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# ALTERATION ZONES ASSOCIATED WITH EOCENE MAGMATISM IN THE OLUR (ERZURUM) **AREA, EASTERN PONTIDES AND THEIR SIGNIFICANCE**

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The Alpine Orogenic Belt with numerous porphyry Cu-Mo-Au mineralizations, starts from Eastern Europe continues through Turkey and the Caucasus and extends into Iran and Afghanistan. The study area of the Eastern Pontides is in this orogenic belt. Using field and laboratory studies an attempt has been made to establish the origin of Yeşilbağlar, Kaban and Köprübaşı alteration zones in the Olur area (Erzurum). In the study area Early Eocene Coşkunlar volcanics and sub volcanic rocks have contact with the Oltu çayı volcanics of Early-Middle Jurassic. Alteration in the study area effects these Oltuçayı and Kaban volcanics. In the study area mineralizations are present in the alteration zones. Disseminated, stockwork, vein/veinlet and fissure type mineralizations are present in the Coşkunlar dacite. Paragenesis in the alteration zones are pyrite, chalcopyrite, sphalerite, galena, pyrrohotite, quartz, calcite and barite. FT-IR and XRD studies showed the presence of clay, sulphate, sulphur, carbonate, silicate and oxide minerals in the alteration zones. Field and petrographical studies showed that alteration types in the Yeşilbağlar, Kaban and Köprübaşı areas are, advanced argillicargillic, pyropylitic and sericitic. They are similar to the alterations present in the upper part of the mineralizations in the porphyry systems of the Alpine Orogenic Belt. In the Eastern Pontides starting in Early Jurassic, continuation of subductions resulted in closure of the İzmir-Ankara-Erzincan ocean and in Early Eocene the Taurid platform collided with the Eurasian active continental margin. Data from Received Date: 27.02.2017 the study area indicate the presence of alteration zones in the upper part of the buried porphyry system Accepted Date: 11.04.2017 and the possibility of mineralized parts in the deeper parts of the system.

**1. Introduction** 

The base metals and precious metals of the Eastern Pontides have for a long time drawn the attention of earth scientists (a) Geological evolution of the İzmir-Ankara-Erzincan suture zone in particular and it's continuation to the East Minor Caucasus are especially important (Okay, 1984; Evans and Hall, 1990; Okay and Sahintürk, 1997; Yılmaz et al., 1997; Okay and Tüysüz, 1999; Yılmaz et al., 2000; Hakyemez and Konak, 2001; Konak et al., 2001; Topuz et al., 2004; Okay et al., 2006; Rice et al., 2006; Konak and Hakyemez, 2008a; Rice et al., 2009; Rolland et al., 2009a, b; Çelik

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et al, 2011; Ustaömer and Robertson, 2010; Topuz et al., 2012; Ustaömer et al., 2012; Robertson et al., 2013), (b) Origin of Late Cretaceous massive sulphide deposits (Kraeff, 1963; Hirst and Eğin, 1979; Çağatay and Boyle, 1980; Akıncı, 1984), (c) Late Cretaceous-Eocene porphyry Cu deposits, (Cağatay and Cağatay, 1978; Aral and Erler, 1981; Er et al., 1995; Soylu, 1999; Singer et al., 2008; Yiğit, 2006, 2009; Oğuz, (d) Ophiolites and their emplacements along İzmir-Ankara-Erzincan suture zone (Rice et al., 2006, 2009; Özen et al., 2008; Colakoğlu et al, 2009, Sarıfakıoğlu et al., 2009; Parlak et al., 2013; Topuz et al., 2013). and in the Minor Caucasus (Galoyan et al., 2007, 2009; Rolland et

al., 2009*b*, 2010; Sosson et al., 2010), the formation and settlement of ophiolites is very important. The presence of metallogenic provinces along the Alpine Orogenic Belt has been described by scientists (Moore et al., 1980; Yiğit, 2006, 2009). The study area is located in the belt extending from the Macedonia-Balkans, Istranca belt in NW Turkey, then diving into the Black Sea, coming out near Sinop in Northern Turkey, it then continues along the coast of Northern Turkey to the Caucuses, into Iran and extending to the Himalayas. Along these belts porphyry copper and Kurokko type massive sulphide deposits are quite extensive.

The study area is located between Eastern Pontides and Torids in the northern part of the East Anatolia accretionary belt. The zone extends from the Balkans into Eastern Turkey along a West-East direction and then enters Iran. In this belt porphyry, copper and Krouko type massive sulphide deposits are quite extensive (Figure 1). The Alpine Orogenic Belt, in which the study area is located has Porphyry copper deposits in the active continental margins (Andes type) and porphyry deposits (Philippine type) forming the inner ocean island arc. Porphyry copper deposits in Bor, in Maydenpek (Yugoslavia), in Medet (Bulgaria), (Sar Çeşme) Shar Cheshme (Iran) are Andes type deposits developed in the active continental margins (Waterman and Hamilton, 1975; Hezarkhani, 2006; Singer et al., 2008). In Turkey Dereköy (Kırklareli, Bakırçay (Amasya) and Ulutaş-İspir (Erzurum) porphyry copper deposits display similar features of the Andes type deposits (Çağatay and Çağatay 1978; Jankovic 1977; Taylor, 1981; Ohta et al., 1988; Er et al., 1995; Soylu, 1999; Popov et al., 2002; Singer et al., 2008; Yiğit, 2006, 2009). Part of the Alpine Orogenic Belt between Samsun and Georgia is named as 'Pontide Metallogenic Belt' and forms 'Philippine type porphyry belt' (Çağatay and Çağatay, 1978).

Yeşilbağlar, Kaban and Köprübaşı (Olur, Erzurum) alteration zones, subject of this study are considered to be in the 'Eastern Pontide Metallogenic Belt' and are located within the Oltu imbricated zone. Metamorphic and sedimentary units outcropping along this zone belong to the rocks of the Olur Group within the Olur-Tortum zone (Figure 2), (Konak et al., 2001). Alteration zones extend East-West direction in the Southern part



Figure 1- Porphyry-Cu occurences along the Alpine orogenic belt and location of the study area (from Çağatay and Çağatay, 1978).

of Olur (Erzurum) (Figure 3). Yeşilbağlar alteration developed in Jurassic Oltuçayı volcanites and in the apophsis of the Early Eocene Coşkunlar dacites. Kaban and Köprübaşı alterations have developed in the Jurassic Kaban dacites and along the contact zone of the Cretaceous Soğukçam formation (Figure 3). All these alterations are believed to have generated from the quartz porphyries of the apophsis of the Early Eocene Coşkunlar dacites (Konak et al., 2001).

The aims of this study are (a) to prepare 1/5000 scale detailed geological map of the host rocks and

intrusive body in which mineralisations are associated and to gain more definite knowledge of the alteration zones, (b) to collect samples from the alteration zones and host rocks to study mineralogy and petrography of the units, (c) to conduct XRD (X-Ray Diffractometer) and FT-IR (Fourier Transform-Infrared Spectroscopy) studies to compute the mineralogy of the alteration zone, (d) to evaluate all of the findings together to be able to carry out regional scale correlations to find out the mineralogical deposit type to which the alteration zone is associated.



Figure 2- Simplified geological map of the tectonic units in the study area and surroundings (from Konak et al., 2001).



Figure 3- Geological map of the units in the study area and surroundings (Simplified from Konak ve Hakyemez, 2008a).

### 2. Regional Geology and Stratigraphy

The study area is located in the Sakarya zone (Okan and Tüysüz, 1999) of the eastern part of the Pontides (Ketin, 1966), forming the western extension of the Trans Caucasians and bound by the East Anatolia Accretionary Complex in the South (Şengör and Yılmaz, 1981). In the Eastern part of the Eastern Pontides, four different tectonic slices with NE-SW orientations, bound by tectonic zones have been identified (Konak and Hakyemez, 1996, 2001). These tectonic slices have been thrusted in South-North direction. From north to south these

tectonic slices are (a) Hopa-Borçka zone, (b) Artvin-Yusufeli zone, (c) Olur-Tortum zone and (d) Erzurum-Kars ophiolite zone (Konak and Hakyemez, 1996, 2001; Konak et al., 2001), (Figure 2). Hopa-Borçka zone is the autochthon units of the Eastern Pontides. Autochthon units mainly have fragments of Permian granites, Early Jurassic-Palaeocene covering units and Middle Eocene volcanics, detritic units (Konak and Hakyemez 2001; Ustaömer and Robertson, 2010; Konak and Hakyemez, 2008*a*, 2008*b*). Artvin-Yusufeli zonu overlay autochthon units with a tectonic contact. On the other hand, the zone consisting ArtvinYusufeli zone, Paleozoic basal metamorphic units, Late Paleozoic-Middle Jurassic sheeted dyke complex and Jurassic sedimentary and volcanic units have been described as 'Basal Tectonic Slice Complex' by Ustaömer and Robertson (2010). Further to the south Artvin-Yusufeli zone was overlain by Olur-Tortum zone with a tectonic contact. The zone in general has small outcrops of basal units, Middle Jurassic volcanics and Late Cretaceous-Early Senozoic volcanics and sedimentary units. This zone has been described as 'Upper Tectonic Slice Complex' by Ustaömer and Robertson (2010). Structurally Erzurum-Kars Ophiolite Zone overlying at the top forms tectonic slice in the further south. This zone in general has rocks of ophiolite suite, high pressure-low temperature (HP/ LT) metamorphics (blue schists) and Late Cretaceous-Palaeocene sedimentary rocks (Konak and Hakyemez, 2001; Ustaömer and Robertson, 2010). All these above mentioned tectonic-stratigraphic/magmatic units observed in the described tectonic zones in the further south, form haphazardly sliced thrust sheets along the southern part of the Tertiary volcano-sedimentary basin. This zone was named as Oltu Thrust Sheets Zone (OTSZ) by Konak et al., (2001).

In the area along the Oltu Thrust Sheets Zone, two different rock units of the Pre Jurassic basement form narrow tectonic slices. These tectonic units are mainly low grade metamorphics of the Kışla metamorphics and gneiss, amphibolite, metagabbro, metadiabase, metabasic like rocks heavily cut by metagranitic, pegmatitic, dioritic, tonalitic, dacitic and diabase dykes and veins of the Güvendik dyke complex. Relations of these rocks with each other are not clearly observed in the field (Konak et al., 2001) (Figure 3).

In the field Early-Middle Jurassic basic, intermediate and acidic lavas and pyroclastics over lay Güvendik dyke complex with a tectonic contact (Figure 3). Between Yeşilbağlar and Kötek Dağı (mountain) Oltucayı volcanites mainly consisting of andesites, basalts and in places dacitic lavas and pyroclastics have large areas of outcrops (Figure 4). In the upper levels of Oltuçayı volcanites, lens shaped epiclastic-sandstone-siltstone interlayers are present. In the East of Yeşilbağlar, in the Körübaşı and Coşkunlar areas Kaban dacite has large areas of outcrops (Figure 4). Contact relation of Oltuçayı volcanite with the Kaban dacite is considered to be transitional (Konak and Hakyemez, 2001; 2008a). Ramli formation of Dogger, mainly consisting andesitic lavas and fine grained sandstones in places interlayered with silicified pyroclastics transitionally overlay Oltuçayı volcanites (Konak et al., 2001). Ramli formation in the area extends about E-W direction in the Northern part of Kırdağ and Yeşlilbağlar and Yolgözler and Olurdere areas (Figure 3). Ramli formation with a possible unconformity is overlain by Oxfordian-Berriasian Olurdere formation (Yılmaz, 1985). The unit mainly consists of volcanic intermixed pebble stone, sandstone, siltstone and marl intercalations (Konak and Hakyemez, 2001, 2008a). Berriasian-Aptian (Early Cretaceous) Soğukçam formation (Altınlı, 1973) concordantly overlies Olurdere formation (Konak et al., 2001). It mainly consists of micrite and clayey micritic limestones and has chert bands and chert concretions in the upper levels. Soğukçam formation in the study area has outcrops along E-W direction to the North of Yolgözler, Yeşilbağlar, Olurdere and Kaban (Figure 3). Karacasu formation of Aptian-Santonian (Early-Late Cretaceous) concordantly overlay Soğukçam formation (Figure 4). The unit, mainly consists of marls intercalated with sandstones and siltstones and some clayey limestones (Konak et al., 2001). Andesitic pyroclastics and in places lens like sandstones are observed at the bottom of the Karacasu formation. In the Olur-Karacasu areas the unit has outcrops oriented along E-W direction (Figure 3). Turonian-Santonian Eğlek formation mainly consisting of andesites and agglomerates concordantly overlay Karacasu formation (Konak et al., 2001). The unit has outcrops in the northern part of the mapped area (Figure 3). Unluca formation mainly consisting of clayey-sandy limestones with sand intercalations and in the upper level marls with clayey limestone intercalations concordantly overlay Eğlek formation (Konak et al, 2001). The age of the unit is determined to be Late Santonian-Maastrichtian. In the area Alos formation concordantly overlays Unluca formation (Konak et al., 2001). The age of this unit is Early Paleocene and it is mainly made of platform carbonates (Figure 4). During Late Palaeocene the platform (Alos formation) became deeper by collapsing and in the deepening basin conditions Kaltarmak formation developed with siltstones and marls with turbiditic sandstones and calcic turbidite intercalations (Konak et al., 2001). Acidic Coskunlar dacite dykes cut all units in the area. Units of the Coskunlar dacite cutting all of the units in the area is in accord with the Eocene fold axis and with the tectonics like thrusts considered to be the products associated with the Early Eocene magmatic activity (Konak et al., 2001). In the area Coşkunlar Dacite intruded Lias-Dogger Kaban dacite



Figure 4- Stratigraphic columnar section of the units in the study area and surrounfings (from Konak and Hakyemez, 2008*a*).

and Oltuçayı volcanites. Extensive hydrothermal alteration and associated mineralizations have large areas of outcrops along the contact zones (Figure 3).

#### 3. Method

To enable our mineralogical, petrographic and geochemical studies to be carried out 94 samples were collected from the host rocks and alteration zones. For the mineralogical and petrographic studies, thin and polished sections of the samples were prepared in the thin section laboratory of the Geological Engineering Department of Çukurova University. Mineral chemistry of the 6 mineralized samples collected from the Yeşilbağlar and Kaban alteration zones were examined in the Mineralogy and Petrology Institute of the Earth Sciences Faculty of Vienna University Austria. Studies were carried out by using CAMECA-SX100 electron microprobe. Standard 27x46 mm rectangular and 1 inch diameter circular samples were prepared. Using electromagnetic lenses, speeded electron rays were focused on to the samples surface producing characteristic X-rays, these energetic electrons were bombarded into a small volume space

(Typically 1-9 micron) of the specimen. As each element has certain X-ray distribution, characteristic X-rays were determined with their wave lengths and concentrations of all elements (except H, He and Li) have been determined. Diameter of the X-ray was set to be 1  $\mu$ m and analyses were carried out at 20 kV and 20 nA.

X-Ray diffractometer analyses have been carried out on the 8 pyrite samples from the alterations from the Coşkunlar dacite. For the mineralogical studies samples were prepared in the crushing-powdering and geochemistry laboratory of the Geological Engineering Department of the Çukurova University and analyses were carried out in the Mineralogy Department of the Geneva University in Switzerland.

92 samples were selected from the alteration zones and host rocks for FT-IR analyses and FT-IR KBr tablet technique has been used. Analyses were carried out in the Chemistry Laboratory of the Science-Arts Faculty of the Çukurova University. For the analyses 1 mg samples were mixed with 900 mgr KBr and the mixture pelletized to 13 mm diameter pellets by using Graseby Specac compaction device. The reference pellet (KBr) and specimen pellets (1 mg specimen/900 mg KBr) were analysed by scanning them in the Perkin-Elmer 1600 FT-IR spectrometer.

# 4. Petrographic Characters of the Magmatic Rocks Outcropping in the Study Area

Late-Middle Jurassic Oltuçayı volcanites, Kaban Dacite, and Late Eocene Coşkunlar Dacite cutting Early Cretaceous pelagic-semi pelagic limestones of Soğukçam formation are the magmatic rocks in the area (Figure 5). From the main trace elements content point of view of the Jurassic-Eocene volcanics, they have calcalkaline origin and they developed as a result of northward subduction of Neo Tethys (Önal, 2015). Petrographic characters of the magmatic rocks which caused the alteration zones are given below.

Late-Middle Jurassic Oltuçayı volcanics are noticeable in the field with their dark green-near black colours. The unit is mainly represented by basalticandesitic lavas (Figure 6a). Basaltic lavas have



Figure 5- a) General view of the alterations and Coşkunlar Dacite cutting the Oltuçayı Volcanites (West of Yeşilbağlar village), b) Field view of the Coşkunlar Dacite, Soğukçam Formation and Kaban Dacite (West of Kaban village).



Figure 6- a) Field view of the volcanic rocks (basaltic andesite) (Oltuçayı Volcanites) in the study area, b and c) Plane polarized view of the thin sections from the Oltuçayı Volcanites (Pl: Plagioclase, Amp: Amphibole).

plagioclase and pyroxenes and display hyalopilitic porphyritic and microlithic porphyritic textures. Plagioclases are phenocrystals and microlites and have euhedral and subhedral forms. Calcites, sericites and albites developed as secondary minerals from the alteration of the plagioclases. Pyroxenes in general have anhedral, subhedral forms. Chlorites are anhedral and have irregularly filled interspaces of the plagioclases and pyroxenes. Calcites in general developed as a result of alteration of the plagioclases and in places through secondary processes filled the cracks and fissures (Figure 6b). Andesitic lavas mainly consist of plagioclases and amphiboles displaying porphyritic and microlithic textures. Plagioclases appear as large phenocrystals and microliths have euhedral and subhedral forms. Amphiboles in general are anhedral or subhedral and some green coloured amphiboles result of chloritization can be seen in the rocks. Amphiboles in places have an opaque rim (Figure 6c). Quartz and chlorite are the secondary minerals developed.

Early-Middle Jurassic Kaban dacite has beige, dirty yellow, light grey colours and has parallel or irregular columnar structures (Figure 7a). Dacitic lavas mainly have quartz, plagioclase and biotite and has porphyritic or micro granular porphyritic textures. In the rocks, euhedral in places corroded quartz phenochrystals and micro granular quartz are in micro granular matrix. Quartz phenocrystals appear highly fractured (Figure 7b). Plagioclases phenocrystals and microlites have been altered to albite and sericite. Biotites are rather limited and have been extensively chloritized (Figure 7c).

Early Eocene Coşkunlar Dacite in the field has beige, dirty white colours and have been heavily altered (Figure 8a). Dacitic lavas mainly have quartz, plagioclase and some biotites and have porphyritic and micro granular porphyritic texture. Quartzs in general have euhedral form and in places have been corroded and phenocrystal and micro granular quartz are embedded in fine grained matrix. Plagioclases in the rocks are in the form of phenocrystals and microlites. Plagioclases have been subjected to alteration and have been albitized and partly sericitized. Biotites have been chloritized (Figure 8b). Pyrite is the opaque mineral in the rocks. Prehnite and sericitizations are also present in the rocks (Figure 8c).

In the field quartz porphyries are found to be associated with Coşkunlar Dacite and they are considered to be the subvolcanic equivalents of the dacites. Quartz porphyries are dykes and apophsis in the dacites. In the 1/5.000 scale geological map it was rather difficult to mark these quartz porphyry dykes



Figure 7- a) Field view of the dacitic rocks (Kaban Dacite), b and c) Thin section views of the Kaban Dacite (Qtz: Quartz, Fsp: Feldspar, Kfs: K-feldspar, Bt: Biotite).



Figure 8- a) Field view of the Coşkunlar Dacite in the study area, b and c) Thin section view of prehnite and sericitization in the Coşkunlar Dacite (Pl: Plagioclase, Bt: Biotite).

and apophsis separately so they were marked together with dacites. Quartz porphyries in the field are noticeable with their beige, light yellow colours and quartz phenocrystals (Figure 9a). Primary mineralogy and texture of the rocks has been intensively effected by the alteration, porphyritic and micro granular texture traces are recognizable. Mineralogical studies indicate that apart from quartz all other minerals have been altered (Figure 9b). Plagioclases have been subjected to argillization and carbonatization, quartz has been corroded. Secondary quartz veins/veinlets are also present (Figure 9c).

From the intensity point of alteration and opaque mineral contents Kaban and Coşkunlar dacites are quite different from one another. Early Jurassic Kaban Dacite is characterized with less intense alteration and with not having opaque minerals. On the other hand, Coşkunlar Dacite has been heavily altered and is rich in opaque minerals.

#### 5. Economic Geology

Yeşilbağlar, Kaban and Köprübaşı alterations have East-West extensions in the South of Olur (Erzurum).

### 5.1. Yeşilbağlar Alterations and Mineralizations

Yeşilbağlar alterations are located aproximately 10 km south of the Yeşilbağlar village. It is about 300 m wide and has 600 m extension along N10°-15°E direction (Figure 3). Basaltic Jurassic Oltuçayı volcanites and Early Eocene quartz porphyry apophsis of the Coşkunlar dacites cutting Oltuçayı volcanites have been altered (Figure 10). In the alteration zones



Figure 9- a) Field view of the quartz porphyries in the study area, b and c) Thin section views of the quartz porphyries (Qtz: Quartz, Pl: Plagioclase, Om: Opaque mineral).



Figure 10- 1/5.000 scale geological map of the alteration zone in Yeşilbağlar (Olur-Erzurum) region (Önal, 2015).

silicifications, argillizations, sulphatizations are common, sericitization and chloritization are limited. Stockwork of limonite and hematite are commonly present. Breciations and elementer sulphurs are also present in the alteration zones (Figures 11a-d). In the advanced argillic alterations in the leach zone of the dacites, hematitization is seen in the upper part, pyrites together with hematization and elementer sulphurs are in the lower part. In the oxidation zone hematitization (iron cap-gossan) along N30°W direction is about 20 m long and 2 m thick. In the alteration zone white coloured stockwork of quartz veins/veinlets in places are chalcedonic and are found together with pyrites. Gypsum is also commonly present. The size of the pyrites in the silicification zone is 1-2 cm (Figures 11e-h). In the parts where rocks are crowded with pyrite, hematitization and limonitization appear to have developed as alteration products from the alteration of iron rich minerals like amphiboles, biotites, hematites and limonitization are also present around the brecciations. In the study area along some fractures from the alteration of pyrites, limonitizations and hematitization have also been noticed to have developed.

### 5.2. Kaban Alteration and Mineralization

Kaban alteration zone is situated aproximately 17km to the Southeast of Olur (Erzurum) and about 10km to the East of Yeşilbağlar alteration zone (Figure 3). Coşkunlar Dacite has intruded into the contact zone between Kaban Dacite belonging to the Olur Group and Soğukcam formation. The alteration zone developed in the Coşkunlar Dacite along this contact zone (Figure 12). Within the Coşkunlar Dacite the alteration zone is quite extensive and along E-W direction it is about 100 m wide, 300 m long (Figure 12). Kaban alteration is quite similar to the Yeşilbağlar alteration. In the alteration zone silicifications, argilization are extensive, chloritization and seritization are also present. In the oxisation zone along with hematitization (iron capgossan) zones, sulphates (barite) and gypsums are also common (Figures 13a-d). In the Kaban alteration zone along with disseminated pyrites, malachites and azurites are also present in the fracture zones. Within the brecciated block there are remains of addit entrances belonging to the pre republic time copper mining (Figures 13e-h).

### 5.3. Köprübaşı Alteration and Mineralization

Köprübaşı alteration is situated between Yeşilbağlar and Kaban alteration zones 8 km to the south of Olur (Erzurum). Alteration is in the Coşkunlar Dacite which has intruded along the contact between Kaban Dacite and Soğukçam formation. These alterations extend about 100 m in an E-W direction (Figure 3). In the Köprübaşı silicifications, limonitizations, hematitization ares common but argilization is less than other alteration zones (Figure 14). In the field outcrop of Köprübaşı alteration zone is very small, so it was not marked on the 1/5.000 scale geological map. Samples could not be collected from the Köprübaşı alteration zone therefore the mineralogy and chemistry of this zone could not be studied in detail.

# 5.4. Mineralization Type

In the alteration zones of the study area, disseminated, stockwork, vein/veinlet and smear like different types of mineralizations are present. Disseminated type mineralizations are commonly present in the quartz porphyry apophsis of the Coşkunlar Dacite and in the host rocks. In these mineralizations pyrite was macroscopically observed (Figure 15a). Limonitization and hematitization are the stockwork type mineralizations in the alteration zones (Figures 15b, c). Vein-veinlet type mineralizations have developed in the grey and grey-white coloured quartz veins which include pyrites. In the Yeşilbağlar alteration zone pyrite bearing zones are mm-cm thick and are 1-2 m long. Veins and veinlets have cross cutting relations (Figures 15d, e). Smears of malachites and azurites are seen in the fracture zones in various directions and have irregular dispositions (Figure 15f).

### 6. Ore Mineralogy and Chemistry

Ore mineralogy and chemistry of the mineralizations in the Yeşilbağlar and Kaban alteration zones have been separately evaluated and mineral paragenesis have been described. In the alteration zones the ore minerals present are; pyrites, chalcopyrites, galena, sphaelerites and pyrrhotites, gang minerals present are quartz, barites and calcites.

### 6.1. Yeşilbağlar Alteration

Macroscopic and microscopic mineralogical studies were carried out on the samples collected from the Yeşilbağlar alteration zone. Paragenesis of the minerals show that pyrite is the most abundant ore mineral. Chalcopyrite, sphalerite, galena, chalcocite, rutile are present in decreasing order. Hematite, limonite, malachite, azurite ore minerals are the



Figure 11- Field views from the Yeşilbağlar (Olur-Erzurum) alteration zone.



Figure 12- 1/5.000 scale geological map of the alteration zone in Kaban (Olur-Erzurum) region (Önal, 2015).

minerals present in the oxidation zone. Details of the mineralogy, texture and chemical compositions of the ore minerals are given below.

Pyrite: Pyrite is the most common ore mineral present in the alteration zone. Size of the pyrite crystals is up to 1 mm, idiomorph, pseudomorph crystals have skeleton textures (Figure 16a, b). In the ore samples chalcopyrites and sphalerites appear to have metasomatised pyrites (Figures 16c, d). This indicates that pyrites were formed earlier then chalcopyrites and sphalerites. Because of the deformations they became subjected to pyrites were fractured and broken and in some cases they were metasomatized by chalcocite. Secondary rutiles are also present (Figure 16e). Cataclastic textures observed in the pyrites indicate that deformations developed in rather low temperatures. As pyrites are harder, they were effected more than the other sulphide minerals present together with pyrite (Craig and Vaughan, 1981; McClay and Ellis, 1984; Craig and Vokes, 1993; Kuşçu and Erler, 1999, 2002) (Figure 16f). Temperature and pressure pyrites give information on the deformation textures and tectonic past of the deposit (Craig et al., 1998; Lianxing and McClay, 1992). In the mineral deposit if changes of textures when pyrite are present in other ore minerals too and have been repeated several times over, this indicates continuous deformations in the process of their developments (Kuşçu and Erler, 2002; Demir, 2010). Pyrites have been analysed for S, Fe, Mn, Co, Ni, As, Pb, Ag, Cu, Ga, In, Sb, Zn and Cd (Table 1). S and Fe are the main content of pyrites. Range of contents of other elements are; Ni 0.01-1.08%, Zn 0.01-0.13%, Cd 0.01-0.21 %, Co 0.01-0.04%. Based on these analyses the chemical formulae of the pyrites have been calculated as Fe<sub>0.81-</sub>  $_{0.85}S_{1.6-1.7}$  (FeS<sub>2</sub>). Chemical compositions and textures of the pyrites reflect the process they were subjected to during and later stages of their developments. Some scientists use Co/Ni ratio of pyrites to understand development processes. Co/Ni ratio gives information on the primary development temperatures and also independent from this metamorphism temperature.

conditions causing changes of textures to develop in



Figure 13- Field views from the Kaban (Olur-Erzurum) alteration zone.



Figure 14- Field views from the Köprübaşı (Olur-Erzurum) alteration zone.



Figure 15- Types of mineralization observed in the study area.

If Co/Ni<1, it indicates sedimentary origin, Co/ Ni>1 indicates hydrothermal origin (Loftus-Hills and Solomon, 1967; Bralia et al., 1979; Roberts, 1982; Xuexin, 1984; Raymond, 1996; Kant et al., 2012). Analyses of the pyrites from the Yeşilbağlar alteration zone show Co/Ni>1 (Co/Ni: 1-2.83) indicating hydrothermal origin (Table 1).

Chalcopyrite: In the Yeşilbağlar alteration, after pyrite chalcopyrite is the most abundant primary Cu mineral. They are all pseudomorph crystals. Chalcopyrites developed after pyrites and have metasomatized pyrites (Figure 17a). Chemical analyses of chalcopyrites show that apart from main elements of S, Fe and Cu, Cd is also present. Analysed all other elements are below detection limits (Table 1). Cd content of chalcopyrites is 0.02%. General chemical formulae of chalcopyrites have been calculated as  $Cu_{0.52}Fe_{0.55}S_{1,10}$  (CuFeS<sub>2</sub>) (Table 1).

Sphalerite: In the Yeşilbağlar alteration zone sphalerite is less abundant than pyrite and chalcopyrite. Under microscope sphaelerite is in various shades of grey colour and has yellowish brown internal reflections (Figure 17b). Fe content of sphalerite is relatively low, this is in accordance with their light coloured internal reflections. Sphalerites have pseudomorphic crystal forms and have metasomatized pyrites (Figures 17c, d). Mineral chemical analyses of sphaelerites are given in table 1. Chemical analyses of



Figure 16- Polished thin section views of pyrites from the Yeşilbağlar alteration zone, d) Back-scattered electron (BSE) image (Py: Pyrite, Cpy: Chalcopyrite, Sf: Sphalerite, Cc: Chalcosine, Ru: Rutile, Hem: Hematite).

sphaelerites show that ranges are; Fe 1.91-12.76%, Cu 0.01-0.21%, Zn 50.76-64.68% and Cd 0.22-0.42%. General formulae of sphaelerites have been calculated as  $Zn_{0.80-1.00}Fe_{0.0-0.2}S_{1.01-1.03}$  [(Zn, Fe)S] (Table 1). Sphalerite is an important mineral indicating origin and mineralizing conditions of the mineralizations (Craig and Vaughan, 1994; Cook, 1996; Holten et al, 2000; L'Heureux and Jamtveit, 2002; Palero and Martin-Izard, 2005). Variations in the chemical compositions reflects variations in developing conditions during crystalization process (Grammatikopoulos and Roth, 2002). Compositional changes in sphalerites are better represented from their primary compositions when

they were first formed then changes that developed at a later stage resulting from balancing conditions (Dibenedetto et al., 2005). Sphalerites in the Yeşilbağlar alteration zone do not show any compositional element zonings. This indicates that during crystallizations physicochemical conditions of the environment were stable (Demir, 2010). Studies on mineral chemistry of the sphaelerites suggest that Cd contents and Zn/Cd ratios could be used to determine crystallization types of the mineralizations (Jonasson and Sangster, 1978; Xuexin, 1984; Brill, 1989; Xu, 1998; Gottesman and Kampe, 2007; Demir, 2010; Kant et al., 2012). In volcano sedimentary deposits Zn/Cd ratios show



Figure 17- Polished thin section views of chalcopyrite, sphalerite and galenite from the Yeşilbağlar alteration zone, d) Back-scattered electron (BSE) image (Py: Pyrite, Cpy: Chalcopyrite, Sf: Sphalerite, Gn: Galenite).

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Table 1- Mineral chemistry	/ analyses of the mine	als of the alteration zones	s (weigth %) (YB	3-Yeşilbağlar, K-Kaban alterations)	
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Sample	Mineral	S	Mn	Fe	Co	Ni	As	Pb	Ag	Zn	Cu	Ga	Cd	In	Sb	Total
YB34_C_pt52	Chalcopyrite	35.15		30.5							32.7		0.02			98.401
YB6_A_pt2	Pyrite	53.32		46.6						0.02	0.01		0.12			100.12
YB6_A_pt3	Pyrite	53.62	0.01	46.8					0.02				0.19	0.03		100.62
YB6_A_pt4	Pyrite	53.29		46.5		0.01			0.01		0.01		0.14		0.03	100.04
YB6_A_pt5	Pyrite	53.3		46.7		0.01			0.02	0.02		0.01	0.13		0.03	100.17
YB6_A_pt6	Pyrite	53.5		46.7							0.02		0.21			100.44
YB6_A_pt7	Pyrite	53.41		46.6		0.01			0.02	0.01			0.13			100.15
YB6_A_pt8	Pyrite	53.38		46.7								0.01	0.09		0.01	100.19
YB6_B_pt9	Pyrite	53.05		46.8			0.01				0.01	0.02	0.06			99.96
YB6_B_pt10	Pyrite	53.13	0.01	46.8	0.01				0.03	0.04	0.03	0.01	0.16	0.03		100.22
YB6_B_pt11	Pyrite	53.2		46.7					0.02				0.08	0.01	0.01	100.01
YB6_B_pt12	Pyrite	52.9		46.6	0.01		0.03					0.01	0.16	0.02		99.717
YB6_B_pt13	Pyrite	53.29	0.01	46.8		0.02	0						0.09	0.05		100.24
YB6_B_pt14	Pyrite	53.13	0.01	46.7			0.07			0.03		0.02	0.11		0.02	100.1
YB6_C_pt15	Pyrite	53.21		46.8	0.02		0.01		0.02	0.02			0.12			100.25
YB6_C_pt16	Pyrite	53.12		46.6					0.04	0.13	0.01	0.01	0.11	0.01		99.994
YB6_D_pt20	Pyrite	53.3		46.9	0.01				0.05		0.01		0.03		0.02	100.32
YB6_D_pt21	Pyrite	53.17		46.7			0.01		0.03		0.02		0.13			100.1
YB13_A_pt23	Pyrite	53.26	0.01	46.6		0.14	0.02		0.04		0.03	0.01	0.08	0.01	0.01	100.23
YB13_A_pt24	Pyrite	52.84	0.01	46.5		0.1	0.02			0.02	0.04		0.13	0.05	0.01	99.664
YB13_A_pt25	Pyrite	53.03	0.01	46.3	0.02	0.53					0.02		0.08	0.01		99.985
YB13_A_pt26	Pyrite	52.89	0.01	46.9		0.02				0.05	0.01		0.05	0.03	0.01	99.939
YB13_A_pt27	Pyrite	53.46		46.4		0.09				0.08		0.01	0.12		0.01	100.18
YB13_B_pt28	Pyrite	53.44	0.01	45.6		1.08			0.05				0.04			100.26
YB13_B_pt29	Pyrite	53.09		46.4		0.17					0.02		0.07			99.782
YB18_A_pt2	Pyrite	53.33		47.1		0.01	0.36	0.08	0.04		0.01				0.03	100.99
YB18_A_pt3	Pyrite	53.73		46.7			0.04	0.11					0.02			100.61
YB18_A_pt4	Pyrite	53.46		46.8			0.05	0.19	0.03		0.02					100.56
YB18_A_pt5	Pyrite	52.58		46.2		0.02	1.8	0.24			0.03		0.03		0.02	100.94
YB18_A_pt6	Pyrite	52.77		46.6		0.01	1.19	0.09	0.02		0.06				0.01	100.69
YB18_A_pt7	Pyrite	53.41		46.8		0.01	0.05	0.1		0.02	0.02		0.10		0.01	100.34
YB18_A_pt8	Pyrite	53.69		47.2		0.01	0.05	0.1		0.02	0.03		0.12		0.01	101.24
YB18_A_pt9	Pyrite	53.74		46.5		0.01	0.01	0.07	0.01	0.05	0.02				0.01	100.44
YB18_A_pt10	Pyrite	52.72		46.3		0.01	1.3	0.12	0.01	0.03	0.04					100.48
YB18_A_pt11	Pyrite	53.22		40.5		0.01	0.08	0.04	0.02	0.03						100.29
VP18 A pt12	Pyrite	51.07		4/		0.01	0.05	0.03	0.02	0.02			0.01		0.01	100.01
VP26 A pt5	Pyrite	53.497		40.2		0.01	2.10	0.07					0.01		0.01	100.41
VP26 A pt6	Purito	52.02		47.2		0.01	2.10	0.02	0.01		0.01		0.15			101.02
VP26 A pt7	Purito	53.02		40.0			0.01	0.05	0.01		0.01		0.13			101.02
VP26 P pt9	Purito	53.40		47.2	0.01		0.01	0.08	0.08		0.02		0.12		0.01	100.97
VB26 B pt9	Pyrite	53.8		40.9	0.01		0.01	0.0	0.01	0.03	0.02		0.00		0.01	101.18
VB26_B_pt)	Durito	52.12		47.2			2.02	0.03	0.01	0.05	0.02		0.06			100.00
YB26 B pt11	Pyrite	53 56		47.2	0.04		0.02	0.05	0.01	0.01	0.04		0.00			101.77
YB26 B pt12	Pyrito	53.66		47.2	0.04	0.02	0.02	0.00		0.03	0.04		0.12			101.07
YB26 C pt13	Pyrite	53.50		47.4		0.02	0.01	0.15		0.05	0.01		0.12			101.20
YB26 C pt14	Pyrite	53.67		47.3		0.01	0.02	0.06	0.04				0.00			101.17
YB26 C pt15	Pyrite	53.66		47			0.02	0.02	0.01				0.1		0.02	100.82
YB26 C pt16	Pvrite	53.28		47.4			0.03	0.06	0.04	0.01	0.01		0.05		0.02	100.96
YB26_C pt17	Pyrite	53.44		47.2			0.03	0.16	0.02				0.12			100.95

Sample	Mineral	S	Mn	Fe	Co	Ni	As	Pb	Ag	Zn	Cu	Ga	Cd	In	Sb	Total
YB26_C_pt18	Pyrite	53.72		47.4				0.09	0.01				0.08		0.02	101.31
YB26_C_pt19	Pyrite	53.66		47.4			0.01	0.06					0.04			101.14
YB26_C_pt20	Pyrite	53.62		47.6			0.02	0.09			0.03		0.05			101.45
YB34_A_pt30	Pyrite	53.07	0.01	46.6									0.09		0.03	99.84
YB34_A_pt32	Pyrite	52.96		46.7			0.01		0.01				0.07			99.71
YB34_B_pt33	Pyrite	52.82		46.5					0.03		0.03	0.01	0.07		0.01	99.494
YB34_B_pt36	Pyrite	52.85		46.5					0.01	0.02		0.01	0.06	0.03	0.01	99.454
YB34_B_pt37	Pyrite	52.9		46.8		0.01	0.06				0.01	0.02	0.05			99.837
YB34_B_pt38	Pyrite	52.76		46.9					0.01	0.02				0.04	0.02	99.74
YB34_C_pt39	Pyrite	53.13		46.8	0.01	0	0.01		0.04	0	0.01		0.05	0.08		100.09
YB34_C_pt40	Pyrite	53.02	0.01	46.6						0.01	0.01		0.02			99.626
YB34_C_pt41	Pyrite	51.83	0.01	45.3	0.02	0.01	2.09				0.02	0.01	0.06	0.06	0.04	99.468
YB34_C_pt42	Pyrite	52.92		46.7		0.02							0.04			99.691
YB34_C_pt43	Pyrite	53.26		46.6					0.04	0.07	0.02			0.02		100.02
YB34_C_pt45	Pyrite	52.89		46.6						0.03	0.02		0.06	0.06	0.03	99.661
YB34_C_pt46	Pyrite	53.1		46.6		0.01			0.03					0.01		99.708
YB34_C_pt41a	Pyrite	51.76	0.01	45.6			1.85			0.02	0.01	0.01			0.08	99.308
YB34_C_pt48	Pyrite	53.56		46.6		0.01			0.04	0.02			0.04	0.01		100.29
YB34_C_pt47	Pyrite	51.34	0.01	45.9		0.02	1.75			0.06			0.09		0.08	99.2
YB34_C_pt49	Pyrite	53.26		46.6							0.02				0.01	99.941
YB34_C_pt50	Pyrite	52.05		45.6			1.99		0.03	0.02			0.07		0.06	99.825
YB34_C_pt51	Pyrite	52.48		46.4			2				0.03		0.07		0.07	101.06
YB34_C_pt53	Pyrite	53.56		46.8			0.01			0.01	0.01		0.04	0.02		100.49
YB6_A_pt1	Galena	14.81		5.22				82.6			0.06	0.05		0.02		102.72
YB26_pt2	Galena	13.59		2.23				86	0.12	0.05	0.04			0.02		102.02
YB26_pt3	Galena	13.64		2.55				86.8	0.04	0.02				0.05		103.06
YB26_pt4	Galena	13.48		1.42				85.9	0.23	0.04				0.04		101.13
YB6_C_pt17	Sphalerite	32.68	0.04	4.54	0.01	0.01			0.01	62.3	0.01		0.22	0.01		99.825
YB6_C_pt18	Sphalerite	35.75	0.01	12.8						50.8	0.01		0.22	0.06		99.571
YB6_C_pt19	Sphalerite	32.45	0.03	3.26			0.14		0.03	63.1			0.31			99.304
YB6_D_pt22	Sphalerite	32.98	0.03	3.15			0.11			63	0.01		0.3		0.01	99.633
YB34_A_pt31	Sphalerite	32.42		2.5	0.01	0.01				64.3			0.42		0.02	99.674
YB34_B_pt34	Sphalerite	32.64	0.01	2.21						63.9	0.11		0.24			99.136
YB34_B_pt35	Sphalerite	32.38		1.91						64.7			0.28			99.257
YB34_C_pt44	Sphalerite	32.64		2.89	0.01				0.01	63.1	0.21	0.02	0.3	0.01	0.12	99.267
K27_B_pt33	Chalcopyrite	34.77		31			0.22		0.01		32.9					98.952
K27_A_pt26	Pyrite	53.3		47.1		0.01	0.06		0.03							100.48
K27_A_pt27	Pyrite	52.79		46.9			0.4				0.01					100.04
K27_A_pt30	Pyrite	52.39		47	0.01	0.01	0.12	İ								99.547
K27_B_pt31	Pyrite	52.74		47	İ	0	0.27	İ								100.01
K27_B_pt32	Pyrite	53.14		47.2		0.01	0.05									100.37
K27_B_pt34	Pyrite	53.21		46.7		0.01	0.25		0.02							100.19
K27_A_pt28	Pyrrhotite	38.26		60.6		0.01	0				0.02					98.899
K27_A_pt29	Pyrrhotite	38.37		60.6			0.16									99.129
K27_B_pt35	Pyrrhotite	39.02		60.4		0.01	0.3									99.754

changes in 417-531 range, in magmatic hydrothermal deposits in 104-214 range and in stratiform deposits related with carbonates in 252-330 range (Jonasson and Sangster, 1978; Xuexin, 1984). Zn/Cd ratio of the sphaelerites in the Yeşilbağlar alteration zone on average is 223.2, suggesting magmatic hydrothermal origin.

Galena: Galena in the Yeşilbağlar alteration zone have idiomorphic and pseudomorphic crystal forms, filling interspaces of other minerals present. In the polished sections idiomorphic galenas are white coloured and have characteristic trinangular shapes (Figures 17e, f). In paragenesis galenas are after pyrite and have metasomathised pyrites. Metasomatism has obscured the contacts of galenas with other minerals and they appear irregular. Like pyrites, chalcopyrites and sphaelerites, galenas have also been fractured. Fractures in galenas are along the cleavages, in other minerals they are rather irregular. Mineral chemistry analyses of the galenas from the alteration zone are given in table 1. Pb and S are the main elements of galena. Apart from these elements, samples were analysed for Fe, Ag, Zn and In. Analyses of these elements in galenas have given the following values: Fe 1.42-5.22%, Ag 0.02-0.23%, Zn 0.02-0.05%, In 0.02-0.05. From these values, general chemical formulae of galena has been calculated as Pb<sub>0.40-</sub> <sub>0.42</sub>Fe<sub>0.03-0.09</sub>S<sub>0.42-0.46</sub> ([Pb, Fe]S) (Table 1).

#### 6.2. Kaban Alteration

Based on the macroscopic and microscopic studies of the samples collected from the Kaban alteration zone. Paragenesis of the minerals in decreasing order are; pyrite-chalcopyrite-pyrrhotite. In the oxidation zone hematite, limonite, malachite and azurite are the minerals present. Details of the mineralogical and textural characteristics and chemical compositions of the minerals in paragenesis are given below.

Pyrite: As is the case in Yesilbağlar alteration zone, pyrite is the most common mineral in the Kaban alteration zone. In general pyrites have idiomorphic pseudemorphic crystal forms and have cataclastic texture. Grain size varies from several microns to 5-6 mm. Polished section studies show that pyrites are highly fractured and have hematite rims developed along the margins (Figure 18a). In general pyrites developed ahead of chalcopyrites and are surrounded by gang minerals. From the alteration zone, in one sample chemical analyses have been carried out on 6 points. Chemical analyses of pyrites gave results S, Fe, Mn, Co, Ni, As, Pb, Ag, Cu, Ga, In, Sb, Zn and Cd concentrations. (Table 1). Fe ans S are the main elements of pyrites. Ni and Co contenta respectively are 0.00-0.01% and 0.01%. Based on these values general chemical formulae of pyrites has been calculated as  $Fe_{0.83-0.84}S_{1.6-1.7}$  (FeS<sub>2</sub>). Co and Ni concentrations of the pyrites from Kaban are rather low (Table 1). Co/Ni ratio of the pyrites is 1.4 (Co/Ni=1.4). As this ratio is greater than 1 (Co/Ni> =1) alteration is considered to have hydrothermal origin.

Chalcopyrite: In the study area chalcopyrites are the second most abundant mineral after pyrites. They in general have irregular, pseudomorphic crystal forms and have metasomathized pyrites (Figure 18b). S, Fe and Cu are the main elements of chalcopyrite, apart from these elements As and Ag are also present. Other elements were under the detection limits (Table 1). Based on the chemical analyses chemical general formulae of the chalcopyrite has been calculated as  $Cu_{0.57}Fe_{0.56}S_{1.08}$  (CuFeS<sub>2</sub>).

Pyrrhotite: In the alteration zone it is not a commonly found mineral. They are generally found in pyrites developed as a result of metasomatism. Pyrites are cataclastic, coarse to fine grained and have developed ahead of pyrrhotites (Figure 18c). In some cases, in cataclastic pyrites, along fretures and cleavages pyrrhotites are seen as metasomatism



Figure 18- Polished thin section views of chalcopyrite, sphalerite and pyrotine from the Kaban alteration zone (Py: Pyrite, Cpy: Chalcopyrite, Po: Pyrotine, Hem: Hematite).

products. S and Fe are the main elements of pyrrhotite. Apart from these elements analyses show presence of Ni 0.01%, As 0.01-0.3% and Cu 0.02%. Other elements are below detection limits (Table 1). On the base of chemical analyses, chemical formulae of pyrrhotite has been calculated as  $Fe_{1.08-1.09}S_{1.19-1.22}$  (FeS).

# 6.3. FT-IR Fourier Transform-Infrared Spectroscopy Analyses

FT-IR analyses carried out on the specimens collected from the Yeşilbağlar alteration zone showed the presence of kaolinite, chlorite (clinochlore), quartz, illite-muscovite, gypsum, jarosite and barite minerals. Some of the findings are given in table 2. IR spectrums of typical mineral peaks of the minerals present in the samples from the Yeşilbağlar alteration are given in Figures 19a-e. In some of the analysed samples characteristic peaks indicating carbonate presence can also be seen (Figure 19a).

FT-IR analyses results of the samples from the Kaban alteration zone are similar to the Yeşilbağlar alteration. In the analysed samples presence of kaolinite, chlorite (clinochlore) quartz, gypsum and barite have been detected (Table 3). IR spectrums of typical mineral peaks of the minerals present in the Kaban alteration samples are given in figures 20f-h.

# 6.4. X-Ray Diffraction Analysis

XRD studies carried out on the samples from the Yeşilbağlar alteration zone showed, presence of

quartz, chlorite group minerals (clinochlore), sulphate minerals (gypsum, bassanite, barite), muscovite and pyrite (Figures 20a-f). In the analysed samples quartz and chlorite group minerals are the main minerals. In all of the analysed samples minor amounts of nonclayey minerals are also present. Among those jarosite  $[KFe_3(SO_4)_2(OH)_6]$  is an alteration product mineral. Oxidation of pyrites produces sulfuric acid. Sulphuric acid reacts with K-feldspars and illite, causing K<sup>+</sup> extractions, and jarosite develops (Karakaya, 2006). Bassanite  $[CaSO_4 1/2H_2O]$  is another mineral detected. It is a pseudomorph of gypsum. Clinochlore is a chlorite mineral containing Mg-Al (Karakaya, 2006). Results of XRD studies are in agreement with FT-IR analyses results.

Table 3- Wave lengths of some of the minerals in the Kaban alteration zone.

Minanal	Wave length of the mineral (cm <sup>-1</sup> )									
Mineral	K-1	K-16	K-18-A	K-27						
Kaolinite		3695 3652 3620	3696	3693 3619						
Chlorite	3635 3420									
Quartz	796 777	796 777		796 780						
Gypsum and Barite			3546 3404 1142 1118 669 602							
Carbonate		1438								

Table 2- Identifying wave lengths of some of the minerals in the Yeşilbağlar alteration zone

	Wave length of the mineral (cm <sup>-1</sup> )												
Millerai	YB-3	YB-4	YB-13	YB-20	YB-26	YB-34	YB-41	YB-48					
Kaolinite	3695	3695 3654 3620	3696	3697									
Chlorite		3695		3557 3433									
Clinochlore			3546 3420				3563 3445						
Illit/Muscovite	3620 3428 827 760			3619 3433	3630 3402								
Quartz	796 777	797 778	799 777	794 779		797 778	797 777						
Gypsum								3546 3405 1147 1120 669 602					
Jarosite ve Barite						3387,1084 632							
Carbonate	1450	1452											



Figure 19- Spectrums of the FT-IR analyses, a-e) Samples from the Yeşilbağlar alteration zone, f-h) Samples from the Kaban alteration zone.



Figure 20- Diffractograms of the XRD analyses, a-f) Samples from the Yeşilbağlar alteration zone, g-h) Samples from the Kaban alteration zone.

XRD studies carried out on the samples from Kaban alteration zone showed the presence of quartz, sulphate (gypsum, barite), clay (kaolinite) and pyrite (Figures 20g, h). As in the Yeşilbağlar alteration, results of the XRD and FT-IR analyses of the samples from the Kaban alteration zone are in agreement with each other.

#### 7. Alteration

The units present in the study area belong to the Olur Group defined within the Olur-Tortum zone (Konak and Hakyemez, 2001) Alteration associated units of Early-Middle Jurassic Oltuçayı volcanics and Kaban Dacite, Early Cretaceous pelagic-semi pelagic limestones all belong to the Soğukçam formation and have been cut by Eocene Coşkunlar Dacite. Quartz porphyry apophysis of the Coşkunlar Dacite also cover large areas. All of the defined alteration zones with some interruptions have 11 km extensions along NE-SW direction. To study the characteristics of the alteration zones, samples were collected from Yeşilbağlar, Kaban and Köprübaşı alteration zones and petrographical, mineralogical, FT-IR and XRD studies were carried out on these samples.

The rocks in the study area have been extensively subjected to hydrothermal alterations. This caused difficulties in the identifications of the rocks. Petrographical studies showed that the rocks in the area are andesitic-basaltic-dacitic volcanics (Oltucayı volcanite, Kaban and Coşkunlar dacite) and their subvolcanic equivalents (quartz porphyries). As a result of hydrothermal alterations their initial primary mineralogical contents have been changed to another new group of minerals. The original compositions and textures of the rocks have been partly or completely destroyed and with the hydrothermal alterations identification of the intrusion and the breccias has been problematical. Early Eocene Coşkunlar Dacite is the most differentiated mineralization containing the youngest intrusive rock. Yeşilbağlar, Kaban and Köprübaşı alteration textures are complicated, so quartz porphyry intrusives and related brecciations have been considered to have been caused by solutions with different chemical compositions.

(a) Advanced Argillic-Argillic Zone: The advanced argillic zone covers large areas in the study area and they are seen along the contacts with breccias. The zone developed from the alteration of andesites, basalts and dacites and towards the upper parts it passes into a silicified zone. In topographically higher parts quartz content of the silicified zone is more than 80% with very small amount of clay. Original mineralogic composition and textures have been completely destroyed (Figure 21). In the field silicified structures stand out like notches and caps. The rocks in this zone are rather hard and have fractures and breaks on their outer faces. In the area starting in Early Eocene volcanic activities rose subsurface and silicified volcanics. In the field breccias in the silicified zones are grey, yellowish grey, brownish red and purple coloured. In the host rock, in most cases as a result of alteration quartz has been infiltrated by iron oxide. As a result of hematitization, rocks in this zone have brownish, purplish appearance. Petrographical studies showed that all of the plagioclases have been fully altered to clay minerals. FT-IR and XRD studies indicated that clay minerals are kaolinite, away from



Figure 21- Schematic illustration of the alteration zone in Yeşilbağlar area.

the zone they are montmorillonite. Considering their topographical distributions limits of advanced argillic zone cannot be marked clearly but they have iron oxide smeared breccias at the top and have a clayey zone below it (Figure 21). The argillic zone in the field is marked with light yellow and white colours. Particularly in the heavily hematitized, limonitized parts plagioclases have mostly been altered to clay minerals. Along the fractures, along with hematitization and limonitization, limited carboatizations can also be observed. FT-IR and XRD studies carried out on the samples collected indicated developments of smectite±illite±muscovite±montmorillonite minerals. The presence of kaolinite mineral in the argillic and advanced argillic zone in the Yeşilbağlar and Kaban alteration zones indicates that clay minerals dominate these zones. Kaolinites dominate the mineralized zones; montmorillonites represent the zones away from the mineralizations. In the field sulphate mineralizations are the guides for argillic alteration zones. The alteration with these characteristics is quite similar to the argillic alteration described by Lowell and Guilbert (1970) with paragenesis of quartz, kaolinite, montmorrilonite and a small amount of leucoxene.

(b) Pyrophyllitic Zone: It is overlain by the advanced argillic alteration zone and mostly observed as protected along the outer zones. It has been subjected to chlorite, carbonate alterations. It is observed in the rocks with basaltic, andesitic and dacitic compositions and has redish bordeaux colour. Towards outer zones where hematitization and limonitization have developed, it passes into advanced argillic zone. Particularly in the Yeşilbağlar alteration zone pyrophyllitic alteration zones have been cut by pyrite containing quartz veins and veinlets. Petrographic studies showed that plagioclases were carbonatized, and argillitized and were slightly sericitized. FR-IR and XRD studies showed that chlorite (clinochlore) and carbonate (calcite) minerals were also present (Figure 21). Alteration is similar to the pyrophyllitic alteration defined by Lowell and Guilbert (1970) with chlorite, calcite, epidote, adularia and albite paragenesis.

(c) Sericitic Alteration: It has been overlain by advanced argillic alteration and has almost been masked or wiped out. In the study area it has limited coverage and mainly has sericite and quartz and a small amount of carbonatization. FR-IR and XRD studies carried out on the samples collected along the contact of host rock-with quartz porphyry showed the presence of quartz, sericites, and pyrites and in some samples chlorite, illite and rutile were also present. In the inner parts of the alteration zone sericites is dominant and illite is dominant at the outer parts. Sericization is mainly related to feldspar minerals. In this zone pyrite is mainly disseminated (Figure 21). This defined alteration is similar to the phyllic alteration defined by Lowell and Gilbert (1970).

Microscopical, FT-IR and XRD studies carried out on the samples collected from the alteration zones showed that the general mineral assemblance consists of quartz, smectite, illite, kaolinite, chlorite, clinochlore, carbonate (calcite), sulphate (gypsum, bassanite). From the points of primary texture and mineralogy, the rocks in the study area have been identified as andesite, basalt and dacite and main alterations are argillization, silicification, chloritization, sericitization. Zones with hematite, limonite and sulphae are common in the oxidation zone. With the increasing alteration clay minerals and quartz also increase. Copper carbonate (malachite-azurite) minerals are also present. By using analytical methods characteristics of the alterations have been defined. Eocene tectonic activities and later developing alterations have masked developments of the previous period consequently during the 1/5.000 scale geological mapping all these mentioned alteration zones could not be marked on the map.

#### 8. Discussion and Results

#### 8.1. Discussion

In this study area it was difficult to make separations on the base of distribution of alteration minerals. Alteration minerals in general show that advanced argillic alteration zones in the study area are quite extensive. Quartz, kalolinite, illite, montmorillonite and jarosite are the commonest alteration minerals. In places they are accompanied by chlorite, and sericite. Paragenesis of this group of minerals are considered to be the evidence of typical advanced argillic alteration. Jarosite and gypsum are also common in this zone. The presence of some alteration mineral relics eg sericite, chlorite and carbonate show that alterations in the field are overlying each other. In general, it is considered that solutions from the alteration zones at relatively shallow depths react with previously developed alterations at depths and replacing them causing alteration mineral types becoming younger towards the upper zones.

In the advanced argillic zones, the roots of the lithocaps have structural control. In the high temperature parts below the lithocaps, sericitic alteration passes into quartz-pyrophyllite. In the low temperature parts also below the lithocaps, quartzkaolinite are dominant. More than mafic magmatic rocks, felsic magmatic rocks have been subjected to argillic alteration. In some locations advanced alterations below lithocaps characteristically display a typical patchy texture. These textures have been embedded into the silicified rocks and contain pyrophyllite and kaolinite.

In the porphyry Cu mineralizations, vertical distributions of the mineralization types depend on to the overlying and the interminglings. In high temperature intermingled systems in the porphyry stocks the advanced argillic lithocap may effect upper parts and in the root parts may effect downwards, down to 1 km depths. In this kind of situation argillic alteration overlying the potassic alteration may be 1-2 Ma younger than the potassic alteration (Sillitoe, 2010). In places where interminglings are limited, lithocap and stocks with potassic alterations may be separated with ~0.5-1 km fron each other. The gap in between is filled with pyritic chlorite-sericite alterations.

Copper deposits developed in the porphyry systems are low grade but with large reserves and have developed in the near surface intrusive rocks in the island arc environments and in the intrusive rocks of the calcalkaline magmatisms near the continents. Most characteristic features of the porphyry systems are defined alteration and mineralized zones. These zones from outer towards inner part are prophylitic, phyllic and potassic zones. The main mineralizations are along the zones between phyllic and potassic alteration zones (Lowell and Guilbert, 1970; Sillitoe, 1972, 1973; Lowell and Gilbert, 1974: Berger et al., 2008; Sillitoe, 2010). In the porphyry systems most of the ore mineralizations containing intrusives, have calc-alkaline character. In general, in the volcanic and pyroclastic rocks, particularly in andesitic, dacitic, rhyodacitic rocks and in their subvolcanic equivalents, veins, breccias and metasomatisms of the sulphur bearing minerals are present (Sillitoe, 1972; Mitchell and Bell, 1973, Sillitoe, 1973; Aral and Erler, 1981; Ayhan, 1991, Sillitoe and Hedenquist, 2003; Berger et al., 2008; Sillitoe, 2010). The main mineralization body is found enclosed by a pyrite rich shell. In the porphyry systems the most important sulphur minerals found are pyrite, chalcopyrite and molybdenite. They are present in the rocks as veins, veinlets and are in accord with the alteration zones (Lowell and Guilbert, 1970; Sillitoe, 1972, 1973; Lowell and Guilbert, 1974; Richards, 2003; Seedorff et al., 2005; Kesler and Wilkonson, 2006; Sillitoe, 2010; Oğuz, 2010).

Hydrothermal solutions described as solutions at 50°C-500°C temperature and have Na, K, Ca and Cl as main elements and Mg, B, S, Sr, Fe, CO<sub>2</sub>, H<sub>2</sub>S, NH4, Cu, Pb, Zn, Sn, Mo, Ag and Au as secondary elements (Skinner, 1979). Hydrothermal solutions could only have magmatic, metamorphic, sedimentary, meteoric or marine origin and could also be a mixture of these sources (Evans, 1987). In host rocks with high permeability, hot acidic hydrothermal solutions with low internal pressure, flow and carry their element contents through cavities and channels. In host rocks with low permeability, solutions move by filtering and in host rocks with very low permeability solutions move by absorption (Pirajno, 1992; Hedenquist et al., 2001; Einaudi et al., 2003; Sillitoe and Hedenquist, 2003; Pirajno, 2009; Sillitoe, 2010) (Figure 22). In the porphyry systems, minerals which have developed numbers of alteration types have been defined and sub groups like chloritization, hematitization, pyritization have been described (Mever and Hemley, 1967: Lowell and Guilbert, 1970, 1974; Pirajno, 1992; Sillitoe, 1993; Pirajno, 2009; Sillitoe, 2010). The subvolcanic intrusive/breccia complex is closely related with time and place of the hydrothermal alteration and mineralization. Silica rich volatile phase is believed to be the mechanism which brought mineralization to the area (Giles, 1973; Pirajno 1992, 2009; Sillitoe, 2010).

The Alpine Orogenic Belt which starts in Turkey, passes through The Caucuses and Iran then extends into Afghanistan, hosts numerous porphyry Cu-Mo-Au deposits. With limited explorations carried out in Turkey some low grade porphyry systems like Bakırçay (Amasya), Güzelyayla (Trabzon), Ulutaş (Erzurum), Balcılı (Artvin), Gümüşhane (Artvin) have been discovered. The ages of the intrusive rocks causing the development of the porphyry systems are Late Cretaceous (80 Ma), Eocene (45 Ma) and Oligocene (25 Ma) (Giles, 1973; Moore et al., 1980; Yiğit, 2006, 2009). In the host rocks of the porphyry copper mineralizations in Eastern Pontides have tonalite, quartz-monzonite, granodiorite and granite mineralogies (Pejatovic, 1971; Çağatay and Çağatay, 1978; Yalçınalp, 1995; Soylu, 1999; Singer et al., 2008; Oğuz, 2010). Among these porphyry systems Ulutaş-



Figure 22- Schematic illustration of the hydrothermal alteration in porphyry system (Simplified from Hedenquist et al., 2001; Sillitoe and Hedenquist, 2003; Sillitoe, 2010).

İspir (Erzurum) porphyry Cu-Mo deposit is quite close to the study area. Developments of Yeşilbağlar, Kaban and Köprübaşı alteration zones may be explained by the presence of Ulutaş-İspir porphyry Cu-Mo deposit. In the Eastern Pontides presence of various porphyry systems in different areas and the data presented in this study support the view that Cu, Mo, As type deposits associated with porphyry systems along belt are all subduction related.

In the study area advanced argillic-argillic, pyrophyllitic and sericitic alterations are the alteration types present. Advanced argillic alteration zones are quite extensive. Because of this, it is considered to be similar to the island arc porphyry system (Pejatovic, 1971; Çağatay and Çağatay, 1978; Yalçınalp, 1995). Mineralizations generally are pyrite, less chalcopyrite, galena, sphalerite and pyrrhotite. The main copper mineralization representing middle-deep sections of the porphyry systems are not clearly seen in the field. In Eastern Pontides from Early Jurassic onwards İzmir-Ankara-Erzincan ocean started closing subduction related (Celik et al., 2011; Topuz et al., 2012; Robertson et al., 2013). Collision between Taurus platform and Eurasia active continental margin took place in Early Eocene. Continent to-continent collision causing crustal thickening, continents gaining heights and erosions being effective. All these processes are believed to have affected the mineralized zone in the study area. Data collected show that Yeşilbağlar, Kaban, Köprübaşı alteration zones in the Olur (Erzurum) area and associated mineralizations show similarities to the upper portion of the porphyry mineralizations in the Pontides as well as in the Alpine Orogenic Belt, meaning, this may be taken as a clue of possible buried porphyry mineralization in the study area. Not having drilling data in the study proved to be a handicap. In the Kaban area there are abandoned addit entrances for copper mining belonging to pre Republic time.

#### 8.2. Results

(a) In the study area in Olur (Erzurum) Yeşilbağlar, Kaban, Köprübaşı, alteration zones are situated in the Eastern Pontides in the Alpine Orogenic Belt. These alteration zones have developed in the quartz porphyry apophsis of the Coşkunlar Dacite where Early Eocene Coşkunlar Dacite have intruded Early-Middle Jurassic Oltuçayı volcanics (basalt-andesite) and Kaban Dacite. (b) Alteration in the study area has been defined as advanced argillic-argillic, propylitic and sericitic zones.

(c) A late stage advanced argillic zone covers large areas and early stage alterations have been wiped out or masked and mineralization types of the advanced argillic alterations like veins-veinlets, smear and limited stockwork-disseminated, are present.

(d) FT-IR analyses showed that kaolinite, chlorite (clinochlore), quartz, illite, muscovite, gypsum, jarosite and barite are the minerals in the alteration zones. XRD studies agreed with the FR-IR results.

(e) Mineralizations present in the Yeşilbağlar, Kaban and Köprübaşı alteration zones are quite similer to the porphyry system mineralizations present in the upper part of the porphyry systems in the Pontides as well as in the Alpine Orogenic Belt. Based on this similarity it is concluded that in the study area there may be some buried porphyry type mineralizations in the deper part of the system.

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