Mineral composition and paragenesis of altered and mineralized zones in the Gadir low sulfidation epithermal deposit (Lesser Caucasus, Azerbaijan)

Novruz Novruzov¹, Anar Valiyev², Aydin Bayramov², Sabuhi Mammadov², Javid Ibrahimov², Aygul Ebdulrehimli³

1. Institute of Geology and Geophysics of ANAS. H. Javid prospect 119, Baku, Azerbaijan
3. Baku State University, Baku, Azerbaijan

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Abstract

Mineralogy, gold mineralization and metal contents of the Gadir deposit have been investigated during current research in order to determine the geological conditions, temporal and spatial relationship with certain mineral assemblages and associations. The mineralogy of orebodies is mainly composed of pyrite, chalcopyrite, sphalerite, galena, petzite, native gold, electrum and subordinate molybdenite. Gold is hosted by pyrite and chalcopyrite minerals in fracture-filling textures and forms a thin dispersion condition. The native gold was observed in chalcopyrite, which is probably related to the second stage of ore deposition. The Gadir deposit can be classified to Au-Ag-Cu-Zn±Pb stockwork-type mineralization which is characteristic of low sulfidation epithermal deposit.

Keywords: Hydrothermal alteration, Ore mineralogy, Gold mineralization, Low sulfidation epithermal deposit, Gadir

1. Introduction

The Gedabek high sulfidation epithermal deposit comprises one of the main producing mining of the Gedabek ore district, Azerbaijan and is the largest porphyry-epithermal ore field in the country. It belongs to the Lesser Caucasus, located in the central part of the Tethys metallogenic belt (Fig 1). The deposit is hosted by the Jurassic-Cretaceous Lok-Karabakh magmatic arc, resulting from the subduction of the Neo-Tethys Ocean along the Eurasian margin (Agakishiyev et al. 2004). The NW Flank of Gedabek Mine is located in the Yogundag Mountain area. Gedabek volcano-plutonic rock units are located at Shamkir uplift of Lesser Caucasus metallogenic zone. The ore perspective areas, also Gedab high sulfidation epithermal deposit (Gadir LSED) is embedded in cone-shaped Mountain Yogundag at elevation 2085m, located approximately 400m from Gedabek Mine (Baba-Zade et al. 1990; Doebirich et al. 2008). This deposit has been discovered by Gedabek Exploration Group (EGG) during an extensive geological exploration across the northwestern flank of the Gedabek Mine, in 2012 (Gadimov et al. 2014). Hydrothermal breccia, silica sinter and lacustrine silicous were considered as the main exploration factors in the study. Exploration boreholes (e.g., AIMCDD86) were performed in contact between rhyolite-dacite subvolcanic bodies in order to characterize the orebody during 2012.

In addition, the Gadir horst structure has been identified during geological-structural mapping and field surveys.

2. Geological setting and deposit geology

The geological history of the Gedabek area and metallogenic processes associated with the Gadir deposit can be related to the Late Paleozoic intensive magmatic activity occurred throughout the Lesser Caucasus. During the Middle-Jurassic to Early-Cretaceous period, volcanism peaked in the Caucasus and thus the geology is dominated by prominent volcanism and intrusions bodies. The volcaniclastic rocks are characterized by andesite in composition and the U-Pb zircon ages of ~168.3Ma and ~166.1Ma were reported for the volcaniclastic rocks, which correlated with the Bajocian and the Bathonian of Upper Jurassic period, respectively (Ismet et al. 2003). In addition, the intrusive rocks in the Gadir deposit were reported by ~157.3Ma, which consistent with the Bathonian to Kimmeridgian in age (Ismet et al. 2003). Gold mineralization in the Gadir deposit is mainly hosted by intrusive bodies, which dominated by quartz porphyry in composition. The host rocks are highly altered by propylitic alteration, primarily in the andesite tuff. Presumably, major regional faults striking NW-SE controlled the mineralization at Gadir deposit.

Aygul Ebdulrehimli

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*Corresponding author.
E-mail address (es): sabuhi.mammadov@aimc.az
represented (from older to younger) by andesite-basalts, andesite porphyries, diabase and diabase porphyries. Upper Bajocian volcanic rocks are represented by rhyolite-dacite lava facies and rhyolite subvolcanic rocks. The rock units of this substage in the investigated area are widely developed and traced from the southeast (Gadir Gallery area) to the center (east contact of Gedabek Hydrothermal Eruption Breccia Pipe) and northwest directions to Umid Area (Veliyev and Talibov 2012; Valiyev et al. 2013).

Fig 1. Tectonic map of the Arabia-Eurasia collision zone. Location of the Gadir deposit is shown by a circle (modified from (Sosson et al. 2010)). Abbreviations: GC-Greater Caucasus; LC-Lesser Caucasus; AT-Achara-Trialeti; R-Rioni; DZ-Dzirula; K-Kura; MB-Mus Basin; EP-Eastern Pontides; KM-Kinichir Massif; EAF-Eastern Anatolian Fault; NAF-North Anatolian Fault; IAES-Izmir-Ankara-Erzincan Suture; MM-Menderes Massif.

The Bathonian volcanic sequences are developed across the upper layer of the Yogundag Mountain. On sediments of Upper Bajocian Substage have transgressively occurred formations of Bathonian stage represented by an alternation of fine- and thin-layered, ashy and agglomerated tuffs with rare interlayers of andesitic-porphyrritic breccia and andesitic-dacitic lavas (Fig 2 and 3).

The Gedabek hydrothermal eruption breccia pipe (GHEB pipe) is located in the central-eastern part of the Yogundag Mountain around the Gadir deposit. The present shape of the pipe with about 50m diameter resulted from both volcanic and erosional processes. Gedabek silica sinter observed around of GHEB pipe in the central part of Yogundag Mountain.

The sedimentary sequences of the lacustrine basin are in the east of Gadir outcrop over an approximately 85000 m² area (Fig 2). The original size of the basin is not known because it is bordered by normal faults to the west and south.

Gadir quartz veins are similar to the most of known epithermal mineralization. The type of the hydrothermal activity is easily decided by studying the textures observed within a quartz vein occurred in the NW Flank. Therefore, the place of this quartz vein in the epithermal system on the paleo-topography can be estimated. It is suggested whether the precious metals zone of the vein was cut by erosion or an ore existence can be expected at depth while there is not any evidence on the surface. As a consequence, the textures of the quartz veins are used as a guide in the exploration.
Two major textural groups are recognized on the hand specimens collecting during the field studies in the Yogundag area: 1) Primary growth textures representing the open-space fillings; 2) superimposed. Primary quartz vein textures are classified as buck, comb and banded textures. Superimposed textures are replacement and breccia textures. These textures can be formed by different quartz species such as quartz, chalcedony, opaline and amethystine. Banded textures of microcrystalline quartz are more dominant at the boiling level or just above. Massive or slightly banded chalcedony exists in the shallow depth. Sinter consisting of amorphous chalcedony was observed at the surface. In general, the high-grade zones of the epithermal vein in precious metals existed at the banded textures, whereas, the base metal content has located in the below levels. In the deeper levels of the vein is representing the comb texture. Mineralization at Gadir consists of semi-massive to massive pyrite and chalcopyrite ranging to sphalerite and galena as an indication of low sulfidation.

3. Hydrothermal alteration zones and their spatial distribution
As above mentioned, Gadir deposit is confined to a low-sulfidation epithermal system, as well as this system characterized by the range of hydrothermal alterations. During the field alteration mapping, the following hydrothermal alteration was obtained in Gadir horst.

Two main zones of hydrothermal alteration were observed in the Gadir deposit (as Gedabek) that is propylitic and quartz ± adularia ± pyrite alteration.

Propylitic alteration
The propylitic alteration has been occurred in the andesitic tuff, in the peripheral parts of the deposit. This
alteration is mainly controlled by the permeability of tuff layers (Fig 4a). This zone is mainly characterized by chlorite and epidote. Despite the alteration, the primary texture of the tuff is still preserved most chlorite grains replaced clasts; epidote is rather disseminated in the matrix together with chlorite (Fig 4b). However, some tuff layers show a preferential replacement by epidote (Fig 4a). Petrographic studies were also indicated local replacement of the matrix by magnetite (Fig 4c).

Quartz ± Adularia ± Pyrite alteration
The main texture observed in the quartz porphyry body (QPB) is a porphyritic texture formed by quartz phenocrysts (up to one centimeter) within a microcrystalline (aphanitic) matrix (Fig 4d). Depending on the location within the QPB, this porphyritic texture is barren (Fig 4e) or associated with disseminated pyrite (Figs. 4f and g). The QPB is spatially associated with the mineralization; therefore it is the most important unit to understand in this deposit. SEM studies displayed the occurrence of microcrystalline K-feldspar and quartz together with subordinate fine-grained adularia, sericite, and barite (Fig 4f). Furthermore, the KFs-staining method using the sodium cobaltonitorite was carried out on 7 sericite-poor samples to examine the presence of adularia associated with quartz and disseminated pyrite within entire QPB (Fig 4g). In most cases, high contents of adularia are associated with pyrite in quartz porphyry intrusions (Fig 4e). This leads to the conclusion that adularia, as well as disseminated pyrite, is not homogeneously distributed within the QPB.

Fig 3. Schematic stratigraphic column and typical core showing the different rock types in the Gadir area (by Gedabek Exploration Group (2015)). Abbreviations: PSZ-Propylitic-silicified Zone; LB-Lower Bajocian; UB-Upper Bajocian.
These interpretations are consistent with other observations:

1. Both the propylitic and quartz ± adularia ± pyrite alterations show a strong lithological control, with the alteration of some preferential tuff layers (Fig 4h). No lower permeability horizon is described at Gadir. However, it is obvious that the pathway followed by fluids is mainly controlled by tuff permeability. Furthermore, the assumption of a less permeable horizon is consistent with the flat-lying contact reported between the quartz ± adularia ± pyrite alteration and the sub-horizontal andesitic tuff.

2. Some samples collected from QPB distinguished by porphyritic texture, which occurs together with remnant clasts are still distinguishable. The shape of clasts is easier to distinguish when highlighted by pyrite mineralization (Fig 4i).

3. Petrographic investigation of dike samples intersecting the QPB, and of the upper part of the diorite intrusion, shows an overprint of the pre-existing texture by microcrystalline quartz (and possibly adularia).

4. Rock classification diagram using major and trace elements demonstrated an andesite composition. It is reflects the initial composition of the rock, which is probably andesitic tuff.

Fig 4: Main alteration types at Gadir mining area (Gadir and Gedabek deposits); (a) Tuff interlayers affected by prophylitic alteration in surface outcrops; (b) Volcaniclastic rock with chlorite replacing clasts and epidote together with chlorite in the matrix; (c) Mineralized orebody consists of magnetite together with chlorite in the matrix of propylitised tuff layers; (d) Transmitted-light photomicrograph of the QPB, which composed of with quartz phenocrysts in a microcrystalline quartz ± adularia ± pyrite matrix; (e) KFs-staining of a barren sample from the QPB; (f) Back-Scattered Electron Image (BSE) of the quartz-adularia-pyrite alteration; (g) KFs-staining of a mineralized sample from the QPB; (h) Preferential quartz ± adularia ± pyrite alteration along individual tuff layers (Darker layer = more altered, Lighter layer = less altered); (i) QPB with clasts in a pyrite matrix.

Abbreviations: ad=adularia; bar=barite; chl=chlorite; ep=epidote; mt=magnetite; py=pyrite; qz=quartz

4. Spatial distribution of mineralization
Mineralized zones at Gadir are spatially associated with Quartz-Porphyry Body (QPB). Disseminated pyrite occurs pervasively through most of the QPB. Fine-grained pyrite displays various intensities of mineralization in different alteration zones (Fig 5a).
Higher pyrite abundances were observed in central parts of the orebody. Ore textures are dominated by semi-massive, vein, veinlets, and disseminated sulfides that generally post-dated the disseminated pyrite stage. Orebodies mainly consist of semi-massive lenses of pyrite (Fig 5a and b), chalcopyrite and sphalerite (Fig 5a and b). Due to underground mining activity, no spatial or temporal relationships of the different styles of the polymetallic mineralization were observed during field surveys. Generally, semi-massive textures of pyrite are not associated with chalcopyrite and sphalerite. However, in some cases, lesser amounts of semi-massive pyrite are associated with chalcopyrite and sphalerite. Semi-massive chalcopyrite and sphalerite, as well as large irregular veins, are only observed in the central parts of the deposit. Minor chalcopyrite and sphalerite mineralization occurred as irregular veinlets and disseminated sulfides are observed throughout the whole QPB (Fig 5c and d).

Fig 5. Spatial distribution and different mineralization styles at Gadir: (a) Massive and semi-massive textures of pyrite and sphalerite; (b) Massive and semi-massive textures of pyrite-chalcopyrite-sphalerite, also barite veinlets; (c) Disseminated pyrite and chalcopyrite, irregular veins of quartz, possible open-space filling; (d) Disseminated pyrite occurred in contact between quartz porphyry and potassic altered rocks.

Abbreviations: Bar=barite; Brt=biotite; Cpy=chalcopyrite; Py=pyrite; Qz=quartz; Sph=sphalerite.
Generally, low-grade Au occurred in pervasively silicified zones lead to a large tonnage of orebody exploitable by underground mining. High-grade orebodies are mainly associated with massive textures located in the central parts of the deposit. Some parts of the ore body are characterized by brecciated textures, which are associated with the abundant occurrence of tourmaline in fractures and voids.

5. Ore mineralization and textures

The main ore minerals consist of chalcopyrite, pyrite, sphalerite, galena, and minor amounts of molybdenite, native gold and electrum. The silver content of the deposit is highly variable. The highest grades silver-bearing zones tend to be peripheral to the high-grade gold-bearing zones (Fig 6a). The majority of the gold mineralization is very fine-grained (0.5 to 30 microns) occurred as native grains in quartz gangue, and locked grains in pyrite, chalcopyrite, and sphalerite.

Gold is also, to a lesser extent, present in galena-tennantite (Fig 6a). Higher gold grades, however, are not directly related to sulfide percentages.

Chalcopyrites are developed in streaky, irregular form of aggregates at the dimension 0.01-10 mm; it rarely forms solid massive ore, cementing sphalerite, pyrite, and silicate gangue minerals (Fig 6). The permanent presence of inclusions of pyrite, arsenopyrite, sphalerite, and tetrahedrite is typical.

Sphalerite was observed in association with chalcopyrite, but in comparison with the last, it doesn’t contain the inclusions. The minerals being in growths with sphalerite might be set in the following by sulfide minerals: chalcopyrite and pyrite (Fig 6a and f).

Galena comprises the second most abundant sulfide mineral, which occurs as euhedral crystals, and in most cases, was co-precipitated with sphalerite and with chalcopyrite on fractures. Sphalerite and galena occur in grain size up to a couple of centimeters in massive veins or as small as 10mm when they occur disseminated in quartz and calcite or included in pyrite (Fig 6e and f).

Pyrite is one of the most common and earliest formed sulfides and most spread sample mineral, it is observed in impregnations (0.01-5.0 mm), reaching 50-60% of rock volume, i.e. impregnation often turns into solid, close to the massive structure. Pyrite occurs as euhedral crystals accompanied by chalcopyrite within early quartz-carbonate filled fractures (Fig 6e). Also, pyrite occurs as subhedral to anhedral crystals accompanied by galena and chalcopyrite (Fig 6e).

Arsenopyrite is quite wide developed and practically detected in all polished sections, containing chalcopyrite (Fig 6a). Graphical structure of growing with chalcopyrite probably arising in decay consequence of solid solution is interesting. Besides, it forms growths with sphalerite, tetrahedrite and gold.

Pyrhothite is met in irregular grains (0.01-0.2 mm), plates in non-metal bulk in association with pyrite, chalcopyrite. Pyrrohbit is generally fine-grained and occurs more commonly as inclusions in iron-rich cores of zoned sphalerite. The two most abundant non-sulfide gangue minerals in the two veins are quartz and carbonate. Quartz crystals in bands are euhedral to anhedral, vary in size from microcrystalline to coarse grained. Colloform and chalcedonic bands of quartz show interlocked grains of irregular shape or spherulites with radial extinction or the typical feathery textures of chalcedony. Carbonate crystals vary in grain-size from fine to coarse and the bands commonly contain microcrystalline quartz in the interstices. Other common gangue minerals associated with quartz and calcite that may form bands are chlorite, dolomite – ankerite, adularia, hematite and undifferentiated phyllosilicates (illite and/or interlayered illite/smectite). Bands of quartz-hematite and epidote have been observed alternating with bands of black and white chalcedony.

6. Mineral assemblages

The mineral associations in Gadir underground mine is typical for low sulfidation epithermal systems (Fig 7). The main ore-bearing mineral associations are described below:

- **Quartz – chalcopyrite – galenite – pyrite – barite±magnetite assemblage** mainly obtained in 1482m levels of Gadir mine. Chalcopyrite, sphalerite, galenite, and pyrite are in disseminated textures. Barite and magnetite occur in veinlets (Fig 5b).
- **Quartz – chalcopyrite – pyrite - sphalerite assemblage** occurs similar to the above-mentioned assemblage. Ore minerals mainly have the fine disseminated structure like stock. These two assemblages consist of the main ore-rich bearing. The highest grade of gold mineralization is located at upper levels in Gadir mine (Fig 5c).
- **Quartz – tournaline-pyrite assemblages** located at marginal parts of the ore-rich zone (Fig 7a).
- **Quartz – pyrite±barite association** occurs as massive pyrite stocks. Pyrite has coarse grain size minerals. Intensive developed the crystal structure pyrite in intergrown with disseminated forms (Fig 5d).
- **Quartz – chalcopyrite±pyrite assemblage** developed in uppers and intermediate levels. Chalcopyrite is disseminated and contains high grade of ore. Pyrite has less quantity and very grain size, located in relics of contact rock (Fig 5c).
- **Quartz – sphalerite±barite assemblage** similar to previous veins occurred in 1482m levels. Massive sphalerite ore-stock intercepted by barite veinlet (Fig 5b).
- **Quartz–amethyst-pyrite assemblage** occurs in the marginal part of the quartz-tourmaline-pyrite mineral assemblage, in the peripheral zone of Gadir deposit (Fig 8). Amethyst may occur in highly silicified zones (or breccia) in quartz porphyry or in volcanic rocks near to contact between andesite and quartz porphyry.
Quartz - biotite - pyrite assemblage occurs in the deepest zone, below quartz porphyry body. This assemblage is associated with potassic alteration. Biotite forms are lamellar or grain crystals substituting the plagioclase phenocrysts and mafic minerals. Together with sericite, apatite and quartz also form grain aggregate in the groundmass. Pyrite has intermediate distribution and substantially is located in hornfels (upper contact of Gedabek intrusion) which closely related to ore mineralization.

Quartz – carbonate ± pyrite±chalcopyrite assemblage developed mainly in phyllic alteration zone in – quartz porphyry host rock, and to lesser amounts in propylitic alteration zone, within andesitic tuff. All these mineral assemblages are intercepted by later carbonate veinlets which mainly occurred along fault and fractures zones.

Based on petrographic and mineralogy studies, mineralization stages can be further subdivided into five stages in Gadir deposit.

7. Vein paragenesis
The vein paragenesis is summarized as follows:

- Early quartz veins with minor sulfides (sphalerite, pyrite, galena) at margins;
- Anastomosing quartz stockwork veins with marginal sphalerite, pyrite, and galena;
- Brecciation of hornfels host rocks;

Fig 6. Photomicrographs (reflected-light) of ore minerals from the Gadir deposit: (a) semi-massive texture of pyrite together with sphalerite and chalcopyrite; (b) I disseminated, euhedral, and fine-grained pyrite and chalcopyrite grains hosted by quartz gangue; (c) A large lath-shaped sphalerite crystal intersecting pyrite and chalcopyrite grains, respectively. (d) Massive textures of sphalerite and chalcopyrite together with chalcocite/covellite replacing the chalcopyrite grains along fractures and crystal boundary. (e) Cubic pyrite grains, chalcopyrite, sphalerite, and galena inclusions within chalcopyrite; (f) Magnetite and chalcopyrite together with small inclusions of chalcopryte and galena. Sphalerite shows exsolution texture with chalcopyrite, forming chalcopyrite disease in sphalerite. Abbreviations from Whitney and Evans (2010): Cpy = chalcopyrite; Gn = galena; Mt = magnetite; Py = pyrite; Sph = sphalerite.
Fig 7. The generalized model of mineral vertical zonation of the Gadir low sulfidation epithermal deposit based on assay and interpretation of mineralogical data (by Gedabek Exploration Group (2015)).

Fig 8. a) Photograph of quartz–tourmaline–pyrite association, b) Close-up photograph of quartz–amethyst–pyrite association.

Abbreviations: Tur=tourmaline, Py = pyrite; Cal=calcite, Amt=amethyst, Qz = quartz

- Breccia cement, with coarse-grained sphalerite, pyrite, and galena in symmetrically banded layers. Chalcopyrite also occurs in particularly high-grade intersections;
- These veins and breccias repeat and cross-cut one another to form thick, high-grade intervals;
- Late unmineralized quartz (locally amethystine or chalcedony) with minor calcite.

Veins show banding, indicative of deposition in open spaces, whereas in other areas they show brecciation or narrow veins in stockwork texture that indicates the structure was closed or partially closed to the fluid passage. At depth, the veins commonly contain coarse massive veins of sulfides, whereas the upper portions generally show barren or low grade coarsely banded veins of quartz and calcite.
The sulfides in these veins can be coarse-grained and massive (massive veins of sulfides), can form bands alternating with quartz, chalcedony and calcite, or can occur as fine disseminations in quartz and calcite. Sulfides are generally fine to medium grained when they form bands. The sulfide minerals present in these veins include pyrite, sphalerite, galena, arsenian-pyrite–arsenopyrite, marcasite, chalcopyrite, and pyrrhotite. One conspicuous feature of these veins is the presence of coarsely banded or massive veins of coarse-grained sphalerite and galena at deeper levels. The sulfides deposited in this event occasionally cement breccias in the host rock. Commonly, the massive veins are cross-cut by the banded veins that extend to higher elevations, which suggest the multiple events of opening and mineralization occurred during vein formation. Banding in the banded veins can be either thinly-laminated, which is commonly associated with ore, or it can be coarse (thicker bands) which is generally low grade or barren.

8. Mineralization Stages

Main sulfide stage is characterized by deposition of medium and coarse-grained quartz, initially euhedral galena, pyrite II, chalcopyrite and tetrahedrite. The alteration assemblage accompanied by the main sulfide stage is muscovite, illite and montmorillonite whereas ankerite–dickite–kaolinite may have formed in the latter part of main sulfide stage and/or during the supergene stage. Moderately deformed arrays of triangular cleavage pits are commonly present within galena, suggesting that galena has undergone some deformation without complete recrystallization during later tectonic events (Bayramov 2014).

Stage 1. This stage is characterized by deposition of coarse-grained galena and sphalerite with fine-grained silver sulfosalts and minor chalcopyrite. Sphalerite in this stage is commonly zoned showing the dark brown to black color, with yellow-orange rims low in iron. Inclusions of chalcopyrite and pyrrhotite are common in sphalerite. Chlorite also occurs associated with this massive vein but it seems to be late with respect to sulfides.

Stage 2. This stage is characterized by deposition of medium- to fine-grained quartz and calcite cross-cutting the coarse-grained sulfides in Stage 1 and the host rock. This quartz and calcite typically show abundant disseminated sulfides and it is possible that at least some of them are reworked grains formed during Stage 1.

Stage 3. This stage is characterized by deposition of alternating bands, rarely symmetrical crustiform-banding of quartz, calcite, and sulfides (sphalerite, galena, pyrite and arsenopyrite). Minor constituents forming thin bands or included in quartz and calcite bands are epidote, hematite and clay minerals. Pyrrargyrite and the other silver sulfosalts occur disseminated in quartz and calcite or associated with sphalerite and galena in the bands of sulfides.

Stage 4. This stage consists of calcite, dolomite –ankerite and quartz veins or stringers with pyrrargyrite that cross-cut stages 1, 2 and 3.

Stage 5. This stage is barren and consists of milky and amethyst quartz and calcite with minor disseminated pyrite and marcasite and sometimes fluorite. Fluorite appears to be the last mineral to have been deposited (Pierre 2013).

9. Textures

Most commonly the breccia zones are strongly silicified and have a very fine-grained rock-flour matrix with pyrite dissemination. The grade of silicification increases towards the veins. Fragments in the breccias are semi-angular-round with variable sizes, up to 5 cm. The fragments are also silicified and originated from the wall rock; however, angular fragments of the silicified fine-grained matrix are also present suggesting repeated brecciation. In the vein outcrops, quartz and the less amount of chalcedony, opal, kaolinite, and smectite are the most common vein-filling minerals. Calcite is more common in the deeper zones of the veins where it is associated with quartz and sulfides. Textures of vein filling quartz have been classified into several groups. These textures are not equivocally distributed in the mineralization. Stockwork-type vein zones with fine-grained (<0.2 mm) equigranular-comb textured infillings, as well as overgrowth of coarse comb textured quartz (up to 2-5 cm) with abrupt change in grain size on the fine grained equigranular quartz, are typical for the veins: these fine grained-equigranular quartz infillings are also characterized by brecciation and occurrences of large (up to 5-10 cm) euhedral water-clear prismatic quartz in the fine-grained quartz matrix. The most developed texture of ore in Gadir deposit is breccia texture which mainly occurs at intermediate and deeper levels. Sphalerite and other ore-bearing minerals located in different size and shape silica breccia. Sugar textured fine-grained quartz infillings the tiny veinlets (max. 10-20 mm width).

10. The precious metal, base metal, and trace element relationships

The Ag/Au ratio (base drill hole assay results) various between 0.01 to 47 (maximum 79), average about 10. As seen from diagram this ratio is not constant into depth which is characteristic for low sulfidation epithermal deposit. Ag is especially enriched in the hydrothermal breccia bodies, as well as in association with the polymetallic ores where the observed concentration is up to 50ppm (Mammadov 2015). The Ag and Au have a good correlation between each other (coefficient is +0.867). The different mineral assemblages have different contents of Au, Ag and Cu grade. The monomineral analyzes mentioned above is one of the provident of this (Mammadov 2015).The monomineral samples were taken by exploration geologist of Gedabek and selected in Scientific
Research Institute of Raw Minerals. Samples were analyzed in the AIMC laboratory of Gedabek. From the results, it is clear that sphalerite minerals contain more Au grade than chalcopyrite (Table 1). In below tables are showed the Ag, Au, and Cu grades of different mineral associations and rock type. All Ag, Au and Cu grades data are summarized in Table 2 and Figure 9. It is clear that quartz-pyrite-chalcopyrite-sphalerite association and andesite-quartz porphyry (contact zone) rock type are the main rich metal containing (Table 2).

Table 1. Results of monominerals for Au, Ag and Cu

<table>
<thead>
<tr>
<th>Monominerals</th>
<th>Grades</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au (ppm)</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>33.56</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>21.29</td>
</tr>
</tbody>
</table>

Table. 2. Mineral associations and rock types

<table>
<thead>
<tr>
<th>Mineral assemblages and rock types</th>
<th>Metal content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au (ppm)</td>
</tr>
<tr>
<td>Quartz-sphalerite-pyrite</td>
<td>1.56</td>
</tr>
<tr>
<td>Andesite (contact with quartz porphyry)</td>
<td>0.46</td>
</tr>
<tr>
<td>Quartz-sphalerite-chalcopyrite-pyrite-barite</td>
<td>1.36</td>
</tr>
<tr>
<td>Kaolinitized quartz andesite porphyritic (contact rock)</td>
<td>6.81</td>
</tr>
<tr>
<td>Quartz-pyrite-chalcopyrite</td>
<td>0.24</td>
</tr>
<tr>
<td>Quartz-pyrite veinlet ± illite</td>
<td>1.15</td>
</tr>
<tr>
<td>Andesite (contact rock) with quartz porphyry ± biotite</td>
<td>0.10</td>
</tr>
<tr>
<td>Andesite with magnetite vein and weak silicifications</td>
<td>0.03</td>
</tr>
<tr>
<td>Quartz porphyry with strong silicified alteration and breccia, sphalerite and pyrite</td>
<td>0.23</td>
</tr>
<tr>
<td>Quartz porphyry with pyrite-tourmaline mineralization and phyllic-potassic alteration</td>
<td>0.13</td>
</tr>
</tbody>
</table>

In order to complete petrographic observations and to establish better relationships between mineralization stages and various elements, several metals were analyzed in 15 samples at the ALS Minerals laboratory of Turkey. Gold was treated by fire assay fusion and analyzed by Atomic Absorption Spectrometry (AAS). Other elements were treated by acid digestion and analyzed by Inductively Coupled Plasma Spectroscopy detection limits (ICP-MS and ICP-OES). Representative samples of the different mineralizations at Gadir were selected. A general description of the samples results are listed in Figure 9.

**Gold mineralization:**
No visible gold is reported at Gadir. However, rarely tiny electrum grains was microscopically observable (Fig 10a). Electrum was only observed in samples from the galena – tennantite – dominated mineralization. Figure 10a indicates deposition of electrum together with hessite, chalcopyrite, galena, and tennantite. This electrum is observed together with large galena and tennantite crystals, which are relatively larger than the usual smaller disseminated crystals from this substage. Analyses of electrum by SEM indicate an Au/Ag ratio of about 3 (qualitative estimation). The galena-tennantite-dominated stage has the highest content of gold measured in this study (~30-40 g/t Au, see Fig 9). Despite the possibility of a nugget effect, it is consistent with microscopic observations of electrum in this mineralization only. Furthermore, analyses indicate a strong correlation between Au and Bi, Te, Pb, and Ag (0.98, 0.91, 0.89, and 0.87, respectively; Figs. 10b and c). These correlations are consistent with the observation of gold occurrence as electrum in association with galena and tellurides.

11. **The metal content of the differentore stages**
Figure 9 shows Au, Ag, Cu, Zn and Pb contents measured in different mineralization stages. The general metal content is significantly lower in the disseminated-pyrite stage affecting the whole QPB (<1 ppm Au). Mineralized zones, which sampled in the central part of the deposit show higher grades, and higher grades are also correlated to more massive mineralization types. Au has a low correlation with Cu and Zn (0.30 and 0.02, respectively), however, chalcopyrite–sphalerite-dominated mineralization has grades of Au (~1 to 10 ppm Au).
Fig 9. Plot of metal content from whole rock analyses of Gadir deposit; Eunaidi diagram (by GEG, 2015)  a) Au/Ag;  b) Au/Cu;  c) Ag/Au;  d) Au/Zn;  e) Ag/Pb;  f) Ag/Zn;  g) Ag/Pb.  1. Galena-tennantite;  2. Chalcopyrite-sphalerite (semi - massive/vein);  3. Chalcopyrite-sphalerite (veinlets/disseminated);  4. Chalcopyrite-sphalerite (oxide zone (sphalerite), veinlets);  5. Quartz-adularia-pyrite (semi-massive);  6. Quartz-adularia-pyrite;  7. Oxidized zone;  8. Argillic alteration;  9. Unmineralized quartz porphyry.
**Other elements:**
Enrichment factors of each element relative to average abundances in Earth’s crust indicate a significant enrichment in As, Sb, Bi, Se, Te, and Hg (±Tl, Mo, and W) are characteristic of epithermal deposits footprint (Simmons et al. 2005). Average abundance of the earth crust is based on values from Web Elements.com (references therein). Correlations are calculated between main elements, taking into account analyses from every analysis. Three groups of significantly enriched elements can be distinguished based on correlations. In each group, elements show a strong correlation with each other, and weak or no correlations with elements from other groups. Only Ag cannot be clearly placed in one group because it shows good correlations with two different groups.

The first group is made of Au, Bi, Pb, and Te. This group clearly represents the *galena-tennantite-dominated mineralization*. It indicates that gold mainly precipitates together with galena (Pb), tellurides (Te; e.g. Hessite) and undefined Bi-rich minerals. This group also shows good correlations with Ag, which can be represented by the precipitation of Ag together with Au (electrum) and Te (Hessite).

The second group is composed by As, Cd, Cu, Hg, In, and Zn (Sh, W). It represents the *chalcopyrite - sphalerite – dominated mineralization (Cu-Zn)*. Cd and In are well known as typical substitutions of Zn in sphalerites; and As was observed in graphic textures indicating an initial high As content in chalcopyrite. Ag also shows good correlations with elements from this group (Cu and As), but this correlation could be due to the late copper event (Cu-and As-rich) replacing chalcopyrite and sphalerites.

The third group is represented by Fe, S, and Se (Mo, Tl). Many sample show S contents above the higher limit of saturation. However, these elements seem to represent the *quartz-adularia-pyrite stage*, with Se known as a common substitution of S in pyrite. Au, Ag, and Cu do not show any correlation with these elements.

**12. Paragenetic Sequence**
Relationships between different mineralization were not observed in the field. Therefore, the paragenetic sequence (Fig 11) is mostly based on petrographic and mineralogy studies. Despite one sample showing a link between the quartz-adularia-pyrite stage and chalcopyrite – sphalerite - dominated mineralization, these two stages are distinguished in the paragenetic sequence. This distinction is supported by metal content analyses showing significantly different patterns for these two stages. There is no evidence if this distinction is due to evolving fluids or to spatial relationships.

Petrographic studies indicate that differences in mineralogy observed within the chalcopyrite - sphalerite -dominated mineralized zones are linked to variations of the sulfidation state of the system. Two extremes are represented in the paragenetic sequences. (1) First the Fe-rich sphalerites in equilibrium with major chalcopyrite. Observation of pyrrhotite inclusions indicates a reduced environment and microprobe analyses indicate a sulfidation state close to the limit between low and intermediate. (2) Then, Fe-poor sphalerites are observed in equilibrium with fine pyrite.
and rare fahloere and chalcopyrite. This mineralization indicates a sulfidation state close to the limit between intermediate and high; furthermore more abundant barite during this later stage as well as sulfur isotopes indicate deposition in a more oxidized environment. However, the close spatial association of Fe-rich and Fe-poor sphalerites, both observed in the central part of the deposit, suggests a progressive evolution of the system in time rather than local spatial variations. The galena – tennantite - dominated mineralization is arbitrarily placed after the chalcopyrite - sphalerite - dominated mineralization. This is suggested by rare occurrences of fahloere in equilibrium with Fe-poor sphalerites. However, galena-tennantite-dominated mineralization is observed in spatial association with the “stockwork-like” structure, and no relationship with other mineralization is observed. This order is defined based on a more linear evolution of the mineralization, linking the earlier disseminated pyrite toward the later copper enrichment. But it is important to note that only rare petrologic observations indicate an evolution in time between these stages.

![Mineral Content](image)

Fig 11. The generalized paragenetic sequence scheme of the Gadir deposit based on the petrography and mineralogy studies. Thick line: dominant mineral; Thin line: common mineral; Dashed line: accessory mineral.

**Discussion**

The Yogundag (Gedabek and Gadir areas) epithermal system was introduced with more lithological factors such as silica sinter, lacustrine siliceous deposit, hydrothermal breccia pipe. The latest international geological models show that the potential ore located around of hydrothermal breccia. These factors are helpful in understanding the model of ore formation in epithermal processes and will be the guideline for future exploration drilling on silica sinter and around of hydrothermal breccia pipe zones. The mineralogy of ores shows considerable overlap, but there are several pronounced differences, based on a compilation of mineral data for more than 130 epithermal deposits (White and Hedenquist 1995); these differences are mainly in the sulfide mineralogy, which reflects the different redox conditions of the hydrothermal fluid.

One distinction is the common occurrence of sphalerite and arsenopyrite in (Gadir) low sulfidation deposits, whereas sphalerite is scarce and arsenopyrite rare in (Gedabek) high sulfidation deposits (White and Hedenquist 1995).

The gangue minerals associated with both two styles of epithermal mineralization also show considerable overlap, but there are clear differences as well, differences that reflect the reactivity (pH) of the altering fluid. Quartz is common in both styles. Adularia and calcite, both indicating near-neutral pH conditions, are common minerals in low sulfidation deposits but are absent from (Gedabek) high-sulfidation deposits. Minerals formed under relatively acidic conditions, such as kaolinite and alunite are common but minor in (Gedabek) high-sulfidation deposits. In (Gadir) low sulfidation deposits kaolinite and alunite do not occur as gangue, except as an overprint (White and Hedenquist 1995).

Gold-sulfide stockwork mineralization in Gadir is characteristic of the low-sulfidation epithermal quartz-adularia type. Just like all mineral deposits, however, Gadir has some subtle differences, which makes it unique. Firstly, the early extensive quartz-adularia-rich veins do not carry appreciable amounts of precious metals, whereas precious metals associated with adularia-quartz stage has been reported from the Gedabek high-sulfidation epithermal deposit (Pierre 2013). It is the later relatively narrower clay-rich veins and breccias that define the mineralized ore shoots. Secondly, the mineralized shoots are of the considerably
greater vertical than lateral extent, a feature not commonly found in epithermal stockwork deposits. The unusual geometry is thought to result from the structural and hydrological complexity in the formation of the veins. Lastly, the presence of electrum as the main silver minerals is also not common. Silver mineralization has been documented at similar deposits such as Gunung Pongkor (Izawa et al. 1990; Milesi et al. 1999; Corbett 2002). The probable age of the gold-sulfide vein mineralization at Gadir can be constrained to a narrow range.

**Conclusion**

The most significant conclusions to research on the mineral composition and paragenesis of altered and mineralized zones in the Gadir deposit and their epithermal type issues include the following:

- Discovering of Gadir deposit with Au-Ag-Cu-Zn ore mineralization gives background to think about the existence of epithermal-porphyry system near Gedabek deposit.
- The deposit is a notable example of quartz-adularia ± calcite ± sericite type of low-sulfidation epithermal gold system.
- Two main zones of hydrothermal alteration were observed in the Gadir deposit (as Gedabek) that is propylitic and quartz ± adularia ± pyrite alteration.
- The deposit is characterized by the presence of chaledonic to crystalline quartz, adularia, illite, and mixed-layered illite/smectite minerals, along with dominant crustiform banding and lattice bladed carbonate replacement (pseudomorphed by quartz) textures.
- Ore mineralization at Gadir is spatially associated with Quartz-Porphyry Body (QPB). Based on mineralogic study observation, polymetallic ore includes different styles of mineralization (semi-massive, vein, veinlets, disseminated) generally post-dating the disseminated pyrite stage.
- The main ore minerals consist of chalcopyrite, pyrite, sphalerite, galena (which constitute the majority of the mineral assemblage); and trace amounts of molybdenite, native gold, and electrum.
- The most developed texture of ore in Gadir deposit is breccia texture which mainly occurs at intermediate and deeper levels.
- Au displays a low correlation with Cu, Zn, and Pb (0.30, 0.02 and 0.01, respectively), but has a good correlation with Ag (0.57), however, chalcopyrite-sphalerite – dominated mineralization indicates has grades of Au.

Considering the above mentioned we (GEG) can suppose that Gedabek gold-copper deposits may relate to the high-sulfidation epithermal system (vuggy quartz and advanced argillic alterations are main factors). Gadir, in turn, may relate to low sulfidation epithermal system (adularia-sericite alteration, silica sinter and quartz-adularia vein type are the main factors).

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**References**


