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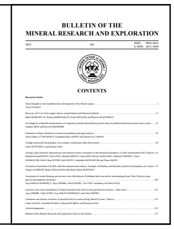

Geology, fluid inclusion characteristics and mineral resource estimation of the Güzelyayla porphyry Cu-Mo mineralization (NE Türkiye)

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Research Article

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ABSTRACT

Magmatic processes that emerged with the evolution of the Neotethys ocean and associated lithospheric plates caused the formation of significant mineralization in the Tethys belt. The Eastern Pontides, which are located in the northeast of Türkiye and are a part of the Tethys metallogenic belt, are particularly rich in porphyry-type mineralization and represent an important region for Cu-Mo exploration. A large number of Cu, Pb and Zn anomalies have been determined in a large region including the Güzelyayla Cu-Mo field by stream sediment sampling. The Güzelyayla occurrence is Cu-Mo mineralization associated with andesitic/basaltic volcanic rocks and intrusive dacites crosscutting these rocks. The Güzelyayla Cu-Mo mineralization developed in the stockwork and fault-controlled silicified zones. Homogenization temperature values vary between 324 °C and 420 °C (average 374 °C). Salinity values range between 2.2 and 18.6% NaCl (average 9.1% NaCl). A concentric alteration zoning surrounding the potassic alteration indicates a gradual change in the physicochemical properties of the solutions forming the mineralization. The Güzelyayla mineralization was formed in the Eocene (50.7 ± 1.0 million years) period in the Upper Cretaceous volcanic rocks in relation to post-collisional processes in the magmatic arc environment. Contrary to previous studies, estimation zone models were created and an estimated 54.2 million tons of extracted/potential mineral resource with an average grade of 0.20% Cu and 0.014% Mo (0.26% Cu equivalent grade) was made in the Güzelyayla field.

1. Introduction

The Pontides, which were formed as a result of the subduction of the Neotethys Ocean along the Eurasian continental margin in the Mesozoic period, collided with the Anatolide-Tauride platform in the Cenozoic period (Şengör and Yılmaz, 1981). As a result of these successive tectonic processes, numerous volcanogenic massive sulfide (VMS), porphyry and epithermal type mineralizations associated with calc-alkaline and

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adakitic magmatism were formed in the Pontides. It was aimed to search for VMS and epithermal type mineralizations in the Pontides (Çağatay and Boyle, 1977; Pejatovic, 1979; Çağatay, 1993; JICA, 1998; Yiğit et al., 2000; Aslan, 2011; Karakaya et al., 2012; Akaryalı and Tüysüz, 2013; Eyüboğlu et al., 2014; Bilir, 2015; Revan et al., 2014, 2016, 2017, 2019; Revan, 2021). Scientific studies on the origins and geological environments of porphyry-type mineralization have been very limited (Doğan, 1980; Yalçınalp, 1992; Soylu, 1999; Delibaş et al., 2016, 2019; Kuşcu et al., 2019). To understand the geological events that control the formation and timing of the porphyry-type mineralization in the region, more detailed geological and geochemical studies at the deposit scale are required. Regional-scale geochemical prospecting data is an important and decisive method in the exploration of mineral resources. In particular, it plays an important role in the selection of priority target areas in explorations. A detailed geochemical sampling study (stream sediment, rock and soil) to be carried out after the selection of the target areas sheds light on the type of possible ore system in the region (Reimann et al., 2002; Zheng et al., 2014). The type of mineralization system also directly influences the selection of exploration strategies. The presence of metal anomalies and metal association is interpreted as a part of the mineralization system from which it originated and indicates target mineralization areas. The statistical analysis of the numerical data obtained from the target areas, on the other hand, has an important place in the determination or re-evaluation of mineral resources. In this context, the latest study by the General Directorate of Mineral Research and Exploration (MTA) on the Güzelyayla porphyry type mineralization in the eastern part of the Pontides and the data obtained in previous studies were examined together. The Güzelyayla mineralization is the first porphyry type occurrence discovered in the Eastern Pontides with regional prospecting geochemistry in terms of Cu and Mo resources (Nebioğlu, 1983; JICA, 1986; Güner and Güç, 1990). A large number of Cu, Pb, Zn and Au anomalies and associations have been determined as a result of geochemical sampling (stream sediment) in a large area where the Güzelyayla Cu-Mo field is located. It has been observed that some of these anomalies match exactly with the Güzelyayla mineralization area known in the region. The existence of potential in the field has been demonstrated numerically with statistical methods prepared by creating a large number of descriptive statistical parameters of the obtained data.

The Güzelyayla Cu-Mo mineralization, which was determined as the target areas for porphyry type systems, was found as a result of the detailed geochemical sampling study carried out in the past. Also, the importance of such systematic and detailed geochemical studies in revealing the mineral resources was also emphasized in this study. The data presented in this article will be the basis for understanding the porphyry type mineralization in the region and will increase the interest in similar regions. In addition, this study has once again confirmed how important geostatistical methods are in the determination of mineralization and their possible potentials.

2. Geological Setting

Güzelyayla Cu-Mo mineralization is located within the Eastern Pontides volcanic belt (Figure 1). The Eastern Pontide volcanic belt is located in the northeastern part of the Anatolian Peninsula, which is a part of the Alpine-Himalayan metallogenic belt. Ketin (1966) divided the Anatolian Peninsula into four main tectonic units, aligned from north to south, as the Pontides, Anatolides, Taurides, and Border Folds, based on the orogenic development of Türkiye. Each tectonic unit has characteristic sedimentary, volcanic, plutonic, and metamorphic patterns that are related to its orogenic development. Located in the north of the northern branch of the Neotethys ocean, the Pontides are a morphological entity extending from the Gulf of Edremit in the west to the Caucasus in the east. Okay and Tüysüz (1999), who rearranged the tectonic units of the Anatolian Peninsula, named the east of the Sakarya Zone and the north of the Ankara-Erzincan Suture, as the Eastern Pontides. The Eastern Pontides is a volcanic belt consisting of Jurassic-Neogene volcanic and sedimentary rocks, ~600 km long and ~150 km wide, extending along the Eastern Black Sea coast. Due to its lithological differences, the Eastern Pontide belt is divided into two zones, generally north and south (Gedikoğlu et al., 1979; Özsayar et al., 1981; Bektaş et al., 1995; Okay and Şahintürk, 1997; Eyüboğlu et al., 2014; Liu et al., 2018). While the northern zone is mostly composed

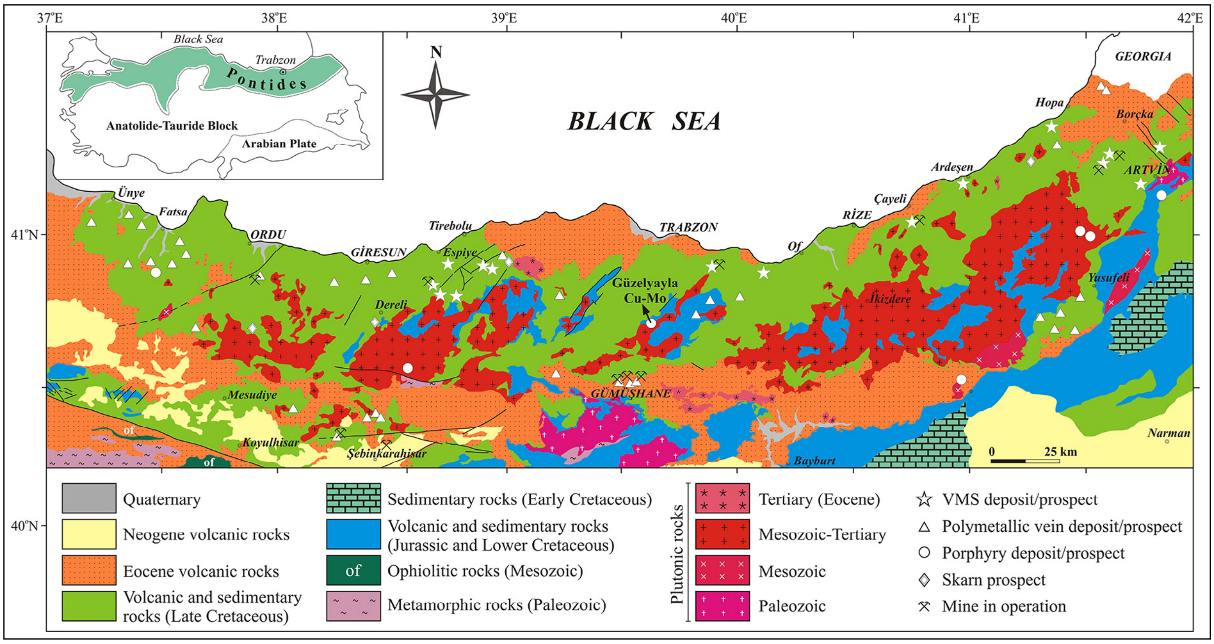

Figure 1- The locations of some important mineral deposits in Northeast Anatolia and the Güzelyayla porphyry type mineralization on the simplified regional geological map. Tectonic units of Anatolia (Ketin, 1966) are given in the upper inset.

of Late Cretaceous and Middle Eocene volcanic and volcaniclastics, the southern zone is mainly composed of pre-Late Cretaceous ophiolitic, sedimentary and lesser igneous rocks (Okay and Şahintürk, 1997). This region is restricted in the south by the Ankara-Erzincan Neotethys suture zone.

The Late Cretaceous period is represented by a volcanic arc in the Eastern Pontides (Peccerillo and Taylor, 1975; Pejatovic, 1979; Şengör and Yılmaz, 1981; Şengör et al., 1985; Robinson et al., 1995; Okay and Şahintürk, 1997; Kandemir et al., 2019). The geological evolution of the eastern Pontides during the Late Cretaceous period is related to the magmatic activity resulting from the subduction of the northern Neotethys lithosphere under the Eurasian continent. The direction and timing of the subduction are still vigorously debated. Many researchers agree that the geological evolution of the Eastern Pontides is originally related to the northward subduction of the Neotethys ocean in the Late Mesozoic period (Şengör et al., 1980; Ustaömer and Robertson, 1995; Okay and Şahintürk, 1997; Yılmaz et al., 1997; Rice et al., 2009; Dilek et al., 2010; Kandemir et al., 2019; Aydın et al., 2020). The view that the Paleotethys oceanic lithosphere was formed by southward subduction from Paleozoic to Eocene has recently gained support (Dewey et al., 1973; Chorowicz et al., 1998; Bektaş et al., 1999; Eyüboğlu, 2010; Eyüboğlu et al., 2011*a*, *b*, 2014; Liu et al., 2018).

The Eastern Pontide volcanic belt consists of Mesozoic and Cenozoic rocks overlying a crystalline basement. The crystalline basement is a part of the Hercynian orogeny and consists of Paleozoic metamorphic rocks and Hercynian granitic intrusives in this region (Schultze-Westrum, 1961; Zankl, 1962; Yılmaz, 1976; Moore et al., 1980; Topuz et al., 2004, Kaygusuz et al., 2016). These basement rocks are overlain by a volcano-sedimentary succession ranging from Early Jurassic to Eocene (Okay and Şahintürk, 1997; Yılmaz and Korkmaz, 1999; Kandemir et al., 2019). Plutonic rocks of different ages and compositions, as well as various dykes and sills cut the entire succession. The ages of the plutonic rocks range from Carboniferous to Neogene (Delaloye et al., 1972; Okay and Şahintürk, 1997; Yılmaz et al., 1997; Kaygusuz, 2000; Arslan et al., 2004; Aydınçakır and Şen, 2013; Delibaş et al., 2016; Eyüboğlu et al., 2017, 2019; Liu et al., 2018). Plutonic rocks have a wide compositional range and are largely composed of tholeiitic and calc-alkaline granitoids and alkaline syenite/monzonites (Yılmaz and Boztuğ, 1996). The emplacement of the plutonic rocks is related to subduction and post-collisional rifting events (Yılmaz and Boztuğ, 1996; Topuz et al., 2005; Karslı et al., 2007; Boztuğ and Harlavan, 2008; Delibaş et al., 2016; Eyüboğlu et al., 2017, 2019; Liu et al., 2018).

3. Material and Method

After the macro structure and textural descriptions of the samples taken for petrographic purposes to represent the mineralizations were made, the rock cutting, etching, polishing and thin-section making and petrographic examinations were carried out in the laboratories of the MTA, Department of Mineral Analysis and Technology (MAT).

MAT of MTA was used for fluid inclusion analyses. Linkam MDSG 600 (motorized) heating and cooling system are used for fluid inclusion studies in MTA laboratories. The heating-cooling table is mounted on the Leica DM 2500 M model microscope. Objectives with 20x and 50x magnification were used for the examinations. Linkam MDSG 600 (motorized) is a fully automatic and programmable system. To be programmed, a software called Linksys32 is used in the computer environment. The temperature ranges of the Linkam table range from -196 °C to 600 °C. Heating and cooling rates increase from 0.1 °C/minute to 150 °C/minute. Liquid nitrogen (N_2) is used in cooling processes. PL-A662 model PIXELINK camera is used while examining transparent samples.

Rock and sediment geochemistry was carried out in the laboratories of the Mineral Analysis Technology Department of MTA. Each rock sample was ground and sieved through 80 mesh size and turned into a 50-gram powder sample. ICP-MS instrument for gold (Au), AAS instrument for silver (Ag), and ICP-OES instrument for 10 other elements (As, Bi, Co, Cu, Mo, Ni, Pb, Sb, V, Zn) were used. For the analysis of Au (10 grams) and Ag (1 gram), the solving process was applied using the aqua regia method. For other elements (As, Bi, Co, Cu, Mo, Ni, Pb, Sb, V, Zn), 1-gram sample was weighed and dissolved in three acids (HNO_3 - HCl - $HClO_4$).

4. Findings

4.1. Research History

Güzelyayla Cu-Mo mineralization is located at 2.5 km southeast of Güzelyayla village in Maçka district, ~30 km south of Trabzon Province. The Cu-Mo anomaly was determined in the mineralization area during the stream sediment geochemistry studies carried out in the region within the scope of the United Nations Development Project in 1973. In the following period, detailed prospecting, soil geochemistry and geological mapping studies were carried out in the field (Nebioğlu, 1983; Çınar and Yazıcı, 1985; Gülibrahimoğlu, 1985). Between 1985 and 1987, Japan International Cooperation Agency (JICA) conducted geophysical and 4969 meters of drilling in 17 locations in total (JICA, 1985, 1986, 1987). As a result of the drilling studies, 186.2 million tons of probable and proved reserves with an average grade of 0.3% Cu and 0.014% Mo were determined (JICA, 1987). To investigate the possible spread of mineralization in the northeast direction, a total of 1191 meters of drilling was carried out by MTA in four different locations from 1987 to 1990 (Güner and Güç, 1990). The data obtained about the geological settlement and geochemistry of the mineralization was examined within the scope of his doctoral study (Yalçınalp, 1992). Recent research in the field of mineralization was carried out by MTA from 2017 to 2019 within the scope of this study.

4.2. Geology and Structure of Mineralized Area

Jurassic (Dogger) basalts are the oldest rocks in the mineralization area (Figure 2). Intense silicification and epidotization are typical in massive and locally amygdaloidal basalts. Late Jurassic-Early Cretaceous crystallized limestones (Gülibrahimoğlu, 1985) are in the form of blocks within the Late Cretaceous basaltic-andesitic volcanic rocks. These platform limestones belonging to the Berdiga Formation are semi-crystalline with the effect of intrusive rocks and faults and have turned into marble in places. Basalt-andesites and pyroclastics of the Çatak Formation, one of the host rocks of the porphyry type mineralization, crop out in large areas in the map area. The primary texture of the minerals in the basaltic-andesitic rocks has been obliterated by intense alteration. Chloritization and epidotization are common in basaltic-andesitic rocks close to felsic intrusives. Sediment deposits composed of siltstone, limestone and micritic mudstone are in the form of irregular lenses in the formation (Nebioğlu, 1983; Çınar and Yazıcı, 1985). Microscopically, the andesitic/dacitic rocks are

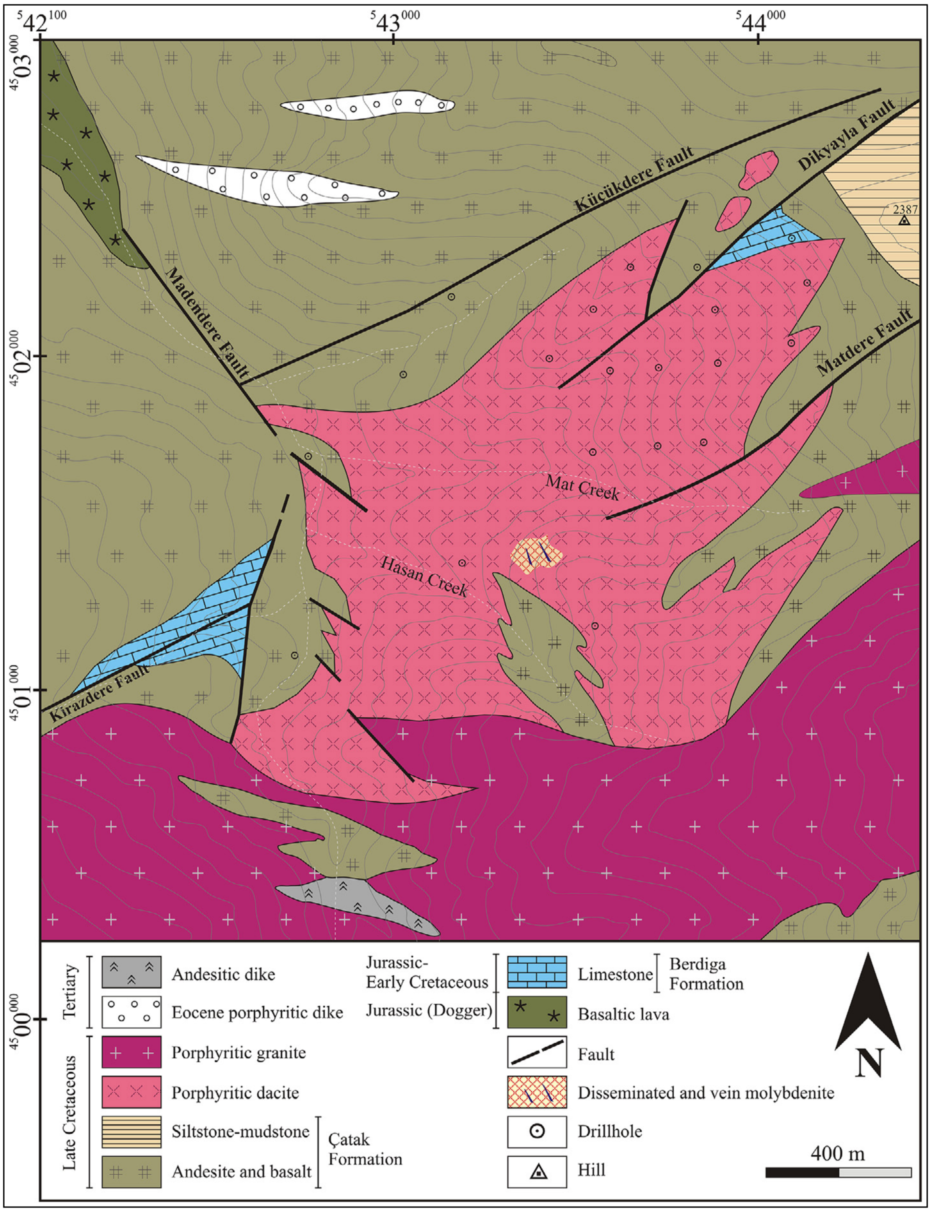

Figure 2- Geological map of the Güzelyayla Cu-Mo mineralization and distribution of important lithologies (modified from Çınar and Yazıcı, 1985 and JICA, 1986).

composed mostly of euhedral plagioclase, to lesser extent quartz phenocrysts filling interstices between other minerals. It is cut by quartz veins in place. The plagioclases are in the form of long laths and are located in the groundmass in argillized and sericitized forms. Mafic minerals are generally composed of weathered pyroxenes. The age of the Çatak Formation is Late Cretaceous (JICA, 1986; Güner and Güç, 1990). All these rock lithologies are intruded by Late Cretaceous porphyritic dacites and granites (Aydın, 2014; Delibaş et al., 2016). Porphyritic dacite has a more fractured/jointed structure compared to the other plutonic rocks in the area, and their primary textures have largely been obliterated. The weathering products are generally sericitization, silicification, argillization and, to a lesser extent, epidotization and chloritization. This felsic intrusion is generally composed of quartz and plagioclase phenocrysts. Their plagioclase is argillized and mafic minerals are weathered. It is considered that the porphyritic dacite intrusion intruded in the form of a vertical body (JICA, 1986). Most of the mineralization in the field is in this unit. The age data of 81 ± 1.1 million years (Upper Cretaceous) were obtained from porphyritic dacites by the LA-ICP-MS U-Pb zircon method (Delibaş et al., 2016). Porphyritic granite is the largest intrusive mass outcropping in the Güzelyayla area. Porphyritic granite is commonly composed of plagioclase and quartz crystals. The mineralization is not observed in the porphyritic granite and the alteration is very weak. The mafic minerals are slightly chloritized and epidotized. Porphyritic granite cuts the volcanic and sedimentary units of the Late Cretaceous Çatak Formation in the map area. The contact relationship with the porphyritic dacite is uncertain due to the dense vegetation. However, porphyritic granite was interpreted as younger than porphyritic dacite due to the low degree of alteration (JICA, 1985). There is no radiometric age data for porphyritic granite. Age data of 78 ± 0.73 million years (Upper Cretaceous) were obtained using the LA-ICP-MS, U-Pb zircon method around Turnagöl area in the northeastern part of the granitic unit (Kaygusuz et al., 2013). The latest magmatic phase is represented by Eocene granodioritic-tonalitic porphyritic dykes and andesitic dykes. Porphyritic and andesitic dykes crosscut Late Cretaceous volcanic rocks and porphyritic granite. The age of a subvolcanic porphyritic dyke representing the late-stage magmatic intrusion in the area was determined as 53.55 ± 0.34 and 51.34 ± 0.27 ($^{40}Ar/^{39}Ar$ - hornblende) million years (Eocene) (Karslı et al., 2011). Andesitic dyke has a porphyritic texture and contains plagioclase, hornblende and pyroxene.

The mineralized area is located on the limb of an approximately N-S/NE-SW oriented anticline structure. The location of the porphyritic intrusions has caused some structural discontinuities (fault, fold, etc.) to form in the area. The positions of the faults are roughly parallel to each other and in the ~N45E direction. The Madendere fault, on the other hand, represents a roughly NW-SE trending fracture system. Local small faults in NE-SW direction cutting these faults were determined. It is thought that the granitic rocks in the area were emplaced along these tectonic lines. In some studies, using aerial photographs (Güner and Güç, 1990; Yalçınalp, 1992), it has been accepted that the Güzelyayla porphyry Cu-Mo mineralization is within the circular depression area.

4.3. Mineralization

Güzelyayla Cu-Mo mineralization was formed within Late Cretaceous porphyritic dacite and andesitic/basaltic volcanic rocks. The mineralization concentrated in the region between the Mat Dere and Hasan Dere has developed mostly in porphyritic dacites (Figure 2). The mineralization in andesitic/basaltic volcanic rocks intruded by porphyritic dacites is less developed and represents the outer parts of the mineralization center. Geochemical anomalies, distribution of alteration minerals, geophysical and drilling studies (JICA, 1986; Güner and Güç, 1990; Yalçınalp, 1992) support such a lithological distribution of the mineralization (Figure 3). In addition, skarn zones have developed at the limestone contacts with porphyritic dacite intrusions. Magnetite, chalcopyrite and pyrite enrichments are observed in these small sized skarn zones in order of abundance.

In the Güzelyayla porphyry Cu-Mo field, three types of mineralization are observed: stockwork (Figure 4a, b), disseminated (Figure 4c) and late-stage quartz veins (Figure 4d, e). The stockwork type quartz veins that crosscut the volcanic rocks with the Late Cretaceous porphyritic dacite intrusion typically contain chalcopyrite, pyrite, pyrrhotite, rutile and very rare molybdenite, while the disseminated mineralizations in the silicified zones of the porphyritic dacites are characterized by chalcopyrite, magnetite and pyrite. Covellite, chalcocite and digenite minerals observed in disseminated mineralization were interpreted as secondary minerals associated with local supergene enrichment (Delibaş et al., 2016). Late-stage quartz veins are a few centimeters thick and contain pyrite, chalcopyrite, molybdenite and sericite. Molybdenite is enriched in these late-stage quartz veins, which crosscut mostly porphyritic dacites and volcanic rocks.

Pyrite, chalcopyrite, magnetite, molybdenite, sphalerite, hematite, galena, pyrrhotite, gold, bornite, chalcocite, covellite and native copper are the ore minerals identified in the Güzelyayla porphyry Cu-Mo mineralization. Pyrite is disseminated all over the field, especially in the propylitic and sericitic zones, and in the form of infilling in quartz veins. Early and late stage phases were determined in pyrites. Magnetite is in the form of veins and disseminations in the propylitic

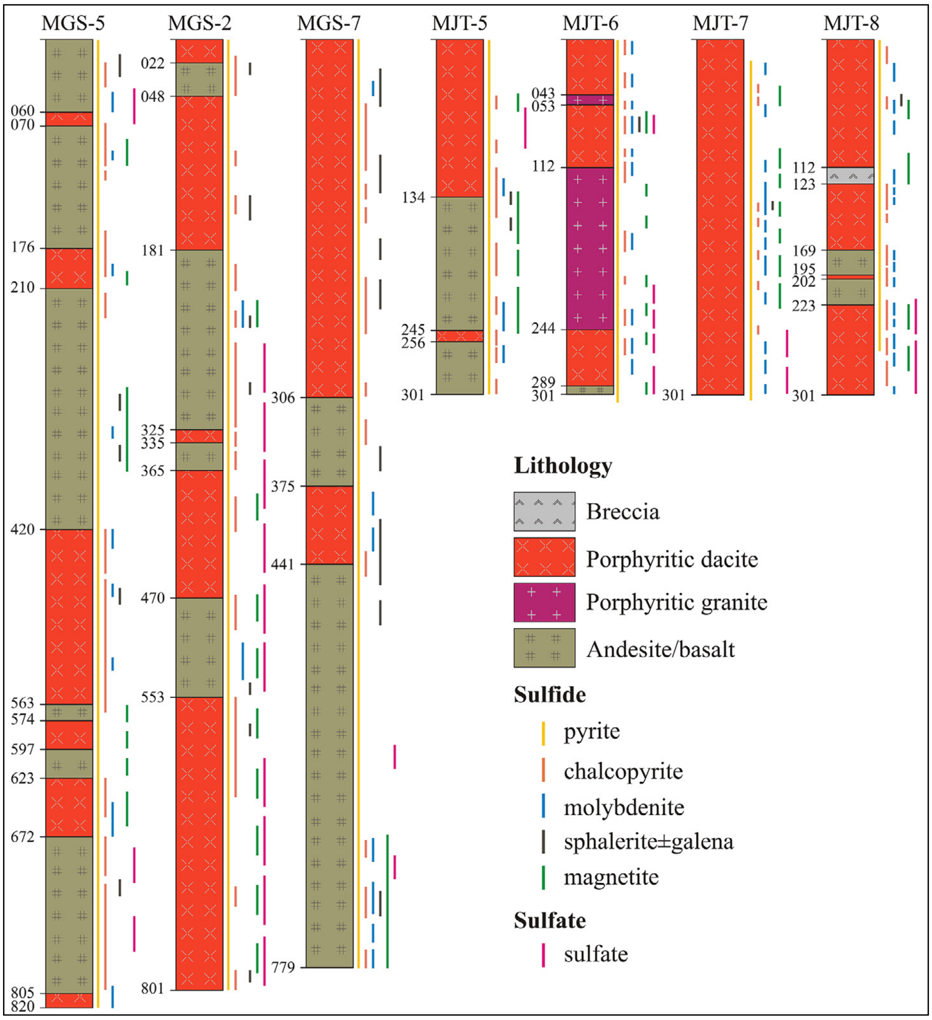

Figure 3- The main geological units and the distribution of some important related ore and gangue minerals in the representative drillings of the Güzelyayla Cu-Mo mineralization.

and potassic zone and is accompanied by very small amounts of hematite. Chalcopyrite increases towards the center of the mineralization. Molybdenite presents a distribution from the potassic zone to the propylitic zone. Sphalerite was observed in the potassic zone in the drillings. Pyrrhotite was identified as inclusions in chalcopyrites. Gold (3-7 microns in size) was identified in quartz. In microscopic examinations, it was observed that pyrite and chalcopyrite cut magnetite in many samples. Therefore, magnetite has been interpreted as one of the first minerals to form (JICA, 1986). Chalcocite, covellite and native copper were defined as secondary enrichments in the phyllic zone. Sulfate veins consisting of anhydrite and gypsum are commonly observed in the potassic zone and represent end-stage mineralization. The relationship between paragenesis and succession of porphyry Cu-Mo mineralization is given in Figure 5.

While carbonates (calcite and dolomite) are common in the near-surface sections of the mineralization, the abundance of sulfate (gypsum and anhydrite) veins is remarkable, especially in the deep (>400m) sections. The source of abundant sulfur in porphyry deposits is problematic because of the relatively low solubility of sulfur in felsic magmas compared to mafic magmas (Sinclair, 2007). The role of mafic melts in the contribution of excess sulfur to felsic magmas has been suggested (Hattori and Keith, 2001). It was also suggested that aqueous magmas might contain abundant oxidized sulfur dissolved as sulfate (or anhydrite) (Strect and Dilles, 1998).

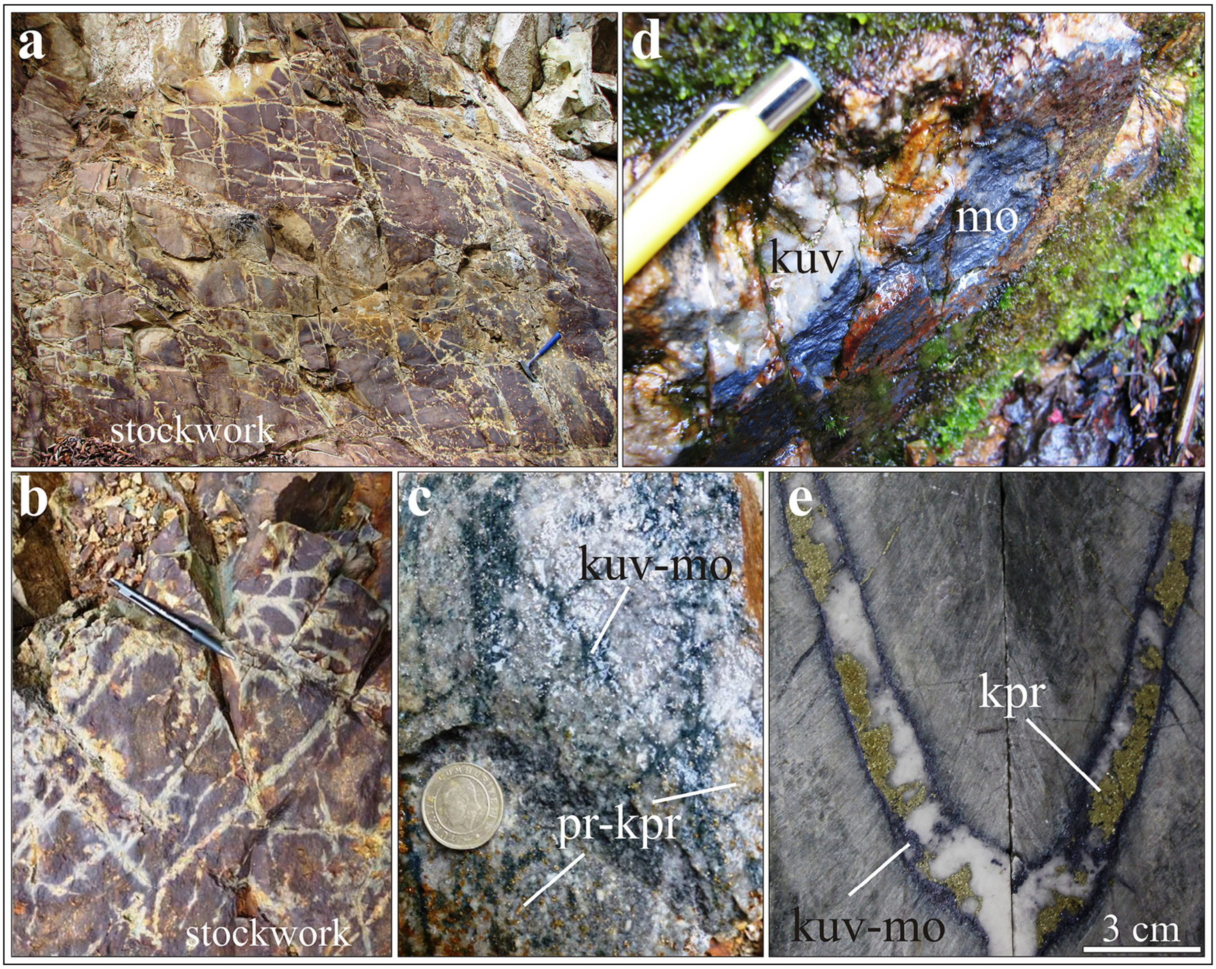

Figure 4- Mineralization types in the Güzelyayla Cu-Mo deposit; a) and b) quartz-pyrite-chalcopyrite stockwork zone developed in Late Cretaceous andesitic/basaltic volcanic rocks, c) disseminated sulfide (pyrite and chalcopyrite) and silicified mesh like sulfide (molybdenite) veins in the stockwork zones of porphyritic dacites, d) and e) late stage silicified sulfide (chalcopyrite and molybdenite) veins in porphyritic dacites. kuv-quartz; mo-molybdenite; pr-pyrite; kpr-chalcopyrite.

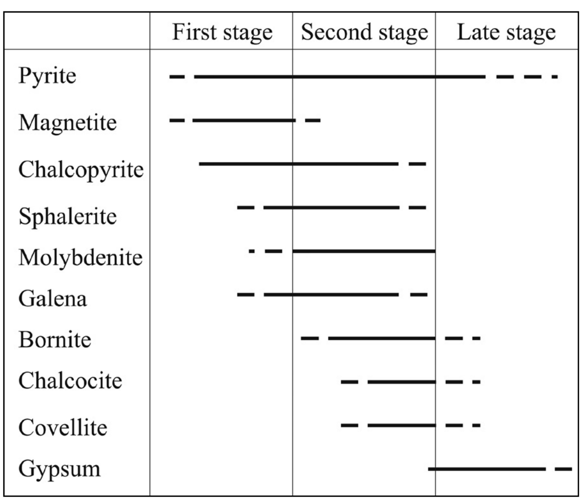

Figure 5- Paragenesis and succession relationship of the Güzelyayla Cu-Mo mineralization.

Alteration minerals are largely composed of sericite, chlorite, kaolinite, pyrophyllite, and montmorillonite. Sericite-rich rocks are defined as phyllic zone, chlorite-rich rocks as propylitic zone, and rocks containing K-feldspar and biotite as potassic zone (JICA, 1987). The alteration area covers an area of 1.8 km x 1.8 km (Figure 6).

The central parts of the porphyritic dacite have been affected by potassic alteration. In the potassic zone, where thin quartz veins are common, disseminated magnetite and biotite veins and a small amount of K-feldspar are observed. The potassic zone is cut by thin quartz and sericite veins. Anhydrite is abundant in the potassic zone (Figure 7a, b). The minerals of sericitic alteration overprint porphyritic dacite and volcanic rocks. Sericitic alteration is remarkable

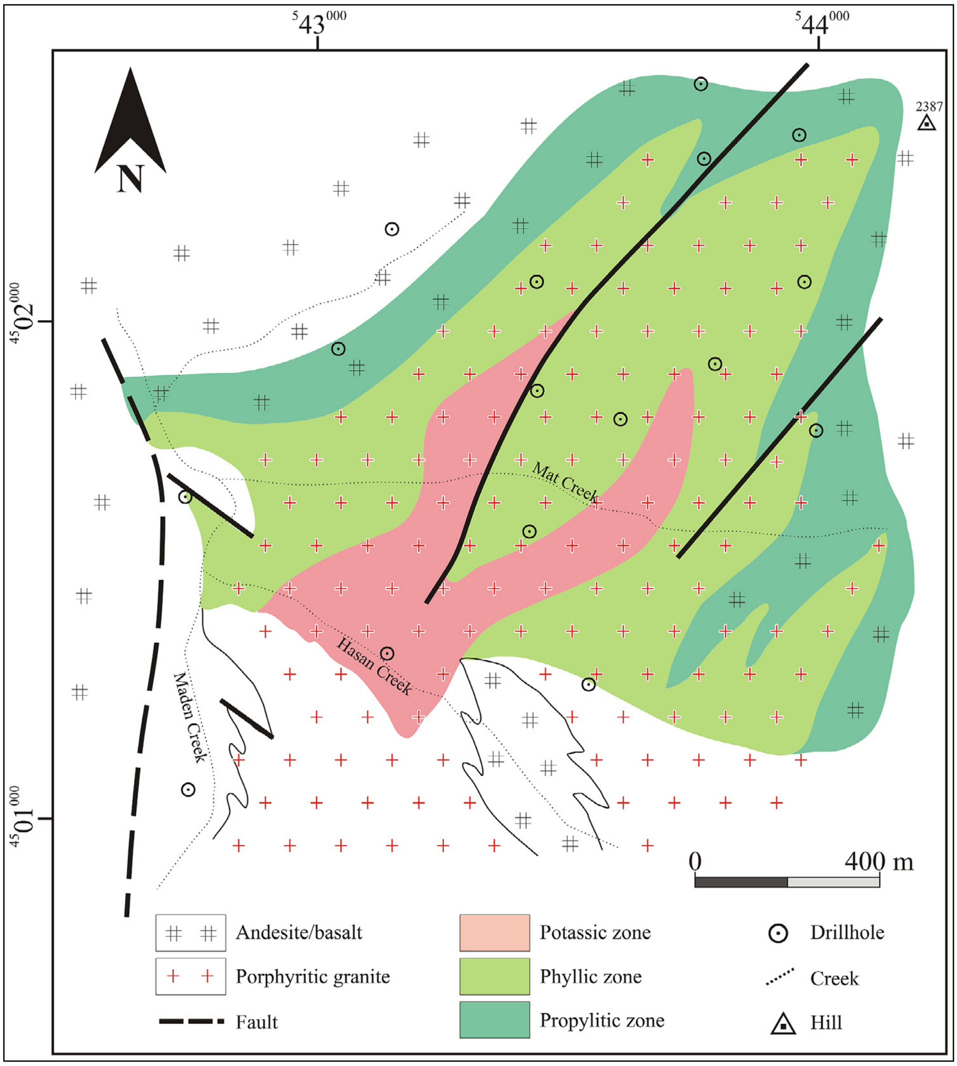

Figure 6- Alteration distribution map defined in the lithologies of the Güzelyayla Cu-Mo mineralization (modified from JICA, 1987).

with quartz, pyrite, sericite, and molybdenite veinlets (Figure 7c, d). The outermost propylitic alteration is more common in volcanic rocks. The propylitic zone contains chlorite, epidote, and magnetite. Pyritic quartz veins are common in the propylitic zone (Figure 7e, f). The argillic zone, which is characterized by kaolinite and montmorillonite, was observed only in the outer parts of the sericitic alteration zone in drillings. This alteration zoning pattern determined in the Güzelyayla Cu-Mo field is consistent with the potassic-phyllic-propylitic (from the center to the outer parts) concentric zoning adapted by Lowell and Guilbert (1970) for porphyry systems. Alteration zoning varying from the central potassic alteration to the propylitic alteration in the outer parts indicates that the physicochemical properties of the solutions constituting the Güzelyayla mineralization have changed gradually. The interaction of deep seated origin magmatic-hydrothermal solutions with host rocks of different permeability by rising and a decrease in the temperature and pressure of the solution are the determining features in the gradual change in the physical chemistry of ore solutions (Seedorff et al., 2005; John et al., 2010).

The geochronological (Re-Os) age of molybdenite in a quartz vein representing the stockwork zone in porphyritic dacites to reveal the formation age of the Güzelyayla porphyry system, was determined as 50.7 ± 1.0 million years (Delibaş et al., 2019).

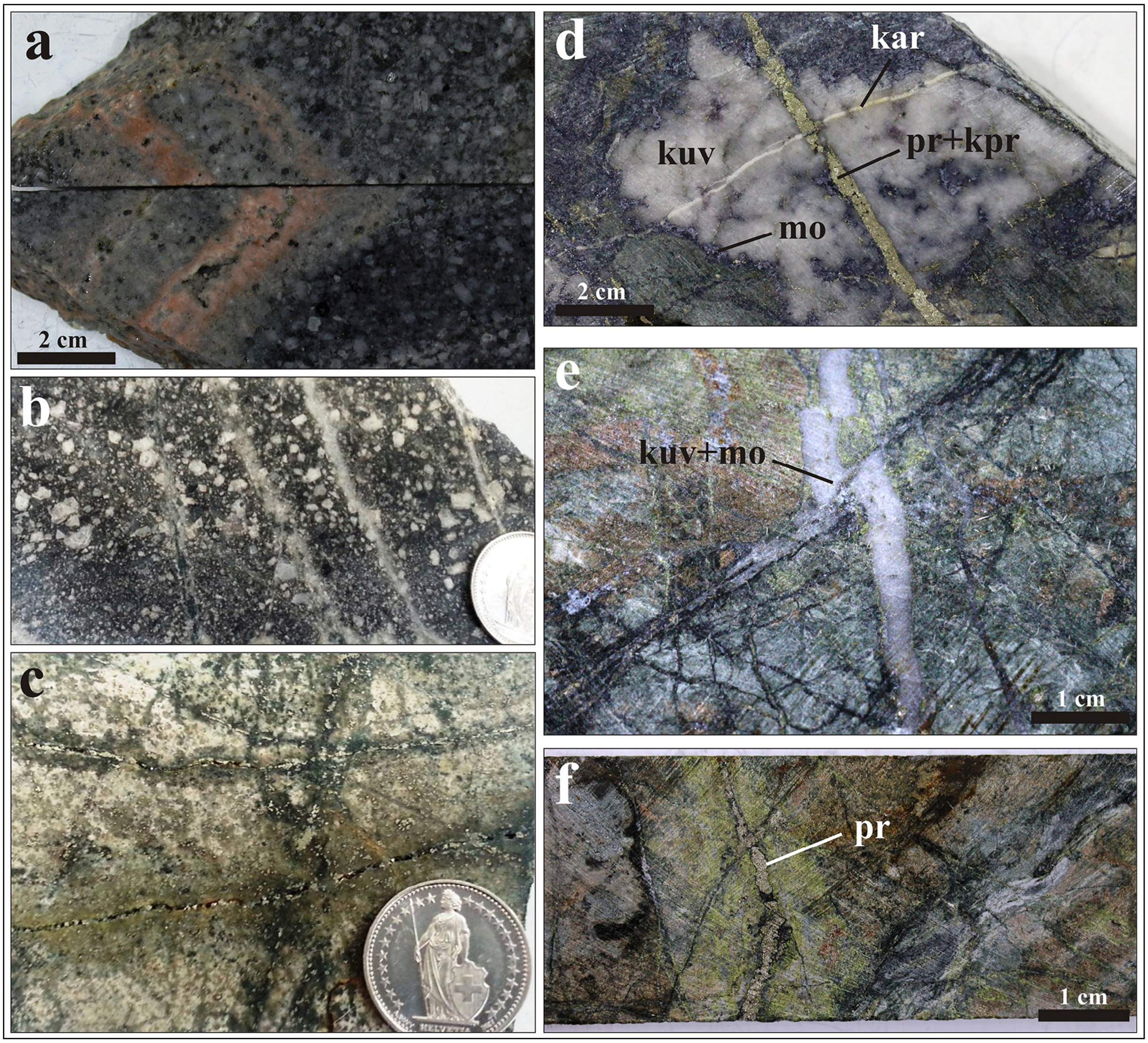

Figure 7- Some examples of alteration types identified in the Güzelyayla Cu-Mo mineralization; a), b) thin quartz and sericite veins that cut through the potassic alteration zone in porphyritic dacite, c), d) phyllic zone with veinlets of quartz, sericite, pyrite, and molybdenite in porphyritic dacite, e) ,and f) pyritic quartz veins observed widely as distributed in the propylitic zone of basaltic/andesitic volcanic rocks. kuv-quartz; mo-molybdenite; pr-pyrite; kpr-chalcopyrite; kar-carbonate.

4.4. Fluid Inclusion Studies

To determine the homogenization temperatures of the solutions, which are effective in the formation of the Güzelyayla Cu-Mo mineralization, fluid inclusion studies were carried out in two quartz veins containing sulfide representing the stockwork zones in the ore-bearing intrusive rocks. A fluid inclusion study was carried out on quartz crystals. Primary two-phase (liquid and gas) inclusions were determined in these crystals. Inclusions are generally rod-like, polygonal and irregular in shape, and their size varies between 2 and 60 microns. Most inclusions are smaller than 20 microns. The homogenization temperatures (Th °C) obtained as a result of microthermometric measurements made in two-phase inclusions are presented as histograms (Figure 8a). Homogenization temperature values range from 324 °C to 420 °C (average 374 °C). Salinity values vary between 2.2 and 18.6% NaCl equivalent (average 9.1% NaCl) (Figure 8b). A total of 1004 fluid inclusions were measured from 50 samples collected from quartz veins and quartz phenocrysts in porphyritic granites and dacites and andesite/basalts in fluid inclusion studies conducted within the scope of JICA-MTA cooperation (JICA, 1986). The majority (90%) of the measurement results are clustered between 350 °C and 450 °C. Salinity values vary between 4.8 and 20.6% NaCl equivalent. Yalçınalp (1992) made a total of 209 measurements from 37 samples taken from porphyry dacite and andesitic/basaltic rocks in his doctorate study. It is observed that most of the measurement results (more than 90%) are clustered between 280 °C and 460 °C. It is observed that the fluid inclusions (homogenization temperatures and salinity) values obtained from this and previous studies are quite compatible. The formation temperatures of the Güzelyayla mineralization indicate a porphyry type formation. When a large number of fluid inclusion microthermometric measurement data compiled from porphyry systems on a global scale were examined, it was concluded that the homogenization temperatures and salinity values of ore solutions were concentrated in three fields (Titley, 1993). Condensation fields are observed to vary from high salinity magmatic waters (Type I) to low temperature and salinity solutions diluted with meteoric waters (Type II and Type III). Hypersaline solutions with more than 30% NaCl equivalent salinity and homogenization temperature greater than 650 °C are defined as Type I. High salinity solutions with homogenization temperature between 350 °C and 550 °C are defined as Type II, and dilute solutions with less than 20% NaCl equivalent salinity and temperatures below 450 °C are defined as Type III (Figure 8b). It can be said that these fluid inclusion data compiled on a global scale are compatible with a scenario where the porphyry system includes solutions diluted by meteoric waters as it cools. When the homogenization temperatures and limited salinity values of Güzelyayla mineralization are examined, we can say that the solutions forming the mineralization are composed of dilute solutions (Type III) at relatively low temperatures. The available data indicate that the contents of ore solutions are not entirely of magmatic composition and that meteoric waters are involved.

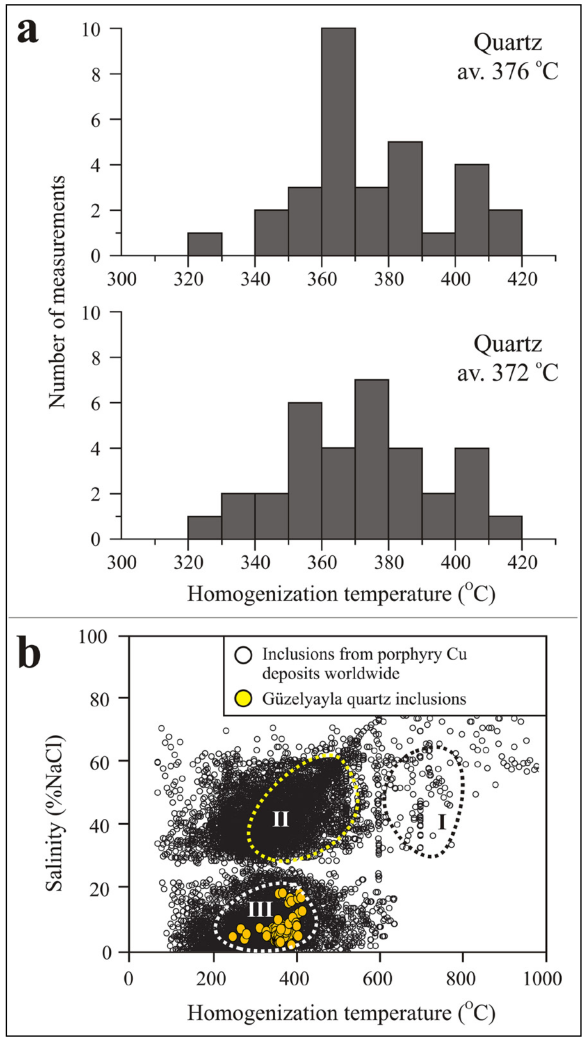

Figure 8- a) Homogenization temperature (°C) diagrams of fluid inclusions in two representative quartz samples compiled from the ore-bearing zones of the Güzelyayla Cu-Mo deposit and b) comparative presentation of the Güzelyayla Cu-Mo mineralization fluid inclusion data in the diagram (modified from Titley, 1993 and Bodnar et al., 2014) of hydrothermal solution type formed from homogenization temperatures and salinity values compiled from porphyry type deposits. Areas I, II and III correspond to areas where homogenization temperatures and salinity values are concentrated, compiled from porphyry systems on a global scale by Titley (1993).

4.5. Geostatistical Evaluation of Numerical Data of the Güzelyayla Porphyry Cu-Mo Mineralization

Geostatistics constitutes the whole of the methods used in the arrangement, presentation and interpretation of the obtained numerical data. The main task of geostatistics is to organize the counting and measurement results in an easily understandable way and to extract information about the mass by making use of the variability in the common features of the objects that constitute a mass (Tüysüz and Yaylalı, 2005; Tütek and Gümüşoğlu, 2008). Statistically, the most useful data is the normal distribution, where the data distribution is symmetrically distributed around the arithmetic mean. However, ideal distributions are not always achieved although many methods are used to approximate the normal distribution of values. This is one of the most common problems for geochemistry data. In such a case, appropriate and practical methods are used in calculating the threshold value to reduce the effect of extreme values.

4.5.1. Geochemical Prospection

Geochemical sampling studies were carried out to reveal the existence and distribution of metal mineralizations in a wide area including Güzelyayla mineralization. In the region with a size of approximately 114 km^2, a total of 160 stream sediment samples were taken and analyzed, with 1 sample per 0.7 km^2 area. In the analysis, the detection limit was determined as 3 ppm for Cu (copper) and Zn (zinc) elements and 5 ppm for Pb (lead). Obtained results were subjected to descriptive statistics. The table of descriptive statistics parameters of Cu, Pb and Zn elements is presented below (Table 1).

The obtained data should conform to or be close to the normal distribution (Hawkes and Webb, 1962). It was visually and mathematically tested whether the distribution of the data conformed to the normal distribution. Descriptive statistical parameters (mean, median, maximum, minimum, etc. values) were created for mathematical tests, and histograms, line and box plots were created for visual tests. In the descriptive statistics table, the mean, median, maximum, minimum and standard deviation values of each element of the samples were given in the 95% confidence interval. Other descriptive statistical data in the table are measures of skewness and kurtosis. These values are decisive in evaluating whether the data show a normal distribution or not. In an ideal normal distribution, the mean and median should be equal, and the skewness and kurtosis coefficients should be zero. If the mean skewness coefficient of the elements is in the range of ±2, the distribution is considered to be normal. If the mean is greater than the median, the distribution of the data is skewed to the right (positive), and the distribution of the data is skewed to the left (negative) if the mean is less than the median (Tüysüz and Yaylalı, 2005; Güriş and Astar, 2015). The data are skewed to the right since the mean of the elements in the area where the Güzelyayla mineralization is located is greater than the median, and they do not present a normal distribution as the skewness coefficients are outside the range of ±2 (Figure 9a). Kurtosis, on the other hand, is a parameter that shows how steep or flat the curve is in a normal distribution. In normal distribution, the kurtosis coefficient is zero. If the kurtosis coefficient is positive, the curve is steeper than the normal and flatter than normal if it is negative (Tüysüz and Yaylalı, 2005; Güriş and Astar, 2015). Since the kurtosis coefficient

Table 1- Descriptive statistical parameters of Cu-Pb-Zn elements in the stream sand samples collected from the Güzelyayla Cu-Mo mineralization and its immediate surroundings.

Element	Cu	Pb	Zn
Number of Sample	155	155	155
Minimum	7.0	5.00	21.00
Maximum	986.00	164.00	501.00
Mean	67.76	27.16	100.64
Median	42.00	20.00	90.00
Standard Deviation (SD)	102.35	19.42	56.78
Coefficient of Variation	0.14	0.71	0.56
Skewness	6.19	2.76	3.01
Kurtosis	47.95	14.91	16.03
Mean+2SD	272.47	66.00	214.22
Median+2MMS	138.60	103.92	71.40
% 25 (weighed average)	30.00	14.00	69.00
% 75 (weighed average)	84.00	40.00	123.00
% 95 (weighed average)	172.00	60.00	204.00

AMD: Absolute Median Deviation.

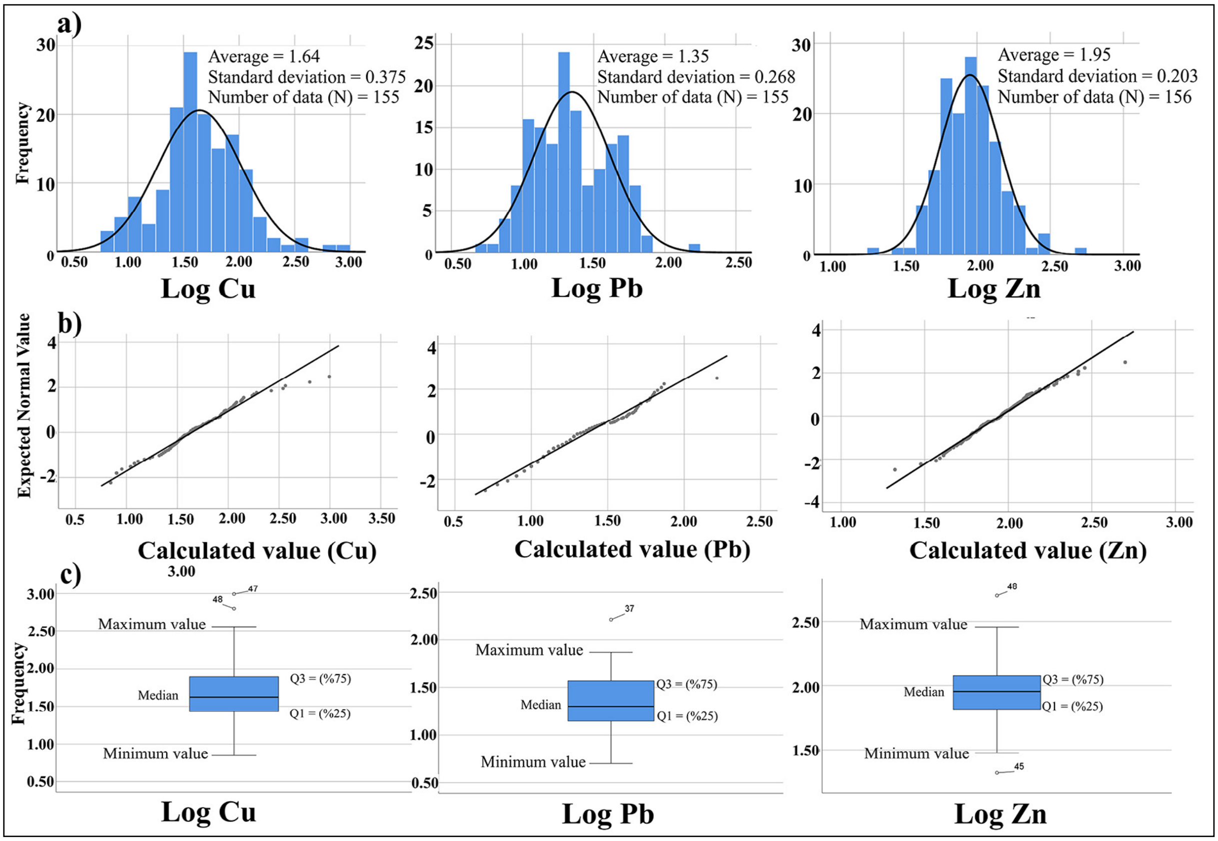

Figure 9- Visual tests of descriptive statistical data of Cu-Pb-Zn elements in the stream sand samples collected from the Güzelyayla Cu-Mo mineralization and its immediate surroundings; a) log normal distribution histograms for Cu, Pb and Zn elements, b) Q-Q diagrams for Cu, Pb and Zn elements, and c) log normal box plots for Cu, Pb and Zn elements.

of the data in the region is positive, the curve is steeper than normal.

It was also observed visually with the help of graphics whether the data set conforms to the normal distribution or not. Visual evaluation of the distributions of the samples, histograms (normal, log normal) and Q-Q (normal, log normal) and box (normal, log normal) diagrams of Cu, Pb and Zn elements subjected to descriptive statistics within 95% confidence interval were made. However, since the normal histograms of the elements do not show a normal distribution, log normal histograms, Q-Q lines and box diagrams were used to approximate the data to the normal distribution in this study. When the histogram diagrams created by taking the logarithmic values of the data belonging to Cu, Pb and Zn elements were examined, it was seen that the right-skewed data mostly approached the normal distribution, but they did not form an ideal normal ensemble (Figure 9b). A normal probability graph is also used while performing normality analysis of data. If the samples are taken from a normally distributed stack, the values should be collected on or around a line (Kalaycı, 2006). In the log normal Q-Q diagrams of the field data, it was observed that the values of the sample populations were mostly gathered on or around a line, but did not form an ideal normal community.

Another convenient way to graphically represent groups of numerical data across their quartiles is box plots (Tukey, 1977). Box plots are used to summarize the distribution pattern of the data set, its central tendency, level of dispersion, kurtosis and skewness, and to identify outliers. With the help of this chart, the asymmetry, clustering and extreme values of the data are also easily defined (Tüysüz and Yaylalı, 2005). The line passing through the middle of the box represents the median value. The bottom of the box is the first quartile (Q1) and the top is the third quartile (Q3). The first quarter part in the box covers 25% of the data, the second quarter part covers 50% (median) and the third quarter part covers 75% of the data. The lines drawn out of the box at the top and bottom of the box are created by extending the data up to 1.5 times the minimum (smallest value without extreme or outlier) and maximum (highest value without extreme or outlier) values (Reimann et al., 2005). It was investigated whether the data groups presented a normal distribution by creating log normal box plots of the elements subjected to descriptive statistics (Figure 9c). When the log normal box plots of the data of Cu, Pb and Zn elements are examined, it is observed that the data is skewed to the right because the line passing through the median values of the elements is closer to the minimum values of the elements, except for the log normal Zn boxplot in the log normal box plots of the elements of the log normal raw data. In the log normal box diagram, the values of Cu (2 samples), Pb (1 sample) and Zn (1 sample) elements fell to the outlier region above the maximum values, and the Zn (1 sample) element fell to the outlier region below the minimum value.

In summary, element distribution maps for Cu, Pb and Zn were created in the relevant region and anomalies were determined with the data obtained by evaluating the data sets created with the geostatistical method with the results of the stream sediment analysis of an area including the Güzelyayla mineralization (Figures 10, 11, 12). Element distribution maps are the most common and final data evaluation step in the evaluation of data in mineral exploration studies. In the creation of element distribution maps, the Inverse Distance Weighting (IDW) interpolation method of deterministic models was used. IDW is the inverse weighting of the distance between the anchor points and the point to be estimated. This method is the easiest deterministic interpolation method. To estimate the value at any unmeasured point, the IDW uses measured values near the point to be estimated. The effect of the measured values closest to the point whose value is desired to be found is more effective than the ones far from the investigated point. Therefore, it was aimed to obtain large weights from points that are close to each

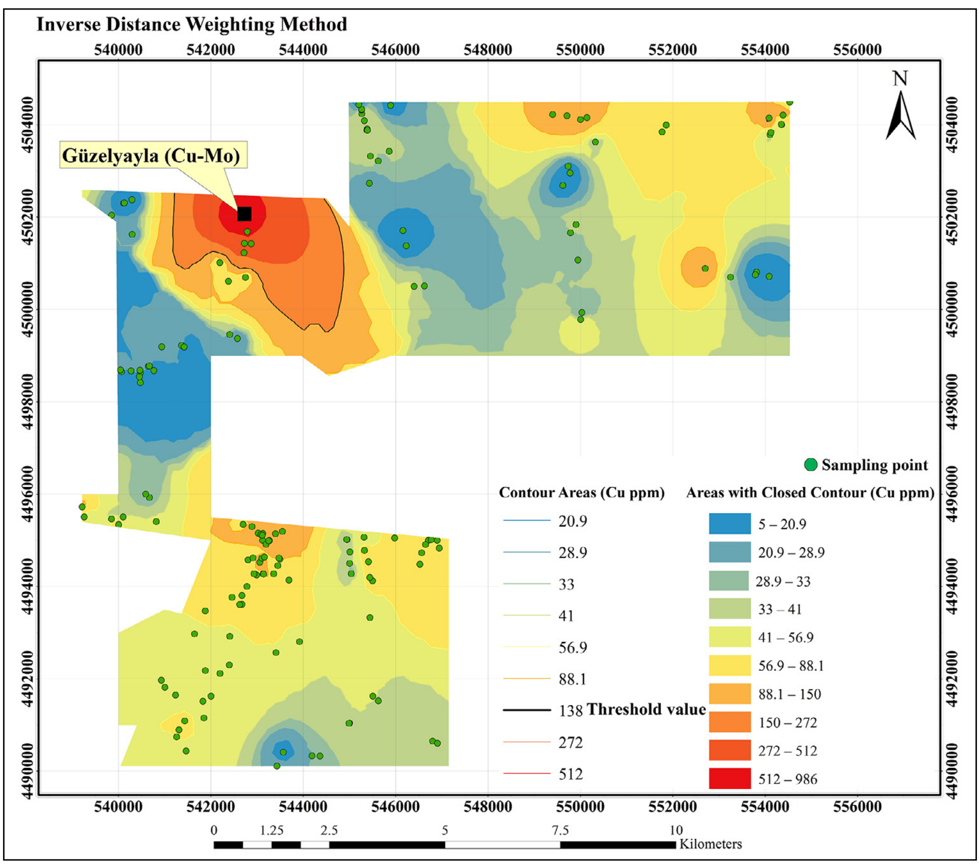

Figure 10- Cu metal anomaly map of the Güzelyayla mineralization and its surroundings, created by stream sediment geochemistry.

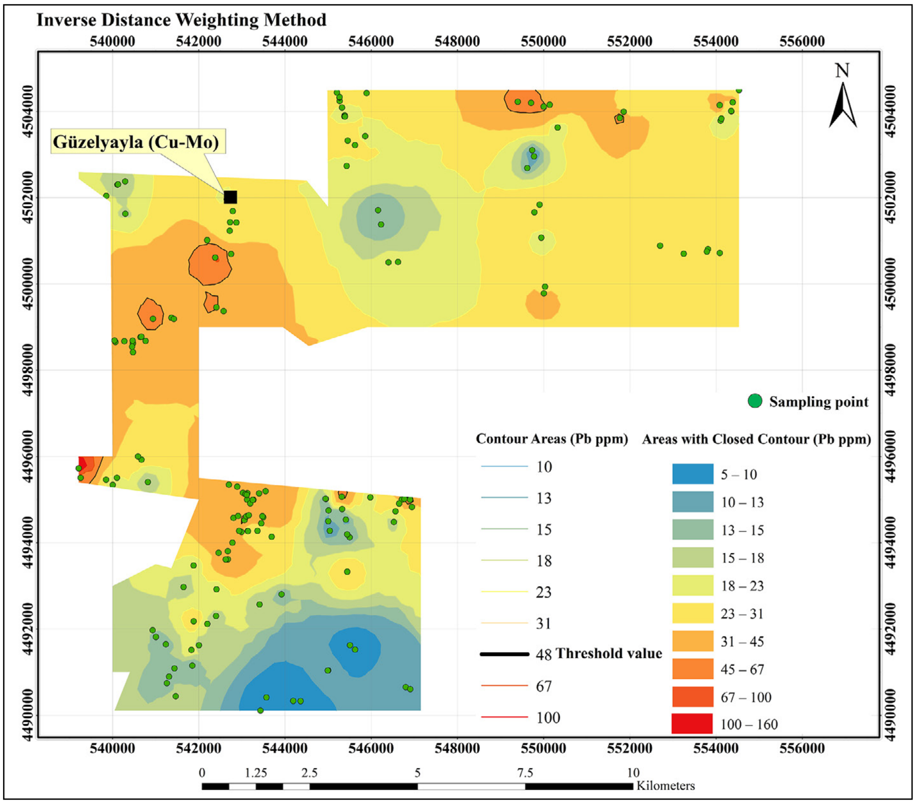

Figure 11- Pb metal anomaly map of Güzelyayla mineralization and its surroundings, created by stream sediment geochemistry.

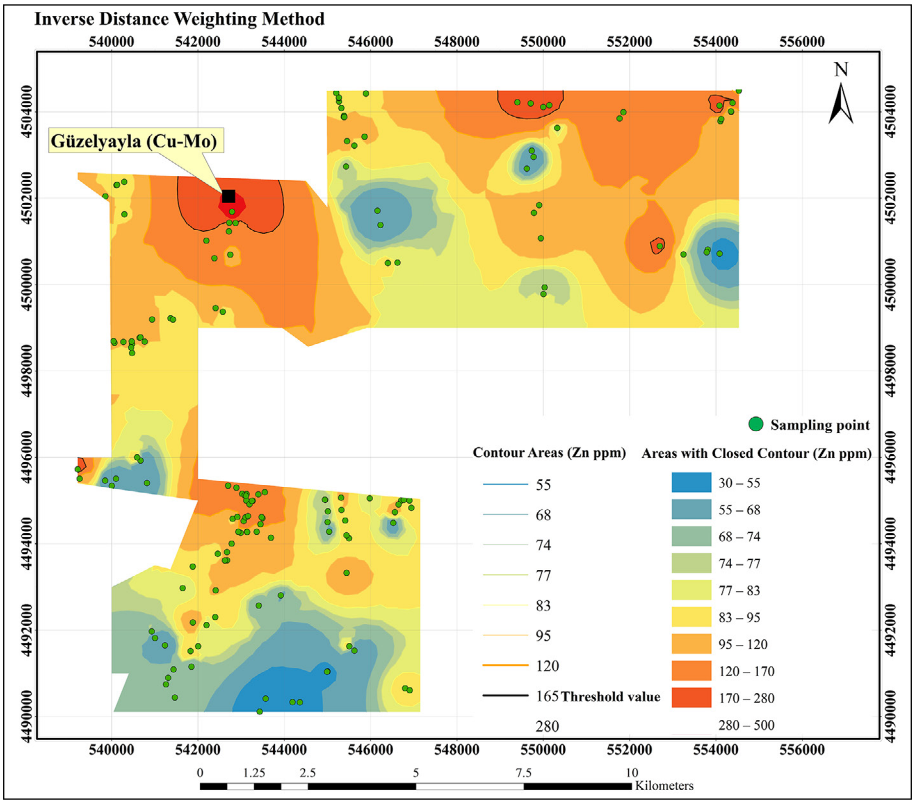

Figure 12- Zn metal anomaly map of Güzelyayla mineralization and its surroundings, created by stream sediment geochemistry.

other and to obtain small weights from points that are far from each other.

4.5.2. Mineral Resource Estimation

Geological and analytical data of core drillings were used in mineral resource estimation studies of the Maçka-Güzelyayla field. Within the scope of this study, mine resource estimation studies using data compiled from 16 core drillings (Table 2) made in previous years are based on 3D block modeling principles. While the majority of the cores belonging to the drillings carried out within the scope of this study were sampled as 1 meter, sample intervals of 3 meters were preferred for the drillings of previous years and the intervals considered to be without ore were not sampled. Alphanumeric data entries (< detection limit value) denoting ranges with a grade lower than the detection limits are assigned as half of the detection limits. The summary statistical parameters prepared for the raw data collected from the Güzelyayla field and obtained as a result of the detailed search studies are given in Table 3.

The linear correlation coefficients prepared by considering the analysis data of 12 elements in the Güzelyayla field drilling database are given in the linear correlation matrix in Table 4. In the correlation matrix, a weak to moderate positive correlation was observed between lead-zinc (r: 0.43), silver-zinc (r: 0.36), nickel-cobalt (r: 0.61), antimony-arsenic (r: 0.56), silver-antimony (r: 0.37) and vanadium-nickel (r: 0.56). A weak positive correlation was observed between the other elements.

Analytical data to be taken as a basis in modeling were obtained by creating a composite sample from the raw data of the field. While forming the composite sample, the sample length was determined as 2.5 meters, taking into account the vertical block size determined for the planned block model. Step compositing algorithm was used in the composite sample process and geological contacts were taken into account. Summary statistics for target metals (Mo and Cu) of 3023 composite samples created by this method are shown on the histograms presented in Figure 13, along with relative frequency graphs. Similar to raw data statistics, the histograms of shared composite data for Cu and Mo elements show rightward (positive) skewness. Grade distribution observed in composite and raw data is frequently encountered in porphyry type mineralizations.

Table 2- The summary presentation of the information about the drillings made in the Güzelyayla Cu-Mo deposit is given together with the analysis numbers used in the mine resource estimation studies.

Drilling no	Drilling year	Number of sampled well	Total Depth	Sample number		
				Mo	Cu	Ag, As, Au, Bi, Co, Ni, Pb, Sb, Zn, V
MGS	MTA - 2018 (this study)	7	4909	4909	4909	4909
MGT	MTA - 1990	4	3653	369	369	–
MJT	JICA - 1986	5	2508	504	504	–
Total		16	11070	5782	5782	4909

Table 3- Summary statistics of raw data obtained from Güzelyayla Cu-Mo deposit.

Element	Ag	As	Au	Bi	Co	Cu	Mo	Ni	Pb	Sb	V	Zn	Cu_{eq}
Sample Number	4909	4909	4909	4909	4909	5782	5782	4909	4909	4909	4909	4909	5782
Minimum	0.5	1.5	10.0	2.5	2.5	1.5	0.0	2.5	2.5	2.5	2.5	1.5	4.0
Maximum	31	1641	300	100	78	15683	10800	109	7276	156	182	4458	48531
Median	0.5	1.5	10	2.5	8.0	443.0	18.0	6.0	6.0	2.5	18.0	55.0	564.2
Mean	**0.6**	**6.1**	**10.9**	**5.5**	**10.1**	**578.8**	**43.9**	**12.5**	**23.9**	**3.3**	**27.3**	**133.6**	**772.2**
Standard Deviation	0.9	32.1	8.9	9.0	6.7	591.1	260.4	17.1	137.9	5.1	25.7	263.5	1320.7
Coefficient of variation	1.33	5.27	0.81	1.62	0.66	1.02	5.93	1.37	5.77	1.52	0.94	1.97	1.71

Table 4- Correlation matrix of 12 elements in drillhole database of the Güzelyayla Cu-Mo prospect.

Element	Ag	As	Au	Bi	Co	Cu	Mo	Ni	Pb	Sb	V	Zn
Ag	1	0.26	0.15	0.07	0.08	0.24	-0.01	-0.04	0.23	0.37	-0.03	0.36
As		1	0.05	0.02	-0.02	0.22	0.02	-0.04	0.02	0.56	-0.08	0.11
Au			1	0.02	0.06	0.23	0.00	-0.01	0.09	0.04	-0.04	0.07
Bi				1	-0.03	-0.01	0.02	-0.11	0.02	0.06	-0.10	0.08
Co					1	0.35	0.02	0.61	-0.03	0.01	0.66	0.01
Cu						1	0.05	0.15	-0.02	0.13	0.10	0.03
Mo							1	0.04	-0.01	0.02	0.00	-0.04
Ni								1	-0.05	0.00	0.56	-0.06
Pb									1	0.01	-0.06	0.43
Sb										1	-0.06	0.02
V											1	-0.01
Zn												1

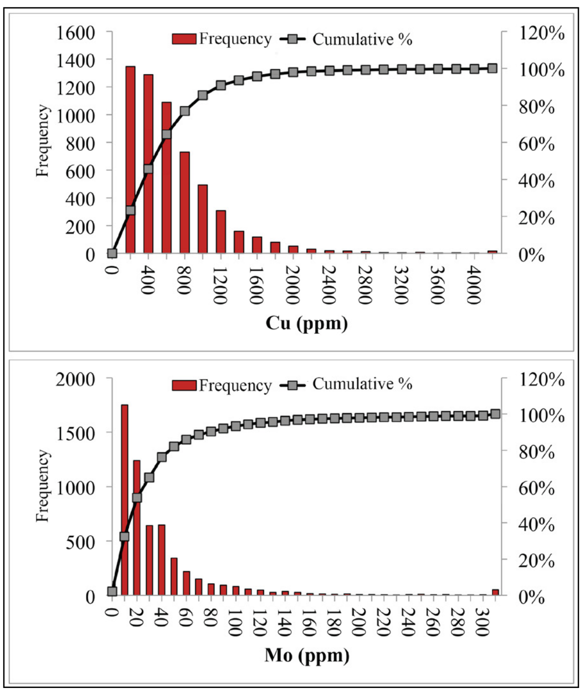

Figure 13- Composite data statistics for copper (Cu) and molybdenite (Mo) metals in the Güzelyayla mineralization.

For mineral resource estimation, 3D estimation zone models were created and by the price and metallurgical recovery assumptions made for the target metals, the copper equivalent formulation was determined as [Cu equivalent grade (%) = Cu (%) + (4.4 x Mo (%))]. In the NW-SE directional sections determined by considering the distribution of the boreholes and the ore geometry, Cu equivalent grades equal to or higher than 0.15% were digitized. For the specified component of the Güzelyayla mineralization with the expectation of final economic extraction, the open pit boundaries determined by the Lerch-Grossman algorithm and the economic limit grade in copper equivalent (0.15% Cu equivalent grade) were taken into account.

As a result, 54.2 million tons of deduced/potential mineral resources with an average grade of 0.2% Cu and 0.014% Mo (0.26% Cu equivalent grade) were estimated in the Güzelyayla field by creating predictive zone models.

5. Results

The mineral deposit types associated with the closure of the Tethys oceanic basins are volcanogenic massive sulfide deposits, porphyry type Cu±Mo±Au deposits and epithermal type Au±Cu deposits. These deposits were formed as a result of subduction, collision and post-collision events, and the characteristics of the magmas with which they are associated are important in determining these processes. Among these deposits, especially porphyry type deposits are decisive in the explanation of the tectonomagmatic processes specific to the environment in which they were formed. Porphyry type formations in Tethys orogen were formed in four periods; Early Mesozoic (Triassic-Jurassic), Late Mesozoic (Cretaceous), Paleogene and Neogene periods (Richards, 2014). Except for a few deposits, no significant porphyry type mineralization associated with the Paleozoic subduction is known. Its absence during the Paleozoic period can be explained by a later erosional removal of the deposits formed early. A large number of porphyry and associated epithermal deposits were described in the Cretaceous period. The most productive period throughout the generation is the Paleogene period. Porphyry deposits of the Paleogene period are associated with subduction (like Türkiye and Iran) or collision (Balkans, Carpathians and Tibet). Neogene deposits formed in the belt (Romania, Greece, Türkiye, Iran and Tibet) have been associated with post-subduction processes (Richards, 2014). Porphyry Cu-Mo systems in the Eastern Pontides, which are part of the Tethys belt, are typically interpreted as Early Cretaceous–Eocene (Soylu, 1999; Yiğit, 2009; Kuşcu et al., 2019; Delibaş et al., 2019). Recent studies (Kuşcu et al., 2019; Delibaş et al., 2019) indicate that the host rocks, including porphyry type mineralizations in the Eastern Pontides, were formed in an arc environment shaped by the subduction of the Neotethys ocean during the Cretaceous period. The ore formation ages of these deposits largely correspond to the Cretaceous period, except for the Güzelyayla mineralization. In the Güzelyayla area, the mineralization-related intrusions have been interpreted as the products of arc magmatism associated with the northward subduction of Neotethys subducting under the Eurasian plate (Delibaş et al., 2019). The age of the porphyritic dacites (LA-ICP-MS U-Pb zircon age 81.4 ± 1.1 million years) and andesitic/basaltic volcanic rocks in which the Cu-Mo mineralization in Güzelyayla is found was determined as Late Cretaceous (Güner and Güç, 1990; Delibaş et al., 2016). However, the hydrothermal system in the Güzelyayla field was formed later from Late Cretaceous porphyritic dacite host rocks, unlike other porphyry-type deposits in the region, and corresponds to the Eocene period (molybdenite Re-Os age 50.7 ± 0.3 million years) (Delibaş et al., 2019). Although the porphyry type mineralization formed during the Eocene period in the Tethys orogeny was considered to be associated with subduction and collision processes (Richards, 2014), the Güzelyayla mineralization was accepted to be associated with post-collisional processes in recent studies (Delibaş et al., 2019). In addition, it has been suggested that the Güzelyayla hydrothermal system was formed in a tectonic environment that offers a transition from compressional to the extensional regime in a magmatic arc environment (Delibaş et al., 2019).

A large number of hydrothermal activities accompanied the Cretaceous and Eocene magmatism, which emerged with the geodynamic evolution processes of the region, and caused the formation of important mineralizations. The Güzelyayla Cu-Mo mineralization, which represents one of these mineralizations, is a part of a polycentric Cu-Mo system. The mineralization is Cu-Mo mineralization associated with andesitic/basaltic volcanic rocks and porphyritic dacite intrusives cutting these rocks. The Güzelyayla Cu-Mo occurrence is mineralization developed in the stockwork and fault-controlled silicified zones. When the ore types were examined structurally and texturally, it was evaluated that the mineralization developed in roughly three main phases. The first mineralization stage is represented by copper - magnetite - (±molybdenite) - containing dissemination, veinlet and brecciated zones and is associated with intense silicifications accompanied by potassic alteration. The second stage of mineralization is Cu-Mo-(±Zn-Pb) containing veins and associated with potassic and phyllic alterations. The last stage is represented by late stage sulfate veins that cut through the whole system and is common in areas with potassic alteration. Mineral contents indicate that solutions at high temperatures initially decrease in temperature over time. When the country rock lithology, alteration features, metal content, mineralization stages and solution temperatures are evaluated together, the Güzelyayla mineralization is a porphyry Cu-Mo type formation. It would not be wrong to say that the solutions forming the Güzelyayla mineralization are composed of dilute solutions at relatively lower temperatures when compared to their global counterparts. The Güzelyayla occurrence is mineralization formed in the Upper Cretaceous volcanic rocks during the Eocene (50.7 ± 1.0 million years) period. This age value is not compatible with the LA-ICP-MS U-Pb zircon age (81.4 ± 1.1 million years) of the porphyritic dacites in which the mineralization occurs. This indicates that the Güzelyayla porphyry Cu-Mo mineralization was formed much later than the host rocks in which it was formed.

Metal anomaly maps, created with systematic and detailed stream sediment geochemistry data, have been a decisive method in determining the type of ore system in the region and the selection of the Güzelyayla Cu-Mo occurrence and mineralizations in its vicinity as target sites.

The existence of potential in the field has been demonstrated numerically with statistical methods prepared by creating a large number of descriptive statistical parameters of the obtained data. Contrary to previous studies, estimation zone models were created and an estimated 54.2 million tons of extracted/potential mineral resource with an average grade of 0.20% Cu and 0.014% Mo (0.26% Cu equivalent grade) was made in the Güzelyayla field. These determining grade and source values are in the range of values predicted for porphyry systems.

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