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Textural and genetic investigations of gold mineralization in fault-controlled quartz-carbonate veins in Bayburt-Zarani area (Eastern Pontides-NE Turkey)

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Abstract: The Eastern Pontides Orogenic Belt (EPOB), geographically corresponding to the northeastern part of Turkey hosts several different types of mineralizations that are closely related to Late Mesozoic-Early Cenozoic arc magmatism. Of these, Zarani gold mineralization, which is located in the southern part of the EPOB occurs as quartz-carbonate veins/veinlets within the Pulur metamorphic massif of Paleozoic age.

Mineral textures indicate low-temperature vein-type mineralization. Gold mainly occurs in quartz and pyrite. The presence of calcite, dolomite, and sericite in the mineralization indicates near neutral pH conditions of ore-forming fluid. Geochemical analyses of chlorites in the quartz-carbonate veins reveal a temperature of ore formation at 140–297 °C, which is compatible with those obtained from fluid inclusions in the mineralized quartz (i.e. 132–226 °C). The average salinity value obtained from fluid inclusions is 4.32% NaCl equiv. O and H isotope values range from ~6.03‰ to +1.47‰ and from ~60‰ to ~119‰, respectively, indicating a mixture of magmatic and meteoric fluids. Mixing is also evidenced by the X_{Fe} analytical data of hydrothermal chlorites associated with ore-forming gangue minerals. Gold precipitation in Zarani mineralization is caused by boiling. The occurrence of mineralization within quartz-carbonate vein/veinlets in metamorphic host rocks, the mineral paragenesis with near-neutral pH conditions of the ore-forming low salinity fluids and the H–O isotopic data imply that the Zarani gold mineralization is an orogenic type epithermal mineralization that may be related to deeply buried Early Cenozoic felsic intrusions, produced by subduction-induced processes in the southern part of the EPOB.

Key words: Eastern Pontides Orogenic Belt, epithermal gold, vein-type, stable isotope, fluid inclusion

1. Introduction

The Eastern Pontides Orogenic Belt (EPOB) is one of the well-preserved fossil magmatic arcs in the Alpine-Himalayan orogenic system. As with many magmatic arcs, the EPOB also hosts several types of ore deposits, which have been the subject of numerous studies (e.g., Güven, 1993; Tüysüz et al., 1995; Akçay et al., 1998; Tüysüz, 2000; Lermi, 2003; Demir et al., 2008; Yaylan-Abanuz and Tüysüz, 2010, 2011; Akaryalı and Tüysüz, 2013; Eyuboglu et al., 2014; Akaryalı, 2016; Deliab et al., 2016; Revan, 2020). The most important ones of these deposits, from north to south, are Kuroko-like volcanogenic massive sulfide (VMS) type Cu-Pb-Zn deposits associated with the Late Cretaceous felsic extrusive rock series (e.g., Murgul, Tunca, Çayeli, Kutlular, Harköy, Lahanos), porphyry Cu±Mo and skarn deposits associated with the Early (?)-Late Cretaceous felsic intrusions (e.g., İspir-Ulutaş, Yomra-Özdil, Maçka-Güzelyayla, Merzifon-Bakırçay) and epithermal gold deposits associated with Early Cenozoic magmatism (e.g., Arvın-Cerattepe, Gümüşhane-Mastra, Gümüşhane-Kaletaş, Gümüşhane-Arzular, Ordu-Akoluk, Ordu-Sayaca, Fatsa-Altunetepe). Considering the type, origin, and regional distribution of ore deposits, the EPOB is divided into three major metallogenic belts from north to south: volcanicogenic massive sulfide, porphyry Cu-Mo and skarn, and epithermal gold. Most of these deposits are small-scale and exploited and abandoned, except Mastra (producing > 25 t of gold) and Altunetepe epithermal gold, and Çayeli and Murgul VMS deposits.

There is a limited number of studies on the origin of gold mineralizations that occur mainly in the southern part of the EPOB. Geological, petrographic and geochemical data indicate that they are mainly intermediate-sulfidation epithermal in the origin (Aslan, 2011; Akaryalı and Tüysüz, 2013; Akaryalı, 2016; Akaryalı and Akbulut, 2016), except Kaletaş mineralization, which is a sedimentary-hosted Carlin-type gold deposit (Tüysüz and Çubukçu, 1999). They are generally hosted by Eocene volcano-sedimentary rocks consisting mainly of andesitic-basaltic volcanic and associated pyroclastic and are mainly controlled by NW-SE and NE-SW-trending structures. Eyuboglu et al., (2011, 2013, and 2017) classified the Eocene felsic...
intrusions exposed in the southern part of the EPOB into two main categories as adakitic and non-adakitic, based on their geochemical characteristics, and suggested that the Lutetian non-adakitic granitoids, which are well exposed along the Gümüşhane-Bayburt-İspir welt, were probably responsible for the economic epithermal gold mineralizations in the EPOB.

The Zarani gold mineralization is located immediately south of the Gümüşhane-Bayburt-İspir welt defined as an epithermal gold belt by Eyuboglu et al. (2011 and 2017) in the southern part of the EPOB and is hosted by medium- to high-grade lithologies of Pulur metamorphic massif. To date, there has been only one study on this mineralization, which was exploration-oriented (Güner and Yazıcı, 2012).

In this study, we present new geological, petrographic, tectonic, whole-rock major and trace element, oxygen and hydrogen isotope, fluid inclusion, and mineral chemistry data from the Zarani gold mineralization and discuss its genesis in the light of new and published data.

2. Geological background

The EPOB stretches over a length of 600 km and a width of 200 km that extends parallel to the southeastern coast of the Black Sea (Figure 1). The Mesozoic-Cenozoic geodynamic evolution of EPOB has been a subject of some controversy over the last forty years. The most widely accepted idea is that the EPOB was shaped by the northward subduction of Tethyan (either Paleotethys or Northern Branch of Neotethys) oceanic lithosphere in the Late Mesozoic and subsequent collision of Eastern Taurides with Eastern Pontides in the Early Cenozoic (e.g., Adamia et al., 1977; Şengör and Yılmaz, 1981; Okay and Şahintürk, 1997; Arslan and Aslan, 2006; Karshi et al., 2007; Aydin et al., 2020; Kaygusuz et al., 2020). Conversely, some researchers suggested that the EPOB was formed above a south-dipping subduction zone from Paleozoic to Early Cenozoic (Dewey et al., 1973; Bektaş, 1987; Bektaş et al., 1999; Eyuboglu et al., 2011, 2017, 2018, 2019, 2021; Maden and Elmas, 2022).

The EPOB can be divided into three subzones: the northern, southern, and axial zones, based on different lithological units, facies changes, and tectonic characteristics (Bektaş et al., 1995; Eyuboglu et al., 2006). Each zone is separated by NE, NW, and E-W trending regional faults which control the emplacement of most of the felsic intrusions and associated mineralizations. The Northern Zone is mainly represented by the Late Mesozoic and Early Cenozoic volcanic and plutonic rocks. The Carboniferous to Triassic metamorphic
lithologies including Pulur, Ağvanis, and Tokat massifs, the Late Carboniferous Gümüşhane and Köse granitoids and Alaskan-type ultramafic-mafic complexes, Early to Middle Jurassic volcano-sedimentary rocks, Late Jurassic to Early Cretaceous carbonate rocks, Late Cretaceous clastic rock-dominated sequences and high-K volcanic and plutonic rocks, Late Paleocene to Early Eocene adakitic intrusions, Lutetian basaltic-andesitic volcanic and felsic plutonic rocks are the main lithological units exposed in the Southern Zone of the EPOB. Serpentinitized ultramafics, an ophiolitic olistostomal melange unit, and Mio-Pliocene volcanic and sedimentary rock assemblages are widespread in the Axial Zone that extends between the Eastern Pontides and Western Taurides blocks (Figure 1).

The Zarani gold deposition is located 7 km south of Demirözü town, which is 30 km WSW of Bayburt city in the southern part of the EPOB. In this region, the oldest rock unit is the Paleozoic Pulur metamorphic massif, comprising two different tectonometamorphic units (Topuz et al., 2004). The high-grade Cenci Unit includes mainly gneiss, amphibolite, and migmatite whereas the low-grade Doğuankavak Unit consists predominantly of metabasite, phyllite, schist, and metachert. Pulur metamorphic massif was cut by Late Carboniferous nonmetamorphic Alaskan-type mafic-ultramafic intrusions (Eyuboglu et al., 2010) and unconformably overlain by Early to Middle Jurassic volcano-sedimentary rocks (Hamurkesen Formation) which grades upward into Late Jurassic to Early Cretaceous carbonate sequence (Berdiga Formation) and continues with Middle to Early Late Cretaceous olistostomal ophiolitic melange unit. The whole sequence is cut by Ypresian adakitic porphryritic and plutonic intrusions (Topuz et al., 2005; Eyuboglu et al., 2011) and is unconformably overlain by a Lutetian clastic rock-dominated sequence (Sirataşlar Formation).

3. Ore geology and structural setting

NE- and NW-trending fractures, resulting from N-S compression are the main tectonic feature of the EPOB. The distribution of the sedimentary basins, plutons, and mineralizations in the region is controlled by these fracture systems (e.g., Bektaş et al., 1995, 1999; Eyuboglu et al., 2006).

The gold-bearing quartz-carbonate veins occur within an N40–60°E trending and 50–70°NW dipping fracture zone developed in the Pulur Metamorphic Massif (Figure 2). The veins have a thickness of about 10 m over a strike length ranging from 50 m to 300 m. Their thickness diminishes at depths. The metamorphic lithologies include silicified zones, which are enriched primarily with gold, pyrite, and Cu-minerals. Alteration zones comprising mainly of silicification, sericitization and carbonatization with about 5–50 m width and 50–100 m length occur over a fracture zone of 3.5 km. Faults in the fracture zone are extending in two different directions. One of them trending in N60°W along the Dağtarla River in the north is not mineralized. On the other hand, the fault zone (Zarani-main fault zone) extending 40–60° NE direction is mineralized. The 60° NW-trending fault is younger than those with mineralization at the northern edge. This fault zone consists of several faults with strike lengths ranging from a few ten to hundreds of m. The mineralizations are recognized along the main fault zone as intermittent vein/veinlets with varying thicknesses. Fracture plane measurements taken from mineralized areas on the major fault and kinematic analysis based on field and drilling data indicate that the main fault in the study area was defined as an N57°E trending right-lateral strike-slip fault with transtensional character and it is accompanied by 35°NE and 75°NE trending splay-faults and riedel shears (Figures 3a and b). Although anti-riedel fractures and faults are not recognized in this resolution, the fault around the north of Sakızlı site in the north of area is thought to be anti-riedel type. It is believed that shear fault starts along the foliation planes within the calcschists-micaschists and then gains a transtensional character depending on pull-apart basin development in the EPOB (Bektaş et al., 1995). In areas where dips of riedel and splay faults are increased (up to 80°–85°) mineralizations are thickened (A–A’ section in Figure 4). Since this is a common feature of dip-slip normal faults, it is suggested that the strike-slip fault wherever it gained oblique (transtensional) character acted as normal faults and hence created open spaces. Opening and shearing caused a grid-like fracture pattern forming stockworks that are filled with quartz-carbonate veinlets (Figure 5). These veinlets create quartz-carbonate-cemented breccias forming rhombic-shaped wall rocks fragments between the fault and veins. These observations indicate that host rock around the fault zone is broken and fragmented by the shear zone and then opened cyclically as a result of transtensional movements and finally filled with quartz and carbonate material with accompanied ore minerals.

3.1. Textural and microstructural features

Several studies have shown that silica and carbonate phases have various textures revealing the physical conditions related to mineralization in the hydrothermal deposits. These different textures are divided into three groups. These are primary growth textures that formed during the deposition, recrystallization textures, and replacement textures (Adams, 1920; Bodnar et al., 1985; Sander and Black, 1988; Saunders, 1990; Dong et al., 1995; Henley and Hughes, 2000; Camprubi and Albison, 2007; Moncada et al., 2012; Yilmaz et al., 2016). The textures observed in the veins are mainly open-space, although some recrystallization textures are also noted.
The comb texture is characteristic of euhedral quartz crystals that grow from a nuclei surface in the empty zones to the space center. It can be either double or single-sided. Comb-texture quartz was recognized in a few samples, and it is the primary growth texture (Figures 6a and b). Quartz represented by this type of texture has micro-fractures that host secondary inclusions (Bodnar et al., 1985).

The void-filling texture is one of the most common textures recognized in epithermal systems. The voids could be either primary or dissolution voids that form as a result of faulting and fracturing of the rock. In the quartz-carbonate veins of the Zarani ore field void texture is quite common (Figures 6c and 6d).

The brecciation occurs by the fragmentation of hematitic and silicified veins due to shearing. The voids are widely filled by quartz and carbonate minerals (Figures 6e and 6f).

The mosaic texture that is one of the texture types observed in the quartz minerals of Zarani ore field is characterized by interlocking of grain boundaries of microcrystalline or crystalline quartz crystals (Dong et al., 1995) and this feature is recognized by only a microscopic study. This mosaic texture is formed by recrystallization of chalcedony or amorphous silica (Dong et al., 1995; Camprubi and Albinson, 2007).

The massive texture is also observed in quartz-carbonate veins. The “massive” term is used to refer to the homogeneous appearance of quartz minerals and the absence of banding and deformation (Dong et al., 1995).

The flamboyant texture was first described by Adams (1920) and Sander and Black (1988). Under a microscope,
Euhedral quartz crystals show extinction from the rims to the center (Figure 7a), similar to the feathery texture. The term feathery originates from spine-like appearance of quartz crystals. For this texture, different names are used just like for flamboyant and plumose quartz textures (Dong et al., 1995; Moncada et al., 2012). It is thought that the recrystallization texture is made up of silica gel and consists of fibrous microcrystalline quartz, which is rounded along the outer rims (Dong et al., 1995). The silica gel is deposited during supersaturation that is triggered by faulting and boiling subsequent to rapid pressure and temperature decrease (Henley and Hughes, 2000). This type of silica comprises the transition phase in the silica deposition cycle and it is deposited following the amorphous silica phase but before the crystalline quartz phase (Camprubi and Albinson, 2007). Feathery and plumose textures are common within the studied samples (Figures 7b, 7c, 7d, 7e).

Zoned quartz texture is a primary growth texture and resembles comb texture (Figure 7f). In this texture, euhedral quartz crystals show growth zones that host primary inclusions reflecting the original deposition conditions (Moncada et al., 2012).

Microscopic determinations revealed that the size of quartz crystals ranged from very fine to very coarse. They grow along their long axis (Figures 7g and 7h). Mosaic, feathery, plumose, and colloform textures recognized in the studied samples are formed by quartz crystallization from silica or directly deposition from the supersaturated solution.

3.2. Ore petrography

The gold mineralization in the Zarani field mainly includes sulfide and oxide minerals that occur in veins/veinlets within the silicified zones. Among the sulphide minerals, pyrite is the most dominant phase associated with chalcopyrite, bornite, and tennantite in the hypogene stage. Malachite, hematite, limonite, and covellite occur in the supergene stage. Quartz, dolomite, calcite, sericite, and chlorite are the primary gangue minerals (Figure 8). Pyrite occurs as euhedral to subhedral grains frequently showing a cataclastic texture and is replaced by other ore minerals such as chalcopyrite, rutile, and hematite (Figures 9a, 9b, 9c, 9d). Chalcopyrite as the second most common ore mineral occurs in subhedral to anhedral forms replacing and surrounding pyrites. Chalcopyrite is locally replaced by bornite and tennantite (Figures 9c and 9d). Bornite is a minor constituent of the mineralization and occurs as subhedral fine grains (Figure 9c) and is replaced by tennantite. Tennantite is also rarely observed as small anhedral grains and replaces both chalcopyrite and
Covellite occurs as anhedral grains replacing chalcopyrite (Figure 9e) and is recorded as the supergene phase product. The gold in bright yellow color coexists with quartz in the gangue ranging from 5 to 20 µm in size (Figure 9f). In addition, it forms part of the pyrite crystal structure as determined by EPMA analyses. The analyses of pyrite minerals indicate significant amounts of gold content with an average of 0.760 (wt.%) Au reaching up to 0.176 (wt.%) Au (Table 1). Gold does not show any significant relationship with other ore-forming elements in pyrites.

Samples collected for chemical analyses (Table 2) from D-1, D-2, and D-3 boreholes drilled in and from P-1, P-2, and P-3 profiles laid out on quartz-carbonate veins revealed gold concentrations varying from 0.50 to 9761 µg/kg with an average of 209.6 µg/kg.

Hematite is macroscopically pale red in color and occurs mostly as decomposed grains (Figure 10b). Limonite is yellow in color and occurs as an alteration product of pyrite.

3.3. Hydrothermal alteration
There is a limited alteration exposed in the surface of the study area. However, silicification, carbonatization,
sericitization, and a minor amount of chloritization occur in quartz-carbonate veins along the fault zones. These alterations are controlled by a NE–SW trending fracture system. Propylitic alteration outside of the fracture system is represented by calcite and chlorite. Disseminated pyrite is common within the quartz-carbonate veins. Drilling data indicated the presence of an alteration zone with a width of 50–60 m (quartz vein + altered silicified zone), which is related to gold mineralization.

XRD analysis reveals the presence of abundant kaolinite and illite with minor smectite. Kaolinite and illite occur in the vicinity of quartz-carbonate veins and smectite is found in low quantity away from the fracture system.

3.4. Chlorite chemistry

Hydrothermal chlorite grains occur as small clusters (Figure 10a) and veinlets associated with quartz, calcite, dolomite, sericite, pyrite and chalcopyrite indicating that chlorite was at least partly contemporaneous with these phases, whereas that of metamorphic origin is associated with a metamorphic assemblage of chlorite, quartz, calcite, sericite, biotite, muscovite, and K-feldspar (Figure 10b). The chlorite flakes all run parallel to schistosity and show some degree of bending and distortion around quartz and feldspar grains. The mode of occurrence of chlorite with hydrothermal gangue and ore minerals suggest their coprecipitation to reliably estimate the temperature of precipitation.

EPMA mineral chemistry analysis was carried out on a total 5 chlorite samples (4 core samples and 1 surface sample). Four samples are from hydrothermal chlorites in quartz-carbonate veins and one sample from chlorites in micaschist. The hydrothermal chlorites have SiO$_2$ contents ranging from 27.35 to 34.91 wt%, Al$_2$O$_3$ from 17.39 to

Figure 5. Core samples (a1, a2) showing brecciation supported by quartz-carbonate cement occurring in association with shearing and opening fractures. b1 and b2 are the sketches.
Figure 6. Various textures recognized in quartz-carbonate veins; a) symmetrical comb texture of quartz, b) asymmetrical comb texture by overgrowth of euhedral quartz crystals within the spaces, c and d) various shaped voids partly filled by secondarily grown calcites in quartz-carbonate veins, e) breccia-fill structures (note to a cockade texture in the inlet), f) a chaotic breccia composed of polymictic clasts of preexisting vein infill cemented by a siliceous and hematitic cement (Qz: Quartz, Cal: Calcite, Hem: Hematite, Lm: Limonite).
Figure 7. a) Flamboyant texture of euhedral quartz crystals, b, c) feathery texture of euhedral quartz crystals, d and e) plumose texture quartz, f) zoning of euhedral quartz crystals, g) coarse quartz intergrowths along the fillings between small quartz crystals, h) coarse quartz overgrowths around the small quartz crystals.
24.58 wt%, FeO from 14.09 to 21.38 wt%, and MgO from 12.23 to 23.05 wt%. They also have a range of Al\textsuperscript{IV} from 1.25 to 2.23 apfu (based on 28 oxygen) and X\textsubscript{Fe} from 0.26 to 0.43 apfu. On the contrary, the metamorphic chlorites have less SiO\textsubscript{2} and MgO contents ranging from 25.69 to 29.07 wt% and from 11.86 to 15.67 wt%, respectively and higher FeO contents from 21.49 to 26.24 wt%. The metamorphic chlorites have a range of Al\textsuperscript{IV} from 2.14 to 2.47 apfu and X\textsubscript{Fe} from 0.44 to 0.55. The hydrothermal chlorites are also enriched with K\textsubscript{2}O with respect to the metamorphic chlorites (Table 3). Relatively low Fe contents of the hydrothermal chlorites may be due to the fact that much of the Fe in solution was preferentially incorporated into pyrites, which is the dominant opaque mineral phase in the veins.

In the X\textsubscript{Fe} vs Al\textsuperscript{IV} diagram, the hydrothermal chlorites are distinctly separated from that of the metamorphic ones with the lower X\textsubscript{Fe} compositions (Figure 11a). In addition, the metamorphic chlorites display a significant negative correlation ($r^2 = -0.86$) with Si (apfu) (Figure 11b), whereas those of the hydrothermal chlorites show no or very weak positive correlation ($r^2 = 0.33$) (Figure 11c).

Hydrothermal chlorites, except one, fall into the field of iron-rich clinochlore whereas metamorphic chlorites are mostly plotted in the Mg-rich chamosite field (Figure 12) (Yavuz et al., 2015).

Although there are several empirical methods to compute the temperature of the formation of chlorites, using those of Cathelineau (1988), Jowett (1991), and...
Kranidiotis, and McLean (1987). The temperatures of hydrothermal chlorites are calculated by the formulas of Cathelineau (1988), Jowett (1991) show similar results (ranging from 140 °C to 297 °C) but differ from that (ranging from 178 °C to 280 °C) of Kranidiotis and McLean (1987) (Table 3).

The formation temperatures of the metamorphic chlorites calculated by three of the methods yield similar ranges from 277 to 342 °C (Figure 13).

3.5. Fluid inclusion studies
Fluid inclusion studies are important for understanding physicochemical conditions of ore formation. Description
and classification of inclusions are very crucial for the assessment of data obtained from fluid inclusion studies. Fluid inclusions have been classified by various workers with respect to trap mechanisms and composition (Roedder, 1984; Shepherd et al., 1985; Samson and Russel, 1987; Kiliás et al., 1996; Wilkinson, 2001). Roedder (1984) classified the fluid inclusions genetically as primary, secondary and pseudo-secondary. Shepherd et al. (1985), made a classification on the basis of phases within the inclusions.

Fluid inclusion studies on quartz-carbonate veins of the Zarani ore field were carried out on 10 quartz samples collected from drill holes and exposures. Measurements were carried out only on primary inclusions, which were classified using the genetic classification criteria by Roedder (1984) and Shepherd et al., (1985). Microscopic examinations reveal that fluid inclusions are represented by gas phase (V) and gas and liquid phase (L + V) compositions (Figure 14). The coexistence of inclusions with only gas phase and gas + liquid phase might indicate boiling process.

Inclusions of gas phase occur only as primary inclusions. Two-phase inclusions occur as both primary and secondary inclusions. Secondary two-phase inclusions are less than 4 μ in size whereas primary two-phase inclusions have lengths between 3 and 10 μ and contain 5%–10% gas phase.

Table 1. EPMA analyses (wt. %) of pyrites from the Zarani quartz-carbonate veins.

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<th>S</th>
<th>Sb</th>
<th>Cd</th>
<th>Te</th>
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<th>Ag</th>
<th>Au</th>
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<td>0.065</td>
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Table 2. The basic statistical parameters of chemical analysis of borehole and surface samples.

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<th>Minimum</th>
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<th>Std. Deviation</th>
<th>Precision %</th>
<th>RSD %</th>
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<td>SiO$_2$ (%)</td>
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<td>Al$_2$O$_3$ (%)</td>
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<td>21.43</td>
<td>9.19</td>
<td>11.30</td>
<td>7.03</td>
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<td>Fe$_2$O$_3$ (%)</td>
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<td>MgO (%)</td>
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<td>2.67</td>
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<td>Au (µg/kg)</td>
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<td>Hg (µg/kg)</td>
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<td>5.70</td>
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<td>0.35</td>
<td>11.50</td>
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The primary inclusions are found in anhedral crystals and show irregular and rarely linear distribution (Figure 14). Inclusions of similar size with only liquid and gas phases are homogenized at nearly the same temperature, which is indicative of boiling (Moncado et al., 2011; Figure 14).

Due to the very small size of fluid inclusions, the first ice-melting temperatures of most inclusions could not be reliably measured. However, some suitable measurements reveal the first ice-melting temperatures in the range of −20 to −18 °C. These temperatures, which are lower than eutectic temperatures suggest a pure H$_2$O-NaCl system due to the size of very small inclusions and thus starting of first melting cannot be accurately recognized. Data for first ice-melting, salinity and homogenization temperature show normal distributions. Last ice-melting temperatures range from −3.8 to −0.4 °C with an average of −2.64 °C (n = 39) indicating that the salinity values (Figure 15a) are in the range of 0.7 to 6.36 (with an average of 4.32% wt.% NaCl equiv) (Bodnar 1993). Homogenization temperatures of fluid inclusions are between 132 and 226 °C (n = 102, average 165.9, standard deviation 21 °C) (Figure 15b). There is no significant difference between temperatures measured for the surface and the core samples.

According to the BULK program (Bakker, 1999), the densities estimated from homogenization temperatures and salinity values of fluid inclusions (Zhang and Frantz, 1987) are found varying from 0.90 to 0.93 g/cm$^3$. 

Figure 10. Photomicrographs of chlorite types and associated minerals a) a cluster of equagranular hydrothermal chlorite (Chl-1) in a fine grained quartz matrix, b) metamorphic chlorite (Chl-2) aligned parallel to the foliation planes in the host rock. (Qz: Quartz, Kfs: K-Feldspar, Ser: Sericite, Cal: Calcite, Ms: Muscovite).

<table>
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<th>Hydrothermal chlorite (n = 40)</th>
<th>Metamorphic chlorite (n = 13)</th>
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<tr>
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<td>Min</td>
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<tr>
<td>SiO₂</td>
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<td>TiO₂</td>
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<td>Al₂O₃</td>
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<td>FeO</td>
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<td>H₂O (c)</td>
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Cations Based on 28 Oxygen

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<td>Fe/(Fe+Mg)</td>
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Chlorite Crystallization Temperature

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<td>Jowett</td>
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<td>Kranidiotis</td>
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Properties

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<td>Flaky</td>
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<td></td>
<td>Mode of occurrences</td>
<td>Equant to rectangular grains and tiny veinlets</td>
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3.6. Hydrogen and oxygen systematics

Stable isotopes provide an important information on physical and chemical parameters related to ore formation such as temperature, pressure, depth, chemical composition of fluids, and origin of ore-forming components (Ohmoto, 1986; O’Neil, 1986; Faure, 1986; Hoefs, 1987). During the assessment of isotope data, field observations, relation between ore and gangue minerals and results of fluid inclusion analysis should be taken into account. Results of H and O isotope analyses of quartz minerals from the Zarani ore field are given in Table 4. Oxygen isotope composition of studied quartz-carbonate veins is between 8.6 and 16.1‰.

In order to estimate the δ¹⁸O fluid value, the average homogenization temperature measured on quartz grains (165.9 °C, 439.05 °K) was used. δ¹⁸O composition of fluid/fluids equilibrated with quartz varies from −6.03 to +1.47‰ (O’Neil and Taylor, 1969). If δ¹⁸O fluid compositions are compared to isotope compositions of various solutions and rocks, the effect of temperature on O isotope composition becomes evident.

4. Analytical methods

4.1. Whole rock geochemistry

Following the petrographic determinations of core and outcrop samples, their major oxides, trace elements analyses were made. Rock samples were crushed with jaw crusher and then ground to 200-mesh size with tungsten carbide ring crusher at the Geology Department of the Karadeniz Technical University (Turkey). The analyses were carried out at Bureau Veritas Laboratories (Canada, LF-202 analyses package). A powdered sample of 0.2 g was
Figure 11. a) Compositional diagram (X_{Fe} vs. Al(IV)), b) and c) correlation diagram of Si vs. Fe/Fe + Mg for metamorphic and hydrothermal chlorites.

Figure 12. Classification of hydrothermal and metamorphic chlorites (Yavuz et al., 2015).

Figure 14. Fluid inclusions images of a quartz sample from the Zarani ore field a) Gas and liquid inclusions over the edge of a euhedral quartz crystal and the area around, b) Enlarged view of fluid inclusions in the juxtaposed area to the euhedral quartz crystal.

Figure 15. a) Salinities estimated from last melting temperatures, and b) homogenization temperatures ($T_h$ °C) measured on primary fluid inclusions in quartz.
weighed in a graphite crucible and mixed with 1.5 g LiBO$_2$ flux. Then the mixture was heated at 1050 °C for about 15 min. The melt was dissolved in 100 5% HNO$_3$ and major oxides were measured with inductively coupled plasma atomic emission spectroscopy (ICP-ES). Rare earth element contents were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) following the dissolution of 0.25 g powdered sample in four different acids. Loss on ignition was estimated from the weight difference after burning the sample at 1000 °C.

4.2. Stable isotope (oxygen and hydrogen) analyses
Oxygen isotope analyses on quartz and hydrogen isotopes from fluid inclusions in quartz were carried out at Queen’s Laboratories (Canada). In hydrogen isotope analyses samples were weighed in silver capsules, degassed for 1 h at 100 °C then crushed and loaded into a zero-blank auto sampler. The hydrogen isotopic composition was measured using a Thermo-Finnigan thermo-combustion elemental analyzer (TC/EA) coupled to a Thermo-Finnigan Delta plus XP Continuous-Flow Isotope-Ratio Mass Spectrometer (CR-IRMS). δ$^2$H values are reported using delta (δ) notation in permil (‰), relative to Vienna Standard Mean Ocean Water (V-SMOW), with a precision of 3‰.

For oxygen isotope analyses, oxygen was extracted from a 5 mg sample at 550–600 °C according to the conventional BrF$_5$ procedure of Calyton and Mayeda (1963) and analyzed via dual inlet on a Thermo-Finnigan Delta plus XP Isotope-Ratio Mass Spectrometer (IRMS). δ$^{18}$O values are reported using the delta (δ) notation in units of permil (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW) international standard, with a precision of 0.3‰.

4.3. Fluid inclusion analyses
To study fluid inclusions on quartz samples doubly polished wafers were prepared at the laboratories of the Geology Department of the Karadeniz Technical University. Thin sections were examined under a microscope with lenses of ×40 and ×100 magnification to study their types, petrography, and microthermometric characteristics. The measurements were made with Linkam THMSG-600 model liquid nitrogen freezing-heating stage temperature range of –196 °C to 600 °C. The densities and pressures at homogenization of fluid inclusions were calculated using the program compiled by Steele-MacInnis et al., (2012).

4.4. Microprobe analyses
Samples for microprobe analysis were cut with diamond disc of 0.5–1 cm thickness and then using epoxy resin mounted on 28×48 mm thin section glass. Samples were dried for about 8 h and abraded to a thickness of 50–70 μ with diamond discs of 80, 220, 600, and 1200 mesh and finally polished with diamond discs of 6 and 3 μ. The final polishing was made with 1-μ diamond paste and 0.3 and 0.05 μ Al$_2$O$_3$ suspensions to Akasel Daran, Akasel Napal and Metkon Fedo1N polishing cloths. The electron microprobe analysis (EPMA) was carried out at the Institute of Petrology and Structural Geology Charles University in 2018 with a JXA-8530F field-emission gun electron microprobe (FE-EPMA) device equipped with a 5-channel wavelength-dispersive spectrometer. The operating conditions were 15 kV and 30 nA beam current for spot analyses. Samples for EPMA analysis were coated with carbon using the Cressington brand device. During the measurements natural and synthetic minerals and elements were used for the calibration standard.

5. Results and discussion
5.1. Mineralization and alteration style of the Zarani gold mineralization
The Zarani (Demirözü) gold mineralization is a fault-controlled ore deposit hosted in N40°–60°E trending quartz-carbonate veins with a total length of 1.5 km in the Carboniferous metamorphic rocks. The quartz-carbonate veins show comb, void-filling, breccia-fill/brecciated, mosaic, flamboyant and feathery textures which are typical of epithermal deposits (Yılmaz et.al, 2010, 2013, Fournier, 1985; Dowling and Morrison, 1990; Dong et al., 1995). Since the ore is deposited as open space-filling within fractures and cracks of the wall rock, it reflects an epigenic character. The mineralization is tectonic-controlled and related to Tertiary (?) granitoid intrusions (Eyuboglu et al., 2011; Eyuboglu et al., 2014; Eyuboglu et al., 2017; Eyuboglu et al., 2018).

<table>
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<th>Sample No</th>
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<th>δ$^{18}$O$_{water}$(165.9 °C)</th>
<th>δD(‰)</th>
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<td>3</td>
<td>Quartz</td>
<td>16.1</td>
<td>1.47</td>
<td>-101</td>
</tr>
<tr>
<td>4</td>
<td>Quartz</td>
<td>10.4</td>
<td>-4.23</td>
<td>-66</td>
</tr>
<tr>
<td>5</td>
<td>Quartz</td>
<td>12.7</td>
<td>-1.93</td>
<td>-60</td>
</tr>
</tbody>
</table>

Table 4. Oxygen and hydrogen isotope compositions of gangue mineral and equilibrated fluids and δ$^{18}$O of water in equilibrium with quartz.
In epithermal systems, the textures of quartzs significantly change with increasing depth. Comb texture is observed below the boiling level in a deeper part of the vein, whilst brecciated+cockade+banded textures are dominated just above this in the area including the boiling level (Buchanan, 1981). The massive texture is common in shallow parts. Precious metal deposition is related to the boiling process (Giggengbach and Stewart, 1982; Hedenquist et al., 2000). Most quartz textures (Figure 7) are an indication of boiling or sudden temperature and/or pressure decrease which result in rapid precipitation and supersaturation. Boiling first starts at depth and then progresses to the surface. In these systems, gold is enriched in boiling zones where banded, brecciated, and cockade textures occur (Buchanan, 1981; Bodnar et al., 1985; Brown, 1986; Simmons and Christenson, 1994; Andrea-Mayer et al., 2002; Etoh et al., 2002; Moncada et al., 2012).

Gold occurs mainly in quartz and carbonate-dominated matrices. However, some sulphide minerals especially pyrites and arsenian pyrites contain a significant amount of invisible gold in their crystal lattice (Fougerouse et al., 2021; Reich et al., 2005). There is no arsenian pyrite among the ore minerals observed but pyrites from Zarani gold mineralization contain considerable amounts of gold (Table 1) and hence contribute significantly to the gold content in quartz-carbonate veins.

The hydrothermal alteration in the Zarani gold mineralization occurs from quartz-carbonate veins to the outer parts of the alteration zone in the order of silicification, carbonatization, sericitization, chloritization, illitization, and kaolinization. Argillic alteration is a common alteration type recognized around the quartz-carbonate veins that form smectite and kaolinite clay minerals in rocks that suffer H+ metasomatism by hydrothermal solutions with the temperature of 100–300 °C.

5.2. Characteristics of the ore-forming fluids
The Th of fluid inclusions in quartz ranges from 226 °C to 132 °C (Figure 15). The salinities of fluid inclusions in quartz ranged from 6.36 to 0.70 wt%NaCl equivalent. Using homogenization temperature and salinity diagrams (Wilkinson, 2001), the data for fluid inclusions in quartz indicate that mineralization at Zarani involved boiling of a deeply circulated dilute fluid. After the precipitation of gold, the fluid cooled down due to wall-rock interaction (Figure 16). Observation of the vapor and liquid rich inclusions in the same quartz crystals also supports boiling (Figure 14).

The XFe values of chlorites are related to the oxygen fugacity of the system (Beaufort et al., 1992). A narrow range of the XFe values (0.43 to 0.55) of the metamorphic chlorites indicates a minor variation in the redox conditions (Pant et al., 2019), whereas a relatively wider range of XFe values (0.26 to 0.43) of the hydrothermal chlorites suggests a significant fluctuation in fO2 conditions in the hydrothermal system at the time of their crystallization. The XFe values of chlorites less than 0.5 point out oxidizing conditions (Pant et al., 2019) prevailing at the time of crystallization of the chlorites and associated minerals. This in turn affirms that increasing fO2 of the system is caused most probably by the mixing of gold-bearing fluids with oxidizing fluids.

The densities of fluid inclusions in quartz range from 0.9 to 0.93 g/cm³, and the pressures at homogenization range from 1 to 25 bar. According to hydrostatic pressure conditions, the Zarani gold mineralization formed at a depth shallower than 280 m, beneath the paleo-groundwater table. This is consistent with the Zarani mineralization being an epithermal gold deposit (Cooke and Simmons, 2000; Hedenquist et al., 2000; Simmons et al., 2005; Zhong et al., 2017).

The temperatures calculated from the hydrothermal chlorite EPMA analyses using empirical formulations of Cathelineau (1988), Jowett (1991), Kranidiotis and McLean (1987) range from 140 to 297 °C and homogenization temperatures obtained from fluid inclusions from 132 to 226 °C. Although temperatures obtained from fluid inclusion data show somewhat less temperatures than those from chlorite data, a large range of temperature overlap exists between them.

It might be of interest at this point to compare some fluid characteristics of the Mastra and Arzular gold mineralizations in the region with those of Zarani gold mineralization.

The average homogenization temperature of quartzs from the first stage of mineralization at Mastra is 270 °C and that from the second stage is found at 230 °C. The average salinities on quartz from the first and second stages are 8.4 wt.% and 6.9 wt.% NaCl equiv, respectively (Aslan, 2011). Similarly, the homogenization temperature and salinity of quartzs from Arzular ore field are 214 °C and 8.5 wt.% NaCl equiv, respectively (Akaryali and Tüysüz, 2013).

It is evident that the average homogenization temperature (165.9 °C) and salinity (4.32 wt.% NaCl equiv) of quartzs from the Zarani field are lower than those of Mastra and Arzular fields. Temperature and salinity values of Zarani field are similar to those of vein-type deposits that are deposited from meteoric fluids with a magmatic component (Roedder, 1984) and this might indicate that the Zarani gold mineralization was formed in an epithermal system. Densities of ore-forming fluids in epithermal deposits generally do not exceed 0.95 g/cm³ and are always lower than 0.8 g/cm³ at high temperatures (Roedder, 1984). Densities of fluids in the Zarani field vary from 0.90 to 0.93 g/cm³ which are largely consistent with those of epithermal deposits.
5.3. Source of ore-forming fluids and gold precipitation

Stable isotope studies can be explicitly used to identify the source, chemical composition, transport, and storage of ore-forming fluids, as well as the temperature of ore formation (e.g., Rye and Ohmoto, 1974; Ohmoto and Rye, 1979; Faure, 2003; Hoefs, 2015). In order to make a comparison between fluids of different origins, \( ^{1}H \) and \( ^{18}O \) isotope compositions of quartz samples from the Zarani gold field are plotted on the diagram proposed by Taylor (1974) and Ohmoto (1986) (Figure 17). \( ^{1}H \) and \( ^{18}O \) isotope values from other gold mineralizations in the nearby regions are also added to the diagram. \( ^{1}H \) and \( ^{18}O \) isotope compositions of quartz samples are –6.03 to +1.47‰ and –60 to –119‰, respectively. Considering the lateral and vertical distributions, the composition of ore-forming fluids is most likely modified by the mixing between magmatic and meteoric waters. The scattered pattern of the data may also indicate local isotopic heterogeneity present during fluid mixing and trapping. In epithermal systems, the hydrothermal solutions are mostly of meteoric origin although magmatic contribution cannot be ruled out (Giggengbach, 1992; Hedenguist and Lowenstern, 1994; Matsuhisa and Aoki, 1994).

Ore-forming fluids in the Mastra and Arzular fields are comprised largely of magmatic waters whereas those in the Zarani field are a mixture of magmatic and meteoric waters. The mixing probably took place before the boiling of magmatic fluids. Boiling as evidenced by quartz texture types (Figure 7), brecciation, and fluid inclusion petrography acts likely the chief process in gold deposition (Figure 16).

5.4. Implications for the Zarani gold deposit type

A combined study of lithology, structural features, fluid inclusions in ore and cogenetic gangue minerals best constrains the ore-forming conditions, particularly for an orogenic epithermal gold deposit. The presence of calcite, dolomite, and sericite in the Zarani gold mineralization indicates the near neutral pH conditions of its ore-forming fluid. The fluid inclusion data for quartz reveal low–medium temperatures and relatively low salinities due to the dilution of magmatic fluids by deeply circulating meteoric waters.

6. Conclusions

Gold mineralization in the Zarani field was formed along N40°–60°E trending quartz-carbonate veins with a thickness of about 10 m and a cumulative length of 1.5 km in the Paleozoic metamorphic units. 60°NW-extending another fracture system in the field does not contain any mineralization. In the Zarani field, gold is accompanied by several metallic minerals such as pyrite, chalcopyrite,
bornite, and tennantite. Quartz, calcite, and dolomite are the major gangue minerals with lesser amounts of sericite and chlorite. Kaolinite and illite are quite abundant around the quartz-carbonate veins. The presence of calcite, dolomite, and sericite in the Zarani gold mineralization indicates the near neutral pH conditions of its ore-forming fluid.

The silica gel hosting gold is deposited during supersaturation that is triggered by faulting and boiling subsequent to rapid pressure and temperature decrease. In the quartz-carbonate veins of the Zarani ore field; massive, comb, space-filling, breccia-fill/brecciated, and zoned growth structures are regarded as the primary growth textures, whilst mosaic, flamboyant and feathery textures are the main recrystallization textures. Many of these textures have resulted from boiling processes that caused gold precipitation. These textures overall indicate depositions from low temperature fluids at shallow levels. The homogenization temperatures and salinities of quartz range from 132 °C to 226 °C and 0.70 to 6.36 wt.% NaCl equiv, respectively. These values are highly compatible with temperatures estimated by the chlorite geothermometer. Although in low abundance, chlorite is one of the main components of the gangue minerals associated with gold. Oxygen (−6.03 to +1.47‰) and hydrogen (−60 to −119‰) isotope compositions of quartz samples vary in a narrow range and lateral and vertical distributions show that the stable isotope composition of ore-forming fluids is modified by mixing between magmatic and meteoric waters. In conclusion, boiling following the mixing of meteoric and magmatic waters enhanced the gold precipitations. The mineralization style and the near-neutral pH conditions of the ore-forming fluid as well as the H–O isotopic data, imply that the Zarani gold mineralization is an orogenic epithermal mineralization that is most likely related to deeply buried Early Cenozoic felsic intrusions.

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