

# Geology and geochemistry of skarn deposits in the northern part of Ahar batholith, East Azarbaijan, NW Iran

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## Abstract

Principal Skarn deposits along the northern margin of the Ahar batholith from west to east include Mazraeh, Vine and Gowdoul skarn deposits. Among these skarn deposits, the Mazraeh Cu-Fe Skarn deposit is the most typical skarn deposit in the NW Iran. This skarn deposit is located 5 km. north of Mazraeh village and 20 km north of Ahar town. The origin and development of the skarn can be related to the granitic intrusion of Oligo- Miocene age which has intruded a sequence of calcareous rocks. On the basis of petrological considerations the skarn can be subdivided into Exoskarn, Endoskarn and Ore skarn. The main mineral constituents of the skarns are garnet, magnetite, calcite, chalcopyrite, epidote, hematite and pyroxene, accompanied by quartz, pyrite, bornite, coevalite, chalcocite, plagioclase and chlorite. The bulk chemistry and spatial variation characteristics indicate that the endoskarn was the result of interaction between Mazreah granodiorite with crystalline limestone and metasomatic alteration through hydrothermal fluid enriched in Mg, Fe, Cu, P, Ag, Zn, Pb, Cd, Mo, Mn, etc. These elements point toward a magmatic source, and have been contributed to the system from the magma as well as the host rock. The crystalline limestone was the source for Ca and Mg in case of endoskarn. The transformation of granodiorite into endoskarn was accomplished by addition of 1.4 to 15% CaO along with 7.17% of total iron into the granodiorite was accompanied by depletion of about 15.5% SiO<sub>2</sub> (average 53.5%).

Keywords: Cu - Fe Skarn, Mazraeh batholith, geochemistry, Ahar, NW Iran.

## 1. Introduction

A number of Eocene - Oligocene age rocks have intruded the Karaj Formation and other rocks in Alborz and the Central Iran. This NW-SE late Eocene-Oligocene plutonic activity, known as the Gharah Dagh - Tarom plutonic belt (Pourhosseini, 1981) in northern Iran, continues as the Karkas and Jebal- Baluch belts of Central Iran (Fig. 1A). The magmatic activities are related to the Laramide Orogeny of late Cretaceous age, triggered by the post-collision convergence during several major compressive movements. The late plutonic Eocene-Oligocene (Mainly Oligocene) activities are reported by Khain (1975), from Lesser Caucasus to the northern Azerbaijan. According to Lescuyer and Riou (1976) the magmatic activity of the north Ahar Quadrangle is the largest granitic intrusion (Ahar batholith), which was emplaced during the early Oligocene. It is located to the north of Ahar town and forms the greater part of the Gharah Dagh range. The Tertiary plutonic bodies (Late Eocene-Oligocene, Oligo-Miocene and Pliocene ages) are associated with some important mineralizations.

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The Ahar region is part of the Alpine Eurasian metallogenic belt which extends from Greece and Caucasus towards Iran. The different ore deposits like porphyry, Skarn deposit, Skarn porphyry and vein type mineralization in this region are attributed to the Pyrenean Orogenic phase (Bazin and Hubner, 1969). The skarn deposits are very important for being the sites of ore localization and concentration. Different types of skarns can be associated to a specifie type of granitoid series. During the last few decades, the skarn deposits have become important repositories for metallic and non-metallic ores and have emerged as a subject for scientific research and investigations (Simirnov, 1976; Burt, 1972 and 1977 and 1982; Einaudi, 1977 and 1982; Einaudi et al., 1981; Einaudi and Burt, 1982; Kwak 1987; Hu Shouxi, 1991; Mollai and Dave, 1991 Mollai, 1994; Mollai et al., 1998 and 2007; Karimzadeh Somarin, 2003 and 2004; Meinert, 1982 and 1984 and 2001; Calagari and Hosseinzadeh, 2006).

Copper Skarns are perhaps the world's most abundant Skarn type mineralization and are particularly common in the subduction related Orogenic belts, both in oceanic and continental settings (Einaudi et al., 1981; Einaudi, 1982; Mollai, 1993; Calagari,and Hossein zadeh 2006) Most of the copper skarns are associated with I-type calc–alkalic, porphyritic plutons, developed along the contact with intrusive rocks (Einaudi et al., 1981, Meinert, 1982).

Majority of copper sulfide–bearing skarns relates to prestigious porphyry copper deposits and were developed within calcareous rocks, siliceous limestone and silty limestone. The Northern Azarbaijan has been identified as an important metallogenic province in studies carried out by Bazin and Hubner (1969) and Khadem (1965) who ascribe the mineralization in the Mazraeh mine related to a contact metasomatic. Some preliminary studies were carried out by Mollai (1993) however; no detailed information is available on the skarn deposits of Iran despite a close relationship between the magmatism and mineralization skarn deposits. This paper mainly focuses on the geology and geochemistry of the copper –iron skarn deposit in the north of Ahar, East-Azarbaijan, Iran.

## 2. Regional Gology

Fundamental differences in crustal character and in age of basement consolidation of Iran allow three major structural units to be distinguished, separated from each other by a ophiolite -bearing suture. Other criteria such as structural style, age and intensity of deformation, age and nature of magmatism, are used to subdivide these major zones into smaller elements. The three major units and their main constituents are as follows. (1) A S unit with a crystalline basement consolidated in Precambrian time and a platform -type Paleozoic development. This unit comprises the Zagros folded belt. (2) The central unit is interpreted as an assemblage of marginal Gondwana fragments that were united with the mother-continent and separated from the N (Eurasian) continent in the Paleozoic, but detached from Gondwana and attached to Eurasia in the Mesozoic, and finally rejoined by Gondwanic Afro-Arabia in the Late Cretaceous. It comprises central Iran and the Alborz. (3) The northern unit sharply separated from the central unit by the North Iran Suture .It is characterized by continental crust including remnants of more or lees cratonized former (Paleozoic) oceanic crust that seems to reflect a Paleotethys. The N unit represents a marginal strip of the Hercynian realm of Central Asia- broadly overlapped by the Alpine realm. It was deformed and largely consolidated by strong early kimmerian folding and a Late Alpine folding (Stocklin, 1977).

The Alborz Mountains, forming gently sinuous E-W range across N Iran. S of the Caspian Sea, constitute a N part of the Alpine-Himalayan Orogeny in W Asia. The Alborz Range in N Iran is stratigraphically and

structurally related to Central Iran. The similarities are particularly evident on its flank. However, some distinctions can be made .In contrast to Central Iran the Late Kimmerian and early Alpine tectonic movements did not cause angular unconformities in the Alborz.

From tectonic point of view, Iran can be divided into two marginal active fold-belts located in the NE (Kopeht-Dagh) and in the SW (Zagros) overlying resting on the Hercynian terrain and the Precambrian Arabian plate respectively. (Nabavi, 1976). The Iranian plateau between these marginal fold belts are the Central Iran, Alborz, Zabol-Baluch and Makran units, (Fig. 1A). Stocklin and Nabavi (1973), on the tectonic map of Iran, have divided the intrusive Intrusive rocks of Iran are of Precambrian, Mesozoic and Tertiary age (Stocklin and Nabavi, 1973). There are three parallel magmatic arcs in the northwest of Iran, of Cretaceous and Eocene-Miocene to Quaternary ages, trending in NW-SE direction between the Main Zagros Thrust (MZT) in the southwest and the Tabriz Fault in the northeast. Magmatic activity is apparent in the Iranian plate at all periods, but the peak activity was in the Eocene .Before the Eocene, volcanicactivity was generally low. Plutonic rocks developed to the south Sanandaj-Sirjan Zone (SSZ), following the Sanandaj Cretaceous (Stocklin 1977, Berberian, and King 1981; Moinevaziri, 1985; Sengor, 1984, Sengor et al., 1993, Sengor and Natalin, 1996; Mohajjel and Fergusson, 2000; Azizi and Moinevaziri, 2007 and 2008; Azizi and Jahangiri, 2008 Azizi et.al 2006). The Tertiary plutonic bodies were mainly intruded during the Upper Eocene-Oligocene, Oligo-Miocene and Pliocene epochs and have important mineralization. The study area is the skarn deposits of the Oligocene Ahar Batholith; located in the Sheyviar Dagh range, part of the Alborz unit in northwestern Iran. The Ahar batholith and related intrusives (Fig. 1B) were responsible for contact metamorphism, contact metasomatic mineralization, and skarn deposits, forming part of the belt of skarn porphyry copper deposits in the Caucasus and Iran (Bazin and Hubner, 1969; Superceanu, 1971; Mollai, 1993).

In the Alborz unit, Precambrian basement rocks are of Gondwanan affinityTectonic. The study area is part of Alburz, North -West of Iran. Eftekharnezhad (1975) believe that, the tectonic movements in the Late Precambrian caused significant uplift in Azarbaijan and locally formed angular disconformities (Eftekharnezhad, 1975). V and vertical movements during the Cambrian are inferred to have occurred based on stratigraphic gapes between the Cambrian and younger rock unites.



Fig. 1. (A) Regional tectonic map of Iran (after Nabavi, 1976) showing location of area under study TF=Tabriz fault. S=Sungun porphyry skarndeposit (B) Geological map of Ahar batholith and related intrusives (modified after Mollai, 1993; Mollai et al., 2009), showing the principal skarns (1–6). The Gharanigh Daragh depositis shown as (7).

Silurian and Early Devonian sedimentary sequences as well as Upper Carboniferous sedimentary rocks are absent in Azarbaijan (Nabavi, 1976). Tectonic activity in the Early Devonian resulted in the formation of NW-trending Tabriz Fault that extends several hundred kilometers NW–SE. A thick sedimentary- volcanic sequence from the Triassic to Late Upper Cretaceous sedimentary- volcanic sequence best regards was subsequently folded by Orogenic movements during Late Cretaceous-Early Triassic Tertiary orogenic movement (Eftekharnezhad, 1975).

During the Upper Late Eocene-Oligocene time, the Alborz and the central - Iran units (Karaj Formation) and other rocks were cut by several-intrusive-bodies. The late Eocene-Oligocene plutonic activities of northern Iran (the Gharah Dagh - Tarom plutonic belt) mainly developed along the have a NW- SE trending (Pourhosseini, 1981). The Oligo-Miocene regional plutonic activity of Iran was developed along the Karkas and Jebal-Baluch belt of Central Iran.The late

(mainly-Oligocene) Eocene-Oligocene plutonicactivities was reported by Khain (1975) from the Lesser Caucasus to the northern Azarbaijan (Stockline and Eftekharnezhad, 1969; Pourhosseini, 1981). According to Lescuyer and Riou (1976) the magmatic activity of the Ahar Quadrangle occurred during the early Oligocene age. This batholith was traditionally referred to as the Sheyviar Dagh range. Mollai (1993) prepared the 1/50000 scale map of this batholith and surrounding rocks, and named as it the Ahar Batholith. Ahar Batholith The occurred in the Ahar Quadranglebatholith map lies in the north of Ahar town and includes the greater part of the Ghrah Dagh range.

## 3. Geological Setting of Area Understudy

The Cretaceous sedimentary and sub-volcanic rocks are the oldest rock units in the area, followed by Eocene latite and ignimbrite (Babakhany, 1977). The Oligocene intrusive rocks, including granodiorite, diorite, gabbro and alkali syenite make up the Ahar batholith (Mollai, 1993) in the Sheyviar Dagh region. The youngest rock units are Quaternary volcanic rocks. The primary geology, petrography and, mineralogy of the Ahar batholith have been studied by Mollai (1993, 2005, 2006), Mollai and Dave (1991), and Mollai et al. (1998, 1999, 2004). In general three main rock types are identified in the Mazraeh mine area, they are (I) Meta -sedimentary rocks. (II) Igneous rocks that is granodiorite and related volcanic rocks and (III) Metamorphic rocks which are mainly Skarn deposits.

#### **3-1** -Meta sedimentary sequences

The metasedimentary terrain originally was an interbedded limestone with pelitic sequence accompanied by some sub volcanic rocks. Due to contact metamorphism, limestone has changed into crystalline limestone (marble). Depending upon the grade of metamorphism, pelitic layer has changed into spotted schists, hornfels schists or hornfels. The silicified and crystalline limestone as well as marble has been named as crystalline limestone in this work. The crystalline limestone has been folded into an antiform plunging towards SW. The pelitic layer now is represented by hornfelsic schist who forms the core of this antiformal structure separating the crystalline limestone into a northern limb or upper limb and a southern limb or lower limb (Fig. 2). The latter is in contact with the skarn. The northern part of the southern limb shows transitional contact with hornfelsic schist and hornfels. The rocks are deeply weathered and have been folded and in addition, show numerous small scale folds and interrupted foliation planes. This structural set up is very well developed in the north -eastern part of the mine area. The foliation planes are interbedded with the light brown silicate minerals or by brown garnet (bimetasomatic skarn). The crystalline limestone has more or less uniform composition and mineralogy. It is coarse to medium grained, off white to grey in color. The crystalline limestone appears to be free from mineralization but under the microscope the chalcopyrite and pyrite have been seen occasionally. The northern limb has been cut by a small wollostonite vein which is restricted to hornfelsic schist contact.

To the north of the copper mines, hornfels developed after the metasomatism of cataclastic rocks. The hornfels are very fine-grained, hard and usually black in colour and occupy the main part of the northern region of the Ahar granodiorite (Atalu 2004). The southern periphary of the elliptical body comprises siliceous recrystallized limestone layers, which have a sharp contact with skarn, whereas the contact between limestone and pelitic rocks is transitional. The hornfels schist and hornfels layers initially have the same composition. The parent rocks were probably composed of volcano sedimentary elements such as, quartzite, pelitic schist (quartz-biotite schist) and tuffaceous material. The difference between the two layers can be related to the contact metamorphism. Both of these rocks are compact, fine grained and black, dark brown, dark green and grey in color. There is not much evidence of additive metasomatism in these rocks, but along the northern slope of the granodiorite, epidote along with mineralization is quite common and quartz-veins are often seen.

The main mineral constituents of hornfels are garnet, pyroxene, plagioclase, magnetite, feldspar, quartz, biotite, and epidote, chalcopyrite, magnetite, hematite, and pyrite along with some amount of galena (Atalu, 2004). Abundant chlorite has developed due to alteration of garnet and pyroxene. Andalusite and cordierite have also been reported by Telemetal (1968).

#### 3-2- Ahar batholith and Mazraeh granodiorite

The Ahar batholith extends E-W for about 30 km and is 3–10 km wide. Generally the rocks are fresh, except in a few places where they been altered or weathered. The batholith has orthogonal Mural Joints, Mollai, 1993) as well as sub horizontal joints, with the former type predominating (Fig. 3). The orthogonal joints strike NNE-SSW and NNW-SSE and sometimes filled by aplite, pegmatite (Fig. 4), some time chalcopyrite, covellite and malachite. Joints formation were previously thought to have been related either to hydrothermal fluid over-pressuring or to the local stress regime (Mollai, 1993). However, given their regular trend and confined nature within the pluton, these joints have most likely resulted from contraction during magma cooling. Etminan (1978) related the development of the fractures and joints to t hydrothermal pressure, however the role of a regional tectonic stress field, generally expected in such large intrusions seems to be more convincing.

The Mazraeh granodiorite is a major component of the Ahar batholith. The Mazraeh granodiorite pluton has been overlain by volcanic rocks of Eocene and meta sedimentary of Cretaceous along a plunging antiformal structure. It is heterogeneous is appearance, and ranges from granite (pink) to diorite (grey).



Fig. 2. Geological map of Mazraeh mine (Modfied after Henry & Haj Hosseini, 1968 and mollai, 1993)

They appear fresh along the western side of the mine site are fresh but altered and sometimes mylonitized along the eastern part of the mine. Recent mining activities in the eastern part show mineralization as well as alteration. This mineralization and alteration are accompanied by a network of very fine quartz veins. The main granodiorite body is a feldspar porphyry granodiorite with preferably aligned and up to 1 cm large phenocrysts of pink feldspar. The main constituent minerals include quartz (6-15%),plagioclase (24 - 43%),K-feldspar (20-48%),hornblende (0-10%), biotite (0-5%), apaite (0-3%); the accessory minerals are titanite and magnetite (Mollai, 1993). Some feldspars display poikilitic textures and perthitic and myrmekitic intergrowths were also observed in some samples. The Mazraeh granodiorites can be classified as I-type on the basis of presence of hornblende and high plagioclase content. Similar to other Cu-Fe skarn deposits of northwestern Iran, the Mazraeh skarn is also associated with a lowsilica, shallow-level I-type pluton, which originated from Fe-rich oxidizing magma under magnetite-stable, O<sub>2</sub> conditions (Mollai, 1993; Mollai et al., 1998; Karimzadeh Somarin and Moayved, 2001). The porphyry skarn deposit and vein type deposit in the Mazraeh area and other places around the Ahar batholith are attributed to the emplacement of plutons during the Pernean Orogeny (Bazin and Hubner, 1969). The effect of pluton emplacement on the host rocks are dependent on the composition, mode and depth of emplacement, and range from development of porphyry skarn deposit to hornfels mineralization, spotted schist and seen as silicification, and recrystallization of limestone (marble).



Fig. 3. Cross joint and typical morphology of Mazraeh granodiorite.



Fig. 4. Quartz and applied veins within the granodiorite in the south of Mazraeh Mine

#### 3-3- Skarn Deposits

There are numbers of Skarn ore deposits formed at or near the contact of felsic intrusive body with Cretaceous limestone. The Oligo-Miocene granodioritic rocks intruded the upper Cretaceous impure carbonate rocks which host the Skarn zones, a series of Eocene arenaceous-argillaceous rocks and a series of Oligocene dacitic breccias, tuffs and trachyandesitic lavas (Mollai, 1993). The results of this intrusion, in addition of the skarnification, and mineralization, are the recrystallization of Cretaceous limestone along with pronounced preserve alteration produced. Most of the skarn minerals in these areas were formed at the northern contacts of intrusive rocks except the Zandabad Skarn which is formed at the southern contact of the Ahar Batholith. At some places like Sungun, Anjerd, Mazraeh and Zandabad, the metasomatism was so intense that the original characters of the Cretaceous carbonate rocks are completely lost. The following skarn deposits from the western limit of the area towards the east include: (1) Sungun Skarn Copper porphyry, (2) Anjerd skarn (3) Zandabad skarn, (4) Javanshaykh skarn (5) Mazraeh Iron-Copper skarn (6) vein garnet skarn and (7) Gowdoul skarn. The Sungun porphyritic skarn, Anjerd, Gowdoul and Mazraeh skarns were also described earlier (Telemetal project 1968) while other skarn deposits were reported for the first time by Mollai (1993). In this paper, the later three skarn deposits (Mazraeh Iron-Copper skarn, vein garnet skarn and Gowdoul skarn) are discussed. The size and shape of skarn deposits are dependent on the lithology, composition, the mode, geometry and depth of emplacement of the host and the intruded body. The first parameter is the geometrical relationship between the intrusive body and the country rocks. In the areas under study the intrusives are discordant, therefore the metasomatizing fluids travel farther and upward through the bedding plane and extensive skarn is likely to form. The second parameter is the lithology of the host rock. The carbonate rocks are very reactive to the involving fluids and very easily convert to skarn. The third parameter is the composition of the invading magma. The intermediate to acidic magmas are recorded to generate more skarns than any other magmatic type (Simirnov, 1976; Einaudi et al., 1981; Einaudi and Burt, 1982; Kwak, 1987; Sawkins, 1990; Hu Shouxi, 1991). At the Mazraeh, the southern contact between the granodiorite and crystalline limestone is steeply dipping ( $60^{\circ}$  to  $70^{\circ}$  S) and is subconcordant, transecting the limestone beds (striking E-W, dipping S). The width of the skarn here ranges from 2 to 25 m (50 m where the granodiorite tongue cuts across the limestone). In general, all of these skarns, irrespective of their size, have sharp contacts with both of the intrusive body as well as crystalline limestone

(Fig. 5) and have almost the same the mineral composition such as, dark brown to light brown garnet, calcite, epidote tremolite-actinolite, magnetite, chalcopyrite and pyrite.

The Mazraeh Skarn deposit is the largest deposit in the area and is being actively mined. The Mazraeh skarn deposit extends for about one km. along the E–W trending contact between the intruding granodiorite and host calcareous rocks. Adjacent to the granodiorite, the calcareous character of the rock has been completely obliterated due to intense magmatism, however, effect of initial metasomatism and still preserved original features can be seen little away from the contact.

The country rock is nearly pure recrystallized limestone inter bedded with alumino silicate layers. This argillaceous limestone consists of angular calcite, subordinate biotite, feldspar and quartz exhibiting lowgrade regional metamorphism and metasomatism. Ladame (1945) initially investigated and reported that this area was promising for copper mining and Khadem (1965) reported polymetallic characteristics and identified it as one of the most promising regions for copper. The total mineable reserves are 400000 tons at 1.2% Cu P The Mazraeh copper deposit is a notable example of the contact metasomatic and metamorphic system that was developed by interplay between a plutonic body, sedimentary rocks. The main skarn zone lies in the southern margin of the structure (i.e., along the northern margin of granodiorite) and becomes thicker at depth (Telemetal report, 1968). The skarn zone is roughly WNW-ESE to ENE-WSW trending (with up to 20° deviation, either N or S), parallel to the contact of granodiorite and southerly dipping crystalline limestone. Although the signs of zonal arrangement are available across the contact as well as along the contact, at Mazraeh (Fig. 6), the zonal arrangement is not easily mapable in these skarn deposits as reported in other skarn deposits like, Corr Fork Area, Bingham, Utah (Reid, 1978), Sonleon Magnetite skarn Deposit, S.W. Sardinia (Verkaeven and Bartholome, 1979) and strata bound skarn of Tonguanshan in China (Cuibin, 1991). In the northwestern part of the Mazraeh mine a large enclave of metasedimentary rock occurs within the skarn. The enclave has more or less been converted into hornfels and exhibits transitional contact. The skarnification of igneous rock at the contact can be seen both megascopically as well as microscopically. The effect of metasomatism on granodiorite and formation of endoskarn is limited and varies from few centimeters to maximum one meter but the reaction is not uniform along the contact. The exoskarn occurs toward the limestone in the field and shows sharp contact. The hand specimens show various shades of brown color when the mineral constituents are garnet and calcite, and grey-green when the exoskarn is rich in epidote and chlorite.



Fig. 5. Contact of Exoskarn with the crystalline marble as country rocks



Fig. 6. Zonation of skarn deposit in the Mazraeh Copper-Iron Mine

## 3-3 - Bimetasomatic Skarn

The term bimetasomatic skarn is used for those skarns which are formed due to the metasomatism of limestone and its inter bedded silico-aluminous subvolcanic rocks (Einaudi et al., 1981). Such skarn in Mazraeh occurs as inter layers within crystalline limestone. The width of bimetasomatic skarn ranges from 0.5 to 5 cm where two layers partly join together and extend towards the north east of the mine. These layers of skarns are parallel to the strike of beds. Their foliation direction is N60E-S60°W and dip 60 towards south. Folding are not uniform, but are essentially open folds sometimes refolded and turned into box folds, isoclinal's to recumbent or other types of folds in this area.

## 4. Classification of Skarn Deposit

Skarns in the field and hand specimen show various shades of brown colour when the mineral constituents are garnet and calcite and the grey-green color when the skarns are rich in epidote and chlorite, (Fig. 7A-7C). At some places, the garnet is fresh and clear. Texturally, the skarns show porphyroblastic, poikiloblastic and sometimes cataclastic textures and anisotropic properties with twinning (Fig. 7D-7E). Due to altration of garnet, chlorite and actinolith have been formed (Fig. 8). In the southwest of the Mazraeh mine, where the tectonic deformation is common, the garnet and associated minerals show cataclastic texture which is more common in comparison to the central part, where the replacement and granoblastic textures are more common. Brecciation and overprinting textures which are formed due to retrograde events are very predominant. Skarn deposit can be petrologicaly classified in to endoskarn, exoskarn and ore skarn. Each of these can be further sub-divided on the basis of mineral assemblage. The complete scheme is summarized below which is based on the predominant primary skarn mineralogy:

I- Endoskarn:1) Plagioclase-alkali feldspar-magnetiteepidote skarn; 2) Epidote-plagioclase-biotite skarn; and 3) Garnet-plagioclase-pyroxene skarn.

II. Exoskarn: 1) Garnet skarn; 2) Garnet-pyroxene skarn; 3) Pyroxene skarn; 4) Garnet-calcite skarn; 5) Epidote skarn; and 6) Bimetasomatic skarn.

III. Ore skarn: 1) Magnetite-garnet skarn. 2) Magnetitechalcopyrite-garnet-pyroxene skarn. 3) Chalcopyritequartz-epidote skarn. 4) Pyrite-chalcopyrite-epidote skarn.

These stages include the initial hydrothermal orebearing and later barren hydrothermal fluid circulation. The hydrothermal events were accompanied by alteration of pyroxene, garnet, plagioclase, and alkali feldspar, leading to chloritization, sericitization and saussuritization. Although the skarns are the main host for ore deposit, mineralization also occurs at the contact of granodiorite and meta-sedimentary rocks. The exoskarn and endoskarn are transected by a set of mineralized quartz veins which are parallel to each other, but a few also exhibit intersecting relations (Fig. 7c). They are cavity-filling type where in quartz was the first phase, followed by iron ore and sulfide sericitization minerals. Chloritization and of granodiorite are common features near such veins. The granodiorite adjacent to these veins is enriched in ore minerals, which may be due to lateral diffusion of mineralizing fluid. The mineralized quartz veins appear to have formed from the late-stage hydrothermal fluids that evolved from the crystallizing magma. In the ore skarn assemblage, chalcopyrite, pyrite, magnetite, hematite, siderite, bornite, coevellite, chalcocite and malachite are present as ore minerals and quartz, garnet, calcite, pyroxene, epidote, actinolite and biotite as the main gangue minerals. The ore minerals are seen

intensively replacing the host rock as well as the silicate gangue minerals. Quartz is coeval with the sulfides and magnetite. Sulfide ores are post-date the iron ores and also occur as intergranular fillings. Chalcopyrite has an affinity with magnetite and shows a positive correlation with epidote. The ore minerals occur along different layers of skarn that resulted from garnetization, epidotization and silicification of carbonate rocks. Based on field and petrographic evidences, at least five paragenetic stages of skarn mineralization can be recognized. The early magmatic Stage I of granitoid was followed by the stage II which included the formation of anhydrous minerals such as clinopyroxene and garnet (mainly andradite). This can also be called as the main metasomatism stage or the stage of prograde. Stage III included formation of iron ores and chlorite and Stage IV, the formation of sulfide ores along with chlorite and quartz veins. The latest episode (Stage V) is represented by the barren hydrothermal veins containing quartz, calcite and alteration of the existing low-temperature assemblage minerals. Magma, especially I-type, has been recognized as a source for Cu-Fe mineralization by a number of workers like Schwartz (1959), Buseck (1966), Holland (1972), Haughton et al., (1974), Burnham (1979), Craig and Vaughan (1981), Einaudi et al. (1981). Dick and Hodgson (1982). Jairath and Sharma (1985), Jairath (1986), Wyborn et al., (1987). A number of workers like, Shimazaki (1980), Einaudi et al., (1981), Kwak (1987) and Sawkins (1990) have established a close affinity for I-type granodiorite, such as at Mazraeh series and iron-copper skarn deposits. The deposits like Sungun in East-Azarbaijan Iran (personal visit) Christmas, (Arizona), Bingham (Utah), Santa Rita and Conception del oro (Buseck, 1966) are associated with mineralized stock and serve as the best examples of the genetic relation between the skarn deposit formation and magmatic processes. The copper skarns are characterized by their association with acidic to intermediate igneous rocks (quartz monzonite, granodiorite), with porphyry textured stock of hypabyssal rocks. The iron-rich oxidizing solution leads to the precipitation of andradite, causes a decrease in Fe/Cu ratio in the ore bearing fluid as the temperature drops, and leads to the deposition of bornite rather than chalcopyrite. Alien and Buseck, 1988; Rose and Burt (1979). At Mazraeh, bornite deposited as exsolution within the chalcopyrite yeins. Therefore bornite is the first sulphide phase separated from ore fluids. The reason is the high Fe-sulfur bearing fluids that are associated with the formation of ore skarn. The result is that at Mazraeh, after the cyrstallization of andradite, iron precipitated as magnetite and this continued until Fe-Cu-S system started precipitating bornite as exsolution within the chalcopyrite veins (Fig. 9).



Fig. 7. Various type skarn in hand spaciments and microphotographs A: Epidot and plagioclase skarn, B: Garnet magnetite ore skarn, C: Magnetite quartz chalcopyrite skarn D: Microphotograph of anisotropic garnet, showing first order birefringence, zoning, twining, overgrowth and fracturing. E: Anisotropic properties, oscillatory zoning and banding with cross cutting of magnetite vein



Fig. 8. Microphotograph of Epidote and Garnet skarn. Showing formation of actinolite and chlorite as green elongated mineral due to alteration of garnet mineral.



Fig. 9. Microphotographs of polish section. Upper micro photo graph showing cross magnetite and hematite which is the result of martitization. Lower micro photo graphs showing chalcopyrite and bornite as exsolution which indicate earlier formation of bornite.

# 5. Geochemistry

## 5.1. Analytical Methods

Representative samples were selected on the basis of thin and polished section studies and XRD analysis.Chemica analysis was done following the method of Shapiro (1975) and Potts (1987). Different techniques were used including instrumental methods. The main instruments used the university of Roorkee were:

a) Inductively coupled Plasma Spectrometer (ICPS.) model- 8440 - Labtam.

b) Atomic Absorption Spectrophotometer model IL751 was used for Pb and Cd. For the determination of Na and K, emission mode was used. Analysis was also carried out, mainly for cross-checking of data on X-ray fluorescence Spectrometer at Wadia Institute of Himalayan Geology. The XRF data in respect of si, Al, Rb, Sr, Zr, Mb, Y, Th and U were found to be more consistent. Therefore, been reported here. Ferrous iron was determined by titration. The carbon and sulfur were analyzed on carbon-Sulfur Analyzer at Welding Research Laboratory of the University of Roorkee.

c) X-ray diffraction of feldspar and calcite for phase identification

The bulk compositions of different skarns, Mazraeh granodiorite and crystalline limestone are shown in tables 1 to 5. These rocks show significant differences in composition, attributable to the intense alteration of granodiorite and carbonate rocks. Field and petrographic studies show that the Mazraeh granodiorite is progressively converted to endoskarn and carbonate rocks in to exoskarn (Mollai, 1993;

Karimzadeh Somarin and Moayyed, 2001). These studies clearly show that the carbonate rocks and the granodiorite are the protolith of the exoskarn and endoskarn at Mazraeh copper-iron skarn deposit, respectively. In the skarn deposit at one end of the spectrum is granodiorite with coarse grained, relatively homogenous, as well as high SiO<sub>2</sub>, Na<sub>2</sub>O and some time K<sub>2</sub>O. At the other end of this spectrum is the crystalline limestone rich in CaCO<sub>3</sub>, with variation in grain size and grade of metamorphism. The Skarn is usually altered or overprinted by new minerals due to hydrothermal activities. Where hydrothermal solution was rich in ore fluid, corresponding ore deposit has formed. These types of activities and changes cause spatial variation in most skarn deposits. For better understanding of this spatial variation, the average of major oxides and trace elements for five major groups of rocks i.e., granodiorite, endoskarn, exoskarn, ore skarn and crystalline limestone have been plotted in Fig.s 10 and 11, respectively. A graphical representation of major oxide has been shown on Harker type variation diagram. The amounts of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in granodiorite are 65.87% and 15.11%, respectively, In Endoskarn SiO<sub>2</sub> is 52.92 % and Al<sub>2</sub>O<sub>3</sub> is 15.85 which are higher in comparison to SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in Exoskarn and crystalline limestone, 36.7% and 7.79%, 18.12 % and 5.37%, respectively. The range of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in different rocks indicates that only 2.43% and 16.5% of these oxides have been infiltrated to the crystalline limestone respectively, whereas the condition for ore skarn is different, the filtration of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in ore skarn are 25.05% and 2.73%, respectively.

Oxide	A13	A14	A15	A16	<b>MZ21</b>	<b>MZ22</b>	<b>MZ26</b>	MZ27	Mz5	<b>MZ55</b>	<b>MZ56</b>	Mz54c	Mz71
SiO <sub>2</sub>	34.25	23.98	41.81	38.75	42.60	47.46	25.63	35.92	37.14	22.17	30.62	37.16	36.56
Al <sub>2</sub> O <sub>3</sub>	6.16	3.97	5.55	7.70	13.55	12.62	2.44	6.91	8.15	4.30	7.51	6.90	5.28
TiO	1.93	0.20	0.21	0.69	1.87	1.86	0.09	0.74	0.43	0.25	0.64	0.73	0.76
FeO	7.17	2.96	9.76	7.94	4.24	6.06	10.17	4.77	3.53	14.01	12.99	4.77	2.64
Fe <sub>2</sub> O <sub>3</sub>	15.18	22.92	36.40	11.80	11.91	8.73	52.04	17.85	10.85	34.91	23.58	17.84	20.5
MgO	2.45	2.17	1.46	3.23	5.13	7.87	1.01	1.45	1.71	1.943	5.94	1.45	0.49
CaO	29.12	25.63	1.32	24.92	17.51	9.9	1.72	30.76	30.45	17.22	14.78	30.76	31
MnO <sub>2</sub>	0.87	0.40	0.10	0.83	0.45	0.15	0.11	0.62	0.12	0.41	0.31	0.62	0.12
K <sub>2</sub> O	0.11	1.01	1.01	0.15	0.77	0.94	0.20	0.14	0.12	1.12	0.45	0.14	0.12
Na <sub>2</sub> O	0.15	0.38	0.75	0.71	0.48	2.48	0.20	0.22	1.07	0.26	0.92	0.23	0.22
<b>P</b> <sub>2</sub> <b>O</b> <sub>5</sub>	0.61	1.02	1.34	0.65	0.51	0.61	2.51	0.71	0.74	1.62	1.11	0.22	0.62
$H_2O^+$	0.45	6.56	0.04	0.78	0.01	0.11	0.13	0.23	0.21	0.18	0.12	0.25	2.14
H <sub>2</sub> O <sup>-</sup>	0.09	0.20	0.11	0.09	0.01	0.10	0.12	0.23	0.21	0.22	0.99	0.23	0.02
Total	99.78	98.72	100.12	100.46	100.33	99.41	99.57	100.84	98.45	99.31	99.25	99.56	0.04

Table 1. Major (as Wt% Oxide) concentration of Mazraeh Exoskarn

Sample	A13	A14	A15	A16	Mz21	Mz22	Mz26	Mz27	Mz5	Mz55	Mz56	Mz54c	Mz71
Ag	68.57	54.14	13.60	79.62	76.20	20.98	55.80	65.15	0	65.18	89.56	0	30.73
Cr	24.92	91.01	21.31	88.71	178.34	55.16	29.93	141.71	77.68	59.71	201.81	77.675	84.43
Со	59.31	76.31	79.51	69.25	70.62	25.91	546.11	69.36	76.08	120.37	107.37	76.078	52.09
Ni	99.45	70.915	126.11	64.06	168.17	57.74	604.02	47.37	74.41	128.57	104.95	74.482	71.54
Cu	129.56	2177.39	385.97	538.77	2214.24	157.81	145.51	713.51	47.38	2379.29	6816.59	47.375	425.15
Zn	106.02	115.27	110.39	152.25	321.17	99.21	412.64	114.52	99.25	217.94	190.11	99.241	73.65
La	89.88	193.57	36.31	73.83	221.43	69.65	42.88	87.54	81.87	66.38	167.32	81.869	59.68
Pb	135.52	191.77	67.91	89.71	187.52	0	486.31	129.91	119.81	91.972	155.93	119.808	115.76
Cd	19.73	20.38	11.51	14.17	17.76	6.91	6.781	22.71	15.18	13.31	10.91	15.176	11.37
Ba	4.11	635.24	117.91	15.97	30.53	116.66	57.84	43.97	13.58	95.98	33.58	13.578	5.38
Мо	57.21	56.74	93.51	56.28	65.83	35.76	115.68	55.57	45.28	90.78	78.77	45.277	43.71
W	149.67	155.42	261.98	153.65	186.52	131.55	520.55	166.41	143.77	277.92	225.81	143.77	122.55
Li	6.78	12.59	3.8	6.39	16.56	13.91	13.17	10.31	16.95	2.71	6.11	16.942	11.57
Ga	14.44	0	0	27.52	23.12	24.51	0	21.68	0	65.18	89.56	15.472	21.92
Rb	0	0	0	0	9.12	42.45	0	0	77.68	59.71	201.81	2.108	0
Sr	57.51	0	0	53.97	682.97	570.48	0	32.76	76.08	120.37	107.37	78.852	31.73
Zr	31.93	0	0	97.05	192.53	279.05	0	96.46	74.41	128.57	104.95	98.661	16.49
Nb	13.71	0	0	3.47	57.21	27.56	0	4.52	47.38	2379.29	6816.59	0	13.59
Th	0	0	0	6.68	5.65	19.91	0	37.43	99.25	217.94	190.11	6.99	0
Y	8.34	0	0	15.05	40.61	11.06		0	17.85	81.87	66.38	9.6	9.6
U	0	0	0	0	0	7.63		0	0	119.81	91.972	0	0

Table 2. Chemical analysis of trace element (in ppm) of Mazraeh Exoskarn

Table 3. Chemical for data of Major oxide of Endo skarn

Sample	A12	MZ28	MZ54	MZ82	Mz54b
SiO <sub>2</sub>	53.28	54.82	55.31	55.67	45.47
Al <sub>2</sub> O <sub>3</sub>	17.39	18.95	15.94	12.3	14.65
TiO <sub>2</sub>	1.00	0.62	1.38	0.33	1.66
FeO	3.34	1.34	3.44	2.49	1.65
Fe <sub>2</sub> O <sub>3</sub>	3.45	1.38	5.38	6.97	6.42
MgO	1.53	1.53	2.60	1.04	3.70
CaO	6.98	7.49	7.75	13.14	20.66
MnO	0.46	0.17	0.16	0.33	0.34
K <sub>2</sub> O	4.90	0.75	1.89	1.25	0.30
Na <sub>2</sub> O	0.60	6.14	4.79	3.48	1.73
$P_2O_5$	0.54	0.42	0.59	0.41	0.53
СО	4.45	4.61	0.15	2.017	1.64
$H_2O^+$	0	4.61	0.15	2.17	0.98
H <sub>2</sub> O <sup>-</sup>	2.00	0.89	0.99	0.51	0.31
Total	100.00	99.24	100.64	99.65	100.07

1000 - 00000000000000000000000000000000	Table 4.	Chemical	data for	Trace of	Endoskarn	element
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Sample	A12	MZ28	MZ54	MZ82	Mz54b
Ag	10.99	20.98	29.14	1129.15	50.22
Cr	46.79	55.15	161.09	165.23	47.03
Со	32.56	25.99	37.52	46.89	58.39
Ni	79.32	57.73	74.85	46.29	86.29
Cu	73.99	157.87	4711.04	5088.80	123.56
Zn	157.44	99.20	149.91	97.58	116.79
La	73.72	69.64	55.09	81.62	76.33
Pb	87.91	0	79.84	67.85	117.58
Cd	10.78	6.98	4.19	12.37	8.769
Ba	105.89	116.66	145.52	79.24	46.23
Мо	49.79	35.75	5.5	44.71	51.42
W	151.44	131.54	79.44	121.73	152.46
Li	26.19	13.98	161.09	10.37	32.28
Ga	0	24.58	249.43	275.88	17.25
Rb	298.00	42.44	52.60	29.06	21.19
Sr	134.60	570.47	990.95	529.35	414.94
Zr	184.02	279.04	122.30	117.31	128.03
Nb	8.60	27.55	105.80	23.97	0
Th	0	19.90	-88	2.38	3.71
Y	43.33	11.05	22.21	20.53	24.26
U	1.63	7.67	1.31	0	0

Table 5a. (Left) The average values for major oxide of different group of rocks in Mazraeh Cupper -Iron skarn deposit.1. Granodiorite2. Endoskarn.3. Exoskarn4. Ore skarn5. Crystalline limestone

Table 5b. (Right) The average values for trace elements of different group of rocks (without ore skarn) 1. Granodiorite2. Endoskarn. 3. Exoskarn4. Crystalline limestone

Oxide	1	2	3	4	5
SiO <sub>2</sub>	65.87	52.91	36.7	25.05	18.12
Al <sub>2</sub> O <sub>3</sub>	15.11	15.84	7.79	2.73	5.37
TiO	0.68	1.00	0.92	0.17	0.26
FeO	2.55	2.38	5.64	12.95	1.04
Fe <sub>2</sub> O <sub>3</sub>	1.3	4.72	15.52	45.87	1.38
MgO	2.01	2.08	4.29	1.51	1.33
CaO	4.34	11.20	23.6	2.82	43.52
MnO	0.15	0.29	0.563	0.21	0.12
<b>K</b> <sub>2</sub> <b>O</b>	2.73	1.81	0.35	0.35	0.62
Na <sub>2</sub> O	3.89	3.34	0.59	0.26	0.66
<b>P</b> <sub>2</sub> <b>O</b> <sub>5</sub>	0.39	0.50	0.71	2.66	0.18
Со	0.61	2.60	1.97	0.94	-
H <sub>2</sub> O	0.57	1.07	0.94	0.33	27.09(LI)
H <sub>2</sub> O	0.59	0.19	0.14	0.23	-

Elements	1	2	3	4
Ag	7.9	26.46	46.66	56.72
Cr	68.78	95.06	165.6	70.01
Со	29.12	40.27	75.66	54.55
Ni	85.16	68.90	99.83	75.45
Cu	202.72	2554.38	1168.06	337.07
Zn	81.67	124.18	166.1	92.08
La	76.64	71.28	135.49	101.76
Pb	67.15	70.63	110.52	146.33
Cd	6.77	8.62	13.78	16.14
Ba	603.28	284.71	40.59	144.9
Mo	37.86	46.83	64.10	36.87
W	124.74	127.32	162.16	78.51
Li	42.38	48.78	18.07	8.86
Ga	47.07	113.43	33.03	23.3
Rb	111.27	88.66	6.26	62.86
Sr	668.21	528.06	164.33	1653.28
Zr	165.55	166.14	94.91	132.47
Nb	34.08	33.18	14.18	153.12
Th	25.77	7.22	12.05	14.07
Y	11.65	24.28	19.01	17.51
Ū	6.88	2.11	0	2.27



Fig. 10. The Spatial variation diagram for average of major oxide in different rock sequences in the Mazraeh Copper-Iron Skarn deposit.





Fig. 11. The Spatial variation diagram for average of minor and trace elements in different rock sequences in the Mazraeh Copper-Iron Skarn deposit.

The rest of these oxides must be due to impurities of carbonate rock. Sphene is the common accessory mineral in the endoskarn and sometimes in the igneous rocks, as seen in high TiO<sub>2</sub> (~1%) in the endoskarn followed by exoskarn (0.92%). The ore skarn shows much lower TiO<sub>2</sub>. The EPM analysis of magnetite shows less than 1% TiO<sub>2</sub> (Mollai, 1993). Therefore the higher value of this element in the skarn in comparison with granodiorite and carbonate rocks indicates the addition of TiO<sub>2</sub> to the system during post magmatic activities.

The total difference between exoskarn and crystalline limestone shows addition of 18.7% of iron oxides to the host rock to develop exoskarn, whereas the total addition of iron into the ore skarn is 56.4%, meaning there by that 37.65% of iron has been added into the system. Because of low iron (2.43%) the metasediment can not be effective source for iron component, therefore the source of this iron is magmatic fluids. In this regard, in the processes of metasomatism the magmatic solutions became ultimately concentrated with iron. Where replacement of carbonate rocks produces iron rich silicate (andradite) the excess iron leads to the formation of iron ore (Lindgrin 1933, Simirnov 1976, Mollai 1993, 1994). Karimzadeh Somarin (2004) Calculated gains and losses of oxides and elements using Grants (1986) approach the high degree of positive correlation between Al<sub>2</sub>O<sub>3</sub> and Zr indicates the relative immobility of these components during skarnification. Based on this study Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Zr, Th, Nb, and Ga are relatively immobile. SiO<sub>2</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, MgO, P<sub>2</sub>O<sub>5</sub>, Ag, Cu, Zn, La, Pb, Cd, Mo, W and Y display gains. Components such as Fe<sub>2</sub>O<sub>3</sub>, CaO, MnO and Ag show substantial gains, such the up to 26-fold increase in Fe<sub>2</sub>O<sub>3</sub>, which favoured the formation of red-brown andraditic garnet in the endoskarn. As the spatial variation diagram shows MgO is contributed by magmatic source. The average values of CaO is 23.6% and 11.21%, in endoskarn and exoskarn respectively, indicating significant interchangeable Ca from limestone and Si from magma have been produced by the process of metasomatism. K<sub>2</sub>O, Na<sub>2</sub>O, Ba, Rb and Sr display losses due to replacement of primary feldspars in the Mazraeh granodiorite. Ba shows the maximum loss (up to 98%). The decrease of K<sub>2</sub>O in the skarn is in accordance with disappearance of alkali feldespar and biotite from the skarn and this is because there is no solid solution between the Ca and K. The negligible amount of alkali component in the skarn indicates that it has not taken part in metasomatism. The ore fraction contains maximum value of P<sub>2</sub>O<sub>5</sub> (3.49%), decreasing steadily towards the either side. The chemical gradient of SiO<sub>2</sub>, CaO, Fe (tot.) and Al<sub>2</sub>O<sub>3</sub> are responsible for the formation of calc sillicates minerals like garnet, clinopyroxens epidote, plagioclase, and iron ores in the skarn. Based on the occurrence of skarn body and

chemical composition, it can be concluded that the crystalline limestone is the source of Ca but Si, Al, Mg, Fe and P were contributed from the magmatic source. During the skarnifiction process, primary biotite, hornblende and titanite in the contact of granodiorite were replaced by garnet, chlorite and sphene. Al rich garnet (grossular) and epidote have been formed by replacement plagioclase and K feldspar and leached the elements such as Na, K, Rb, Ba and also the other soluble elements also. In addition, the formation of epidote indicates post-magmatic activities and addition of Al, Si and H<sub>2</sub>O from the hydrothermal sources.

## 6. Discussion and Conclusion

A general increase in concentration of metal elements and their non uniform distribution indicate a magmatic source. The local control by the microstructures and weak plane along the contact provide the pathway for the migration of hydrothermal ore bearing fluids. The concentration of Al2O3 and SiO2 can easily be explained as both the Al and Si are tied up with feldspar and TiO<sub>2</sub> with sphene that were introduced during magmatic intrusion and induced contact metasomatism. In normal cases MgO and MnO should have negative correlation with SiO<sub>2</sub>, but the scattering is due to additional post magmatic activity. The alkaline elements are the most mobile components, but this mobility can take place under a set of favourable geochemical conditions. In contact metasomatism, , solid solution between Ca and K cannot take place because of high concentration CaO, but Na and C, solid solution is possible, therefore the concentrations of K and K-rich minerals are very low in the contact as well as in the skarn, especially in the exoskarn. Likewise concentration of Na is high in comparison K due to solid solution. Therefore, the concentration of K increases towards the granodiorite body. In general, the values of trace elements like Cr, Ni, Pb, Nb, Th, W and Co in exoskarn are very low and generally show negative trends with trend with SiO<sub>2</sub> or a data scatter whereas the rest of the elements like Mo, Li, Ga, Rb, Ba, Zr define positive trend. Relatively immobile components include TiO<sub>2</sub>, Zr, Ga, Nb, etc. however, there are significant abundance variations in these trace elements, reflected in their relatively high standard deviations (Karimzadeh Somarin 2004). Alteration of granodiorite to endoskarn at Mazraeh was mainly by mineral dissolution, which created open spaces; these open spaces were then filled by precipitation of later minerals. This volume increase is manifested as open spaces and developed via hydro fracturing and leaching. The enhanced porosity and permeability allowed mineralizing solutions to percolate and deposit sulfides, oxides, quartz and calcite veins in the late stages of skarn formation. High Cl content in the Mazraeh mineralizing fluid is suggested by the presence of high salinity fluid inclusions with up to 63 wt% equivalent NaCl (Mollai, 1993). This relation is clearly seen in the spatial variation diagram.

On the basis of the field studies, petrography and mineralogy, geochemistry and fluid inclusions studies of granodiorite, skarns and crystalline limestone, it can be concluded that skarnification in Mazraeh has taken place under the five stages of skarn evolution under fluid infiltration. (1) Automagmatic stages, which is the emplacement of magma at the contact of limestone. Thermal metamorphism took place in the range bewteen 754 and 698 °C which resulted in limestone recrystallization and hornfels development. (2) Main stage of metasomatism: this stage is marked by the growth of skarn. The magmatic fluids reacted with crystallized calcite to produce typical skarns. (3) Culmination Stage: this stage represents the culmination of the prograde skarn formation, and beginning of the retrograde changes along with mineralization. Based on fluid inclusion studies this stage was within the temperature ranges between 700 to 420 °C. (4) Hydrothermal stage: the metsomatic ore minerals were followed by epigenetic hydrothermal vines bearing chalcopyrite, bornite, and covellite and magnetite, accompanied by silicate minerals. (5) The last episode in the Mazraeh is represented by barren hydrothermal veins of quartz, calcite and chlorite. Chemical gradient of SiO<sub>2</sub>, CaO, Fe (tot.) and Al<sub>2</sub>O<sub>3</sub> were responsible for the formation of calc-silicate minerals like, garnet, clinopyroxene, epidote, and plagioclase and iron ores in the skarn. Based on the occurrence of skarn body and chemical composition, it can be conclude that the crystalline limestone has been the source for Ca but Si, Al, Mg, Fe and P were contributed from the magmatic source. During the skarnifiction process, primary biotite, hornblendes in the contact of granodiorite were replaced by garnet, chlorite and sphene. Al rich garnet (grossular) and epidote were formed by replacement of plagioclase and K feldspar and leached the elements like Na, K, Rb, Ba and also the other soluble elements. In addition the formation of epidote indicates post-magmatic activities and addition of Al, Si and H<sub>2</sub>O from the hydrothermal sources. Skarn associated with epizonal granodiorite, absences of intense alteration of this rock at contact, Fe rich calc- silicate gangue minerals consisting of garnet, epidote, and pyroxene with retrograde metamorphism chloritization. along with ssassuratization. carbonatization indicate intermediate to high oxidation of the skarn deposit. All the above mentioned features are the characteristic of Mazraeh Skarn deposit associated with epizonal granodiorite. Fe rich calcsilicate gangue minerals consisting of garnet, epidote, pyroxene with retrograde metamorphism along with martitization indicate intermediate to high oxidation of skarn deposit. All the above mentioned features of Mazraeh skarn deposit are the characteristic of Island

Arc Skarn formation within the temperature ranges between 700 to 420 °C (Mollai, 1993)

#### References

- Alien, P.M., Buseck, P.R., 1988. XRD. FTIR and TEM studies of optically anisotropic grossular garnets. American Mineralogist, vol. 73, pp. 568-584.
- Atalu, A., 2004. First stage of Copper, Gold and Zinc exploration in south Sheyviardagh, north of Ahar, East Azarbaijan. Iran (In Persian) 256p.
- Azizi, H., Moinevaziri, H., Mohajjel, M., Yaghubpur, A., 2006. PTt path in metamorphic rocks of the Khoy region (northwest Iran) and their tectonic significance for Cretaceous–Tertiary continental collision. Journal of. Asian Earth Science, 27, pp. 1–9.
- Azizi, H., Moinevaziri, H., 2007. Petrology and Geochemistry of Saquez Cretaceous volcanic rocks based on REE elements, Isfahan University Journal of Sciences. (In Persian) pp. 27-38.
- Azizi, H., Jahangiri, A., 2008. Cretaceous subduction-related volcanism in the northern Sanandaj-Sirjan Zone, Iran. J. Geodyn. vol. 45, pp. 178–190.
- Azizi, H., Moinevaziri, H., 2008. Petrology of Cretaceous volcanic rocks in northern Sanandaj. Tehran University Journal of Sciences. vol. 35, pp. 15–23.
- Babakhany, A., 1977. Explanatory text of the Ahar Quadrangle Map, 1:250000.
- Berberian, M., King, G.C., 1981. Towards a paleogeography and tectonic evolution of Iran Canadian Journal of Earth Sciences. vol. 18, pp. 210-265.
- Bazin, D., Hubner, H., 1969. Copper Deposits in Iran, Geological Survey of Iran, Report No. 13.
- Burnham, C.W., 1979. Magmas and Hydrothermal Fluids, In Barnies: Geochemistry of Hydrothermal Ore deposits. New York Wiley, pp. 71-136.
- Burt, D.M., 1972. The facies of some Ca~Fe Si skarns in Japan, 24th IGC.
- Burt, D.M., 1977. Mineralogy and petrology of skarn deposit, Society, Italian Mineralogia Petrologia Rend, vol. 33. pp. 859-873.
- Burt, D.M., 1982. Skarn deposits, historical bibliography through 1970: Economic Geology, vol. 77, pp. 775-763.
- Buseck, P.R., 1966. Contact Metasomatism and ore deposition, conception Del Ore Mexico Economic Geology, vol. 61, pp. 97-136.
- Calagari, A.A., Hosseinzadeh, G., 2006. The mineralogy of copper-bearing skarn in the east of Sungun Chay river, East-Azarbaijan, Iran. Journal of Asian Earth Sciences, vol. 28, pp. 423-438.
- Craig, J.R., Vaughan, D.J., 1981. Ore Microscopy and Ore Petrography. John Wiley & Sons.
- Dick, L.A., Hodgson, C.J., 1982. The MacTung W-Cu (Zn) contact metasomatic and related deposits of the northeastern Canadian Cordillera: Economic Geology, Bulliten vol. 77, pp. 845-867.
- Eftekharnezhad, J., 1975. Brief Description of tectonic history and structural development of Azarbaijan. the Ministry of industry and mines geological survey of Iran, Tehran, Iran.12p.
- Einaudi, M.T., 1977. Petrogenesis of the copper-bearing skarn at Nason Valley mine, Yerington District Navada, Economic Geology, vol. 72, pp. 769-795.

- Einaudi, M.T., 1982. Deposition of skarns associated with porphyry copper plutons South western North America in Tit. ley., S.R.(Edt.) Advance in geology of the porphyry copper deposits, southeastern North America. Tuscon University Arizona press, pp. 139-183.
- Einaudi, M.T., Meinert, L.D., Newbery, R.J., 1981. Skarn Deposits, Economic Geology, 75th Annual, pp. 317-391.
- Einaudi, T.M., Burt, M.D., 1982. A Special issue Devoted to skarn deposits, Introduction Terminology, Classification and Comp. of Skarn Deposits. Economic Geology, vol. 77.
- Etminan, H., 1978. Discover of copper and Molibdinum porphyry near Sungun village NW Iran, Report to Geological Survey of Iran (1356).
- Grants, J.A., 1986. The isocon diagram a sample solution to Gresens equation for metamorphic alteration. Economic Geology, vol. 81., pp. 1976-1982.
- Haughton, D.R., Roeder, P., Skinner, B. J., 1974. Solubility of Sulfur in Mafic Magmas, Economic Geology. vol. 69, pp. 451-462.
- Holland, H.D., 1972. Granites solutions and Base metal Deposit. Economic Geology, vol. 67.
- Hu Shouxi., 1991. Skarn Deposit in Eastern China, In: Skarn their Genesis and Metallogeny: A.K. Syuk, A.M. Collins L.G., Dobrovals kaya, M. Hulun-chi-Beidai He, Lowell, G.R.
- Jairath, S., 1986. Igneous source of sulfur of sulfides from Madhan Kudhan and Kol.lhan deposits, Khatri copper belt Rajasthan: Journal Geological Society of India. vol. 77,
- Jairath, S., Sharma, P.I., 1985. Physico-Chemical conditions of ore deposition in Malonjkhand copper sulfide deposit: Proceedings of the Indian Academy of Sciences, Earth and Planetary Sciences.
- Karimzadeh Somarin, A., 2003. Garnet composition as an indicator of Cu mineralization: evidenc from Skarn deposits NW Iran. Journal of Geochemical Exploration, vol. 81, pp. 47-57.
- Karimzadeh Somarin, A., 2004. Geochemical effects of endoskarn formation in the Mazraeh Cu-Fe Skarn deposit in Northwestern Iran. Geochemistry Exploration, Environment Analysis. Vol. 4, pp. 307-315.
- Khadem, N., 1965. Type of copper ore deposit in Iran, Geological Survey of Iran, Internal Report 11p.
- Khain, V.E., 1975. Structure and main stages in the tectonomagmatic development of the Caucasus: an attempt at geodynamic interpretation. American Journal of Sciences vol.275. pp. 1.31-156.
- Kwak, T.A.P., 1987. W. Sn, Skarn Deposits and related metamorphic skarn and granitoids: Book Elsevior.
- Ladame, G., 1945. Les ressources metallifères de l' Iran. Schweiz. Mineralog. und Petrogr. Mitt. vol. 25, pp. 165-298.
- Lescuyer, J.I., Riou, R., 1976. Géologie de la région de Mianeh (Azarbaijan). Contribution de la volcanisme tertiare de l' Iran. Thèse 3 cycle, Grenoble, 234p
- Lindgren, W., (1933). Mineral Deposits, McGrnw hil Book Company, (Fourth Edition).
- Meinert, L.D., 1982. Skarn, Matno, and Brecciapipe Formation in Sedimentary Rocks of the Cananea Mining District, Sonora, mexico. Economic Geology, vol. 77, pp. 919-949.

- Meinert, L.D., 1984. Mineralogy and Petrology of Iron Skarn in Western British Columbia, Canada, Economic Geology. vol. 79. pp869–882.
- Meinert, L.D., 2001. Skarns and Skarn Deposits in all about skarns web site updated 2001.
- Mohajjel, M., Fergusson, C.L., 2000. Dextral transpression in Late-Cretaceous continental collision, Sanandaj–Sirjan zone, Western Iran. Journal of Structural Geology. vol. 22, pp.1125–113.
- Moinevaziri, H., 1985. Volcanisme Tértiaire et Quatérnaire en Iran. Thèse d' Etat, Paris-Sud Orsay, 290 p.
- Mollai, H., Dave, V.K.S., 1991. Geochemistry and genesis of the Mazraeh granodiorite NW of Iran. Abstract volume, national seminar and 8<sup>th</sup> Indian Geological Congress. Ujjin, India 1991.
- Mollai, H., Dave, V.K.S., Sharma, R., 2004. Copper mineralization at Mazraeh North West of Iran: Evidences for fluid evolution and Skarn deposit. Abstract volume of 32nd International Geological Congress. Florence, August, p. 223.
- Mollai, H., 1993. Petrochemistry and genesis of granodiorite and associated Iron-Cupper Skarn deposit of Mazraeh, Ahar, East Azerbaidjan, Iran. Ph.D. thesis university of Roorkee, India.
- Mollai, H., 1994. Geochemistry and genesis of Iron-Copper Skarn deposit in Ahar. The 11<sup>th</sup> conference of geological Sciences, Geological Survey of Iran. Theran, Iran. (In persian)
- Mollai, H., 2005. Magmatic activities and magmatic effect on the Cretaceous sedimentary rocks in the Ahar region, North West of Iran. Abstract volume of the-7<sup>th</sup> International Symposium on the Cretaceous 5-9 Sep. 2005. University of Neuchatel, Switzerland, pp. 146-147.
- Mollai, H., 2006. Petrology And Geochemistry Of Skarn Deposit In The North Of Ahar, North West Of Iran, Scientefic program and abstracts volume of 6th International Conference on the Geology of the Middle East March 20-23 Al-Ain,U.A.E. p. 190.
- Mollai, H., Dave, V.K.S., 1991. Geochemistry and genesis of the Mazraeh granodiorite NW of Iran. Abstract volume, National Seminar and 8<sup>th</sup> Indian Geological Congress. Ujin, India, pp. 52-53.
- Mollai, H., Dave, V.K.S., Darvishzadeh, A., Yaghubpur, A., 1999. The study of petrology and mineralogy to determined the physico-chemical condition of Ahar Batholith North-West. Iran. Proceeding of the 3rd symposium of geological society of Iran 31Aug-2Sep. Shiraz University Iran, pp. 632-637.
- Mollai, H., Dave, V.K.S., Darvishzadeh, A., Yaghobpour, A., 1998. Distribution and role of fluid inclusions in Iron-Copper skarn deposit, North of Ahar, N-W of Iran. Proceeding of the 2nd Symposium of Geological Society of Iran 18-20, Aug. Ferdowsi University of Mashhad, Iran, pp. 60-62.
- Mollai, H., Sharifiyan Attar, R., Darvishzadeh, A., 2007. Mineralogy and mineral chemistry of Epidote in Mazraeh Skarn Deposit north of Ahar, Eastern Azarbaijan. The proceeding volume of the first Applied Geological Congress of Iran. pp. 252-259
- Mollai, H., Sharma, R., Pe-Piper, G., 2009. Copper mineralization around the Ahar batholith, North of Ahar (NWIran): Evidence for fluid evolution and origin of Skarn ore deposit. Ore geology Reviews 35. pp. 401-414.

- Nabavi, M.H.,1976. An introduction to the geology of Iran. Geological Survey of Iran, 109 p. (In Persian)
- Potts, P.J., 1987. A hand book of Silicate Rock Analysis. Published by Bell and Bain (Glosgow), Ltd. Britain, 622p.
- Pourhosseni, F., 1981. Petrogenes is of Iranian Plutons: a study of the Natanz and Bazman Intrusive complexes, Ph.D. Thesis Published by Geological Survey of Iran, 1983.
- Reid, J.E., 1978. Skarn Alteration of Commercial Limestone Carrfork Area Bingham Utah, Economic Geology. vol. 73, pp. 1315-1325.
- Rose, W., Burt, D.M., 1979. Hydrothermal alteration, pp. 173-235, in H.L. Barnes, ed., Geochemistry of hydrothermal ore deposit, 2<sup>nd</sup> ed., John Wiley & Sons, New York, 798 p.
- Sawkins, F.J., 1990. Metal Deposits in Relation to Plate Tectonics: (II edition), Book Springer-Verlag.
- Schwartz, G.M., 1959. Hydrotherraal alteration, Economic Geology. vol. 54, pp. 161-183.
- Shimazaki, H., 1980. Characteristic of skarn Deposits and related acid magmatism in Japan. Economic Geology. vol. 75, pp. 173-183.
- Simirnov, V.I., 1976. Geology of Mineral Deposit, Moscow, MIR, 520 P.
- Sengor, A.M.C., 1984. The Cimmeride orogenic system and tectonics of Eurasia. Geological Society of America, Special Paper, 195 p.
- Sengor, A.M.C., Cin, A., Rowley, D.B., Nie, S.Y., 1993.

- Space-time patterns of magmatism along the Tethyan sides: a preliminary study. J. Geol. 101, pp. 51–84.
- Sengor, A.M.C., Natal'in, B.A., 1996. Paleotectonics of Asia: fragments of a synthesis. In: Yin, A., Harrison, T.M. (Eds.), The Tectonic Evolution of Asia. Cambridge University Press, pp. 486–640.
- Stocklin, J., 1977. Structural correlation of alpian ranges between Iran and Central Asia.Memorie Hors. Serie.No.8de la Soc.Geolo.de France 8. pp. 333-353.
- Stockline, J., Eftekharnezhad, J., 1969. Explanatory text of the Zanjan Quadrangle Map, 1,250000, Geological Survey of Iran, D4, 59 p.
- Stocklin, J., Nabavi, M.H., 1973. Tectonic map of Iran Scale 1/1000000 Geological Survey of Iran.
- Superceanu, C.I., 1971. The Eastern Mediteranean Iranian Alpine Copper Molybedenum Belt, Society of Mining Geology of Japan, Spec, Issue 3, Proc. IMA-IAGOD Meeting 70, IAGOD vol.pp 393 – 398.
- Telemetal Project, 1968. Report on exploration of Mazraeh copper mine. Edited by Henry. 225p.
- Verkaeren, J., Bartholome, P., 1979. Petrology of the Sanleone Magnetite Skarn Deposit S.W. Sardinia. Econpmic Geology. vol. 74, pp. 53-66.
- Wyborn D., Turner, B.S., Chappell, B.W., 1987. The Boggy Plain Super suite a distinctive belt of I type igneous rocks of potential economic significance in the Lachlan Fold Belt. Aust. J. Earth Science. vol. 34, pp. 21-43.