetites as opaque and periphery minerals compose chlorite to 5 % of the volume of the samples and can be seen in the forms of fine grain, coarsegrained, and amorphous in the texture of these rocks.

Andesite basalt: These rocks contain medium to coarse-grained crystals of plagioclase, clinopyroxene, hornbelende, sanidine in the form of finer grains, and metal minerals which are placed in a microlite to very fine grain and sometimes glassy context. The microlite context includes fine crystals of plagioclase and sanidine [11]. Formed and semi-formed plagioclase minerals in the form of phenocrysts and fine grains constitute 40 to 50 % of the constituting minerals of the rock. These minerals show high levels of darkness in some sections, which possibly includes a variety of more mafic form of the mineral such as labradorite. Pyroxenes, including clinopyroxene and orthopyroxene, are seen in the rock in the form of phenocryst and fine grains. Some sections of the matrix of the rock are more covered with iron oxides than the other sections. The presence of burnt areas in hydrous biotite and hornblende minerals indicates high levels of PH2O at the end of crystallization time and high levels of oxygen fugacity at the time of lava eruption. Some others believe that the reason for this is a reduction in pressure due to the lava getting close to the surface of the earth, exit of magmatic gases, increased cooling speed, and stickiness of the lava and call it opacity margin [12]. Plagioclases have mostly changed to clay sericite minerals due to alterations, and pyroxene s have change to chlorite, iron oxides, and magnetite in the marginal areas. Effects of magmatic mixing can be seen in these rocks as well.

Latite and pyroxene latite: These rocks are dark to light gray in color in the manual sample. The constituting minerals in this rock include plagioclases (40%), pyroxenes (10%), and biotites and orthose feldspars (5%), which are put in a glassy to fine grain matrix and are covered with iron oxide in some areas. Quartz phenocrysts are either very scarce or do not exist at all. In addition to the minerals mentioned above, slabs of volcanic rocks are rarely seen in the matrix of the rock. The textures existing in the rock are porphyry, vitrophyry and intergranular. Plagioclases have a variety of forms and have changed to sericite and clay minerals due to alteration. Pyroxenes, which are often of clinopyroxene type, have altered fractionally to chlorite and iron oxides and in some cases to opaque minerals. Biotites with burnt margins can also be seen in the rock in the form of coarse and extended grains but very scarcely (5 %), which have fractionally altered to chlorite [13].

Dacite-rhyodacite: The constituting minerals of this rock include plagioclase phenocrysts (40-50 %), sanidine (about 20%), orthoclase and quartz (about 10%). Plagioclases are in some cases very coarse-grained and have polysynthetic twin. Zoning is also seen in these minerals, whose composition varies from labradorite and rarely bytonite in the center and olicoclase in the periphery. Quartz is in the form of fine grains and are sometimes coarse-grained. The percentage of alteration in these rocks are lower compared to other rocks. Plagioclases have changed to clay, sericite, and carbonate minerals. Part of plagioclases have fractionally altered to sericite and also to clay minerals. Ferromagnesian minerals are mostly biotites and amphiboles which have changed to iron oxides and opaque

minerals. The texture of the rock is felsophyry and sometimes vitrophyry, and no sign of mixing is seen.

Pyroclastic rocks: The tuff units in the investigated area include lithic tuff and vitric tuff, which are considered the equivalent of Karaj formation and are found more in the northern part of the area. The lithic tuff unit together with andesite units are regarded as the host rock for mineralizations in the area. In addition to it constituting slabs, the matrix of the rock is covered with iron. The vitric unit is seen as light green fine grains in the manual sample. The matrix of the rock is almost completely glassy and the slabs of extended glass are seen as welded, which indicate as otaxitic texture. Also, the matrix of the rock has a fluid state. Phenocryst plagioclases with marked zoning are also seen in both type of tuff units. Fine grain quartz are generated as result of the devitrification of welded glasses of the matrix of the rock. Zeolites as other secondary minerals have also filled the spaces between crack and broken areas.

Volcanic breccias: These rocks include a series slabs from volcanic rocks with carbonate and silicate matrix whose rock slabs are at the extent of latite, andesite, and trachy andesite. The existing plagioclases in rock slabs are extremely altered and have mostly changed to clay and to a lesser degree to sericite. Some constituting slabs of this rock unit have sharp edges and some others have rounded edges. The filled hollows in these rocks are often filled with fine grain quartz (chalcedony) and have made a spherulite texture in a beautiful way. The matrix of the rock is covered with iron oxides and silicate veins and subveins can also be seen in the rock.

Geochemistry and determining the tectonic environment

Given the relatively extensive alterations in volcanic rocks of the area and the emergence of secondary minerals, it was tried to focus the geochemical analyses on the sound and less-altered samples. The results of geochemical analysis of volcanic rocks samples. Since the possibility of alteration, mineralogy and chemical changes in volcanic rocks is high, elements that are less likely to be displaced were used to name these rocks in a more precise way. Therefore, the proposed diagram is used to name these rocks (Figure 1). The amount of SiO₂ in these rocks varies from 43 to 67 %, the amount of Al₂O₃ in the samples is high, being around 15%. The high amount of Al₂O₃ in basalts is an indicator of the crystallization of mafic minerals from their constituting primary melt in relatively high pressures which causes aluminum concentration in the remaining melt and causes crystallization of plagioclase in lower pressures.



Figure 1: The location of the investigated volcanic rocks in the division.

According to AFM diagram, most of the samples are within the range of calc-alkaline which are inclined toward tholeiitic (Figure 2). The K_2O change range of these rocks is relatively wide (0.08 to 3.31), and most of the samples are in the high-potassium calcalkaline series. Variation and spread of samples in terms of K_2O can be due to the mobility of potassium elements during the alteration process of the rocks in the area.



Figure 2: AFM digaram for determining magmatic series of the investigated rocks.



TiO₂, FeO, and MgO changes to SiO₂, whose amounts follow a descending pattern (especially in the two samples KH9 and KH10), which can be an indication of the fractional crystallization of clinopyroxene during the crystallization of lava. Also, the amounts of CaO to SiO2 follows the same trend and can be dependent on the formation of plagioclase composition from calcic to sodic. In the two andesite-basalt samples mentioned earlier, we can see pyroxene crystals in coarse microscopic sections, which causes MgO to higher in this sample compared with other samples. Also, the amounts of the three elements chromium, cobalt, and nickel are high in these two samples which shows that they are highly inclined to separate from the lava at the beginning of magmatic separation. Among the rare elements, compatible elements like chromium, cobalt, nickel, and vanadium to SiO₂ have a relatively decreasing trend. These elements are separated from the basalt lava at the beginning of the separation process and enter pyroxene and magnetite minerals (Figure 3).

In Figure 3, the chemical composition of volcanic rocks in the investigated area is normalized to the primary mantle. In this diagram, the elements Pb, K, Ba, and Sr show positive abnormality in all the samples. These elements are mobile and LILE elements (with low ionic potential) whose concentrations are a function of fluid phase. On the contrary, elements Nb, Rb, and Ce show negative abnormality in all samples and are low mobility elements and HFSE (with high ionic potential) whose concentrations are controlled by the chemistry of the original rock and the crystalline-molten processes that occur during the formation of the rock. Also, the elements Ti, P, and Zr show negative abnormality in some samples.

Due to low ionic potentials, LILE elements are easily dissolved in hydrous fluids and transferred in high pressure and temperature, while the solubility of HFSE elements in hydrous fluids is low. Therefore, during the fractional melting or dehydration of the subducted oceanic crust, the mantle wedge is enriched in LILE elements relative to HFSE elements due to metasomatism of hydrous fluids. The subducted region lava van usually be identified by the depletion of HFSE elements relative to LILE elements. The source of this depletion can be due the effect of fluids or melting material produced by the slab-derived on the mantle wedge. During the subduction zone magmatism, hydrous fluids are responsible for transferring some of the incompatible elements from subducted crust to the continental crust in the arc zone. The high ratio of LILE/HFSE in the arc zone rocks is the result of the components of LILE existing in the subducted plate entering the mantle wedge above it. Also, the subduction process has an effective role in increasing the ration of LILE/HFSE.

The Pb positive abnormalities point to the metasomatism of mantle wedge by the fluids caused by the subducting oceanic crust or the contamination of lava by the oceanic crust. The enrichment of samples with Ba and Sr is also the result of fluids derived from hydrous sediments and the oceanic crust to the transferred mantle wedge. The negative abnormality in P, Nb, and Ti elements which has caused the genesis of a cross pattern

Rad GF

in the change process of rare elements in the samples can indicate the formation of rocks in the subduction region, since in subduction areas the fluids released from subducting lithosphere, which are low in Nb and high in LILE, increase in the mantle wedge.

In order to precisely study the tectonic environment of the rocks in the investigated area, the diagrams were used, in which the rocks in the area are in the range of calc-alkaline basalt and in relation with volcanic arc. In order to distinguish the active peripheral magmatic volcanic arc from ocean island magmatic arc, diagram was used, in which the investigated rocks are in the range of oceanic arc, and it seems that the constituting magmatic arc of the rocks is caused by the subduction of a oceanic crust underneath a continental crust. Also, the ratio of Zr/Y can be used to identify the magmatic arc, in a way that if the ratio is larger than 3, the arc is of a continental type, otherwise it is of an oceanic type.

Mineralization

In the investigated area, metal mineralization has occurred in the two forms of primary and secondary. Magnetite with the chemical formula Fe₃O₄ constitutes 50-56 % of metal mineralizations in the investigated area and is seen as light brown in the vicinity of hematite, and in some sections which have lower densities in the matrix of the rock can be identified as self-shaped crystals. In later stages, this mineral is altered to hematite from the edges under the influence of hydrothermal solutions. The alteration has mostly occurred in peripheral sections, and magnetite has remained in the central section. In some other parts, hematite has completely replaced magnetite. Magnetites have also changed to martyte along fracture and cleavage surfaces. Magnetite mineralization, as hematite and to a lesser extent goethite, has been completely separate from copper mineralization and, according to desert evidence, it seems to have had a magmatic origin.

Bornite with the chemical formula Cu5FeS₄, as the only copper mineral which is genetically primary, has constituted about 5% of metal mineralizations. This mineral along with other minerals and under the influence of hydrothermal solutions have caused the formation of surface-grown copper minerals in the enriched zone. Bornite is amorphous and is seen in the very beautiful color of peacock in the sections. Pyrite with FeS₂ formula is in the primary form in the investigated polished sections, is amorphous, and constitutes around 5% of metal mineralizations. This mineral can be seen in the form of fine and dispersed grains in a matrix of sericite along with magnetite. Oxidation in the area has changed it to martyte along fracture surfaces and has finally led to its destruction. In some sections, pyrite is seen in the presence of chalcosine, which points to two separate mineralization phases of copper and iron in the area.

Hematite with the formula Fe_2O_3 constitutes around 20-30 % of metal mineralizations in the investigated area. According to hematite mineralization Figure, hematite can be seen both in the form of needles and strings and in an amorphous and peripheral form around magnetites, and it can be stated that hematite has been formed from the oxidation of magnetites

both in a primary and a secondary way. Goethites are secondary and constitute around 5% of the mineralization.

Covellite with the CuS formula constitutes around 10% of metal mineralizations. Its aggregate has a twisted and grain form. Chalcocites constitute the highest percentage of copper mineralization. Chalcocite under the influence of Bornite oxidation and other possibly present minerals of copper like chalcopyrite and the dissolution of sulfates released from minerals such as pyrite has caused enrichment in this area. This mineral has changed to covellite in some parts in a substitution manner. Also, malachite as an oxide and surface mineral of copper constitutes 3-5 % of mineralizations and is seen as dark green. In sections, this mineral has occupied the edges of the holes filled by secondary minerals. Paragenetic sequence of mineralization in the investigated area.

Petrography and thermometry of fluid inclusions

The best samples for fluid inclusion studies are large, selfshaped, light and transparent to semitransparent in color and at the same time as the mineralization samples. To get better results, samples were taken from quartz crystals that, as gapfillers, had filled cracks and gaps. In the investigated samples, a variety of fluid inclusions including primary, secondary, and false secondary were present, which had a variety of shapes including needle, star, triangular, negative crystal, and irregular. Also, it was found out that the investigated fluid inclusions have a high filled percentage between 85 to 90 % and consist of only the two phases of gas and liquid (L+V) and lack any girl phase, carbon dioxide, and hydrocarbon materials (Figure 4 A, B, and C).



Figure 4: A, B and C: primary single fluid inclusions with different filling percentage C string-shaped fluid inclusion.

In the heating stage, after putting the doubly polished sample in the device, a fluid and primary inclusion was selected and was heated at a speed of 30 °C/min. with the temperature getting close to the inclusion homogenization temperature, the heating rate was reduced to 10 °C/min, and finally an inclusion homogenization temperature change range of 200-220 °C was obtained.

In the freezing stage, some inclusions were cooled down to different temperatures (up to -80 degrees centigrade) using liquid nitrogen. However, because the frozen samples made the field of vision obscured and due to lack of access to an objective LD with a magnification of larger than 400, it was impossible to record the melting point of the last ice crystal. Finally, due to the reasons mentioned above for failing to record the intended temperatures in the freezing stage of fluid inclusions, based on petrographic observations of fluid inclusions like the absence of halite solid phases and high degrees of filling in most inclusions

Rad GF

and by reference to the statement that when the concentration of sodium chloride is unknown and the halite girl phase is also absent in the inclusions, the salinity degree of the mineralizing inclusions in the area can be considered to be low and a weight of around 10-12 percent of the weight equivalent to table salt.

As for determining the placement pressure of sub-volcanic masses and semi-deep dikes as mineralizing factors, which seem to have originated from deeper penetrating masses and have penetrated through volcanic and igneous layers, it should be stated that, according to stratigraphy evidence in the area, a pressure of around 50 mega-Pascal can be assumed for them. Texture evidence including textures with microlite to granophyre matrix with the same dimension as fine grains approves this issue. The temperatures obtained as the fluid inclusion homogenization temperatures are temperatures recorded in laboratory settings and under a pressure of 1 atmosphere, while the fluid inclusions in question are trapped in depth, therefore, diagrams were used to obtain the real trapping temperature of fluid inclusions with the results being drawn as a diagram.

CONCLUSION

The rocks in the investigated area include andesite, trachy andesite, basalt andesite, latite, dacite to rhyodacite, tuff, and volcanic cuts. Also, the chemical analysis placed the investigated rocks in the range of andesite to trachy andesite and dacite to rhyodacite. The lava nature of the investigated rocks was considered of high-potassium calc-alkaline series toward tholeiitic based on the geochemistry data. The negative abnormality of P, Nb, and Ti elements and positive abnormalities of Pb and K elements in the host ore deposit indicate the properties of subduction region rocks.

Iron mineralization is present in the form of magnetite, hematite, and specularite as primary, and goethite as secondary. Bornite as primary, and chalcocite, covellite, and malachite as secondary constitute copper mineralizations. The presence of iron and copper mineralizations alongside and in two separate phases indicates the magmatic origin of iron mineralization, besides the desert evidence for that. The presence of Bornite and pyrite as sulfide phases in very small amounts and the absence of other primary copper sulfide minerals in the area along with secondary phases of copper mineralization in very larger amounts indicates a hydrothermal solution with a high oxidation degree which has passed the final stages of magmatic subtraction and has caused the formation of copper surfacegrown minerals such as chalcocite in the enriched zone. Thermometric studies of the fluid inclusions based on stratigraphy and petrology evidence determined a 10% salinity equivalent to the weight of table salt, a pressure of 50 mega Pascal, and a temperature range of 200-20 degrees centigrade for these mineralizations. Therefore, based on the investigations and the temporal and spatial settings of mineralization host rocks and the type of mineralizations, it can be concluded that the above-mentioned rocks correspond to magmatism caused by subduction in arc islands, and that the genesis of upper sections is a porphyry copper system which shows a lower temperature. Therefore, the existence of a porphyry copper mineralization which has formed under the influence of primary lava phases at deeper points is likely.

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