Barite Ore Deposits in the Central Iran - Ardakan Province: Genesis and Alterations

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Abstract

Carbonate rocks of upper Paleozoic host barite ore deposits in the Central Iran. Main ore mineral is barite that shows crosscut relationships with its host rocks and occurs as veins and veinlets. Barite is associated with gold-bearing chalcopyrite. Faulting, fracturing and brecciation were important ground preparation processes in the host rock. Jasperoidization of the host rock prior to barite deposition is another ground preparing process. Open space structures had been filled by ore minerals, hydrothermal calcite and white sparry dolomite. Boiling episodes in the ore-bearing fluids, upon their arrival to the lowpressure dilation zones, along with influx of highly oxidized groundwater provided ideal conditions for ore mineralization. The studied ore deposit could be classified as epithermal based on its temperature of formation (167±11°C), shallow depth, open-space filling structures, mineral assemblages, and jasperoid alterations. Secondary alterations in the primary sulfide minerals had been induced by galvanic reactions, which resulted in formation of various secondary ore minerals. Mineralization in the studied area is in association with the magmatic activities of the early Kimmerian orogeny.

Key words: barite, Ardakan, carbonates, fluid inclusions, secondary alteration

1- Introduction

Carbonate-hosted barite ore deposits are among the most important barite deposits in Iran, which occur in different ages. One of the important ore deposits of this type is situated in Central Iran, near the Ardakan City. In the studied area it appears as six separate bodies with similar features such as mineralogy, ore structures, type and age of the host rocks. The host rocks are mainly limestone and dolomite of undifferentiated Upper Devonian-Lower Carboniferous to Permian age. The main ore mineral is barite, which occasionally is associated with fluorite. Ore bodies present crosscut relations with their host rock and occur as veins and veinlets. In some ore mines, ore body occurs as dyke structures along faults. An important feature of the studied ore deposits is the association of the barite with gold-bearing chalcopyrite.

In this study different methods, including thin and polish sections examination, fluid inclusion study along with geochemical analysis, had been employed to define temperature of formation, ground preparation processes, paragenetic sequences of mineral deposition and finally postulate a model for ore genesis.

2- Geological setting

Iran had been subdivided into nine tectonic zones including Central Iran Tectonic zone. The latter covers extensive area of Iran and is surrounded by Alborz mountain chains in the north, Zagross mountain chains in the southwest to northwest, and Naybandan fault in the east (Nabavi 1976). Several important ore deposits, which are hosted by sedimentary units, are situated in this tectonic zone. The studied ore deposits are hosted by Upper Paleozoic sedimentary units of different lithology, but are mainly carbonaceous (Fig. 1).

The oldest unit that crops out in the northern domain of the studied area is the Soltanieh Formation of the Neoprotrozoic (Fig. 1). This unit consists of limestone and dolomite with chert nodules. This unit is overlain by the Barut Formation, which consist of dolomite, limestone, and shale. Barut Formation is the latest Neoprotrozoic unit in the area that itself is overlain by Lower Cambrian Sandstone of Zagun. Some red and white sandstones and quartzite, known as Lalun Formation, overlies the former unit.

Ore bearing strata in the studied area are the undifferentiated Upper Devonian-Lower Carboniferous units and Permian carbonates. The former consists of limestone, sandstone, shale, and dolomite, with basal conglomerates that overlay the older units with unconformity. Tectonic activities caused extensive displacement, faulting, and thrusting in this unit. The calcareous members (upper part) of this unit host two ore bodies. Permian carbonate unit, with about 250m thickness, is the main ore bearing strata in the area and include dolomites, dolomitic limestone and limestone. This unit conformably overlays the older strata and is overlain by Jurassic shales with fault contact. The latter is comparable with the Shemshak Formation, which is a predominating Jurassic unit in different tectonic zones of Iran.



Figure 1 - Location map and stratigraphic column of the study area.

Early and late Kimmerian orogeny in the Central Iran besides metamorphism, caused major magmatisms including intrusion of several complexes. The most important intrusion in the Ardakan area is the Tut Granites. This intrusion shows close mineralogical and

compositional similarity with EsmailAbad Granite of Saghand area. The latter had been emplaced during the early Kimmerian orogeny and Crawford (1972) by isotopic dating (Rb/Sr) has determined a 204Ma age for this granite.

Barite ore deposits in the studied area are located in the southern limb of the main Ardakan anticline with a SE-E trend. Open space structures such as fractures, faults and breccia zones developed in this area are evidence of extensive tectonic activities. Ore emplacement occurred along these open space structures.

3-Methods

Extensive field studies along with 80 thin and 15 polish sections were employed to determine the mineralogy and textures of these ore deposits. Fluid inclusions of the suitable samples were studied for Microthermometry by using Linkam system, Model HFS91 of the Tarbiat Modaress University. In addition, EDXA (Energy Dispersive X-ray Analysis) had been employed to determine secondary copper minerals.

4-Results

4-1- Ore-Host Rock Relationships: Ore deposits in the area could be subdivided into eight major units; nonetheless, veinlets of barite and fluorite are also scattered throughout the area.

The main ore mineral is barite that occasionally coexists with fluorite. Barite along with its gangue minerals shows crosscut and sharp contacts with their host rocks and usually occur as veins and veinlets. These open space structures, shaped by tectonic activities, are the main ore-bearing structures in the area and display pinch and swell systems. For example, host rock in the ore-bearing unit II is a yellow Permian dolomite. This unit contains barite and hydrothermal calcites that occur as fracture filling ore bodies. In some units ore bodies are emplaced in the brecciated zones or manifest as crosscut vertical dykes (regarding bedding planes) (Figs. 2 and 3).

In epigenetic ore deposits, such as the studied one, the chemical and physical changes in the host rocks are vital processes prior to ore deposition (e.g., Guilbert and Park 1986, Clark et al., 1999). In general, structures that provide maximum encounter between hydrothermal fluids and host rocks are the most convenient places for mineralization (Schneider 1967, Chen-Xianpei 1996, Paradis et al., 1999). Fracturing of the host rock, brecciation and dilation structures were the convenient places for ore mineralization (Figs. 2 and 3).



Figure 2 - Brecciation and dolomitization are important ground preparation mechanisms in the area.



Figure 3 - Relationship between fault mirror, brecciation and ore mineralization.

4-2- *Mineralogy:* Minerals (metallic and nonmetallic) in the studied ore deposits could be divided into two types: primary and secondary minerals. The primary minerals include quartz (with inclusions of gold), barite, fluorite, calcite, dolomite, pyrite, chalcopyrite and chalcocite. The main ore mineral in the studied area is barite, but occasionally, fluorite is economically important. Barite occurs as milky to reddish euhedral large crystals (up to 10 cm) and massive masses in the fractures and voids, however, not infrequently, it has replaced the host rock. Inclusions of calcite within barite crystals denote replacement of the former by barite (Fig. 4). However, this form of replacement is rather exceptional, and barite usually appears as open-space fillings. Fluorite appears as white, gray or violet single euhedral crystals that in some places exhibit intergrowth with the barite.

Calcite is the main gangue mineral and turns up as large pink to brown saddle shape calcite crystals or massive masses. Crystalline calcite formed earlier than the barite, but it had been partially embedded and replaced by barite (Fig. 5). White sparry saddle dolomite, which appears as fracture filling cements, had been formed earlier than barite (Fig. 6).



Figure 4 - Arrow shows calcite relicts in the barite. The host rock is silicified (thin section, polarized light)



Figure 5 - Barite replaced calcite (stained thin section, polarized light).



Figure 6 - Fracture filling saddle dolomite (thin section, polarized light).

One of the kinetic barriers for the dolomite formation is the hydration of Mg ions. Dolomite only forms where Mg exists as bare ion (nonhydrous). In deep burial settings, due to geothermal temperatures, and in surficial shallow zones due to influence of hot hydrothermal fluids, these kinetic barriers are suppressed and consequently dolomite forms (Mattes and Mountjoy 1980; Mountjoy and Amthor 1994; Morrow and Coniglio 2000). Using fluid inclusion microthermometery, a temperature range of 150 to 182°C is postulated for mineralization of the Ardakan ore deposits. Therefore, presumption of a heated ore bearing hydrothermal fluid as a source for saddle dolomite seems convincing.

Quartz is the other gangue mineral, which turns up as partial replacement for host rock (jasperoid alteration) and void filling cements with large crystals (up to 1cm) and comb structure. Jasperoid alteration was the introductory ground preparation process and has happened along fractures of the host rocks. Its crystals are fine grained with granular and reticular textures (Fig. 7), moreover, they contain voids with different size and shapes. Barite and crystalline quartz of the next generations had occupied these voids. Presence of abundant fluid inclusions in jasperoid and large quartz crystals denotes hydrothermal origin of the mineralizing fluids (Fig. 8). Meanwhile, relicts of the calcite and dolomite of host rock in the jasperoid and crystalline quartz indicates replacement of the former minerals by the silicification processes. The primary fluid inclusions are usually parallel with the crystal growth faces (e.g., Shepherd and Rankin 1985, Wilkinson 2001). Some quartz crystals show two sets of fluid inclusions (Fig. 9) that indicate they have been formed in two generations.

Metallic minerals such as pyrite, chalcopyrite, chalcocite are mostly accompanied with the secondary minerals such as covellite, goethite, lepidocrocite, malachite and azurite. Pyrite occurs as euhedral crystals and broken pieces, which are cemented by chalcopyrite. The latter texture denotes that pyrite predates chalcopyrite. Chalcopyrite is the most abundant metallic mineral in the study area and occurs as disseminated crystals in the host rock and along with barite in the void



filling cements. Chalcopyrite shows at least two generations, first Figure 7 - Jasperoid alteration along fractures (arrow) (stained thin section, plane-polarized light).



Figure 8 - Granular jasperoids glutted with fluid inclusions (thin section, polarized light).



Figure 9 - Two sets of fluid inclusions in quartz crystals (stained thin section, polarized light).

precipitation before hydrothermal calcite and then formation after calcite and along with barite. Anhedral chalcopyrite crystals display intergrowths with barite.

Gold occurs as micron sized inclusions in the crystalline quartz (Fig. 10) and chalcopyrite crystals. It seems gold mineralization began with quartz crystallization and continued during chalcopyrite formation.

The secondary minerals include: 1- Secondary copper sulfides such as covellite, yarrowite, spionkopite, geerite and anilite, 2- Hydrous copper carbonates such as malachite and azurite, 3- Copper oxides such as cuprite, and 4- Iron oxides and hydroxides such as goethite and lepidocrocite.

Secondary copper sulfides are distinguished by SEM-EDXA. Covellite in less altered samples appears as deep blue color rims around chalcopyrite crystals. Yarrowite happens as scattered bright blue veinlets in the chalcopyrite. Bladed anilite crystals show up at right angle with the chalcopyrite cleavages. Yarrowite, spionkopite, geerite and anilite turn up in deeply weathered chalcopyrites but covellite is present in slightly weathered samples. Malachite occurs as



Figure 10 - Gold inclusions in crystalline quartz (polished section, polarized light).

void filling and replacement in the host rock. In some cases malachite forms green haloes encircling amorphous iron hydroxides. This texture is an indication of copper migration from the primary metallic ore mineral, and its subsequent entrapment (in the form of malachite) by calcite crystals of the host rock. Cuprite with deep red color is the main copper oxide.

General paragenetic sequences of the mineral formation in the studied ore deposits is illustrated in figure 11.

4-3- Ground Preparation Processes: Ground preparation processes in the host rock are divided into physical and chemical processes. The former includes porosity development and increase in the brittleness of host rocks. The latter occurs by different alterations in the host rocks such as silicification and dolomitization. The nature of ground preparation processes depends upon the characteristic of the host rocks and the type of the ground preparation agents (temperature, fluids, tectonic activities and so on). Dominant physical ground preparation processes in the studied area include fracturing, brecciation and development of dilation structures. Chemical ground preparation processes were less important and occurred as jasperoidization and some dolomitization.



Figure 11 - Paragenetic sequence of mineralization in the study area.

4-4- *Fluid Inclusions:* Crystal growth is never complete and usually minor amount of mineralizing fluids entraps in the growing crystals, which have been termed fluid inclusions. They manifest substantial details concerning temperature and pressure of mineral formation, boiling episodes during mineralization and fluid's density and origin (e.g., Roedder 1984, Evans 1987, Wilkinson 2001).

Fluorite crystals have been formed contemporaneously with barite and exhibits higher brightness and copious fluid inclusions. Hence, it has been preferred for microthermometery study. Primary and secondary inclusions have been distinguished in the fluorite crystals of the studied area. The former shows euhedral negative crystal shapes that are scattered throughout the fluorite crystals, but the latter displays irregular small inclusions along the fractures in the fluorite (Figs. 12 and 13). Primary inclusions contain both liquid and vapor phases. Based on their liquid/vapor (L/V) ratios they are subdivided into gas-rich (GRI) and liquid-rich inclusions (LRI). In the GRI, about 60% of vacuoles is occupied by gas phase (degree of filling 0.4-0.5) (Fig. 13). In this group liquid phase disappears by heating and converts to a homogeneous gaseous inclusion. Microthermometery on these inclusions is not precise enough to distinguish the homogenizing temperature (Shepherd and Rankin 1985, Wilikinson 2001). However, co-occurrence of GRI with the LRI indicates boiling events in the

hydrothermal fluids during mineralization (Shepherd and Rankin 1985; Guilbert and Park 1986, Zwart 1995, van den Kerkhof and Hein Ulrich 2001). During heating steps, only the LRI converted to an aqueous homogenous phase and GRI converted to a gaseous phase. Such an observation indicates boiling episode during mineralization, which gave rise to formation of two types of inclusions with different gas/liquid ratios.

decline hydrothermal Pressure in the fluids may induce destabilization of dissolved complexes, reduction of solubility, and subsequent mineralization (Guilbert and Park 1986, Jeffrey 1997, Wang et al., 1999). On the other hand, barite and fluorite occur in the fractures and breccia zones that indicate introduction of hydrothermal the low-pressure dilation systems fluids to and subsequent mineralization due to instability of dissolved ions. Generally, mineralization in the superficial zones is associated with boiling events (White et al. 1971; Plumlee et al. 1995, Wang et al., 1999).



gas with negative fluorite crystal (double polished thin section, plane-polarized light).

Figure 12 - Primary fluid inclusion rich in Figure 13 - Primary fluid inclusion rich in liquid with negative fluorite crystal (double polished thin section, plane-polarized light). L/V ratio is about 80/20.

Accordingly, pressure corrections are not necessary for calculated homogenizing temperature and they are close to the true temperature of mineral formation. Boiling happens when vapor pressure in the fluid is higher than the lithostatic pressure, so that, again, pressure correction is not necessary (Evans 1987). Boiling episodes in the hydrothermal fluids impel significant effects on the fluid's chemistry, inasmuch as even insignificant boiling may causes substantial changes in the solubility various ions, and hence mineral precipitation (Roedder 1979, Wilkinson 2001). Boiling causes selective evacuation of CO_2 and the other volatiles from the fluid phase; this in turn induces pH increase and subsequent mineralization (Rose and Burt 1979).

Microthermometry studies in the Ardakan ore deposit revealed that mineralizing fluids had low salinity (0.6 mole % NaCl) with temperature of about $167 \pm 11^{\circ}$ C (Fig. 14 and Table 1).



Figure 14.- Homogenizing temperatures for fluid inclusions in fluorite crystals from study area.

Salinity of the mineralizing fluids is an important tool for ascertaining their origins (e.g., Bellanca et al 1987; Romberger 1993). Subias and Fernandez – Nieto (1995) showed two stages for fluorite mineralization in the Valle de Tena in the west of Spain, and by utilizing salinity data postulated origin of the mineralizing fluids. They showed that moderate to high salinity fluids (21.3-12.5 equivalent weight percent of NaCl) derived from basinal brines, and low salinity fluids (11.6-4 equivalent weight percent of NaCl) originated from heated meteoric waters. Regarding low salinity of fluid inclusions of jasperoids in the Bonanza gold mine of cordillera (Chile), Romberger (1993) declared the heated meteoric waters (by intrusions) as mineralizing agent.

No	Туре	V/L	Size (?fn)	Tm (°C)	Th (°C)	Phases	Salinity (wt%NaCl eq.)	m NaCl
1	Primary	10/90	3*6	-1.6	174.5	L+V	3	0.48
2	Primary	20/80	4*10	-1.3	182.5	L+V	2.51	0.4
3	Primary	10/90	4*8	-1.6	170	L+V	3	0.48
4	Primary	15/85	6*20	-2	182	L+V	3.65	0.6
5	Primary	15/85	6*12	-1.8	172.5	L+V	3.33	0.54
6	Primary	10/90	3*12	-4	162.5	L+V	6.71	1.18
7	Primary	20/80	4*6	-2.6	167	V+L	4.6	0.78
8	Primary	10/90	5*6	-1.2	155.5	L+V	2.34	0.37
9	Primary	15/85	4*14	-1.5	174	L+V	2.84	0.46
10	Primary	15/85	3*12	-3.1	180	L+V	5.37	0.92
11	Primary	10/90	3*10	-1	173.5	L+V	2	0.3
12	Primary	10/90	3*6	-3.4	176	L+V	5.82	1

Table 1 - Features of two-phases fluid inclusions in a fluorite sample from study area.

Several mechanisms have been proposed for barite and fluorite deposition (Blount 1977; Holland and Malinin 1979; Richardson and Holland 1979; Richardson and Pinckney 1984; Tornes et al. 1991; Plumlee et al. 1995, Kontak et al., 1999). The important mechanisms include: A) simple cooling plus boiling of mineralizing fluids, B) reaction of low pH fluids with alkaline host rocks (carbonates), C) reaction and mingling of reduced Ba and S-bearing fluids with highly oxidizing fluids, plus inversion of H₂S to SO_4^{-2} (for barite only), D) mingling of fluids with different Ca/F ratios (for fluorite only).

It could be suggested that boiling and reaction of low pH fluids with carbonate host rocks were the main mineralization mechanisms in the studied area.

4-5- Secondary Minerals: The secondary minerals resulted from alteration of primary minerals, mainly chalcopyrite. Five distinct Cu-sulfides secondary minerals including, covellite, yarrowite, spionkopite, geerite and anilite have been identified by EDXA analysis.

Covellite (Cu_{0.9} Fe_{0.03}S, Cu_{0.9} Fe_{0.01}S, Cu_{0.91}Fe_{0.08}S) displays deep blue color and appears as thin reaction haloes around the less altered chalcopyrite. Yarrowite (Cu_{1.12}Fe_{0.08}S, Cu_{1.1}Fe_{0.03}S, Cu_{1.09} Fe_{0.04}S) appears as scattered veinlets in chalcopyrite. It is characterized by its bright blue color, and occasional occurrences as

thin reaction haloes encircling chalcopyrite. Spionkopite (Cu_{1.45}Fe_{0.1}S, Cu_{1.3}Fe_{0.07}S, Cu_{1.29} Fe_{0.02} S) and geerite (Cu_{1.62}Fe_{0.05}S, Cu_{1.59}Fe_{0.05}S, Cu_{1.51}Fe_{0.07} S) occur as reaction haloes surrounding chalcopyrite crystals. Anilite (Cu_{1.77}Fe_{0.05}S) shows gray to white colors under the microscope. Composition of anilite in the studied area and those from other ore deposits is compared in Figure 15.



Figure 15- Mole percent diagram (after Sikka et al.,) for Cu-Fe-S chalcopyrite and its secondary minerals.

The sequence of the secondary mineral formation (Figs. 16,17 and 18) is:

Covellite ? Yarrowite ? Spionkopite ? Geerite ? Anilite

Galvanic reactions proceed if conductors to semi-conductor minerals come to immediate contacts or get locked together (Sikka et al. 1991). Differences in the electric potential of diverse minerals in such associations provoke initiation of galvanic reactions. In these conditions mineral with higher electric potential behaves as cathode and low potential mineral as anode. Electric potential of a mineral varies in response to the conditions of the ambient environment such



Figure 16 - Yarrowite developed as veinlets and haloes within and around chalcopyrite (polished section, polarized light).

Figure 17 - Spionkopite and geerite as secondary minerals around chalcopyrite (polished section, polarized light).light).



Figure 18 - Relicts of chalcopyrite in geerite. Anilite is also seen as parallel blades at right angle to chalcopyrite (polished section, polarized light).

as pH, presence or absence of oxygen and nitrogen (Abramv 1965; Abramv et al. 1975; Clark et al., 1999). Galvanic reactions proceed unhindered in the presence of an ideal electrolyte such as water. During such reactions the anode mineral suffers alteration which its extend depends on the difference of the electric potential between the anode and cathode minerals (?•V). Association of pyrite (V= 0.424) with chalcopyrite (V= 0.364) in the studied ore deposits gave rise to severe alteration of the latter. It is presumably due to high ?EV values. Another galvanic circuit contrived between gold (V= 1.63) inclusions (in chalcopyrite) and chalcopyrite itself (as anode). These reactions induced severe alterations in the chalcopyrites.

Goethite euhedral crystals occur as pseudomorph of pyrite and, sometimes, with cuprite and lepidocrocite. Goethite is the dominant mineral phase in the pH ranges of 3 to 6. Coexistence of this mineral with cuprite could be shown by the following reaction (Thornber 1985):

 $Fe^{+2} + Cu^{+2} + 7H_2O$?* 2Fe (OH) $_3 + Cu_2O + 8H^+$

Malachite is the main copper carbonate mineral in the studied ore deposit which occurs as internal linings in the open-space structures, in association with some azurite. Abundance of the malachite and scarcity of the azurite are indication of pH > 6.95 and CO_2 fugacity of about

<10^{-3.45} during mineral alterations (Vink 1986). Acidic solutions resulted from chalcopyrite alterations were neutralized by carbonate host rock. Therefore, despite of Cu solubility in these solutions, descending migration of Cu had been inhibited. Due to these processes no Cu enrichment zone formed under oxidation zone of ore deposit. Instead, Cu-bearing acidic solutions reacted with carbonate minerals of host rock and upon neutralization malachite and azurite were precipitated. Malachite haloes around iron hydroxides, verifies these reactions (Fig. 19).



Figure 19 - Malachite haloes around iron hydroxides is indication of neutralization of acidic Cu-bearing fluids by carbonate host rock (thin section, polarized light).

$$Cu_2O + 2H_2O + HCO_3$$
 ?~ $Cu_2 (OH)_2 (CO_3) + H^+ + 2e^-$
(Cuprite) (Malachite)

5- Discussion

Several genetic models have been proposed by different researchers for barite formation, and source of Ba^{2+} , F⁻, SO_4^{2-} and metallic ions. Dunham and Hanor (1967) showed genetic relations between granitoid intrusions and barite mineralizations in the barite ore deposits of the western United States. These ore deposits had been emplaced along faults and fractures in particular tectonic zones in association with typical magmatisms (granodiorite).

Experimental studies on the granitic systems (e.g., Tuttle and Bowen 1958; Luth et al. 1964) showed that saturated granitic magma releases some water vapors during crystallization. In such a system if the plagioclase is the first mineral phase that continues to crystallize (along or without ferromagnesian minerals), therefore remaining fluid would be enriched in Ba^{2+} ions (fractionation factor of Ba^{2+} between plagioclase and remaining liquid is less than one). Consequently, this water-saturated magma became (before potassium feldspar crystallization), hence, Ba²⁺ ions readily rush into vapor phase and leave the system. Barite mineralization is the next step by these Ba-rich fluids.

Low salinity of the fluorite fluid inclusions from studied area (6.71-2 equivalent weight percent of NaCl), homogenizing temperature of 182.5-150°C, boiling events during mineralization and occurrence of ore minerals in low-pressure dilation structures, all are indications of mineralization by moderately heated, meteorically-originated hydrothermal fluids in a shallow settings.

In vicinity of the studied area, Tut Granite has been emplaced during early Kimmerian (204Ma) compression phase. Therefore, it could be suggested that the Tut Granite behaved as a heat engine for the meteoric (water-dominated) hydrothermal system and, presumably, source of the mineralizing ions. Because of absence of the evaporite deposits and other similar sources of sulfate ions in the study area, magmatic origin for reduced sulfur ions could be suggested. Destabilization of thiosulfate complexes $(S_2O_3^{-2})$ (of magmatic origin) by bacteria and soluble organic materials of mineralizing fluids, increases activity of the sulfate ions and results in barite mineralization (Spirakis and Heyl 1995). Regarding to the higher temperature of ore precipitation in the study area (deduced from microthermometery) bacterial reduction as a source for sulfur ions is not warranted.

Mineral precipitation, caused by mixing of the reduced Ba-bearing fluids and highly oxidized waters, is an important mechanism in barite mineralization (Torens et al. 1991). Barite mineralization in the study area, which is associated with chalcopyrite, pyrite and chalcocite, is compatible with the mixing model. This mineral assemblage indicates companion of the reduced sulfur with mineralizing fluids. Mixing associated with boiling of fluids were the main controlling mechanisms for barite mineralization.

Mole percent Cu-Fe-S diagram displays the successive trend of the chalcopyrite alteration to the covellite and finally to the anilite. As shown in this diagram, during this consecutive alterations decrease in sulfur content from covellite is corresponding with Cu increase in anilite. Chalcopyrite alteration to covellite is accompanied with Fe decrease and Cu increase.

6- Conclusion

In the study area, mineralization is not stratabound and has occurred in stratigraphic Devonian-Lower different levels. from Upper Carboniferous to Permian units, during early Kimmerian orogeny (204Ma). It mainly appears as open-space fillings with some jasperoid alterations. Boiling events upon introduction of the Ba-bearing fluids to the low-pressure dilation zones, besides mixing with meteoritic and highly oxidized groundwater, was the main mechanism for mineralization. Low temperature of mineralization (167±11°C), shallow depth of ore deposition, open-space filling structures, mineral assemblage and jasperoid alterations all are characteristics of epithermal ore deposits. Galvanic reactions induced secondary alterations in the primary sulfide minerals and resulted in secondary ore mineral formation.

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