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Mineralogy of the sulfate-sulfide mineralizations at the Garus District; NW of Iran

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Abstract

There are some vein type sediment hosted sulfate-sulfide mineralizations in Garus district, NW of Iran. They occur in a (shale) host rock of Precambrian age and they show evidence of some deformation. The field, microscopic, XRD and SEM-EDS techniques were used in this investigation. Mineralogical, the veins are composed of barite (Sulfate phase), galena, chalcopyrite, covellite (main sulfide minerals) and dolomite, ankerite, quartz, cerussite, anglesites', calcite, goethite as gangues. Microscopic and XRD investigations indicated the presence of more than 15 minerals at Garus. The SEM-EDS assessments show some probable minor phases present in the investigated galenas. Field and microscopic investigations show barite formed earlier than the sulphide mineralization. The objective of this research is to reveal the new horizons in the mineral exploration in NW of Iran.

Key words

Barite; galena; mineralogy; sulfate; sulfide

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Mineralogía de las mineralizaciones sulfato-sulfurosas del Distrito Garus, NW de Irán

Resumen

Existen algunas mineralizaciones de sulfatos y sulfuros que albergan venas de sedimentos en el distrito Garus, en el noroeste de Irán. Estas mineralizaciones ocurren en rocas calizas (esquistos) precámbricas con evidencias de deformación. Se utilizaron en este estudio datos de campo, microscópicos, DRX y técnicas de SEM_EDS. Mineralógicamente las venas están compuestas de barita (fase de sulfatos), galena, calcopirita, covelina (principales sulfuros) y dolomita, ankerita, cuarzo, cerustira, anglesita, calcita y goethita como ganga. La microscopía y la DRX indicaron más de 15 minerales en el distrito de Garus. Las valoraciones de SEM-EDS muestran probables fases menores en las galenas estudiadas. Las investigaciones de campo y a nivel microscópico muestran que las baritas se formaron antes que la mineralización de sulfuros. El objetivo de este artículo es revelar nuevos horizontes de exploración para la exploración minera en el NW de Irán.

Palabras clave

Barita; galena; mineralogía; sulfatos; sulfuros

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INTRODUCTION

The sediment hosted mineralizations are important for base, noble, precious and trace metals exploration. The shale hosted vein type mineralizations from the North of Tabriz city (NW of Iran), are reported for the first time in this paper. In the Garus sediment hosted resources, barite is the main mineral and many sulfide-carbonate minerals are associated with it. These resources occurred as vein and veinlets in their Precambrian age shale-siltstone host rocks. They are under the tectonic controls. On the other hand, the main veins formed in similar tectonic trend structural features.

This paper shows the mineralogical characteristics of the poorly exposed sediment hosted vein type mineralization in North of Tabriz. The main objective of this paper is to show the new horizons in the mineral exploration in NW of Iran.

MATERIALS AND METHODS

Field work included geological mapping, delineating approximately the host rocks, their various members and mineralized veins and sampling from ore bodies. The samples were thin sectioned and polished and examined microscopically. The XRD technique was used when microscopic studies of minerals were uncertain. The XRD analyses was done by SHIMADZU type diffract meter with Cu/Kα radiation and at a goniometric speed of 2º/min. SEM-EDS (scanning electron microscopy-energy dispersive system) method was employed for the assessment of the semi-quantities variations of the barite-galena crystals at very small scales. Vega-VG2080573 equipment (4-Channel-30 Kev) was used for this purpose. All the sample preparations, microscopic and XRD studies were carried out at the Geology Department of Payame Noor University of Iran. SEM-EDS were carried out at the Razi Metallurgical Institute, Karaj (Iran).

Geological setting

The Morow Mountains are located about 25Km north of the city of Tabriz, in the northwest of Iran. In the classification of the structural units of Iran (Nabavi 1976), this area is situated in the Western Al-

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borz-Azerbaijan zone (Fig.1), which is part of the Alpine-Himalayan Fold belt.

The greater part of the studied area is covered by Neogene sedimentary rocks. They are composed of red conglomerates of Pliocene age and Quaternary deposits. The Kahar formation of Precambrian age (Riphean) (Dedual 1967) as the host rocks of the studied mineralization have limited outcrops. In addition, the other Paleozoic-Mesozoic sedimentary rocks are observed at the southern part of the investigated area.

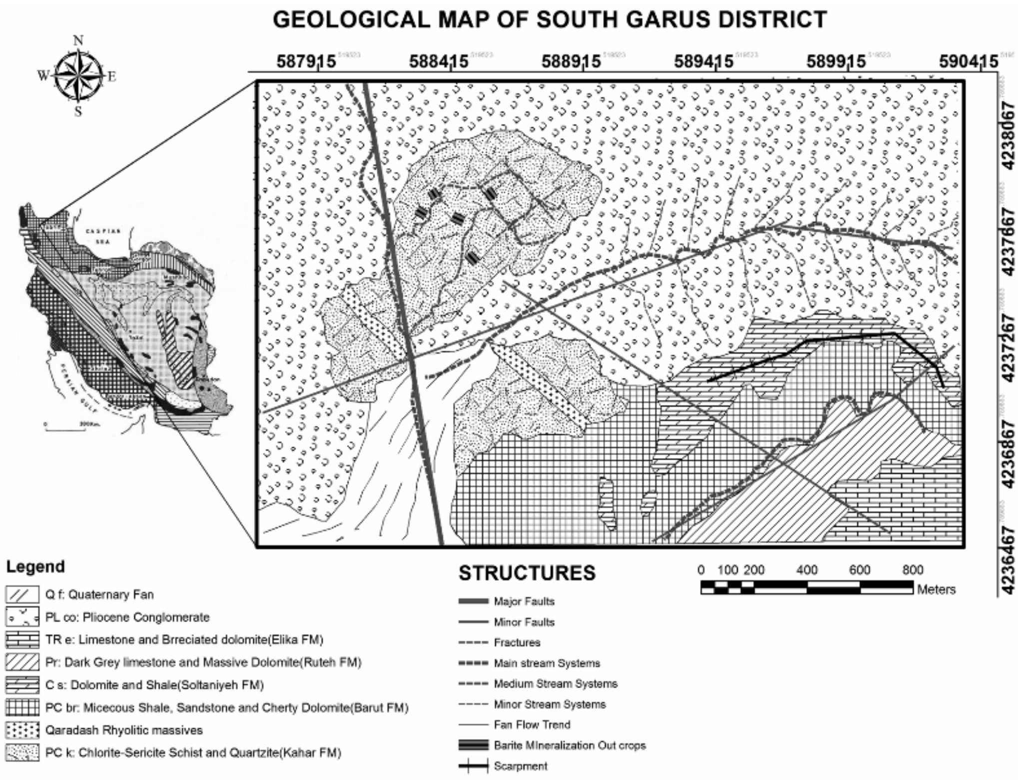

Figure 1. Geological map of the south Garus (Vusuq 2010) and the location of the studied area in the structural units of Iran (Nabavi 1976)

RESULTS AND DISCUSSIONS

Mineralization

- *Barite:* Barite occurs as euhedral-subhedral coarse grained aggregates (Figure 3 - A) with epigenetic relationship between mineralization and the host rock (Figure 3 - B). The space filling, geode (Figure 3 - C), concretion, skeletal, framework and laminated textures-structures are observed in barite.

Some optical disorders formed in barite crystals as a result of tectonic stress. Concrete relation between barite crystals (Figure 3 - D) and ondulatory extinction indicates endurance to tectonic stress in barite crystals (Figure 3 - E).

Some barites show poly-synthetic twinning - poly lamellar bounding (Figure 3 - E) and some of them show zoning and plastic deformation (Jurkovic 1995, 1996, Jurkovic *et al.* 1999).

Barites have tabular shapes and elongation in C optic axis (Figure 3- F). Some of them are over 30 mm long. According to Pastor *et al*. (2006) and Beker *et al*. (2006), high senior contents can help {011} form barite and led to the formation of tabular barites.

Microscopic assessments indicated two race barite mineralization events in the studied case. In the first stage we can see big euhedral crystals that filled the fractures after ground preparation in the host rock. These crystals have ondulatory extinction and are cut by some silica veinlet's. The second barite mineralization event occurs as cross cutting of the above mentioned silica veinlet's.

- *Pyrite:* Pyrites occur in both pre ore and ore forming stages. Framboidal digenetic pyrites formed in the host rock. They are pre ore forming pyrites. Their average sizes are at about 0.05mm. Ore forming stage pyrites occurs as subhedral aggregates. They are forming the islands into goethite matrix. Beside pyrites, the chalcopyrites and galenas are solved and are destroyed under galvanic reactions between pyrite and the above mentioned minerals. Pyrites can be rarely observed as euhedral and fresh crystals (Figure 4 - A). Their sizes are between 0.08mm - 0.2mm.

- *Chalcopyrite:* Chalcopyrite as the main Copper sulfide mineral occurs after barite as anhedral, space filling-veinlet type –disseminated aggregates. They have fresh and altered faces with intensive tarnishes (Figure 4 - B). Chalcopyrites generally are altered to covellites and rarely diagenite in their fractures. Chalcopyrites formed as the veinlet forms and replaced by galenas (Figure 4 - C).

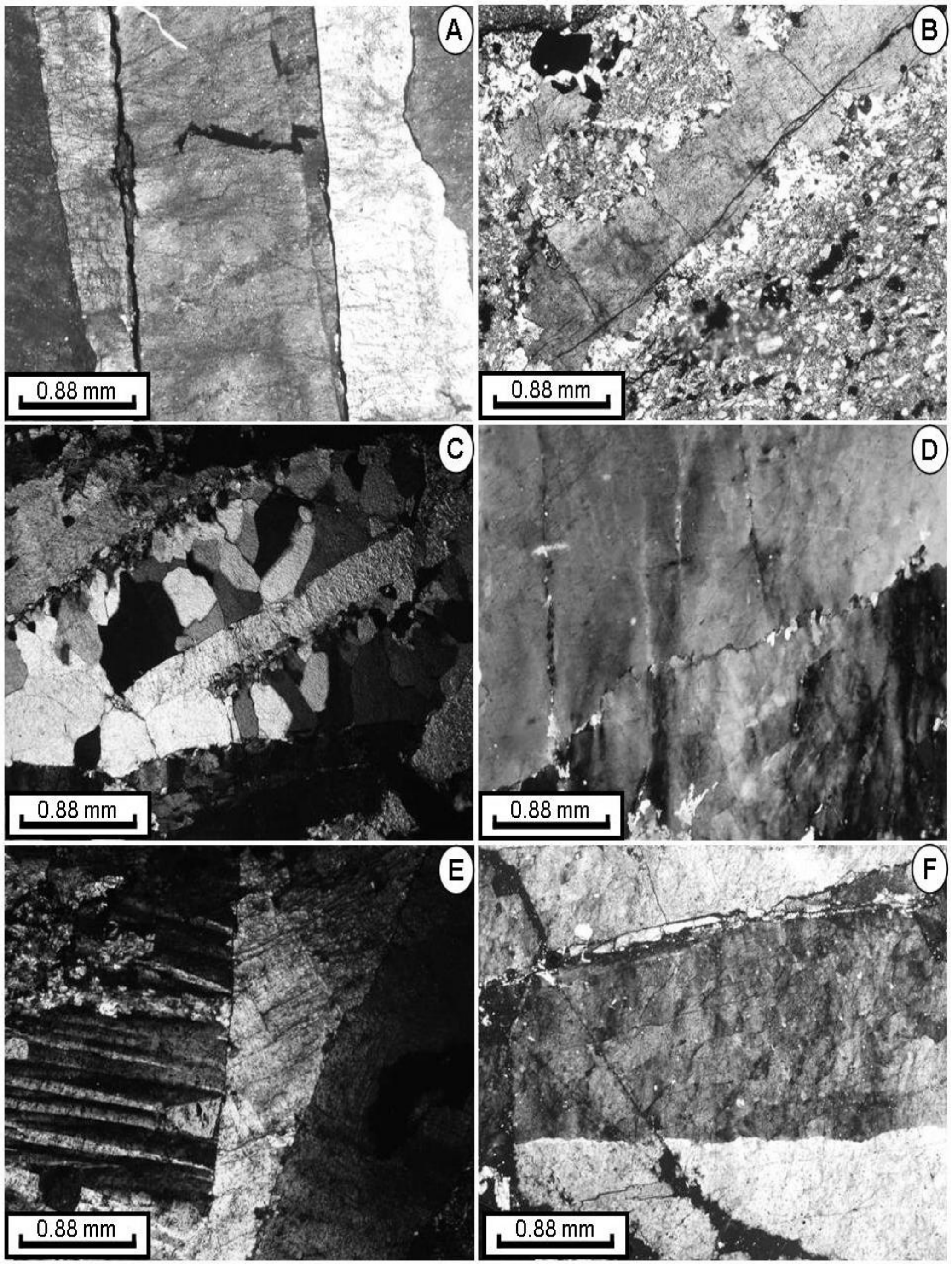

Figure 3. Photomicrographs of barites: (A) euhedral - subhedral coarse grained barites; (B) epigenetic relation with regard to mineralization host rock and barite; (C) geode aggregates of barite; (D) Concrete relation between barite crystals; (E) ondulatory extinction and poly-synthetic twinning - poly lamellar bounding in barites; (F) tabular barites.

- *Galena:* Galenas formed as very small crystal subhedral (microcrystalline) aggregates. Their size is up to 0.3mm and they are replaced with chalcopyrites. There are some chalcopyrites and barite remains islands in the galenas. This fact indicates the formation of galenas after barite and chalcopyrite. The absence of pits in some of the studied galenas is an interesting fact (Figure 4 - D). In addition, there are elongated bayonet-shaped pits in some of them (Figure 4 - E). The authors believe stress can eliminate the pits. Galenas replaced by cerussite, anglesite, quartz and calcite. The studied galenas are widespread tarnished. Hanilci and Ozturk (2005) believe the galena tarnish consists of cerussite and anglesite. Although, Ramdohr (1980), thought the galena tarnish shows some Ag bearing phases (for example tetrahedrite and argentite) as inclusion in galena. To confirm this idea, some of the galenas were analyzed for silver and it was found that some of them contained an average 35 ppm Ag.

- *Covellite:* Microscopically, covellites are observed as dark blue haloes around chalcopyrites. As secondary minerals, covellites occur as anhedral fracture filling aggregates. Covellites are found around the galenas (Figure 4 - F). Covellites can indicate a high content of chalcopyrite formation in the primary mineral formation stage. They show the first stage of chalcopyrite alteration under anaerobic conditions.

- *Goethite:* The goethite formed by alteration of pyrite. They filled the pyrites molds. Microscopically, they are detectable by their distinctive metallic color (Figure 4 - G).

- *Cerussite:* They are pale brown-grey massive phases that filled galena fractures. XRD techniques indicate that they are cerussite. In the presence of carbonate and lead sulfide on surface condition, cerussite can be formed by the following reaction: $Pb + H_2CO_3 \rightarrow PbCO_3 + H2S$

- *Anglesite:* Colloidal phases of them surrounding galena crystals; which are identified as anglesite by the XRD technique.

- *Dolomite:* Dolomites occur as coarse grained euhedral lozenge-shaped crystal aggregates (Figure 4 - H). There are two phases of dolomite formation: pre-ore and ore-forming dolomites. The pre-ore dolomitization acted as ground preparation.

- *Ankerite:* Brown color, good relief, boiling with thick-hot HCl and radular-undulatory extinction (Figure 4 - I) are the factors that contribute to the identification of ankerites. Secondary barites were found as small veinlet in ankeritic masses (Figure 4 - J). Ankerites mainly occur after barite mineralization. Iron-bearing dolomites and ankerites mainly formed by biogenic processes under reduction condition (Habibi 1994).

They can form from low-temperature hydrothermal fluids as coarse grained space and joint filling shapes (Mattes and Montjoy 1980, Choquette and Pray 1970, Greg and Shetton 1990, Saller 1980, Withaker and Smart 1990, Baker and Burns 1985, Zenger *et al*. 1980).

- *Calcite:* Three race calcite formations are observable in this case. Pre-ore forming stage, ore-forming stage and post-ore forming stage. They have poly-synthetic twinning - poly lamellar bounding, which indicates the resistance of calcite to deformation (Ferill et al. 2004).

- *Quartz:* Quartz formed in the pre-ore and the ore forming stages. In pre-ore stages (Figure 4 - K), it contributed to ground preparation. Secondary quartz forms silica vein-veinlets (Figure 4 - L).

- *Pyrolusite:* Occurs as dendritic aggregates and impregnated with barite masses. Sometimes they form as cement and space fillers in oxidation zones. They can be only found in hanging-wall veins and are not observable in foot-walls. Piskin (2002) believed that Mn-dendrites can form by diffusion in an oxidizing zone.

- *Malachite:* Malachite is abundant in Cu-rich veins as a result of chalcopyrite oxidation. Based on Vink (1986), malachite can form under log.HCO_3>-4.3, high CO_2 and O_2 fugacity.

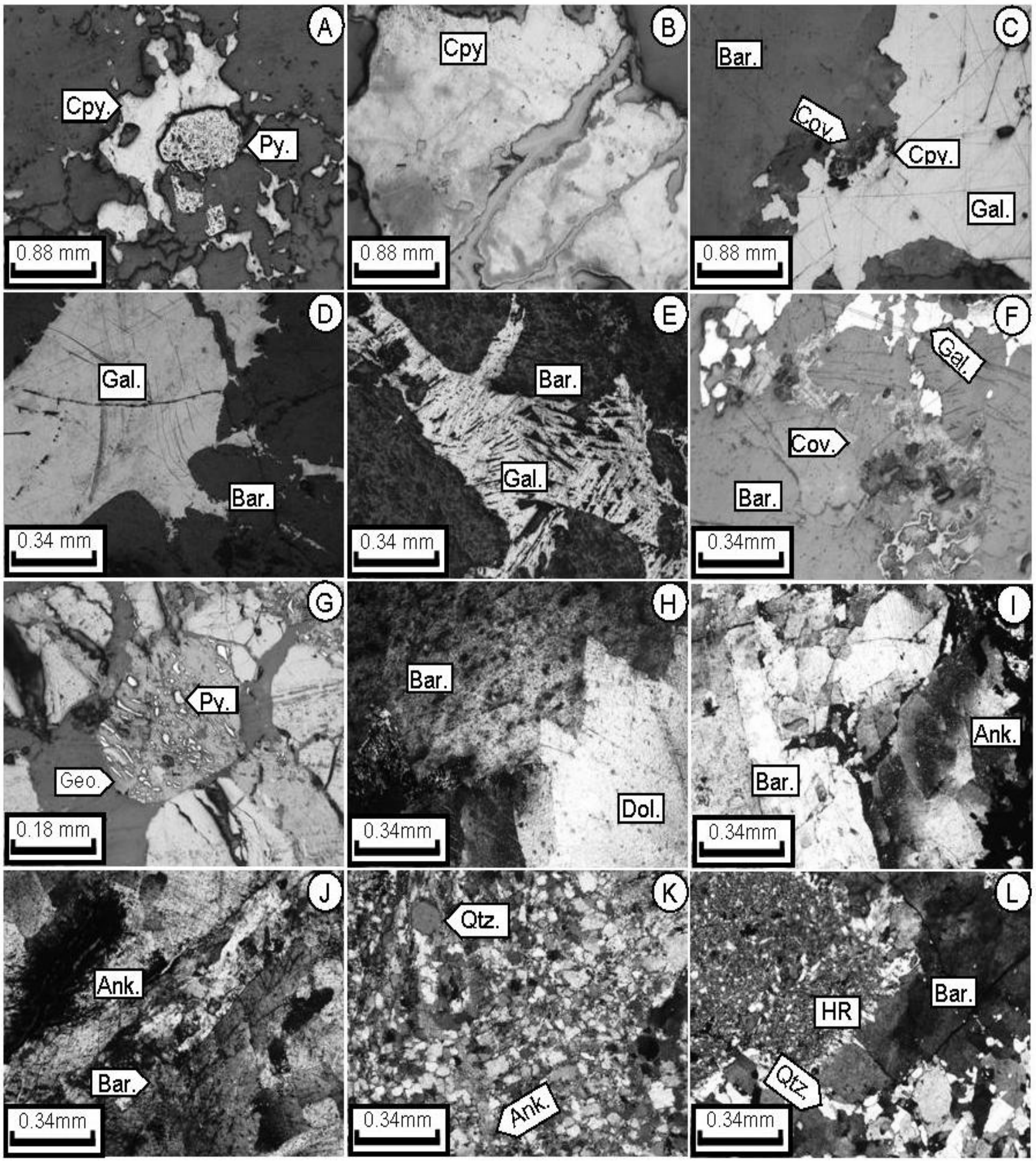

Figure 4. Photomicrographs of metallic and non-metallic minerals: (A) Pyrite in contact with chalcopyrite; (B) Tarnished chalcopyrite; (C) replacement of chalcopyrite to galena; (D) Galena without pit; (E) Elongated bayonet-shaped pits in galena; (F) Covellite around a galena; (G) Pyrite islands in the goethite matrix; (H) Coarse-grained euhedral dolomites; (I) undulatory extinction in ankerite; (J) Barite veinlet in ankerite; (K) Pre-ore forming quartz aggregates; (L) Secondary quartz

Figure 5 shows the arrangement and dependent events of mineralization in the Garus district. Based on microscopic and XRD investigations over 15 minerals were detected from the Garus mineralization. All of the metallic minerals in the studied area are reported in this paper.

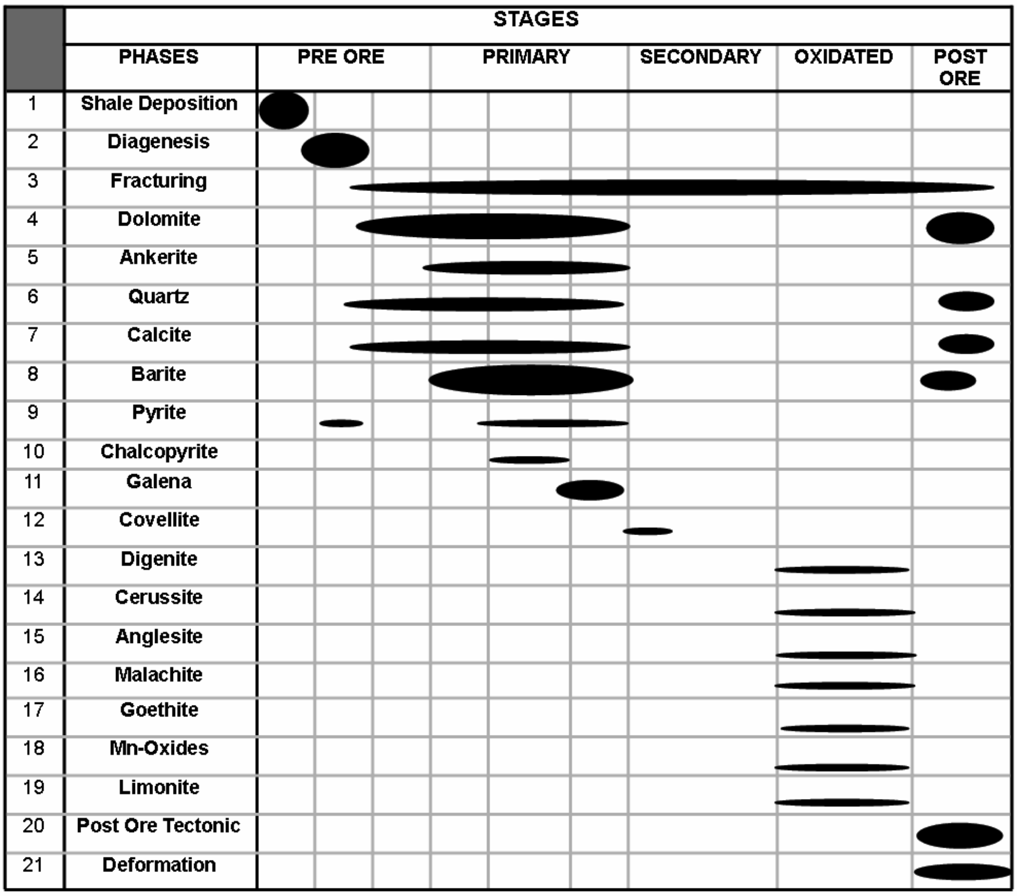

Figure 5. The arrangement of the mineralization and dependent events

SEM-EDS assessments

The SEM-EDS technique was applied to investigate microstructures and semi-quantitative distribution of the elements in barite and galena crystal structures. As a result, there is an obvious copper frequency from margins to central parts of galena crystals. We can see the maximum copper content in marginal parts of the galena. The frequencies of Silicon and Iron do not have a significant variation in the structures of galena. These assessments can show the potential existence of some Lead-copper chloride (Dseveilline- Serperite - Rapidcreekite) and Djerfisherite - Thalfenit groups (particularly Owen site being their most outstanding component) (Strunz 1980) as galena impurities. EDS analysis shows some of the following phases present in galena micro-structures.

$(Pb_{0.9620} \sum x_{0.0308})S$
$(Pb_{0.8112} Ba_{0.0824} Cu_{0.0650} Ca_{0.0347})S$
$(Pb_{0.9549} Cu_{0.0379} Fe_{0.0071})S$
$(Pb_{0.4992} Ba_{0.0202} Cu_{0.0649} Fe_{0.0398} Ca_{0.0721} Cl_{0.3444})S$

The presence of a small quantity of Si in barites structures is interesting. It appears to be that this fact can be dependent on existence of sanborite as a Ba silicate impurity in barite structure. SEM imaging shows large tabular barite crystals (Figure 6). Pastor *et al*. (2006) believed that tabular barite crystals can form under low temperature condition such as low-temperature hydrothermal or diagenetic ore forming processes.

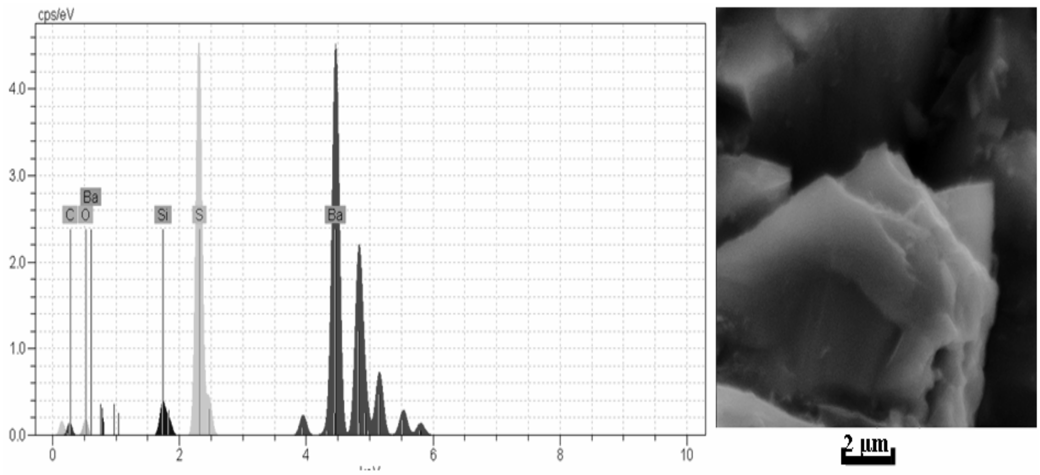

Figure 6. SEM image of tabular barites and its EDS spectrum.

CONCLUSIONS

Vein type mineralizations were developed along the faults and joint in shales of Precambrian age (Kahar Formation). Field evidences, analytical data, mineralogical and textural criteria show that in the study area mineralization generally occurs in four stages: (1) faulting and its subsequent fracture and Si-Mg alteration ground preparation processes (2) Formation of dolomites, ankerites as gangues and barites as the economic mineralization. Barite formation occurred in an oxidizing condition (3) Reduction of SO_4 to H_2S, formation of Cu-Pb mineralization. Chalcopyrite and galena are the main sulfide ore minerals in this stage (4) Oxidizing condition under the surface status followed by pyrolusite, malachite and goethite mineralization. Microscopic and XRD investigations indicated the presence of more than 15 minerals in the Garus mineralization.

EDS assessments show the potential existence of some Pb-Cu chloride (Dseveilline - Serperite - Rapidcreekite) and Djerfisherite - Thalfenits groups (particularly Owen site being their most outstanding component) as galena impurities and the SEM studies indicate low-temperature conditions for the formation of barite.

Although the bounded and covered outcrops of Kahar formation as the exclusive host rock of the Garus district mineralization, the possibility of occurrence of significant base metal sulfide mineralizations in deep horizons is not unreasonable.

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