GENETIC INVESTIGATION AND COMPARISON OF KARTALDAĞ AND MADENDAĞ EPITHERMAL GOLD MINERALIZATION IN ÇANAKKALE-REGION

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

GENETIC INVESTIGATION AND COMPARISON OF KARTALDAĞ AND MADENDAĞ EPITHERMAL GOLD MINERALIZATION IN ÇANAKKALE-REGION, TURKEY

Ünal, Ezgi

M.Sc., Department of Geological Engineering Supervisor: Prof. Dr. Nilgün Güleç Co-Supervisor: Prof. Dr. Ilkay Kuşcu

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This thesis study is concerned with the genetic investigation of two epithermal gold deposits (Madendağ and Kartaldağ) in Çanakkale, NW Turkey. The methodology comprises field and integrated laboratory studies including mineralogic-petrographic, geochemical, isotopic, and fluid inclusion analysis.

Kartaldağ deposit, hosted by dacite porphyry, is a typical vein deposit associated with four main alteration types: i) propylitic, ii) quartz-kaolin, iii) quartz-alunite-pyrophyllite, iv) silicification, the latter being characterized by two distinct quartz generations as early (vuggy) and late (banded, colloform). Primary sulfide minerals are pyrite, covellite and sphalerite. Oxygen and sulfur isotope analyses, performed on quartz (δ^{18} O: 7.93- 8.95 ‰) and pyrite (δ^{34} S: -4.8 ‰) separates, suggest a magmatic source for the fluid. Microthermometric analysis performed on quartz yield a temperature range of 250-285 °C, and 0-1.7 wt % NaCl eqv. salinity.

Madendağ deposit, hosted by micaschists, is also vein type associated with two main alteration types: illite and kaolin dominated argillization and silicification, characterized by two distinct quartz phases as early and late. Oxygen isotope analyses on quartz (δ^{18} O: 9.55-18.19 ‰) indicate contribution from a metamorphic source. Microthermometric analysis on quartz yield a temperature range of 235-255 °C and 0.0-0.7 wt % NaCl eqv. salinity.

The presence of alunite, pyrophyllite and kaolinite, vuggy quartz and covellite suggest a high-sulfidation epithermal system for Kartaldağ. On the other hand, Madendağ is identified as a low- sulfidation type owing to the presence of neutral pH clays and typical low temperature textures (e.g. colloform, comb, banded quartz).

Keywords: Kartaldağ Gold Deposit, Madendağ Gold Deposit, Hydrothermal Alteration, High Sulfidation Epithermal Systems, Low Sulfidation Epithermal Systems, Fluid Inclusion, Oxygen and Sulfur Isotopes

ÇANAKKALE YÖRESİ KARTALDAĞ VE MADENDAĞ EPİTERMAL ALTIN CEVHERLEŞMELERİNİN KARŞILAŞTIRMALI JENETİK İNCELEMESİ

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Bu tez çalışması, Çanakkale (KB Türkiye)'deki iki epitermal altın yatağının (Madendağ ve Kartaldağ) kökensel incelemesini konu edinmektedir. Metodoloji, arazi çalışması ile mineralojik-petrografik, jeokimyasal, izotopik ve sıvı kapanım analizlerini içeren bütünleşik laboratuvar çalışmalarını kapsamaktadır.

Kartaldağ yatağı, dasit porfiri yankayacında bulunan damar tipi bir yatak olup, dört ana alterasyon zonuna sahiptir: i) propilitik, ii) kuvars-kaolin, iii) kuvars-alünitpirofillit, iv) silisleşme. Silisleşme zonu, "vuggy" dokulu erken kuvars ve bantlıkolloform dokulu geç kuvarstan oluşan iki ayrı kuvars türü ile tanımlanmaktadır. Birincil sülfid mineralleri pirit, kovelit ve sfalerittir. Kuvars (δ^{18} O: 7.93- 8.95 ‰) ve pirit (δ^{34} S: -4.8 ‰) örneklerinin oksijen ve kükürt izotop analizleri, akışkan için magmatik bir kaynak önermektedir. Kuvarslardaki mikrotermometrik analizler ile 250-285 °C sıcaklık ve 0-1.7 % NaCl eşdeğeri tuzluluk aralıkları elde edilmiştir.

Madendağ yatağı mikaşist yankayacı içine yerleşmiş olup iki ana alterasyon türüne sahiptir: illit ve kaolen hakim arjillik alterasyon ve iki ayrı kuvars fazıyla (erken ve geç) betimlenen silisleşme. Kuvars minerallerinde yapılan oksijen izotopları ile elde

edilen aralık (δ^{18} O: 9.55-18.19 ‰) metamorfik bir kaynaktan katkı belirtmektedir. Kuvars üzerinde yapılan mikrotermometrik analizler, 235-255 °C sıcaklık ve 0-0.7 % NaCl eşdeğeri tuzluluk aralığı vermiştir.

Alünit, pirofillit ve kaolinit, "vuggy" kuvars ve kovelitin varlığı, Kartaldağ için yüksek sülfidasyonlu epitermal bir sisteme işaret etmektedir. Diğer taraftan Madendağ, nötr pH koşullarındaki kil mineralleri ve tipik düşük sıcaklık dokularının varlığından dolayı (kolloform, taraksı, bantlı kuvars) düşük sülfidasyonlu bir epitermal sistem olarak tanımlanmıştır.

Anahtar Kelimeler: Kartaldağ Altın Yatağı, Madendağ Altın Yatağı, Hidrotermal Alterasyon, Yüksek Sülfidasyonlu Epitermal Sistemler, Düşük Sülfidasyonlu Epitermal Sistemler, Sıvı Kapanım, Oksijen ve Kükürt İzotopları

To my family...

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CHAPTER 1

INTRODUCTION

1.1 Purpose and Scope

Western Anatolia is considered to be an important region within the framework of Tethyan metallogenic belt from the Balkans to Iran. Biga Peninsula hosting especially epithermal type deposits is regarded as an important component of this belt. Within the Biga Peninsula, Çanakkale is a metallogenic province hosting several epithermal and porphyry systems. The porphyry systems are usually localized within the Çan area, and usually co-exist with epithermal occurrences. The epithermal systems are more wide spread, and are recognized as high-sulfidation and low-sulfidation types.

This thesis is concerned with the genetic investigation and comparison of two epithermal gold deposits (Madendağ and Kartaldağ ancient gold mines) in Çanakkale from the perspective of a possible differentiation into high- and low-sulfidation type deposits. To accomplish this goal, field, petrographic, geochemical, isotopic and fluid inclusion studies were conducted on the samples from wall rocks and altered (mineralized) rocks.

1.2 Geographic Setting

Kartaldağ and Madendağ deposits (both are abandoned) are located in Biga Peninsula of western Anatolia, Turkey. The UTM coordinates outlining the study area are in between 462000 – 467000 Easting and 4427000 – 4434000 Northing coordinates in h17 d4 quadrangle of Turkey (Fig. 1.1). Kartaldağ deposit is situated 55 km southwest of Çanakkale (~6 km south of Terziler village), and accessible through the main from Çanakkale-Çan highway. Madendağ mine is located 50 km southwest of Çanakkale and \sim 3 km south of the Terziler village. The distance on topographic map between Madendağ and Kartaldağ mine is nearly 6 km.





1.3 Methods of Study

The thesis study was conducted through two main stages, a) field studies, b) laboratory studies.

a) Field studies were carried out in two field campaigns between September 2008 and October 2009. In the first field campaign, systematic sampling and mapping studies including revising present maps of the study area were accomplished. In the second field campaign, geological works focused more on alteration mapping and sampling for the fluid inclusion studies. In the study area, sampling was performed from several distinct locations for both Madendağ and Kartaldağ mine districts and they were explained in detail in the "Ore Deposit Geology" chapter of the present study.

b) Laboratory studies consist basically of petrographical, geochemical, fluid inclusion and geochronological studies. Thin and polished sections of selected samples for both Madendağ and Kartaldağ mine areas were examined to identify the mineral assemblage and the textural features of the fresh wall rocks and altered rocks, which are in turn used to define wall rock alteration type. Subsequently, XRD (X-Ray Powder Diffraction), SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-ray spectroscopy) analyses were performed to accompany petrographical identification of the alteration characteristics. Then, the wall rock (fresh and altered) samples were dated by Ar/Ar methodology to link the petrography, alteration and local geology. Together with the petrographical and geochronological data, whole rock geochemistry, stable isotope (oxygen and sulfur), and fluid inclusion studies of the selected samples representing two mineralization sites were utilized for completion of the data accomplished.

Among the laboratory studies;

i) Petrographical studies were performed in the Geological Engineering Departments of Middle East Technical University (METU), Muğla University, and Ankara University. 83 thin sections (75 for the ancient mine areas, 8 for the local geology) and 20 polished sections were prepared in the sample preparation laboratory of Department of Geological Engineering, METU. Transmitted and reflected light microscopes equipped with cameras were used for the mineralogic and petrographic identifications. The petrographical studies enabled selection of samples for geochemical and more detailed analyses including XRD, SEM/EDX and geochronology.

ii) XRD analyses of selected 13 samples were undertaken in the XRD laboratory of Geological Engineering Department of METU following a sample preparation stage. During sample preparation, 1 random and 4 oriented sample powders (< 2 μ m in grain size) were prepared for each sample. Random samples were prepared by placing the sample powders on glass slide holders (dry, random < 170 mesh (~63 μ m) samples). Oriented samples were prepared by first subjecting the sample powders to acid treatment to eliminate their carbonate and iron contents (Moore and Reynolds, 1997); treated sample powders were then placed on thin sections (oriented, wet samples of clay fraction). These oriented samples were X-rayed under air-dried; ethylene glycolated (overnight at 60 °C); heated in oven (300 °C) and fired at 550 °C in furnace in order to identify different clay mineral groups qualitatively. During the XRD analysis, standard 2- theta (degree) data were collected by using Rigaku MiniFlex II X-ray diffractometer. The XRD result for each sample is plotted by using software package of Rigaku Miniflex II.

iii) SEM/EDX studies of 5 selected samples were carried out in the SEM facility of Central Laboratory and SEM laboratory of the Metallurgical & Materials Engineering (METE) Department of METU. Monitoring of prepared (crushed, airdried, and reduced to sizes about 1 cm) samples was realized by using the devices of QUANTA 400F Field Emission SEM (Central Laboratory, METU) and JSM-6400 Electron Microscope (JEOL) equipped with NORAN System 6 X-ray Microanalysis System & Semafore Digitizer (METE-METU). Both morphological and compositional information were gathered about the samples via these microscopes combined with EDX equipments.

iv) ⁴⁰Ar /³⁹Ar geochronology was carried out at the The Pacific Centre for Isotopic and Geochemical Research (PCIGR) of the University of British Columbia (Canada), on hornblende, biotite, and sericite separates gathered from the fresh magmatic and altered rocks. A total of 5 samples selected from two deposits (1 sample from the altered metamorphic rock, 2 samples from the fresh and altered volcanic rocks, 2 samples from the fresh and weakly altered plutonic rocks were crushed, washed in deionized water, dried at room temperature, and sieved to obtain the size fraction between 0.25 mm and 0.15 mm. Mineral separates in an irradiation capsule with similar-aged samples and neutron flux monitors (Fish Canyon Tuff sanidine (FCs, 28.02 ± 0.16 Ma, Renne et al., 1998) were irradiated at the McMaster Nuclear Reactor in Hamilton, Ontario. The samples were analyzed at PCIGR by the Laser-Equipped Noble Gas Mass Spectrometer-Micromass VG 5400. All measurements were corrected for total system blank, mass spectrometer sensitivity, mass discrimination, radioactive decay during and subsequent to irradiation, as well as interfering Ar from atmospheric contamination and the irradiation of Ca, Cl and K The plateau and correlation ages were calculated using Isoplot version 3.09 (Ludwig, 2003). Errors are quoted at the 2-sigma (95% confidence) level and are propagated from all sources except mass spectrometer sensitivity and age of the flux monitor.

v) Whole rock geochemistry analyses were performed on 24 samples containing magmatic, metamorphic and altered rock samples in the ALS Laboratories, Canada. Analyses were carried out based on the commercial geochemical package named as CCP-PKG01"Complete Characterization". This package combines a number of methods: 1) ME-ICP06 method (uses Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)) for the major elements, 2) ME-MS81 method (uses Inductively Coupled Plasma - Mass Spectroscopy (ICP - MS)) for the trace elements including the rare earth element suite, 3) Leco Methods (analytical method

for total C: Infrared Spectroscopy, for total S: Leco sulphur analyzer) for the carbon and sulphur contents, 4) ME-MS4 method (uses Inductively Coupled Plasma - Mass Spectroscopy (ICP - MS)) for the volatile, Au related trace elements after an aqua regia digestion, and 5) ME-4ACD81 method (uses Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP - AES)) for the base metals after a four-acid digestion.

iv) Stable isotope measurements were carried out in the Stable Isotope Research Unit of Scottish Universities Environmental Research Center (SUERC), England.

Hand-picked quartz separates from the 6 silicified samples were analyzed for their oxygen isotope ratios using a CAMECA IMS-4f Ion Microprobe at the University of Edinburg (located 40 miles east of SUERC laboratory) using the technique described in detail by Graham et al., (1996). Analytical precision using this technique is +1 ‰.

For S-isotope analyses, a total of 2 pyrite separates from mineralized, crushed samples were hand-picked. A portion of each pyrite separate was classified between the size fractions of coarse (>100 mm) and fine (<100 mm). A few milligrams of each aggregate and size separate was combusted with Cu₂O at high temperature (1075 0 C) in *vacuo* to produce SO₂ (Robinson and Kusakabe, 1975) and purified to obtain the average δ^{34} S value of the bulk sample in a VG SIRA II [©] isotope ratio mass spectrometer. The precision of the isotopic measurements was about 0.2 ‰ (1 σ).

vii) Fluid inclusion studies were performed on the polished thin-sections (80-90 mm in thickness) in Fluid Inclusion Technologies (FIT) laboratory, Oklahoma, USA. For both Kartaldağ and Madendağ areas, a total of 6 sections were prepared from the quartz separates, and were studied for their petrographic features. The sections were examined in both planes light and under UV illumination. Fluid inclusion assemblages were identified according to their presence, relationship to the host, consistency of visual parameters (e.g. apparent vapor/liquid ratio) and applicability for determining required information such as homogenization temperatures and

salinities. As a result of petrographic studies, 3 out of 6 sections were found to be suitable for microthermometric analyses. A Fluid Inclusion Inc. modified U.S.G.S. - type gas-flow heating/freezing stage was used to measure the aqueous inclusion homogenization temperatures, final melting temperatures, and salinities.

1.4 Layout of Thesis

In this thesis, two abandoned gold mines from the Madendağ and Kartaldağ deposits, within Çanakkale were studied for a genetic investigation and comparison of two epithermal types. To accomplish this goal, a literature survey was followed by field, laboratory, and data evaluation studies.

Following this chapter (Chapter 1) which introduces the aim and scope of the thesis, as well as the geographic setting and methodology, information about the tectonic setting and regional geology of western Anatolia and Biga Peninsula are given in Chapter 2. An overview on the epithermal deposits, their general characteristics combined with the previous studies on the epithermal deposits known to occur in the Biga Peninsula constitute the subject of Chapter 3. In Chapter 4, local geology is presented, including field observations and correlations with the previous studies. Chapter 5 focused mainly on the ore deposit geology on the basis of mineralogic-petrographic features of the alteration zones and mineralization. Chapter 6 is concerned with the alteration geochemistry and stable isotope compositions, and geochronological characteristics of fresh magmatic rocks and altered rocks. In chapter 7, fluid inclusion studies are presented and the distinguishing features (including both petrographic and microthermometric analyses) are summarized for both areas. Finally, the discussions and the conclusive remarks of the whole thesis are outlined in the Chapter 8.

CHAPTER 2

TECTONIC SETTING AND REGIONAL GEOLOGY

The study area is regionally located in the northern part of the West Anatolian region within the Sakarya zone which represents one of the paleotectonic units of Turkey. Metamorphic basement of the area is intruded by several episodes of post-collisional granitoids and extension-related volcano-plutonic bodies.

2.1 Western Anatolia: Tectonic Setting and Geologic Outline

Western Anatolia comprises an integral segment of the Eastern Mediterranean belt. Geodynamic evolution of the Eastern Mediterranean belt is described basically within the framework of the plate tectonic movements resulting from the closure of the NeoTethys Ocean along the Aegean-Cyprian subduction zone and the subsequent continental collision of Anatolian and Afro-Arabian plates in eastern Anatolia and in the Caucasus (Dewey and Şengör, 1979; Taymaz et al., 2007). Presently, the western Anatolian region is undergoing an extensional regime represented by a number of E-W and NE-SW trending grabens and is referred to as "West Anatolian Extensional Province" (Fig. 2.1). The province is bounded by the structural systems of the Aegean–Cyprian subduction zone in the south-southwest, the dextral North Anatolian Fault System (NAFS) in the north and the dextral Tuzgölu Fault System (TFZ) in the east (Fig. 2.1).

Being one of the active components of the Eastern Mediterranean region, West Anatolian extensional province is an area of interest, the tectonics of which is still a debatable subject of a number of studies that have been recently summarized by Bozkurt (2001), Güleç and Hilton (2006). The commonly accepted models for the presently active extension in western Anatolia are follows:

- In most of the published papers (Dewey and Şengör, 1979; Şengör, 1979, 1987; Şengör et al., 1985; Taymaz et al., 1991; Görür et al., 1995), the westward tectonic escape (since the middle-late Miocene) of the Anatolian block along North Anatolian Fault Zone (NAFZ) and East Anatolian Fault Zone (EAFZ) as a consequence of the northward subduction of Arabian plate underneath the Anatolian plate is proposed as the main driving mechanism of the extension.
- 2) In connection with the subduction (since about the late Oligocene) along the Aegean-Cyprian trench, back arc extension related geological model is claimed by the studies of McKenzie, 1972, 1978; Le Pichon and Angelier, 1979; Jackson and McKenzie, 1988; Meulenkamp et al., 1988; Taymaz et al., 1990; Kissel and Laj, 1998; Okay and Şatır, 1999)
- 3) A gravitational or orogenic collapse model proposed by Seyitoğlu et al., 1992; Seyitoğlu and Scott, 1996- is claiming that the main cause for the Aegean and western Anatolian extension is the spreading and thinning of the over-thickened crust since the closure of the Neo-Tethys recorded back to the late Oligocene.
- 4) An episodic, two stage extensional model (Koçyiğit et al., 1999; Bozkurt, 2000, 2003; Bozkurt and Sözbilir, 2004) of the Aegean and Anatolian region combines the ideas that concern both the orogenic collapse as a first stage (since about the late Oligocene) and the tectonic escape (since late Miocene) as a finalizing stage of the extension.
- 5) The differential velocity of convergence across the African plate (the convergence of Greece being faster than Cyprus and Anatolia) constitutes the reason for the north- northwestern velocity increase towards the Aegean region and so for the extensional regime (Doglioni et al., 2002).

The paleotectonic evolution of western Anatolia is associated with a number of Mesozoic-Cenozoic closures of Neo-Tethyan oceanic branches and related micro continental collisions, as well as subsequently occurring post-orogenic events (Şengör and Yılmaz, 1981; Bozkurt and Mittwede, 2001; Okay et al. 2001; Dilek and Pavlides, 2006; Robertson and Mountrakis, 2006). Specifically, openings and closures of the Neo-Tethyan oceanic basins have played the role to characterize the nature and the location of the paleotectonic and neotectonic units confined to distinct representative suture zones (e.g İzmir-Ankara-Erzincan, Intra-Pontide, Inner Tauride, Antalya and Bitlis-Zagros sutures, Okay and Tüysüz, 1999) in the area.



Figure 2.1 Simplified map showing the tectonic setting of western Anatolia within the overall framework of the neotectonic units of Turkey (Bozkurt, 2001)

Western Anatolia comprises two major paleo-tectonic units, Sakarya zone in the north and the Menderes Massif in the south, the boundary of which is defined by İzmir-Ankara suture (Fig.2.2). The study area is located within the Sakarya zone and the regional geology of the study is given in the following sections within the overall framework of the Sakarya zone.



Figure 2.2 The map showing the major paleo-tectonic units of western Anatolia (Bozkurt and Oberhänsli, 2001)

2.2 Biga Peninsula: Regional Geology

The study area lies within the Biga Peninsula that constitutes the western end of the Sakarya Zone (Fig. 2.2). The rock units outcropping in the Biga Peninsula can be grouped as Pre-Tertiary and Tertiary units (Fig. 2.3, 2.4), and correlate with the "Ezine Zone" of Okay et al. (1991). Ezine Zone is composed of three NE-SW trending rock associations: a) Karadağ metamorphics, b) Denizgören Ophiolite, and c) Çamlıca metamorphics.

In this section, regional rock associations of the Biga Peninsula are explained on the basis of their ages as Pre-Tertiary - basement rocks, and Tertiary - overlying rocks. While basement rocks are mainly composed of metamorphics, overlying units are formed by Eocene-Miocene marine sediments, Eocene and Oligo-Miocene granitoids

and their volcanic equivalents together with Late Miocene - Pliocene volcanics and siliciclastic sedimentary rocks (Fig. 2.3, 2.4).



Figure 2.3 Regional geologic map of Biga Peninsula (modified from Okay and Satır, 2000)
2.2.1 Pre-Tertiary – Basement Rocks

The lowermost geologic unit of Biga Peninsula is the Paleozoic, high-grade metamorphic rocks (phyllite, amphibolite, marble, metaperidotite, and gneiss) referred to as either the Kazdağ Massif (Bingöl et al., 1973; Duru et al., 2004) or Kazdağ Group (Okay et al., 1991) or Kazdağ metamorphic complex (Okay and Satır, 2000). This Paleozoic metamorphic basement is tectonically overlain by the Triassic Karakaya Complex (Fig 2.3). The metamorphic rocks of the Karakaya Complex (metabasites, marbles, schist, and phyllites) are generally metamorphosed in greenschist facies (Bozkurt and Mittwede, 2001; Okay and Göncüoğlu, 2004) The Karakaya Complex is unconformably overlain by the Jurassic-Lower Cretaceous sedimentary rocks and Upper Cretaceous-Paleocene subduction-accretion mélanges (Okay and Satır, 2000). In addition to these units, Okay et al. (1991) and Okay and Satır (2000) distinguished another metamorphic unit in the pre-Tertiary basement of Biga Peninsula which is entitled as Camlica metamorphics (micaschists) that seem to be tectonically overlain -in places- by ultramafic bodies. The Camlica metamorphics with serpentinite slivers are also the common rock types exposed in the study area forming the Pre-Tertiary basement rocks in this thesis. Camlıca metamorphics are considered as an overlying unit of the Kazdağ massif by Kalafatçıoğlu (1963) and Bilgin (1999), while Sengün and Çalık, (2007) and Sengün et al. (2010) suggest that the Çamlıca metamorphics are equivalent of the İznik metamorphics in Armutlu Peninsula. On the other hand, Göncüoğlu (1995), Göncüoğlu et al. (1997), Okay and Satir (2000), Beccaletto (2003), and Beccaletto and Jenny (2004) propose that Çamlıca metamorphics have affinities with the Rhodope and Serbo-Macedonian Massifs of Bulgaria and Greece.

The Çamlıca metamorphics extend from the north and northeastern part of Ezine to west of Karabiga and covers an area of nearly 500 km² in the Biga Peninsula (Fig. 2.4). As investigated separately by Okay et al. (1991) as well, the Çamlıca micaschists in the north of Ezine differ from the micaschists outcropping to the west of Karabiga and called recently as Kemer micaschists (Bonev and Beccaletto, 2005, 2007). While reference section of the Çamlıca metamorphics (or micaschists) is defined on the highway between Ezine to Çanakkale to the northeast of the Ezine,

close to the Çamlıca village, Kemer micaschists are entitled from the Kemer village on the Marmara sea coast. The çamlıca micaschists, outcropping in the north of Ezine, is structurally bounded by two faults, i) 33 km long, reverse Ovacık fault in the north, and ii) poorly exposed Karıncalı fault in the south (Okay and Satır, 2000).

In the north of Ezine, Şengün and Çalık (2007) grouped the Çamlıca metamorphics basically into three tectonostratigraphic units as i) Andıktaşı, ii) Dedetepe, and iii) Salihler formations. Andıktaşı formation is made up of metavolcanics and metapelite; Dedetepe formation, which is seen in the study area, is composed of muscovite - quartz schist, chlorite - muscovite - quartz schist, garnet - micaschist garnet-chlorite-micaschist, calc-schist, amphibolite, and marbles; Salihler formation is, as an uppermost stratigraphic unit, formed by chlorite phyllite, calc-schist, and marble (Şengün and Çalık, 2007). According to the index metamorphic minerals, they are thought to be metamorphosed initially in eclogite facies and affected by the facies of amphibolite and greenschist from the core to the margins of a regional large-scaled anticline.



Figure 2.4 Geological map of northern Ezine showing the study area (from Okay and Satır, 2000)

2.2.2 Tertiary rocks of the Biga Peninsula

The sedimentary, volcanic and volcano-sedimentary rocks (Tertiary in age) overlying the pre-Tertiary basement in the Biga Peninsula are called overlying rocks in this thesis, along with the Eocene and Oligo-Miocene granitoids.

2.2.2.1 Neogene sedimentary sequences

These consist of Eocene-Miocene marine sediments and Miocene-Pliocene continental sediments (Fig. 2.3). The Eocene to Miocene sedimentary rocks within the Biga Peninsula, predominantly marine type, include conglomerate, sandstone, siltstone, mudstone, marl, calc-arenite, and oolitic and neritic limestones, whereas Miocene-Pliocene continental sedimentary rocks include conglomerate, sandstone, and mudstone.

2.2.2.2 Cenozoic volcanism

Following the closure of Neo-Tethyan Ocean between Sakarya continent and Anatolide-Tauride platform during Late Paleoecene-Early Miocene (Bozkurt and Mittwede, 2001), beginning of the post collisional regime (Latest Early Eocene, Yılmaz et al., 1995; Genç and Yılmaz, 1995) is regarded as the controlling mechanism for the extensive Eocene – Miocene magmatism in the Biga Peninsula.

Regarding the genesis of the Cenozoic volcanism in Biga Peninsula, the proposed models commonly accept two types of volcanic associations; i) Middle Eocene - Miocene calc-alkaline associations, and ii) Late Miocene alkaline associations (Güleç, 1991; Aldanmaz, 2000; Yılmaz et al., 2001; Altunkaynak, 2007; Altunkaynak and Genç, 2008). While the former group suggests a subduction and collision-related interplay in the process (Yılmaz et al., 2001; Altunkaynak, 2007; Dilek and Altunkaynak, 2009), the latter favors the present extensional regime (Güleç, 1991; Aldanmaz, 2000; Yılmaz et al., 2001).

2.2.2.3 Granitoids of the Biga Peninsula

In the recent studies by Altunkaynak (2007) and Karacık et al. (2008), the granitoids in Biga Peninsula are grouped into two as i) Marmara and ii) suture zone (i.e., Izmir Ankara Erzincan Suture Zone) granitoids that intruded into Paleozoic-Mesozoic metamorphic basement of Sakarya continent. Marmara granitoids are mostly composed of monzogranite, granodiorite, and granite, while suture zone granitoids are classified generally as diorite, quartz diorite, granodiorite, and syenite.

Plutonic rocks in Biga Peninsula are grouped into two, by Altunkaynak (2007) and Altunkaynak and Genç, (2008), as the products of i) Eocene, and ii) Oligo-Miocene magmatism (Fig. 2.5). They show calc-alkaline, high-K calc-alkaline and shoshonitic, affinities (Altunkaynak and Genç, 2008). According to the geochemical constraints, they are regarded as the evolutionary products of melts derived from subduction-influenced lithospheric mantle. While Eocene plutons are exemplified by Fıstıklı, Karabiga, Kapıdağ in the north and Orhaneli, Topuk, Göynükbelen, Gürgenyayla, Kuşçayır in the south, Miocene granitoids are represented by Evciler, Çataldağ, Kestanbol, Ilıca-Şamlı, Eybek (Fig. 2.5) (Genç, 1998; Altunkaynak 2007).



Figure 2.5 Simplified geological map of Altunkaynak (2007) showing the distribution of Eocene and Oligo-Miocene granitoids of NW Turkey (1: Kestanbol Pluton, 2: Kuşçayır Pluton, 3: Evciler Pluton, 4: Karabiga Pluton, 5: Eybek Granodiorite, 6: Kapıdağ Granitoid, 7: Ilıca - Şamlı Granodiorite, 8: Çataldağ Granodiorite, 9: Fıstıklı Granitoids, 10: Orhaneli Granitoid, 11: Topuk Granitoid, 12: Göynükbelen Granitoid, 13: Gürgenyayla Granitoid)

CHAPTER 3

EPITHERMAL DEPOSITS: AN OVERVIEW

3.1 General Characteristics of Epithermal Deposits

The term *epithermal* was first defined by Lindgren (1922, 1933) as a term in which "epi" means shallow, "thermal" refers to heated fluid. Epithermal deposits are formed in an environment that is shallow in depth and typically hosting deposits of Au, Ag, and base metals formed at low temperatures (200- 300°C). They are related to intrusive and eruptive igneous rocks forming veins at shallow depths (maximum depth of 1 km) that contain open-cavity filling textures and source of "bonanza" metals/deposits (Berger and Henley, 1989).

Epithermal deposits generally form at the top of magma-related hydrothermal systems but their development is strongly affected by fluids of external origin (meteoric water). Presently, it is accepted that the weakly saline (<1 to ~5-15 wt % NaCl eqv.) fluids at slightly higher temperatures (200-300°C) and at pressures less than a few hundred bars are predominantly responsible for the formation of epithermal deposits. Basically, ore bearing fluids forming such systems have a low temperature range of 50 to 300 °C; usually between 160° and 270°C, and low to moderate pressures < 500 bar or depths equivalent to 1 - 1.5 km (Pirajno, 2009).

Epithermal associated ore minerals are generally native gold, native silver, electrum, argentite, sulfosalts, tellurides, and selenides, and often the sulfides, namely, pyrite, sphalerite, galena, and chalcopyrite. Gangue minerals are quartz, amethyst, chalcedony, pyrite, carbonates (e.g. calcite), barite, rhodochrosite, adularia, and fluorite.

Open space filling textures (typical for the low pressure environments) such as comb structure, crustification, symmetrical and colloform banding, crystal-lined vugs, and hydrothermal breccias are common and distinctive features for the epithermal systems. Hydrothermal alteration is commonly widespread especially in the upper portions of the epithermal vein systems and alteration products include quartz, adularia, illite, chlorite, alunite, kaolinite and/or dickite and sericite (Hedenquist et al., 2000; Deb, 2008).

Based on alteration mineralogy and fluid chemistry, epithermal deposits are classified genetically into two end-members as low sulfidation (LS) or adulariasericite type and high sulfidation (HS) or acid-sulfate type. A transition type, intermediate sulfidation (IS) systems, is defined as a subtype of the low sulfidation systems (Hedenquist et al., 2000; Hedenquist and Sillitoe, 2003). The dominant factor used for the nomenclature of the types differs widely such as fluid chemistry, oxidation, sulfidation, and alteration mineralogy (Table 3.1).

1	LS	HS	Reference
Au-Q veins in an Ag-Au, Ag, Au-T Base metal vei Cinnabar, s	desite and rhyolite e, and Au-Se veins. ns with Au, Ag, atibnite veins	Au-Alunite	Lindgren,1922,1933
Alk	aline	Acid	Sillitoe,1977
Low	Sulfur	High Sulfur	Bonham,1986,1988
Adulari	a-Sericite	Acid Sulfate	Hayba et al., 1985 Heald et al., 1987
Low Sulfidation		High Sulfidation	Hedenquist,1987
Adulari	a-Sericite	Alunite-Kaolinite	Berger and Henley, 1989
Type 1 adularia - sericite	Type 2 adularia – sericite	-	Albino and Margolis,1991
High sulfide + base metal, low sulfidation	Low sulfide + base metal, low sulfidation	High Sulfidation	Sillitoe, 1989, 1993
Intermediate Sulfidation	Low Sulfidation	High Sulfidation	Hedenquist et al., 2000;

Table 3.1 Nomenclature used for the two end-member epithermal environments(modified from Hedenquist et al., 2000; Hedenquist and Sillitoe, 2003)

LS and HS deposits exhibit certain differences summarized as follows: Low sulfidation type epithermal systems are characterized by: i) the predominance of reduced S species (HS⁻, H₂S), ii) sericite, intermediate argillic and chloritic alteration with adularia (K-feldspar), and thus, known to be formed by near-neutral pH, S-poor (low sulfur) and reduced fluids. High sulfidation type, on the other hand, is characterized by: 1) the presence of a significant component of oxidized S species (H²SO₄-, SO₃⁻², SO_{2(g)}), 2) advanced argillic assemblage, dominated by alunite (Ksulfate) and pyrophyllite at deeper levels, and, therefore, known to be formed by acidic (low pH), S-rich (high sulfur), oxidized fluids. Intermediate sulfidation type combines some of the distinct features of both types. It is dominated by sphalerite, galena, tetrahedrite, tennantite, chalcopyrite, and sericite (other than adularia) indicating higher temperatures (probably higher formation depths) than low sulfidation type and generally associated with calc-alkaline andesite-dacite volcanics. Indeed, low, intermediate, and high sulfidation refer to the oxidation potential and sulfur fugacity of the fluid that deposited the sulfides; not to the S content of the sulfides (Einaudi et al., 2003) (Fig. 3.1). Phase diagram of $\log f_{S2}$ versus temperature yield the zones of certain sulfidation states, from very low and low, through intermediate, to high and very high, which are reflecting distinct compositional areas such as arc volcanic rocks, high temperature volcanic fumaroles, magmatic hydrothermal, and geothermal areas.



Figure 3.1 *f* S₂–T phase diagram showing the sulfide minerals in epithermal deposits defining the *sulfidation states* (Hedenquist and Sillitoe, 2003)

There is no clear relation that typifies the connection between the epithermal deposits and their sedimentary hosts, but it is universally recognized that such deposits are generally associated with volcano-plutonic environments either in the form of near surface veins and stockworks or disseminations. Subaerial volcanism and intrusion of calc-alkaline magmas that range from basaltic andesite through andesite and dacite to rhyolite compositions constitute the probable host rocks and related tectonic settings of epithermal deposits (Fig. 3.2).



Figure 3.2 Tectonic settings of gold-rich epigenetic mineral deposits (Groves et al., 1998)

Similar to the porphyry deposits, global distribution of epithermal deposits reflect the genetic linkage to the magmatic centers, especially along the Circum Pacific Belt (Fig. 3.3). Best – known examples of epithermal deposits are generally in Cenozoic age, but there are Paleozoic and Mesozoic examples as well (Simmons et al., 2005). Cenozoic epithermal deposits located in Italy, Turkey, Spain, and the Carpathians comprise the examples of epithermal related deposits in the Alpine-Himalayan orogenic belt. Since the ancient examples of epithermal systems are exposed to erosion and thus not preserved to recent times, well known epithermal deposits are all in Cenozoic age.



Figure 3.3 Global distribution of epithermal and intrusion related Au deposits (Taylor, 2007)

According to Hayba et al., 1985, the epithermal systems can be differentiated on the basis of their proximity to a heat source. While high sulfidation systems develop above or as a lateral offset of a porphyry system at the subvolcanic depths, low sulfidation systems evolve at a slower rate, relatively away from the heat source. A diagrammatic view of high and low sulfidation systems are illustrated in the study of Hedenquist and Lowenstern (1994) (Figure 3.4). This diagram shows the physico-chemical environments of the geothermal and volcanic hydrothermal systems related to the epithermal systems. In this illustration, near neutral pH and reduced, relatively deeper boiling fluids below the geothermal environment, form the low sulfidation deposit in equilibrium with the wall rocks. In the opposite site, near the volcanic-hydrothermal centers, highly oxidizing, acidic fluids yield the high sulfidation deposit which is thought to occur faster than the low sulfidation counterpart.



Figure 3.4 Sketch view displaying the formations of two end-member epithermal deposits and their relation with the subvolcanic source (Hedenquist and Lowenstern, 1994; Hedenquist et al., 1996, 2000)

Hydrothermal alteration shows both similarities and differences among the low and high sulfidation types. In the low sulfidation type, due to the neutral and reduced fluids, wall rocks (hosting mineralization) have alteration mineralogy characteristic for neutral environment. Following an ore vein towards the wall rocks, argillic (mostly illite, smectite, kaolin, and adularia), sericitic (sericite, pyrite, quartz), and propylitic (chlorite, calcite, epidote, and albite) alterations are observed generally. On the other hand, high sulfidation deposits, being formed by an acidic, oxidizing fluid, display the advanced argillic, argillic, sericitic, and propylitic alterations from the margins of the vuggy ore zone towards the wall rocks. Advanced argillic alteration is mainly composed of alunite, kaolinite, dickite, pyrophyllite, whereas argillic alteration includes kaolin and smectite group clay minerals. Vuggy ore zone refers to the early leached zone formed by this acidic, highly oxidizing fluid influx. Typical hydrothermal minerals that form these alteration assemblages are summarized in the Figure 3.5 with their pH values and commonly observed temperatures ranges. Given alteration minerals characterize typical epithermal

environment, thus the related epithermal ore deposit, and are examined as alkaline, neutral, and acidic based on the thermal stabilities.



Figure 3.5 Thermally induced hydrothermal minerals in the epithermal ore zone (White and Hedenquist, 1995; Hedenquist et al., 2000)

3.1.1 Low Sulfidation (LS) type epithermal deposits

Low sulfidation type epithermal deposits are generally associated with the volcanic rocks of andesite-rhyodacite and bimodal rhyolite-basalt. Deposit form might be veins, stockworks, and/or disseminations. Ore textures can be crustiform banding (Fig. 3.6), combs, and hydrothermal breccias. Alteration and gangue mineralogy is summarized commonly with the minerals of sericite, carbonates (e.g. calcite), kaolin, smectite, illite, pyrite, quartz, chalcedony, and rhodochrosite. When the deposition occurs at the shallow depths (0-300 m), mostly colloform chalcedonic formations with abundant calcite, illite, and adularia are observed; when it is developed under deeper conditions (300-500 m), gangue and alteration mineralogy changes into the assemblage of quartz, carbonate, rhodochrosite, sericite, adularia \pm barite \pm anhydrite

 \pm hematite \pm chlorite. Cinnabar, stibnite, pyrite/marcasite-arsenopyrite, galena, sphalerite (generally Fe-rich), chalcopyrite, and tetrahedrite minerals are common sulfides typified with the low sulfidation systems.



Figure 3.6 Crustiform and colloform banding and comb textured ore at the McLaughlin mine, California, USA (Deb, 2008)

As previously stated, the low sulfidation state minerals that formed by reduced, neutral-pH waters are in equilibrium with the host rock alteration minerals and the fluid is characterized by low salinity (0-4 wt %), and low temperature (150-300 °C) and pressure.

Alteration and mineralization style of LS type is modeled by Hedenquist et al. (2000) (Fig. 3.7) basically showing that a steam heated chalcedonic blanket covers (i.e. overlying cover) the low sulfidation ore zone which is composed of disseminated and vein ores. Mineral based alteration of the host rock diverging from the vein is divided into three as sericite/illite \pm adularia, smectite/mixed layered clay \pm chlorite, and calcite \pm epidote.

In LS epithermal deposits, boiling is widely accepted as the critical process to deposit high concentration of Au from bisulfide complexes due to gas loss (see the reaction 1 below) (Fig. 3.8)

$$Au(HS)_{2}^{-} + H^{+} + 0.5H_{2(aq)} = Au_{(s)} + 2H_{2}S_{(g)}$$
 (rxn.1)



Figure 3.7 General model created for the LS alteration style (Hedenquist et al., 2000)

As in the case of the geothermal systems - active counterpart of the low sulfidation epithermal systems-, the concentration of CO_2 and the salinity degree in solution are the principal controls on pH. Therefore, mechanisms including boiling and loss of CO_2 to the vapor result in an increase in the pH which, in turn, gives rise to the formation of adularia from illite depending on their stability. Additionally, the deposition of calcite, mostly developed as a late stage alteration product, occurs due to the loss of CO_2 . Boiling is the process that explains the common occurrence of adularia and bladed calcite seen as gangue minerals in low sulfidation ore veins (Hedenquist et al., 2000; Cooke and Simmons, 2000). Bladed calcite formations are often accompanied by the quartz pseudomorphs. Evidences known for the boiling are hydrothermal breccias, steam-heated blankets, adularia, and bladed calcite, two of which (first two evidences) can be grouped as indirect; other two (last two evidences) as direct evidences.



Figure 3.8 A sketch displaying the boiling process in the low sulfidation systems (Cooke and Simmons, 2000)

3.1.2 High Sulfidation (HS) type epithermal deposits

High sulfidation type epithermal deposits are related to volcanic rocks of andesiterhyodacite, dominated by calc-alkaline magmas. Deposit forms are generally veinlets, dissemination, and hydrothermal breccia. Vuggy quartz hosts replacements, late veins, minor stockworks, and hydrothermal breccias comprise the common ore textures. Alteration styles are dominated by the silicic (vuggy) quartz-alunite (Fig. 3.9), pyrophyllite-dickite-sericite. Enargite-luzonite, covellite, pyrite, chalcopyrite, bornite, and chalcocite are the common sulfides formed in such epithermal systems.



Figure 3.9 The silicic vuggy host in Summitville HS deposit, Colorado, USA (Deb, 2008)

Alteration and mineralization style of HS type is modeled and displayed in Figure 3.10. This model is based on a hypogene acidic fluid derived from the volcanic-hydrothermal environment, leaching the rock, creating a core of residual, commonly vuggy silica (crystallizes to quartz). These silicic zones comprise the core of an advanced argillic alteration and represent an aquifer channel for a subsequent ore (e.g. Au and Ag) bearing fluid.

In detail, the fluids ascending through a discontinuity (mostly a fault) interact with groundwater to form highly acidic solutions. These solutions decompose and dissolve the surrounding rock leaving only silica behind, often in a sponge-like texture known as vuggy silica. Gold and sometimes copper rich brines that also ascend from the magma then precipitate their metals within these vuggy silica formations. If the acidic fluids encountered a broad permeable body of rock unit, vuggy silica zone can even be larger enough to host large bulk-tonnage mineralization with lower grades. After forming the core of the alteration zone, the acidic fluids are progressively neutralized by the wall rock the further they move away from the fault. The rocks in turn are altered by the fluids into progressively more neutral-stable minerals from the assemblages of advanced argillic through argillic to propylitic alterations (Fig. 3.10) (Hedenquist et al., 1994; Hedenquist et al., 2000; Cooke and Simmons, 2000).



Figure 3.10 Diagrammatic alteration model created for HS epithermal deposits (Hedenquist et al., 1994; Hedenquist et al., 2000)

For the HS epithermal deposits, mixing is thought to be the most accepted mechanism for the ore deposition as proved by many isotopic evidences (Cooke and Simmons, 2000). Precipitation of the metals (e.g. Au) derived from the magma and transported by the acidic fluids is believed to occur while the fluids mix with the groundwater which in turn causes the decrease in the solubility of Au (or any other precious and base metals related with such physicochemical environments) (see the example reaction 2 below).

$$AuHS_{(aq)} + 4H_2O_{(l)} = Au_{(s)} + SO_4^{-2}{}_{(aq)} + 2H^+ + 3.5H_{2(aq)}$$
 (rxn.2)

A two stage genetic model (Fig. 3.11) is proposed for the evolution of the HS deposits (White, 1991; Rye, 1993; Hedenquist et al., 1994a; Arribas, 1995) in which stage A considers the alteration, whereas stage B involves the two ore deposition hypothesis. As shown in the Figure 3.11, high temperature magmatic volatiles (including the vapors of SO₂, HCl, and H₂S etc.) derived from a shallow intrusion encounter with the ascending heated ground water to generate acid sulfate high sulfidation fluids (with the temperatures of 200-350 $^{\circ}$ C, pH values of 0-2, and salinities of 2-5 wt % NaCl eqv.) which causes the strong leaching of the wall rocks and, in turn, causes porous residual silica (vuggy quartz) and advanced argillic alteration (e.g. alunite, pyrophyllite). In the main ore-deposition stage, i) absorption of high pressured vapor at depth or ii) mixing with the shallow cooler meteoric water of the ore bearing hypersaline liquid come into consideration. Both hypotheses of ore deposition stage explain the low salinity and magmatic – meteoric characteristics of the high sulfidation ore fluids.



Figure 3.11 HS alteration and ore deposition model based on the previous model of White, 1991 (Arribas, 1995; Cooke and Simmons, 2000)

3.2 Epithermal Deposits in Turkey

Regarding the tectonic setting of Turkey, Turkish epithermal systems tend to occur in two regions: northeastern and western Turkey (Yiğit, 2009) (Fig. 3.12). While Late Cretaceous to Eocene submarine and subaerial volcanic rocks are hosting the epithermal mineralization in NE Turkey, Neogene subaerial rock associations (generally volcanic rocks) comprise the host rocks for the western epithermal mineralization. Main base and precious metals associated with Turkish epithermal deposits are Au, Ag, Hg, Pb, Zn, and Sb.

In western Turkey, especially the N-S trending extension related magmatism, though its genesis is still under debate, is thought to control the structural setting that enables the emplacements of the volcanic and plutonic rocks (Fytikas et al., 1984; Güleç, 1991; Seyitoğlu and Scott, 1992; Setiyoğlu et al. 1997; Aldanmaz et al., 2000; Aldanmaz, 2002; Yılmaz et al., 2001). Thus, the jointing and faulting attributed to this extensional regime constitute the proper structural controls for the epithermal mineralization in western Turkey. Hereby, the exploration projects on epithermal mineralization (for both high sulfidation and low sulfidation types) have been recently focused on this region. Apart from the national mining companies, many international mining companies have been exploring epithermal gold in western Turkey since late eighties. Quite a number of economic epithermal deposits were discovered in this region by studies that have been carried out since 1991. While the high sulfidation type epithermal deposits are mainly concentrated in the Biga Peninsula (Pirajno, 2009) (for instance, Kartaldağ (Watanabe et al., 2003) and Kirazli (Pirajno, 1995) in Çanakkale), best known low sulfidation epithermal deposits are located both in western (Ovacık-İzmir (Yılmaz, 2002; Yılmaz et al., 2007), Efemçukuru-İzmir (Oyman et al., 2003)) and in northwestern Turkey (Küçükdere-Balıkesir (Çolakoğlu, 2000)).



Figure 3.12 Distribution of the epithermal deposits and prospects of Turkey showing Madendağ and Kartaldağ deposits (from Yiğit, 2009)

3.3 Biga Peninsula: Previous Studies

The distribution of the epithermal systems in Biga Peninsula is associated with Eocene to Pliocene volcanic and plutonic rocks overlying the Paleozoic (mostly) metamorphic basement (see Chapter 2). Concerning the tectonic and magmatic history of the Biga Peninsula, the nature (calc-alkaline/alkaline) of the host rocks seems to control the type of the deposits in terms of alteration styles and capability of metal transport. Since the ancient times (e.g. ancient Troy), dating back to nearly 3200 BC with the archeological evidences, many of the epithermal deposits in Çanakkale and the surroundings were exploited and the present study presents two examples of those ancient abandoned mines.

Previous studies regarding the epithermal deposits in the Biga Peninsula are summarized under the headings of high (HS) and low (LS) sulfidation types in Tables 3.2 and 3.3, respectively.

Reference	Watanabe et al., 2003 ⁽¹⁾ , JICA, 1989	Yiğit, 2006 ⁽²⁾ , 2009; Pirajno, 1995; 2009, Alamos Gold Inc., web Release, 2009	Yiğit, 2009	Yiğit, 2006 ⁽⁴⁾ , 2009, Alamos Gold Inc., 2009 ⁽³⁾	Eldarado Gold Co. 2005 ⁽⁵⁾ , Yiğit, 2009 ⁽⁶⁾	Yiğit, 2009 ⁽⁶⁾	Yılmaz, 2003 ⁽⁷⁾ ; Watanabe et al., 2003	Pirajno, 2009
Mineral reserve and/or resource with average grades	50 000 t with 1.38 g/t Au and 29.5 g/t Ag	10 900 t, 20 g/t Au in the high grade oxide zone ⁽²⁾ , 316 000 oz Au ⁽³⁾ , 5,295,000 oz Ag ⁽³⁾	0.50 g/t Au and 0.53 % Cu in the porphyry zone	1.8 Moz Au $^{(4)}$ and 12.3 Moz Ag $^{(4)}$, 991 000 oz Au (indicated) $^{(3)}$ and 5,371,000 oz Ag (indicated) $^{(3)}$	14 g/t Au (west) and <1 g/t Au (east) ⁽⁵⁾ , 1 Moz Au resource ⁽⁶⁾	1.79 g/t Au in one drill hole $^{(6)}$	Average 0.4 g/t $Au^{(7)}$	10 g/t Au and 2.8 % Cu in Bakırlık vein
Ore texture	Veins, breccias	Stockworks, breccias, dissemination, replacements	Stockworks, veins	Disseminations and breccias	Vuggy silica zone, veins	Veins	Stockworks, replacements, and breccia zones	Stockworks, brecciation
Age of the host rock	Eocene (present study), Miocene	Oligo-Miocene	Oligocene?	Oligocene	Miocene	Oligo-Miocene?	Eocene	Oligo-Miocene
Host rock	Dacite porphyry	Andesite, Dacite	Andesite	Volcanic rock	Andesite	Andesite, Dacite?	Granodiorite porphyry and andesite volcanics	Andesite
Precious / Base Metal	Au, Ag	Au, Cu, Ag	Au, Cu	Au,Ag,	Au	Au	Au, Cu, Mo	Au, Cu
Province	Çanakkale	Çanakkale	Çanakkale	Çanakkale	Çanakkale	Çanakkale	Çanakkale	Çanakkale
Deposit Name	Kartaldağ (Serçeler)	Kirazlı	Halilağa	Ağı dağı (Deli and Baba deposits)	Keditaşı	Pirentepe	Kuşçayır	Doğancılar

Table 3.2 Known HS type epithermal deposits with their principal features in Biga Peninsula (superscript numbers refer to the references)

Reference	MTA 1993; Yiğit, 2006; Watanabe et al., 2003	Yıldırım and Cengiz, 2004	Çolakoğlu, 2000; Watanabe et al., 2003	Yiğit, 2009	Watanabe et al., 2003	1
Mineral reserve and/or resource with grade	15 000 t possible reserve at 5.8 g/t Au	7.5 Mt at 8.5 g/t Au	1500 Mt. of ore with 5.0 g/t Au and 11.8 g/t Ag	56 537 Mt at 0,55 g/t Au	Under project	
Ore textures	Breccia zones, stockworks, veins	Veins	Veins, breccia	Breccia, stockworks, and alteration zones	Disseminations, breccia	Veins, breccia zones
Age of the host rock	Paleozoic	Paleozoic and Paleocene- Eocene	Miocene	Miocene	Miocene	Miocene
Host rock	Micaschist	Volcanics and schist	Andesite porphyry	Dacite, rhyodacite, andesite	Andesite	Andesitic tuff
Precious / Base Metal	Au	Au, Ag	Au	Au	Au	Νu
Province	Çanakkale	Çanakkale Çanakkale Balıkesir Çanakkale		Çanakkale	Balıkesir	Çanakkale
Deposit Name	Madendağ (Akbaba)	Şahinli (Lapseki)	Küçükdere (Havran)	Kısacık (Ayvacık)	İvrindi (Kınık)	Küçükkuyu (Avcılar)

Table 3.3 Known LS type epithermal deposits with their principal features in Biga Peninsula

CHAPTER 4

LOCAL GEOLOGY

4.1 Rock Units

The rock units exposed within the study area by which two ore deposits are hosted, are integral parts of the regional metamorphic and ophiolitic rocks, collectively termed as the Pre-Tertiary rocks (see Chapter 2), and overlying Tertiary volcanic, plutonic and volcanoclastic rocks. The pre-Tertiary units are also termed as the basement rocks in this study. These include Paleozoic metamorphic rocks and overlying ophiolitic rocks of Late Cretaceous age. Tertiary rocks include middle Eocene granodiorite, middle Eocene dacite, Eocene-Oligocene tuff, Oligocene-Miocene andesite, Miocene siliciclastic sedimentary rocks, and Quaternary alluvium (Fig. 4.1; Fig. 4.2).

4.1.1 Pre-Tertiary Rocks

The basement in the study area is represented by micaschists widely exposed as the most common rock type defined within the Çamlıca metamorphics (Okay et al., 1991) elsewhere (Fig. 4.1 and Fig. 2.4). An occasional ophiolitic sliver is also exposed in the Madendağ mine area.

A great majority of the Çamlıca metamorphics (over 80 %) consist mainly of quartzmicaschists that are grey, brownish yellow, greenish brown, partly oxidized, and well foliated (Fig. 4.3). Similar to the definitions by Okay and Satır (2000), and observations based on petrographical analyses, the micaschists, particularly those exposed in the northern part of study area, are grouped into two types; as quartzmicaschist (Fig. 4.4) and calc-micaschist (Fig. 4.5). Quartz-micaschist is composed dominantly of metamorphic quartz (equigranular and medium grained), muscovite and minor amounts of chlorite, sericite, and opaque minerals, whereas calcmicaschist is composed of metamorphic quartz, muscovite, sericite, and calcite. Unlike those in the quartz-micaschist, muscovite and metamorphic quartz in calcschist, are subhedral to euhedral and perfectly crystallized along the foliation planes (Fig. 4.5).

Calcite in calc-micaschist is coarse grained (Fig. 4.5) and generally displays gliding and deformation twinning.

Apart from the yellowish calc-micaschists and the quartz-micaschists observed in the study area, the presence of one to ten meters thick bodies of black and yellow marble, white meta-quartzite, and albite-chlorite schist units are reported by Okay et al. (1991).

The quartz-micaschist in the study area is tectonically overlain by two serpentinite bodies; green, brownish green in color (Fig. 4.6). The serpentinites are said to be associated with the Denizgören ophiolite (Şengün and Çalık, 2007).







Figure 4.2 Tectonostratigraphic section of the study area (Not to scale)



Figure 4.3 Field photo showing grey to greenish grey, slightly oxidized quartzmicaschist (Çamlıca metamorphics)



Figure 4.4 Photomicrograph illustrating general mineralogical and textural features of quartz-micaschist Q: Quartz, Mus: Muscovite (Sample no. MD14)



Figure 4.5 Photomicrograph illustrating general mineralogical and textural features of of calc-schist. Q: Quartz, Mus: Muscovite, Cc: Calcite (Sample no. MD18)



Figure 4.6 Serpentinized ultramafic rock (mostly harzburgite) outcropping in the vicinity of Çiftlikdere village

An initial eclogite-facies metamorphism with a peak metamorphism temperature of ~ 510 °C and an intensively overprinting greenschist-facies metamorphism have been reported by Okay and Satır (2000) for the Çamlıca metamorphics which is assumed to be a clue that these units are belonging to the Rhodope metamorphic complex (Beccelatto, 2003).

In the present study, Ar-Ar dating is carried out on a sericite separate taken from micaschist and yielded an age of 55 Ma (Kuşcu, 2008; unpublished data; Table 4.1) probable clue for resetting by regional Eocene magmatic heating.

4.1.2 Tertiary rocks

The cover rocks include Middle Eocene granodiorite and dacitic rocks at the bottom followed by tuffaceous rocks (ignimbrite, acidic lavas and block ash flows), and followed by volcanic and volcanoclastic and pyroclastic rocks, and overlying sedimentary rocks. According to a recent work by Dönmez et al. (2008), the rock units in the study area and surroundings are named as Yeniköy Volcanics (dacite), Şahinli Formation (genereally Eocene basaltic volcanoclastics), Hallaçlar Volcanics (Upper Oligocene-Lower Miocene occasionally altered andesitic rocks), and Gazhanedere Formation (Middle Miocene sandstone, mudstone, pebblestone).

The dacitic rocks, the next unit in the sequence, are generally crop out at the eastern parts of the mapped area (Fig. 4.1), and occur as NNW trending outcrop. The dacitic rocks in the field occur as intensely altered rocks with light grey to green in color, and show generally holocrystalline porphyritic texture (Fig. 4.7). Therefore, these rocks were termed as dacite porphyry. The petrographical analyses showed that they consist of mineral assemblage including hornblende (euhedral-subhedral and coarse to medium grained), chlorite, biotite (fine grained), quartz, plagioclase (generally argillized, coarse, and twinned albite minerals), opaque minerals \pm epidote. The dacitic rocks are important in that they act as one of the host rocks of mineralization in the study area, and its detailed alteration mineralogy is given in Chapter 5 (Ore Deposit Geology). The field macroscopic features and textural, mineralogical and compositional characteristics suggest that they have close resemblance to the Yeniköy volcanics defined by Dönmez et al. (2008). The Yeniköy volcanics of Oligocene age are described as porphyritic andesite lavas and pyroclastic rocks including greenish grey, coarse grained amphibole and pyroxene, and are moderately chloritized and argillized. Yeniköy volcanics are covered by the "Stage 2-Oligocene volcanics" of Altunkaynak and Genç (2008), which are also correlated with the Oligocene volcanics of Ercan et al. (1995).

The Ar-Ar geochronology performed on the biotite separates from dacite unit in this study yielded 42.19 ± 0.45 Ma (performed on fresh dacite porphyry) and 42.27 ± 0.96 Ma (performed on a weakly altered dacite sample) (Table 4.1). These ages suggest a possible temporal and genetic (?) link between the Eocene granitoid intrusions within the Biga Peninsula (Delaloye and Bingöl, 2000; Altunkaynak, 2007; Altunkaynak and Genç, 2008) and felsic to basic volcanism in the area.

In addition to the dacite porphyry, a small granitoid body is exposed to the eastern part of the study area (Fig. 4.1). It is usually exposed within the low-lying areas along the course of the main streams, and hard to recognize elsewhere (Fig. 4.1). The contacts with the metamorphic rocks are characterized by pervasive silicification accompanied by hydrothermal biotite-quartz and K-feldspar veinlets. The granitoid consists dominantly of euhedral, coarse grained, and weakly altered (chlorite and epidote) hornblende (up to 2 cm in dimension) (Fig. 4.8), coarse to medium grained, twinned and zoned plagioclase, generally medium grained quartz, euhedral to subhedral, brownish titanite, generally euhedral apatite and zircon, tourmaline, and opaque minerals (Fig. 4.9). Based on these petrographical characteristics, it is defined as granodiorite.



Figure 4. 7 Dacite porphyry outcrop and hand specimen photo (host rock of Kartaldağ gold mine)

Ar-Ar geochronology of the biotite separates from the granodiorite yielded an age of 40.8 ± 0.36 Ma (Table 4.1). In addition to this data, a weakly altered (sericitized) sample from the same granitoid yielded a sericite Ar/Ar age of 39.57 ± 0.47 Ma (Table 4.1). These ages coincide with the dacite porphyry volcanism in the area. Therefore, it is highly likely that dacite porphyry and granodiorite should be formed during the same magmatic pulse that took place during Middle to Late Eocene in the region.

Sample No.	Rock Type	Analytical Method	Mineral	Age (Ma)	
MD-1a	Micaschist	⁴⁰ Ar/ ³⁹ Ar	Sericite	55 Ma	
KD-18	Dacite porphyry	⁴⁰ Ar/ ³⁹ Ar	Biotite	42.19 ± 0.45	
KD-1a	Weakly altered dacite porphyry	⁴⁰ Ar/ ³⁹ Ar	Biotite	42.27 ± 0.96	
KD-25	Granodiorite	⁴⁰ Ar/ ³⁹ Ar	Hornblende	40.8 ± 0.45	
KD-26	Weakly altered granodiorite	⁴⁰ Ar/ ³⁹ Ar	Sericite	39.57 ± 0.47	

Table 4.1 Results of the geochronologic analyses for the rock units in this study



Figure 4.8 Photograph showing granodiorite handspecimen. Hbl: Hornblende, Pl: Plagioclase (Sample no. KD-25)



Figure 4.9 Photomicrograph of granodiorite sample (No. KD25) showing coarse grained, weakly altered hornblende, quartz, and plagioclase minerals, Hbl: Hornblende, Pl: Plagioclase, Q: Quartz

Except for the northwestern edge, nearly all the northern and easternmost part of the study area is occupied by tuffaceous rocks (Fig. 4.1). These rocks appear to represent the volcanoclastic equivalents of the Şahinli Formation, Eocene in age (Dönmez et al., 2005). The tuffaceous rocks consist of basaltic tuff (Fig. 4.10), and acidic tuff (Fig. 4.11) cut by and intercalated by several basaltic rocks (e.g. basalt dykes). This formation is correlated with the Paleocene-Eocene aged Akçaalan volcanics of Siyako et al. (1989) and a part of Balıklıçeşme formation of Ercan et al. (1995). These volcanics are also named as the "Oligocene volcanics" by Ercan et al. (1989).

The petrographical analyses (Fig. 4.12; Fig. 4.13) have revealed that the tuffaceous and basaltic rocks are mainly of andesitic-basaltic tuff, and olivine-basalt in composition, respectively. Porphyritic acidic tuffs which are occasionally exposed in the area, have phenocrysts of quartz, sanidine and show intense argillization. Main phenocrysts of basaltic rocks and basaltic dikes are plagioclase, clinopyroxene, olivine, opaque minerals, and biotite (Fig. 4.14). Plagioclases are coarse to medium

grained, zoned, and generally euhedral. Calcite, chlorite and clay minerals are observed as secondary (alteration) minerals.



Figure 4.10 Basaltic tuff (Şahinli Formation) exposed in the north of the study area



Figure 4.11 Photograph showing acidic tuff (oxidized) outcrop within the study area


Figure 4.12 Photomicrograph of andesitic-basaltic tuff unit. Ti: Titanite, Pl: Plagioclase



Figure 4.13 Photomicrograph of olivine basalt. Ol: Olivine, Pl: Plagioclase (Sample no. MD2)

The andesitic and basaltic lavas and pyroclastics exposed mostly to the NE and SE of the study area (Fig. 4.1) occur as overlying the older units. These are affected by surface oxidation and weathering giving rise to white, yellow, brown, and reddish brown exposures. The stratigraphic position, lithological characteristics of the andesitic and basaltic lavas and pyroclastic rocks show some resemblance to Hallaçlar volcanics (Krushensky, 1976) which is also correlated to the Nil and Kirazlı volcanics of Ercan et al. (1995). The unit seems to be intensely altered in the study area with brownish to reddish colored and/or stained fractures. The mineral assemblage consists of coarse-medium grained, euhedral plagioclase, biotite, pyroxene, K-feldspar, apatite, and opaque minerals in devitrified volcanic glass and mineral microlites. Alteration and supergene assemblage is composed of calcite, chlorite, hematite and goethite. In the north of Madendağ mine district, intensely oxidized and altered outcrops are thought to belong to this volcanic group. Hand specimen and thin section views of a sample (with brecciated texture) collected from this area is shown in Fig. 4.14.



Figure 4.14 Handspecimen photo and photomicrograph of dacitic volcanic breccia. Quartz, Arg.: Argillic matrix, Lm: Limonite, Pl: Plagioclase (Sample no. MD-15)

The sedimentary rocks including siltstone, sandstone, mudstone, and pebblestone which are partly preserved as local exposures to the NW and W of the study area are collectively displayed as the siliciclastic sedimentary rocks in the local geology map (Fig. 4.1). These Middle Miocene aged sedimentary rocks are known as the Gazhanedere Formation (Dönmez et al., 2008) and can be correlated with the Sarıyar member of Çanakkale Formation defined by Şentürk and Karaköse (1987).

CHAPTER 5

ORE DEPOSITS: GEOLOGY AND ALTERATION PETROGRAPHY

5.1 Kartaldağ Gold Mine

The Kartaldağ gold mine is an ancient gold mine once mined by Trojans (Ancient Troy). Information concerning the possible mining operations of Troy before 1914 is not available. It was, then, operated by a British company called Astyra Gold Mining, during 1914-1918 (Molly, 1961; Higgs, 1962a). Based on the exploration studies, mainly drilling (K1B, K2B, K3B, K4B, and K7) and trenching, carried out by the General Directorate of Mineral Research and Exploration (MTA) between the years 1960-1962, a possible reserve of 50 000 ton (with an average grade of 1.38 g/t Au) was assigned to the deposit (Higgs, 1962a; MTA, 1993; Watanabe et al., 2003). The mineralized zone is developed along E-W, NE-SW trending faults with about 200 m vertical depth and reserve was estimated according to two-meter thick goldbearing zone. Gold grade can reach up to 5.5g/t Au and average grade of silver was assigned to be 29.5 g/t Ag (Higgs, 1962a). Lens-shaped ore body is determined within the E-W trending fault with N20°-30° strike and dips NW70° (JICA-Japan International Cooperation Agency-, 1989). Presently, the license of the area called "Serçeler" region is held by Çanakkale Mining Co. since 1987 (JICA, 1989). Some of the old adits were re-opened by Canakkale Mining Co., and a detailed exploration survey was performed including geological mapping, alteration zonation, and geochemical analysis.

5.1.1 Field Aspects

During the field studies carried out in the September 2008 and October 2009, a total of 40 samples were collected from Kartaldağ gold mine. In order to identify the rock

units and the quartz veins outcropping in the area, 10 samples were collected from the neighborhood of the main gallery (which now appears as a NW-trending depression formed by the collapse of the ancient underground mining, Fig. 5.1.), whereas 30 samples were systematically collected to represent the mineralogical assemblage and textural variations across the alteration/mineralization zones (Table 5.1). The sampling was done along; i) a ~200 m long NE-SW- trending traverse (named as traverse line #1, Fig. 5.2) towards the main gallery, ii) a ~125 m long NNE-SSW- trending traverse (named as traverse (named as traverse line #2) crossing the main gallery, and finally iii) a ~500 m traverse within the altered volcanic-plutonic rocks at the southern part of the study area (Fig.5.2).



Figure 5.1 The main inclined gallery driven through the main quartz vein by the Astyra Mining Co.

Samples were taken at almost 1 m intervals for the traverse line #1 (sample no. KD1to KD4, Table 5.1); after the sample "KD2", sampling interval was increased to 25 m on average (from 10 m to 33 m) (Fig.5.3) depending on the field observations.



Figure 5.2 Alteration map of Kartaldağ mine district



Figure 5.3 Cross sections showing the traverse lines # 1, 2, and 3

Traverse # 2 consist of two types of sampling campaigns as; sampling from the tailings of the galleries opened by Çanakkale Mining Co. (sample no. KD5, KD6, KD8, KD9, KD10, KD11; Table 5.1; Fig.5.3-a; Fig.5.4) and from NNE-SSW trending line (sample no. KD7, KD12 to KD15, Table 5.1; Fig. 5.4) performed to see the changes across the main gallery (Fig.5.3; Fig.5.4-b).

Traverse #3, (sample no. KD16 to KD19, Table 5.1) is drawn to show the transition from almost fresh granodiorite (intrusive counterpart of the dacite porphyry) to clayaltered dacite porphyry which is host rock for mineralization; samples were collected randomly along this traverse to find out the possible mineralogical and alteration systematics between the extrusive and intrusive rocks around the Kartaldağ deposit (Fig. 5.3)

Along the traverse #1 (Fig. 5.3) a total of 13 samples were collected (Table 5.1); from SW to NE direction, a color transition was observed from white spotted pale green dacite porphyry (propylitized dacite) to strongly oxidized reddish altered volcanic rock (pervasively argillized dacite).

Along traverse # 2, a total of 17 samples were collected from silicified (white to pale yellow) and clay-altered (argillized) (red to yellow) volcanic rocks, i) along approximately 15 m long segment transversing the main gallery (Fig. 5.3.), and ii) from tailings of galleries (located southwest and northeast of the main gallery). Samples from the tailings include altered, as well as mineralized samples. The samples taken along the traverse, which transverses the main gallery, display textural and mineralogical changes reflecting argillic and silicic alterations.

From the samples KD16 to KD19 along the traverse #3 (Fig. 5.3), a gradual change is observed from (reddish) argillized dacite porphyry, through (greenish) propylitized dacite porphyry, to slightly altered (most probably argillized) granodiorite.

Apart from the traverses, the alteration zones and rock units were also sampled randomly where the alteration and/or textural characteristics are intriguing. Likewise,

the southeastern and northwestern extension of the main quartz vein on both sides of the Yokuşyayla Tepe- was sampled (samples KD20, KD21 and KD22) (Fig.5.2, Fig. 5.6 Table 5.1).

A total of 40 thin sections (one thin section per sample except sample no. 1 and 22) and 14 polished sections (from traverse line # 2) were prepared from all of the samples collected from the traverses, tailings and the surroundings of the mineralized areas (Table 5.1). In addition, i) 12 samples (KD1-a, KD1-c, KD2, KD3-d, KD5-a, KD5-c, KD8-c, KD9, KD18, KD19-a, KD25, KD26) representing the main fresh and rocks along the traverses, and random sampling locations were analyzed for the whole rock geochemistry (App. 2), ii) 7 samples (KD1-b, KD2, KD3-a, KD3-d, KD5-a, KD5-b, KD8-b) from different alterations recognized at the field were analyzed by XRD, and three of these samples (KD2, KD5-b, and KD8-b) were also analyzed by SEM/EDX (Table 5.1).



Figure 5.4 The main gallery at Kartaldağ and approximate positioning of the samples taken. A: Picture is looking towards NW, B: Looking towards NE (numbers labeled as KD represent sample no.)



Figure 5.5 Recent extension of the main gallery by Çanakkale Mining Co. (Northeast of the main gallery) (KD8a, b, c representing samples taken)



Figure 5.6 Quartz veins towards summit of Kartaldağ silicified vein

Sample	ss (ID)	Sampling	Coord	linates	Original Rock	Field Decovirtion	A nalvtia Mathod
Main ID	Sub ID	Location	Northing	Easting	Type		Allary uc ivieliou
KD-1	KD-1a	Traverse #1	4428345	464932	Dacite porphyry	Green to white colored, dacite porphyry	Thin section, whole rock geochemistry, geochronology
	KD-1b	Traverse #1	4428345	464932	Dacite porphyry	Green to white colored, dacite porphyry	Thin section, XRD
	KD-1c	Traverse #1	4428345	464932	Dacite porphyry	Green to white colored, dacite porphyry	Thin section, whole rock geochemistry
	KD-1d	Traverse #1	4428345	464932	Dacite porphyry	Green, yellow to white colored, dacite porphyry	Thin section
KD-2		Traverse #1	4428350	464952	Dacite porphyry	Green to yellow colored dacite porphyry showing weathering and alteration	Thin section, XRD, SEM/EDX, whole rock geochemistry
KD-3	KD-3a	Traverse #1	4428369	464962	Dacite porphyry	Greenish yellow to white, argillaceous dacite porphyry	Thin section, XRD
	KD-3b	Traverse #1	4428369	464962	Dacite porphyry	Yellow to white argillaceous dacite porphyry	Thin section
	KD-3c	Traverse #1	4428379	464986	Dacite porphyry	Yellow to white, argillic dacite porphyry	Thin section
	KD-3d	Traverse #1	4428384	465011	Dacite porphyry	Yellow to white argillized dacite porphyry	Thin section, XRD, whole rock geochemistry
	KD-3e	Traverse #1	4428398	465030	Dacite porphyry	Slightly silicified, yellow – white, argillic dacite porphyry	Thin section
KD-4	KD-4a	Traverse #1	4428404	465039	Dacite porphyry	Argillic \pm silicified dacite porphyry	Thin section
	KD-4b	Traverse #1	4428404	465039	Dacite porphyry	Argillic \pm silicified dacite porphyry	Thin section

Table 5.1 Samples collected in the Kartaldağ mine district

Samp	les (ID)	Sampling	Coordi	nates	Original	Field Description	Analytic Method
Main ID	Sub ID	Location	Northing	Easting	Rock Type		
	KD-4c	Traverse #1	4428404	465039	Dacite porphyry	Argillic \pm silicified dacite porphyry sample	Thin section
KD-5	KD-5a	Traverse #2	4428419	465057	Quartz vein	Silicified and argillized sample taken from the gallery (opened by Çanakkale Mining Co.), includes sulfides (pyrite, sphalerite and covellite)	Thin and polished section, XRD, SEM/EDX, whole rock geochemistry, stable isotope (S)
	KD-5b	Traverse #2	4428419	465057	Quartz vein	Intensely silicified sample taken from Kartaldağ gallery	Thin and polished section, XRD, SEM/EDX
	KD-5c	Traverse #2	4428419	465057	Quartz vein	Silicified and argillized sample taken from the Kartaldağ gallery	Thin and polished section
KD-6		Traverse #2	4428471	465099	Quartz vein	Intensely silicified and argillized sample showing coarse quartz crystals	Thin section, stable isotope (O), fluid inclusion
KD-7		Traverse #2	4428458	465117	Quartz vein	Silicified ± argillized sample with distinct colloform banded appearance	Thin section, fluid inclusion
KD-8	KD-8a	Traverse #2	4428587	465110	Quartz vein	Argillized and silicified sample collected from the newly opened gallery (by Çanakkale Min. Co.) in northeastern part of the Kartaldağ vein. Coarse pyrite minerals are visible.	Thin and polished section
	KD-8b	Traverse #2	4428419	465057	Quartz vein	Sample taken from newly opened gallery located in northeastern part of main Kartaldağ vein, coarse sulfide (pyrite, sphalerite) formations are visible	Thin and polished section, XRD, SEM/EDX
	KD-8c	Traverse #2	4428419	465057	Quartz vein	Intensely silicified and argillized sample (taken from the newly opened gallery) containing abundant visible pyrite	Thin and polished section, whole rock geochemistry, stable isotope (S)

Table 5.1 (cont.)

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Sample	es (ID)	Sampling	Coord	inates	Original	Diold Docomination	A wolvetio Mothod
Main ID	Sub ID	Location	Northing	Easting	Rock Type		Allaly us mentou
KD-9		Traverse #2	4428504	465099	Quartz vein	Yellowish white colored, silicified and argillized sample	Thin section, whole rock geochemistry, stable isotope (O)
KD-10		Traverse #2	4428487	465083	Quartz vein	Argillized and silicified, pale yellow (supergene alteration) sample	Thin section
KD-11		Traverse #2	4428457	465045	Quartz vein	Intensely argillized and silicified, white sample	Thin section, stable isotope (O)
KD-12		Traverse #2	4428474	465080	Quartz vein	Silicified ± argillized sample taken below 2m of the sample KD-7, colloform banding is distinctive feature	Thin section
KD-13		Traverse #2	4428474	465080	Quartz vein	Silicified \pm argillized sample	Thin and polished section
KD-14		Traverse #2	4428299	465083	Quartz vein	Silicified ± argillized sample with intensive limonitic cover	Thin section
KD-15		Traverse #2	4428305	465089	Quartz vein	Brown to red colored silicified and oxidized sample	Thin section
KD-16		Traverse #3	4428084	464900	Dacite porphyry	Green to yellowish, argillized host rock sample	Thin section
KD-17		Traverse #3	4427949	464957	Dacite porphyry	Altered (probably, argillized) dacite sample	Thin section
KD-18		Traverse #3	4427826	464997	Dacite porphyry	Least altered (probably, argillized) dacite sample with visible mafic minerals	Thin section, whole rock geochemistry, geochronology
KD-19	KD19-a	Traverse #3	4427786	465337	Granitoid	Almost fresh (low alteration degree) granitoid sample with coarse grained hornblende and medium grained feldspar	Thin section, whole rock geochemistry
	KD19-b	Traverse #3	4427786	465337	Granitoid	Sample taken from the same location with KD19-a, includes distinctive mafic enclaves	Thin section

Main ID Sub II	Sampling	Coordi	inates	Original	Field Decorintion	Analytic Mathod
) Location	Northing	Easting	Rock Type		
KD-21	Surrounding unit	4428209	465406	Quartz vein	Silicified ± argillized, red to white colored sample taken from the quartz vein located eastern side of the Kartaldağ mine	Thin section
KD-22	Surrounding unit	4428495	464593	Quartz vein	Silicified and argillic altered sample	Thin section
KD-23	Surrounding unit	4428349	464987	Dacite porphyry	Greenish carbonatized sample taken from the westernmost part of the Kartaldağ quartz vein	Thin section
KD-24	Surrounding unit	4428349	464987	Dacite porphyry	Argillized sample taken from the westernmost part of the Kartaldağ quartz vein	Thin section
KD-25	Surrounding unit	4431084	466707	Granodiorite	Fresh (almost) granitoid outcrop with visible hornblende minerals	Thin section, whole rock geochemistry, geochronology
KD-26	Surrounding unit	4427957	464391	Granodiorite	Altered (probably, argillized) granitoid outcrop	Thin section, whole rock geochemistry, geochronology

Table 5.1 (cont.)

5.1.2 Wall Rock Alteration

During the field works held in two field campaigns, 4 main alterations were recognized and mapped. These alterations are spatially oriented with respect to a regional structure that displaced the dacite porphyry almost E-W to NW direction. In general, the predominant alteration is argillic alteration that occurs as envelope to main ore-bearing silicified rocks. The mineral assemblage necessary to define these distinct alterations were identified using ordinary petrographic analyses of thin and polished sections supplemented by XRD (X-Ray Powder Diffraction), SEM/EDX (Scanning Electron Microscope/Energy Dispersive X-ray spectroscopy). From the fresh (?) dacite porphyry to the main quartz vein, the alterations are mapped as propylitic, quartz-kaolin, quartz-alunite -pyrophyllite, quartz vein and residual silica (vuggy quartz).All these alteration types with their distinctive textures and mineral assemblages are explained in detail as follows:

5.1.2.1 Propylitic Alteration

The propylitic alteration was recognized and mapped by tracing the exposures of green-looking rocks (due to intense chlorite and epidote in the rock). In general, the propylitic alterations restricted to the southern parts of the mapped area (Fig. 5.2), are usually hosted by volcanic rocks. An almost arc to sub-spherical map pattern is diagnostic for this alteration, and western and northern margins closely fit into the lithological boundary of the dacite porphyry (Fig. 5.2). Thin and polished section, XRD, and SEM/EDX studies of samples from the traverse #1 reveal characteristic assemblage of propylitic alteration dominated by the minerals of chlorite-smectite mixed layer, illite, carbonates (e.g. calcite), quartz (α -low temperature) with lesser amounts of epidote and albite. Based on field observations and XRD analyses, propylitic alteration extents along the traverse #1 for a distance of nearly 47 meters and passes to quartz-kaolin alteration with the sample KD3-a towards NE direction. The areal extent of propylitic alteration is spatially controlled by the volume of exposure of dacite porphyry (Fig. 5.2) in the deposit area. It is observed that all hornblendes of dacite porphyry were converted into chlorite, carbonates (e.g. calcite) and/or epidote (Fig. 5.7; Fig. 5.8). The propylitic assemblage seems to be (spatially)

overlapping with argillic alteration (illite, smectite, and kaolin minerals); the latter being intense in some samples (Fig. 5.9). Although argillization is rather widespread in KD1 series of samples, this is highly likely to be argillic "overprint" of propylitic alteration as evidenced by the XRD studies which revealed distinct propylitic assemblage (i.e. chlorite, illite, smectite, calcite, quartz, and albite, Fig. 5.10 and Fig. 5.11), and petrographic analyses show intense carbonatization both on hornblendes and groundmass. Furthermore, SEM/EDX studies on sample KD2 prove the propylitic alteration both via the typical smectite and chlorite morphologies (mixed) and the intensities of the A1, Mg, Fe and K concentrations (Fig. 5.12). Supergene effect due to surface oxidation is seen as FeO staining in most of the fractures and late, banded calcite veining (Fig. 5.13).



Figure 5.7 Photomicrograph of epidotized-chloritized hornblende, propylitic alteration (Sample no. KD1-a) (Chl: Chlorite, Arg. Alt: Argillic alteration, Ep: Epidote)



Figure 5.8 Hand specimen photo of the sample KD1-a, propylitic alteration sample



Figure 5.9 Argillic alterations (Arg. Alt) within the dacite porphyry with typical quartz-eye structure and plagioclase. (Sample no. KD1-a) (Plg: Plagioclase, Q: Quartz)



Figure 5.10 Result of XRD analysis of KD1-b, propylitic alteration, Chl -Sm: Chlorite - Smectite mixed layer, I: Illite, K: Kaolin, Chl: Chlorite, Q: Quartz (low temperature), Alb: Albite, Cc: Calcite (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.11 Result of XRD analysis of KD2. Propylitic alteration; Chl & Sm: Chlorite – Smectite mixed layer, I: Illite, K: Kaolin, Q: Quartz (low temperature), Alb: Albite (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.12 Result of SEM-EDX analysis of KD2 (propylitic alteration sample). Chlorite – Smectite mixed layer is exposed with Mg, Fe, and Al peaks, Illite is associated with K and Al peaks, Kaolin and Quartz (low temperature) display Si and Al peaks



Figure 5.13 Supergene oxidation, supergene argillic overprint and late banded calcite (Sample no. KD1-c) (Cc: Calcite, Arg. Alt: Argillic alteration)

5.1.2.2. Quartz-Kaolin Alteration

The quartz-kaolin alteration appears to be the most wide-spread alteration in the deposit area enclosing quartz-alunite and vuggy quartz alterations. This alteration is exposed within an area covering the northern half, and western, southwestern parts of the mapped area (Fig. 5.2). Although this alteration was mapped as a single alteration, the field works revealed that supergene argillic alterations - formed by the leaching of the propylitic zone and disseminated sulfide-bearing (mostly pyrite) dacitic rocks - are also observed either as large patches (more than 100 m long) or as fracture-controlled oxidized bleached outcrops. These two are hard to map, and not differentiated by petrographical and/or other means.

Quartz-kaolin alteration is best observed within the samples of KD3-a - e, KD4-a c, and KD22, KD23, along traverse line # 1 (Fig. 5.3-a; Table 5.1). The XRD studies on the samples KD3-a (Fig. 5.14) and KD3-d (Fig.5.15; Fig. 5.16), revealed that chlorite content decreases, while kaolin (most probably kaolinite) and α -quartz increase towards NE – nearly towards the Kartaldağ main gallery. On the cross section of traverse line #1 (Fig. 5.3.a), the observed thickness of the quartz-kaolin alteration is about 145 meters, and then it passes into the silicified zone towards the main gallery. To the north of the main gallery, the quartz-kaolin zone re-appears and envelopes the silicified zone around the main gallery (Fig. 5.2, Fig. 5.17). Quartzkaolin alteration is defined based on an assemblage including kaolin, and quartz (low temperature) as predominant constituent, and chlorite, illite, \pm pyrophyllite as occasional constituents. The petrographical analyses have shown that the matrix and pheonocrystal assemblage (plagioclase and hornblende) of dacite porphyry were pervasively altered to clay minerals (illite and kaolin). The minerals of illite, kaolin \pm pyrophyllite increase in abundance with the degree of argillization, particularly at samples KD3-d, KD4-b (Fig.5.18), and KD4-c. A zone composed of illite is locally seen as patches, or intensively over the whole section with hydrothermal quartz and pyrite dissolution features, and sometimes with kaolinite on the groundmass. The transition from argillic to advanced argillic alteration might be considered by using information that confirms reasonable increase in pyrophyllite and pyrite content determined in the sections of KD4 samples (Fig. 5.18).



Figure 5.14 Result of XRD analysis of KD3-a, sample of quartz-kaolin alteration zone. Chl: Chlorite, I: Illite, K: Kaolin (possibly, kaolinite), Q: Quartz (low temperature) (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.15 Argillic alterations on sample no.KD3-d. Arg. Alt: Argillic (illitedominated) alteration



Figure 5.16 Result of XRD analysis of KD3-d, sample for quartz-kaolin alteration zone. I: Illite, K: Kaolin (possibly, kaolinite), Q: Quartz (low temperature) (AD: Airdried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.17 Northeastern part of the main gallery in the quartz – kaolin alteration (See opening to the main gallery, sampled as KD23, 24)



Figure 5.18 Pervasive argillic alteration (illite, kaolin) and euhedral pyrite minerals. Sample no.KD4-b, Arg. Alt. Argillic Alteration (illite and kaolin dominated) Py: Pyrite

5.1.2.3 Quartz-Alunite-Pyrophyllite Alteration

The quartz-alunite-pyrophyllite zone is characterized by pinkish to grayish-green ridges with abundant euhedral alunite crystals accompanied by quartz. This alteration is difficult to map in the field, but has common exposures at and around the Kartaltepe and Yokusyayla hills. It is distinguished from the quartz-kaolin alteration by the abundance of pinkish alunite crystals within the cavities and vugs of the silicified rock. Although it forms an envelope around the main quartz vein, it is hard to differentiate the silicified rocks from the quartz-alunite alteration at megascopic scale since both occur as prominent ridges within the study area. Their differentiation is mainly based on a simple test of abundance of alunite (pinkish) and/or clay mineral.

This alteration is best exposed along the traverse # 2 (Fig. 5.3.b) characterized by the minerals similar to that of advanced argillic alteration assemblage: pyrophyllite,

kaolinite, alunite and α -quartz ± zunyite, accompanied by pyrite, covellite, and sphalerite. At the southern part of the main gallery, Kartaldağ fault (possible normal fault in Fig. 5.2) is interpreted to be the boundary for this alteration. The results of XRD and SEM/EDX studies performed on samples collected from this zone are presented in Fig. 5.19 - 23. Samples KD5 (KD5-a, b, and c), KD8 (KD8-a, b, and c), KD10, and KD11 which are representative samples for alunite-pyrophyllite-quartz zone, were collected from north and south walls of the main gallery re-opened by Çanakkale Mining Co. Based on the field observations and petrographic analyses on thin and polished sections, these samples were believed to be collected from the silicified rocks (main quartz vein) of the Kartaldağ mine area, but the existence of euhedral to subhedral alunite minerals developed in the ghosts of parental grains and pyrite veinlets (Fig. 5.24 and 25) called for a detailed definition of this zone as quartz- alunite-pyrophyllite alteration.



Figure 5.19 Result of XRD analyses of KD5-a showing pyrophyllite (Pyr), kaolinite (K), and α- quartz (Q) (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.20 Result of XRD analyses of KD5-b showing alunite (Al), kaolinite (K), and α- quartz (Q) (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.21 Result of XRD analyses of KD8-b showing pyrophyllite (Pyr), alunite (Al), kaolinite (K), and quartz-α (Q) (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.22 Result of SEM/EDX analysis of KD5-b (see Al and S peaks supporting the existence of alunite, kaolinite and pyrite, and Cl peaks showing the existence of zunyite (?)



Figure 5.23 Result of SEM/EDX analysis of KD8-b (Al and Si contents representing kaolinite and quartz)



Figure 5.24 SEM photomicrograph showing pyrophyllite and kaolinite crystals. K: Kaolinite, Pyr: Pyrophyllite (?), Sample no. KD8-b



Figure 5.25 Photomicrograph showing pyrite-alunite-quartz vein (sample KD5-c. Al: Alunite, Py: Pyrite)



Figure 5.26 Photomicrograph of showing euhedral alunite crystals, A: crossed polar, B: single polar (sample no. KD10, Al: Alunite)

5.1.2.4 Vuggy Quartz / Pervasive Silicification

The silicified ridges, trending almost E-W to NW direction and forming an accurate shape from the Yokusyayla to Çataltepe hills, are termed as vuggy quartz/pervasive silicification (Fig. 5.27a and b). Silicification is represented by two most common hydrothermal quartz textures such as massive replacement (Fig. 5.28) and vuggy textures (Fig. 5.29). These are accompanied by sporadic banded, comb, and colloform textures. The petrographic analyses and cross-cutting relationships enabled recognition of two different quartz generations within the silicification and vuggy quartz as; i) early and ii) late phase silicification. The early phase (massive) silicification refer to massive or vuggy quartz generation, very fine to medium grained, and resulted in precipitation of commonly subhedral quartz and massive replacement of the pheonocrystal assemblage and matrix of volcanic host. The pheonocrystal assemblage is no more persistent and kept as vugs and ghosts/pseudomorphs left behind due to intense leaching (e.g., hornblende and plagioclase) (Fig. 5.30). These vugs and ghosts are also lined with fine grained euhedral quartz crystals referred to as vuggy quartz. This is a very diagnostic criterion for pervasive leaching of the host rocks due to very acidic fluids forming the high sulfidation epithermal systems. The late phase silicification refer to silicification and quartz generation, coarse to medium grained, banded, comb, sometimes colloform, and generally zoned quartz crystals truncating early phase massive silicification (Fig. 5.31).

The term "pervasive silicification" refers to the core of residual zone of Kartaldağ epithermal system where all leaching and boiling processes – typical for epithermal systems - occurred. Traverse # 2 is a good line of section where the internal structure, and mineralogical assemblage and textural variations within this alteration can be observed. The internal compositional change and textural changes are best detected along a 15 m long segment of traverse #2 from sample KD7 to KD15 (see Figure 5.3-b). In many samples along this segment, both early and late silicification phases co-exist (Fig. 5.32, 33, and 34) with a clear cross cutting relationship. In some samples, though, only early phase silicification or late silicification textures are recorded (Fig. 5.35, 36, 37, and 38).



(b)



Figure 5.27 The field exposure of silicified ridges through which the ancient mining operations were focused (a) ridge looking SE, (b) ridge looking NW from Çataltepe



Figure 5.28 Massive replacement of dacite porphyry with occasional alunite (pinkish minerals)



Figure 5.29 Vuggy quartz formed by leaching hornblende and plagioclase (refer to insets for ghosts/pseudomorphs for leached minerals)



Figure 5.30 Fine grained quartz (Q) crystallized around the vugs left behind the leached out minerals during early silicification and alunite crystals (Al) displaying infilling textures (Sample no. KD10)



Figure 5.31 Medium grained quartz vein formed during late silicification phase cutting through the fine grained-massive quartz of early silicification (leaching) phase (Sample no. KD5-c)



Figure 5.32 Early and late phases of silicification, massive and banded quartz generations representing the phases, respectively (Sample no. KD7)



Figure 5.33 Pervasive silicification (early phase) replaced by quartz vein (late silicification) (Sample no. KD14)



Figure 5.34 Photomicrograph showing early (fine grained, massive and vuggy) and late (comb, banded) silicification (see vuggy quartz with euhedral pseudomorphs of hornblende and plagioclase veined by late comb quartz) (Sample no. KD15)



Figure 5.35 Pervasive leaching and vug generation (vugs not filled), early silicification sample - KD13-



Figure 5.36 Multi-banded, colloform quartz, late silicification sample (Sample no. KD12)



Figure 5.37 Vuggy quartz (early silicification phase) in sample no. KD15



Figure 5.38 Coarse grained quartz crystals with well developed growth zones (Sample no. KD6) formed during late silicification phase

5.1.3 Ore Petrography

In order to identify the ore and gangue mineral assemblages and supergene minerals for the Kartaldağ deposit, 11 polished samples were prepared in the laboratory of Department of Geological Engineering, METU and examined by reflected light microscopy in Geological Engineering Departments of Ankara and Muğla Universities. The samples from which polished sections were prepared are KD5-a (3 polished sections), KD5-b, KD5-c, KD8-b, KD8-c (3 polished sections), and KD13. They were selected on the basis of the possible content of sulfide and supergene formations.

The primary ore minerals in the Kartaldağ deposit are pyrite, covellite, and sphalerite. Pyrites can be grouped broadly into two as i) subhedral, fine grained crystals within veinlets or as dissemination, ii) euhedral, fine to medium grained disseminated crystals. First group of pyrites are generally seen on the margins of early and late silicification (Fig. 5.39), with a common occurrence within the early phase silicification close to margins of late quartz veins. Second group, on the other
hand, are seen generally as disseminations within the quartz crystals formed during the late silicification phase. These exhibit textural features suggesting a cataclastic deformation (Fig. 5.40).



Figure 5.39 Pyrite concentrations along the margins of late silicification replacing the early silicification (Sample no. KD5-c) Py: Pyrite



Figure 5.40 Cataclastic deformation observed on pyrite (2nd group) (Sample no. KD5-a) Py: Pyrite

Blue, medium-fine grained covellite and light gray, fine grained sphalerite are seen generally as either replacing or intergrown with pyrite formations (Figures 5.41 to 43). Covellite formations might have changed from chalcopyrite which was present as overprinting minerals on pyrite minerals (Fig. 5.42).

Hematite, goethite, jarosite, malachite, and azurite (Fig. 5.44) are seen as common supergene minerals in the Kartaldağ mineralization system.



Figure 5.41Pyrite and sphalerite minerals (intergrown) in sample KD5-c. Sph: sphalerite, Py: Pyrite



Figure 5.42 Covellite and pyrite minerals in sample KD5-a. (Intergrown/replaced?) Co: Covellite, Py: Pyrite



Figure 5.43 Covellite replacing pyrite. Co: Covellite, Py: Pyrite (Sample no.KD5-c)



Fig. 5.44 Azurite and malachite formations in the main gallery where KD8 series of samples were collected

5.2 Madendağ Gold Mine

The Madendağ gold mine was operated by a British company- Astyra Gold Mining Co. during 1914-1918 (Molly, 1961; Higgs, 1962b; JICA, 1989), at the same period with Kartaldağ gold mine. The mine was being operated even before 1914 by Trojans, but there is no written evidence for period of ancient Troy' mining activities. MTA initiated a series geological survey in the Madendağ area in 1958. Based on the surveys between 1960-62, a small reserve of 15 000 ton (possible reserve) at 5.8-6.8 g/t Au was estimated by means of tunneling and drilling studies (Higgs, 1962b; MTA, 1993; Watanabe et al., 2003). As reported by MTA (1989), Tüprag-joint Venture Company of Eurogold Co. have explored the silicified zone in the andesitic pyroclastics to the west of the old Madendağ mine and used the methods of trenching and drilling in the exploration program. JICA, on the other hand, has performed the exploration studies in the andesitic rocks in the north of old underground operations (JICA, 1989). Trenching at 50m interval, grid drilling and heavy mineral study of the soil of the silicified and argillized zones have been performed during those studies and the existence of gold grains was recorded (JICA, 1989).

5.2.1 Field Aspects

The Madendağ gold deposit is hosted by strongly clay-altered mica-schist overlain by dacite flows and intruded by subvolcanic dacite domes. The known mineralization is strictly confined to three vein-breccia system in more or less E-W to WNW-ESE direction (Fig.5.45). There also occur quartz veins oblique (N-S) to the main orebearing zone. The operations by Astyra Mining appear to be focused on argillic alterations (at vein no. 2 zone, Fig. 5.45) between two silicified vein-breccia systems. Field works performed during the thesis study included alteration mapping and sampling. The alteration mapping focused mainly on outlining the areal extent of the silicified rocks, clay altered metamorphic and volcanic rocks. However, the vegetation and soil cover obscured mapping of the entire area. The Paleozoic micaschist (Fig 5.46) units are identified as the host rock of Madendağ mineralization based on the locations that the quartz veins are observed. The contacts between schist and dacitic rocks in the study area are not clearly observed due to intense argillic alteration and oxidation. However, the field mapping showed that the metamorphics are usually exposed to the western part, while dacite dominates to the eastern part of the silicified ridges. The micaschist is intensely folded and brecciated particularly within the deposit site. The dacitic rocks are generally exposed within low-lying areas along the valleys.

The sampling was carried out in conjunction with mapping, and a total of 36 samples were collected separately from dumps/tailings, altered rocks around the dumps, main silicified ridges (dump #1, vein #1, vein #2, dump #2, 28), and surrounding units (8 samples) (Table 5.2). A total of 18 samples were collected from vein #1 (Fig. 5.45), 4 samples from vein #2 area. From Dump #1 and #2 areas a total of 6 samples (tailing samples) were chosen randomly.

Vein #1 (Fig. 5.47) with two smaller quartz veins crossing the argillized and oxidized schist (Fig. 5.48) are regarded as the main ore-bearing horizons for the Madendağ hydrothermal system. A series of systematic sampling (i.e. rock chip samples traversing whole vein and the wall rocks) was carried out in order to obtain mineralogical and textural variations among the veins and altered host rock (argillized schist), contact zones. From WSW to ENE, the samples of MD6-1 - MD6-14 were taken from the main ore-bearing horizon (Fig. 5.45 and 47). The length of the sampling section along this outcrop is nearly 19.60 meters and average spacing between each sample is 1 meter. Although there were several adits and shafts in the district, the dumps appear to be washed or eroded away. Therefore, the sampling at Dump # 2 left behind after mining operations by Astyra Gold Mining Co, is particularly important since this corresponds to one of the most preserved dump/tailing to better understand what was mined, and which were the wall rocks, in front of the adit (Fig. 5.49). The samples MD9-1, MD9-2 were collected from the dump #2. The next sampling was carried out at a dump/tailings site close to an inclined gallery (Fig. 5.50) at the 340 m level up on the Meydan Tepe (Fig. 5.45), in the vicinity of old trenches by MTA (1960-62). The brecciated sample -MD8- was taken from this area.

The Dump #1 and Vein # 2 were sampled during second field campaign in October 2009. There are several drill holes in the vicinity of Dump #1 by MTA (JICA, 1989) and drilling locations are shown in Fig. 5.45. 3 samples (MD-17a and 17b, and MD-U.P.) were collected from this area (Fig. 5.51). Several isolated to continuous silicified rocks are exposed in the vicinity of the Dump#1 close to Gökçekaya Tepe (Fig. 5.45). Vein # 2 sampling was performed along the strike of the quartz vein (approximately 780 m in length and 50 m in height) located on summit regions of Meydan Tepe (Fig. 5.45). The samples named as MD12, MD13, and MD14 were taken from vein area.

A total of 35 thin and 6 polished sections were prepared in the sample preparation laboratories of Department of Geological Engineering, METU. 12 samples (MD2, MD3, MD6-1, MD6-4, MD6-8, MD6-14, MD6-Ust, MD7, MD9-1, MD12, MD13, MD18) were analyzed for the whole rock geochemistry, and 7 samples (MD-1, MD6-1, MD6-2, MD6-12, MD9-1, and MD-U.P.) from the alteration zones were analyzed for the clay mineralogy by XRD (from which MD6-1 and MD9-1 were also analyzed by SEM/EDX).



Figure 5.45 Alteration map of Madendağ mine district



Figure 5.46 Photograph showing the micaschist as the host rock of the Madendağ deposit (Sample no. MD-1)



Figure 5.47 General view of the Vein #1 in Madendağ district within altered micaschist



Figure 5.48 Photograph illustrating the field exposure of an argillized and oxidized micaschist (Sample no. MD6-1)



Figure 5.49 Closed gallery opened by Astyra British Co. during 1914-1918



Figure 5.50 A gallery driven through the clay-altered micaschist at Meydan Tepe



Figure 5.51 Dump # 1 area towards the north of Vein # 1

Sample	es (ID)	Samuling	Coordi	nates	Original Bock		
Main ID	Sub ID	Location	Northing	Easting	Type	Field Description	Analytic Method
MD-1		Surrounding Unit	4433971	462422	Micaschist	Altered pale gray to green, intensely oxidized schist sample	Thin section, XRD, geochronology
	MD-1a	Surrounding Unit	4433971	462422	Micaschist	Silicified schist sample taken from a contact between small quartz vein and schist units	Thin section
MD-2		Surrounding Unit	4433602	462609	Basalt	Sample taken from a -4-5 m thick- basalt dyke	Thin section, whole rock geochemistry
MD-3		Surrounding Unit	4433430	462569	Dacite or Rhyodacite	Intensely altered dacite porphyry	Thin section, whole rock geochemistry
MD-4		Surrounding Unit	4433307	462894	Dacitic rock	Intensely altered, light gray to green volcanic rock	Thin section
MD-5		Surrounding Unit	4433002	463167	Dacitic rock	Silicified volcanic rock sample	Thin and polished section
MD-6	MD-6-1	Vein # 1	4433687	462854	Quartz vein	Red, brown to yellow, strongly weathered, altered schist sample	Thin and polished, section, whole rock geochemistry, XRD, SEM/EDX
	MD-6-2	Vein # 1	4433687	462854	Quartz vein	Contact zone of a small quartz vein and altered schist	Thin section, XRD, stable isotope (O isotope)
	MD-6-3	Vein # 1	4433687	462854	Quartz vein	Sample representing a -1,20 m thick- quartz vein	Thin and polished, section
	MD-6-4	Vein # 1	4433687	462854	Quartz vein	Brown to light yellow altered schist	Thin section, whole rock geochemistry
	MD-6-5	Vein #1	4433687	462854	Quartz vein	Contact zone of gross (6.5 m in thickness) quartz vein and altered schist	Thin section

Table 5.2 Samples collected in the Madendağ mine district

(cont.)
5.2
Table

Samp	oles (ID)		Coordi	nates	Original Rock		· · · · · · · · · · · · · · · · · · ·
Main ID	Sub ID	Sampling Location	Northing	Easting	Type	Field Description	Analytic Method
	MD-6-6	Vein # 1	4433687	462854	Quartz vein	Yellowish contact zone of gross (6.5 m in thickness) quartz vein and altered schist	Thin section
	MD-6-7	Vein # 1	4433687	462854	Quartz vein	Gross, 6.5 m thick, oxidized, red to brown quartz vein	Thin section
	MD-6-8	Vein # 1	4433687	462854	Quartz vein	Gross, 6.5 m thick, oxidized, red to brown quartz vein, sample taken from ~1 m northeast of MD6-7	Thin section, whole rock geochemistry,
	MD-6-9	Vein # 1	4433687	462854	Quartz vein	Gross, 6.5 m thick, oxidized, red to brown quartz vein, taken from ~ 1 m northeast of MD6-8	Thin section
	MD-6-10	Vein # 1	4433687	462854	Quartz vein	Gross, 6.5 m thick, oxidized, red to brown quartz vein, taken from ~1 m northeast of MD6-8	Thin section
	MD-6-11	Vein # 1	4433687	462854	Quartz vein	Yellowish, silicified and argillized schist	Thin section
	MD-6-12	Vein # 1	4433687	462854	Quartz vein	Northeastern contact zone of gross quartz vein and altered schist	Thin section, XRD
	MD-6-13	Vein # 1	4433687	462854	Quartz vein	Sample taken from the northeastern contact of gross quartz vein and argillic schist	Thin section
	MD-6-14	Vein # 1	4433687	462854	Quartz vein	Last sample for the systematic sampling in Vein # 1 location. Brownish, altered schist sample	Thin section, whole rock geochemistry
	MD6-UST	Vein # 1	4433687	462854	Dacitic volcanic breccia	Sample representing an outcrop of 3-4 m thick and oxidized, red to brown matrix accompanies dark grains	Thin section, whole rock geochemistry

Sample	es (ID)	Sampling	Coordin	lates	Original Rock		A walness Mathad
Main ID	Sub ID	Location	Northing	Easting	Type	FIELD DESCRIPTION	Analytic Method
MD-7		Surrounding Unit	4431412	463056	Dacite or Rhyodacite	Altered dacitic volcanic rock outcropped within the schist units	Thin section, whole rock geochemistry
MD-8		Dump # 2	4431295	463018	Quartz vein	Hydrothermal breccia sample taken from 317 m level of Meydan Tepe, open gallery	Thin and polished, section, stable isotope (O isotope)
9-0M	MD-9-1	Dump # 2	4431782	462981	Micaschist	Altered, light grey to green, vitreous, calc- micaschist sample	Thin section, whole rock geochemistry, XRD, SEM/EDX
	MD-9-2	Dump # 2	4431782	462981	Quartz vein	Hydrothermal breccia sample taken from the tailings of closed gallery, white quartz grains are seen within black silicified matrix	Thin and polished, section, fluid inclusion
MD-10		Vein # 2	4430262	462442	Quartz vein	Sample taken from 414 m. level of Meydan Tepe, a representative quartz vein (50 m length and 20-30 m height)	Thin section, stable isotope (O isotope)
MD-11		Vein # 1	4432780	462855	Dacite or Rhyodacite	Sample taken from ~5 m above the Vein # 1 systematic sampling location, from oxidized and argillized outcrop	Thin section
MD-12		Vein # 2	4431780	462879	Quartz vein	Representing ~120 m in north – south and ~50 m high outcrop of quartz vein, from the northernmost part of Meydan Tepe	Thin section, whole rock geochemistry
MD-13		Vein#2	4431680	462877	Quartz vein	Silicified sample taken from nearly middle of the Vein $# 2$	Thin section, whole rock geochemistry
MD-14		Vein # 2	4431088	462957	Quartz vein	Silicified sample taken from the northern part of Vein # 2	Thin section

Table 5.2 (cont.)

(cont.)
Table 5.2

Sampl	les (ID)		Coord	inates	Original Rock		A second a Made
Main ID	Sub ID	Sampling Location	Northing	Easting	Type	FIEID DESCRIPTION	Analytic Method
MD-15		Vein # 1	4432793	462870	Dacitic volcanic breccia	Sample taken from a small reddish volcanic outcrop, similar sample with MD-11 and MD-16	Thin section
MD-16		Vein # 1	4432977	462807	Volcanic (dacitic) Breccia	Intensely oxidized (reddish) sample bearing limonitic minerals	Thin section
MD-17	MD-17a	Dump # 1	4433089	462924	Quartz vein	Intensely silicified hydrothermal breccia sample	Thin section
	MD-17b	Dump # 1	4433089	462924	Quartz vein	Silicified hydrothermal breccia sample	Thin section
MD-U.P.		Dump # 1	4433089	462924	Quartz vein	Colloform textured silicified sample	Thin section, XRD
MD-18		Surrounding Unit	4431100	462961	Micaschist	Argillized and intensely weathered schist sample	Thin section, whole rock geochemistry

5.2.2. Wall Rock Alterations

The wall rock, micaschist has been subjected to moderate to intense silicification and argillic alterations mostly in E-W direction. The silicification is the most prominent alteration as continuous ridges enclosed by argillic alteration. Two main (nearly) parallel veins characterize the silicification, and the area between the two is occupied by argillic alteration. The present adits, trenches and shafts appear to be opened between these two forming a zigzag pattern from south to north.

The mineral assemblage and textural characteristics of the wall rock alterations in the Madendağ district were examined through an integrated study of field aspects, thin and polished sections prepared from systematically collected samples, XRD, SEM/EDX analysis.

There are broadly two types of wall rock alterations; argillic alteration (illite and kaolin-dominated) and silicification. The order of alteration zonation (from argillic to silicic) can especially be followed in local sampling area, Vein #1 (sample set MD6, Fig. 5.45) Silicification with typical epithermal quartz textures such as comb and colloform banded quartz (which are generally characteristic for the evolving hydrothermal conditions) are observed in both gallery and vein areas.

5.2.2.1 Argillic Alteration

The argillic alteration is the most widespread alteration observed dominantly in micaschists (Fig. 5.52), as well as in dacitic and andesitic rocks in the district. Based on XRD and SEM/EDX analysis data, argillic alteration is classified into two groups as kaolin-rich argillic alteration and illite-rich argillic alteration. Samples of MD6 series (Fig. 5.53), which were collected in a systematically crossing the vein #1, display the transition from illite-rich argillization in schists to kaolin-rich argillization towards the quartz veins. Along the cross section of Vein #1, alteration mineralogy can be summarized as hydrothermal α -quartz, illite, kaolin and pyrite (Fig. 5.53, 54, and 55).

Argillic alteration observed in Dump # 1 area consists dominantly of kaolin and hydrothermal quartz, which is referred to as quartz-kaolin zone (Fig. 5.56), whereas in Dump # 2 area, illite is the predominant constituent together with chlorite (Fig. 5.57 and 58). The difference in argillic alteration might be result of composition differences of the wall rocks in the north and south of Madendağ epithermal system. If the clay mineralogy is taken into account, chlorite and illite for the schist; kaolin for the andesitic/dacitic volcanic breccia samples (Hallaçlar volcanics) are recognizable. Besides, the association of illite-chlorite away from the quartz veins, and quartz-kaolin or montmorillonite close to quartz veins is very common for epithermal systems.



Figure 5.52 Photomicrograph of argillized schist (Sample no. MD6-2) showing clayaltered muscovite



Figure 5.53 Result of XRD analysis of sample MD6-1. I: Illite, Q: Quartz (AD: Airdried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.54 Result of XRD analysis of sample MD6-12. I: Illite, Q: Quartz (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.55 Result of SEM/EDX analysis of MD6-1 showing illite ± kaolin (K, Al, Si) and quartz (Si) peaks



Figure 5.56 Result of XRD analysis of sample no. MD - U.P. K: Kaolin, Q: α-Quartz (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.57 Result of XRD analysis of MD9-1 (calc-micaschist). Chl: Chlorite, I: Illite, K: Kaolin, Q: Quartz (low temperature), Cc: Calcite (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 500 °C: Heated in oven (300 °C) and fired at 550 °C)



Figure 5.58 Result of SEM/EDX analysis of MD9-1 showing illite (K, Al, Si) ± kaolin (Al, Si) chlorite (Mg, Fe, Al, Si), calcite (Ca), and quartz (Si) peaks

The petrographic analyses of samples from the argillic alteration have revealed that it is also accompanied by quartz crystals, fine to coarse grained and both metamorphic and hydrothermal in nature. Quartz crystals of metamorphic origin are observed in the least altered samples from schist, conformable with the foliation planes and generally medium grained. The hydrothermal quartz crystals, on the other hand, are observed in the rocks with little or no foliation plane, and their sizes change from fine to coarse, and are associated with pyrite. Pyrites are very fine to fine grained, euhedral to subhedral. They are generally disseminated, or observed as infilling the fractures. They also occur as oxidized grains resulting in dark red, black colored staining and/or bleaching (altered to goethite) (Fig. 5.59). Oxide-hydroxide staining features-effect of supergene alteration- is observed together with the argillic products and is especially common in the Vein #1 area. In the sections, where chlorite and illite are detected, euhedral and medium to coarse grained calcite crystals become dominant.



Figure 5.59 Goethite infilling the fractures, crossed-polar (Sample no.MD6-1) Gth: Goethite, Py: Pyrite, Hem: hematite

5.2.2.2 Silicification

Silicification is not spatially wide spread as the argillic alteration. However, it is the main ore-bearing alteration at which past mining operations was focused. This alteration is commonly exposed at the summit and eastern skirts of the Meydan Tepe and Gökçekaya Tepe. Two main silicified ridges are said to be prominent in the Meydan Tepe area, and these are almost parallel to each other. The ridges consist of silicified breccia and massive silicification (Fig. 5.60; 5.61). The dump/tailings in front of the galleries and trenches have shown that there are two main types of silicification; pyrite-quartz (as massive or brecciated) and quartz-only (banded-comb textured). The pyrite-bearing silicified rocks also exhibit ghost blades (quartz after calcite-type or silicification after bladed calcite; Fig. 5.62).

Silicification is characterized by two distinct phases of quartz generations; as early and late phases of silicification. Early phase silicification is identified by its clear crosscutting relationship with the foliation planes of the micaschist. Quartz crystals formed during this phase are characterized by colloform, comb and banded textures (Fig. 5.63 to 5.66), typical for low sulfidation epithermal deposits. They are generally medium to coarse grained and occasionally very fine grained truncating the schistosity planes (Fig. 5.64). Given that pyrites and their alteration products are limited to the hydrothermal quartz generations; early phase is accompanied with pyrite disseminations (Fig.5.67). Late phase of silicification (Fig 5.68-5.71) is characterized by the hydrothermally brecciated samples showing occasionally the typical brecciation texture of jig-saw puzzle. The temporal and spatial relationships between early and late silicification phases are illustrated in the Figure 5.67 to Figure 5.71.



Figure 5.60 Continuation of Vein # 1 towards NE



Figure 5.61 Vein # 2 from the northern side of Meydan Tepe



Figure 5.62 Silicified bladed calcite from the silicified rocks in the Madendag deposit



Figure 5.63 Open space filling, banded quartz (early phase silicification) within massive quartz (note relict metamorphic (Met.) rock) (Sample no. MD6-1)



Figure 5.64 Banded-comb quartz formations (early phase silicification) truncating the schistosity planes (dotted lines) (Sample no. MD6-13)



Figure 5.65 Early phase silicification, banded-comb quartz vein (Sample no. MD12), form Vein #2 location



Figure 5.66 Crustiform - banded and comb quartz crystals, early phase silicification (Sample no. MD6-3)



Figure 5.67 Late phase silicification truncating the pyrite (disseminated) bearing early phase silicification (Sample no. MD6-1)



Figure 5.68 Hydrothermal breccia showing the late silicification (Sample no. MD8) from Dump # 2 sampling area



Figure 5.69 Relatively fine grained quartz crystals of late silicification phase veining banded, coarse grained early phase (Sample no. MD9-2), from Dump # 2 sampling area



Figure 5.70 Late phase silicification, quartz breccia veining comb-banded quartz (early phase) (Sample no. MD9-2), from Dump # 2 location



Figure 5.71 Quartz breccia from the Dump # 1 area (early and late silicification phases) (Sample no. MD17A and B)

5.2.3 Ore Petrography

As revealed by ore microscopy studies, the sulfides of the Madendağ epithermal system have sulfide assemblage containing only pyrite and sphalerite (Fig. 5.72). Fine grained and unhedral-subhedral pyrites are detected in early silicification phase in the sections of Vein #1 area. Occasionally, they are observed in late silicification phase as well. Pyrites display intensive cataclastic deformation and replacement by the limonitic material. On the sections collected from Dump # 2, pyrites are euhedral, coarse grained, and more or less aligned along a vein, and are accompanied by sphalerite. For example in the sections of MD8 (Fig. 5.72), totally euhedral and coarse pyrite formations are remarkable with light gray to gray colored sphalerite. Especially for the sampling area Vein #1, hematite and goethite minerals are observed as supergene minerals in almost all sections (Fig. 5.73).



Figure 5.72 Sample MD8 showing coarser, euhedral (low temperature) pyrites (Py) and sphalerite (Sph)



Figure 5.73 Goethite infilling the fractures, Gth: Goethite (Sample no. MD6-1)

CHAPTER 6

ORE DEPOSITS: ALTERATION GEOCHEMISTRY AND STABLE ISOTOPE COMPOSITIONS

6.1. Alteration Geochemistry

In the present study, altered rocks of the Kartaldağ and Madendağ districts, together with the least altered magmatic and metamorphic rocks (totally 24 samples), were analyzed for their whole rock geochemistry. The analyses were carried out at ALS laboratories (Canada) based on the methods described in Chapter 1 (Tables 6.1 and 6.2). According to the major, trace and Rare Earth Element (REE) compositions of the representative samples from the main alteration zones (distinguished on the basis of alteration petrography studies), isocon diagrams (i.e. best-fit isocons) were plotted. In the following isocon diagrams, the oxide and trace element distributions of the protoliths hosting the Kartaldağ and Madendağ mineralization were compared with the distributions in the altered rocks.

Best-fit isocons were plotted by using the software called Geochemical Data Toolkit (GCDkit) 2.3 written in R language. They were constructed to estimate (and/or calculate) the bulk gain (above the isocon) and losses (below the isocon) of the elements associated with main alteration assemblages and are passing through the selected immobile oxide and trace element concentrations as well as the origin. Thus, the relative mobility (gain or loss) of an interested individual element is calculated based on the slope of these isocons. Commonly, Al₂O₃, TiO₂, Y, Zr, and Nb are considered as the immobile constituents in the altered rocks (MacLean, 1990). Although Al₂O₃ is selected as the immobile oxide in most hydrothermal alteration study (MacGeehan and MacLean, 1980; Robinson, 1984), in this study, owing to the intense argillization, TiO₂ was chosen instead of Al₂O₃. Thus the isocons were established and discussed based on the TiO₂ concentrations.

6.1.1 Alteration Geochemistry of Kartaldağ Deposit

The representative samples of propylitic, quartz-kaolin, quartz-alunite-pyrophyllite and massive silicification zones versus least altered dacite porphyry and granodiorite of Kartaldağ mine district are listed with their whole rock geochemistry in Table 6.1. As can be seen from Table 6.1, dacite porphyry and granodiorite have similar geochemical compositions, suggesting a genetic relation between the two such that the granodiorite represents the plutonic equivalent of the dacite porphyry (Fig. 6.1). Since the dacite porphyry (not the granodiorite) is determined as the host rock for the Kartaldağ mineralization system, KD18 was selected as the original (least altered) rock sample for the isocon analyses despite its rather high loss on ignition value.



Figure 6.1 MORB normalized REE spider diagram showing the similarity between the samples KD25 and KD18

										(
	Alteration	Least	altered m	agmatic	rocks	Propy	litic alter:	ation	Quartz- Kaolin	n P P	artz - Alı yrophyll	ınite ite	Massive silicification
*Method	**Sample	KD18	KD19-a	KD25	KD26	KD1-a	KD1-c	KD2	KD3-d	KD5-a	KD5-c	KD8-c	KD9
	SiO_2	62,5	6'09	60,6	62	64	58,9	65,6	73,6	95,5	66,99	48,8	74,4
	Al_2O_3	15,2	15,25	16,15	15	15,75	14,65	16,5	15,6	1,41	10,45	11,3	15,25
	Fe_2O_3	4,2	4,09	6,08	4,13	4,48	4,19	4,25	0,8	1,48	8,67	16,4	2,19
	CaO	3,55	5,39	5,6	4,26	3,41	7,04	0,45	0,03	0,05	0,02	0,03	0,04
	MgO	1,8	1,4	2,43	1,29	1,48	1,86	1,9	0,79	0,01	0,01	<0,01	<0,01
90d	Na_2O	3,01	2,69	3,02	3,49	3,22	2,3	1,97	0,05	0,03	0,15	0,26	0,03
ICI-	$\mathrm{K}_2\mathrm{O}$	1,54	1,82	3	1,78	2,3	1,71	2,33	4,49	90'0	0,61	1,43	0,05
ME	Cr_2O_3	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0,01	$<\!0,01$	$<\!0,\!01$	<0,01	<0,01	<0,01
	TiO ₂	0,46	0,39	0,56	0,42	0,45	0,43	0,45	0,49	0,02	0,29	0,22	0,41
	MnO	0,07	0,11	0,13	0,09	0,09	0,14	0,13	0,01	$<\!0,\!01$	<0,01	<0,01	<0,01
	P_2O_5	0,31	0,27	0,29	0,25	0,27	0,24	0,24	0,05	0,21	0,19	0,23	0,24
	SrO	0,04	0,06	0,07	0,05	0,06	0,05	0,04	<0.01	0,07	0,05	0,09	0,12
	BaO	0,05	0,07	0,07	0,05	0,09	0,07	0,07	0,05	0,04	0,04	0,08	0,05
	IOI	6,31	7,8	2,06	6,5	2,97	7,86	5,63	3,45	1,34	11,6	19,9	7,04
	Total	66	100	100	99,3	98,6	99,4	9,66	99,4	100	66	98,7	96,8
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*see Chapter 1 for details ** Samples KD18: dacite porphyry, KD19-a: granodiorite, KD25: granodiorite, KD26: altered granodiorite

	Alteration	Lea	st altered m	agmatic roo	cks	Propy	litic alter	ation	Quartz- Kaolin	Qua P	ırtz - Aluı yrophylli	nite- te	Massive silicification
*Method	**Sample	KD18	KD19-a	KD25	KD26	KD1-a	KD1-c	KD2	KD3-d	KD5-a	KD5-c	KD8-c	KD9
	Ba	421	524	565	412	753	665	553	415	321	299	624	399
	Ce	38,2	46,5	60,2	47,3	49,5	49,9	102,5	51,1	8,9	30,4	30,5	50,7
	Cr	10	10	10	10	10	20	10	10	20	10	10	10
	C_S	4,19	7,67	7,17	9,51	10,1	16,2	6,91	8,77	0,13	0,11	0,07	0,09
	Dy	2,4	2,59	3,69	2,65	3,11	2,82	2,64	2,76	0,18	0,37	0,41	0,74
	Er	1,43	1,62	2,27	1,72	1,88	1,74	1,64	1,75	0,05	0,32	0,26	0,66
	Eu	0,95	0,96	1,2	1,01	1,12	96,0	0,82	0,94	0,16	0,36	0,42	0,54
Ľ	Ga	15,1	15	16,4	14,7	15,8	15	16,6	16,2	7,8	43,6	33,3	38,9
8SI⁄	Gd	2,94	3,22	4,66	3,32	3,74	3,42	3,13	3,32	0,42	1,4	1,4	1,93
IE-I	Ηf	3,4	3,2	3,6	3,1	3,4	3	3,1	3,6	<0.2	2,3	1,8	3,1
N	Но	0,5	0,55	0,78	0,58	0,66	0,59	0,54	0,59	0,03	0,08	0,08	0,18
	La	20,1	25,8	30,8	26,1	27,9	26,5	21,7	29,4	4,2	16,4	17,3	26
	Lu	0,24	0,26	0,37	0,3	0,32	0,29	0,29	0,29	$<\!0,01$	0,08	0,08	0,15
	ЧN	5,3	6,7	7,6	7,2	7,7	7,3	7,7	8,5	0,3	4,8	4	7
	Nd	15,2	17	23,6	17,6	19,9	18,3	17	17,5	3,5	10,9	10,6	17,9
	\mathbf{Pr}	4,28	5,03	6,55	5,15	5,71	5,36	4,86	5,26	0,98	3,21	3,17	5,35
	Rb	55,8	63,3	100	67	76,7	68,1	94	233	0,9	1,3	1,8	0,5
	Sm	2,97	3,28	4,64	3,27	3,83	3,58	3,19	3,24	0,54	1,9	1,72	2,81
*see Chapter ** Samples K	1 for details CD18: dacite pc	rphyry, KD1	9-a: granodio	rite, KD25: g	ranodiorite,	KD26: alt	ered grano	diorite					

Table 6.1 (cont.)

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Alteration Least altered magmatic rocks Propylitic alteration Xion Yronovinte Billification Strend Display Editeration Strend Display Editeration Strend Display Editeration Strend <trend< th=""></trend<>										Onartz-	Oli	ntz – Ali	inite	Massive
(4.10.1) ************************************		Alteration	Least	altered ma	igmatic r	.ocks	Prop	ylitic alter	ation.	Kaolin	P	yrophylli	ite	silicification
Sin I	Iethod	**Sample	KD18	KD19-a	KD25	KD26	KD1-a	KD1-c	KD2	KD3-d	KD5-a	KD5-c	KD8-c	KD9
Sr 295 496 611 394 508 468 308 9,8 575 443 715 899 Tb 0,5 0,6 0,8 0,49 0,57 0,5 0,6 0,1 0,1 0,1 0,1 0,1 Tb 0,44 0,47 0,68 0,49 0,57 0,5 0,44 0,49 0,1 </td <td></td> <td>Sn</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>2</td> <td>16</td> <td>12</td> <td>1</td>		Sn	1	1	1	1	1	1	1	1	2	16	12	1
Ta 0,5 0,6 0,8 0,7 0,6 0,6 0,8 0,1 0,3 0,6 0,1 Tb 0,44 0,47 0,68 0,49 0,57 0,5 0,44 0,47 0,61 0,12 0,12 Tb 0,44 0,47 0,68 0,49 0,57 0,5 0,5 0,6 0,11 0,12 0,19 0,19 Th 8/8 11,1 15,3 12 12,75 11,2 12,15 10,95 2,65 7,91 7,54 12,3 U 2.78 0,57 0,50 0,56 0,52 0,55		Sr	295	496	611	394	508	468	308	8'6	575	443	715	668
Tb 0,44 0,47 0,68 0,49 0,57 0,5 0,44 0,49 0,10 0,12 0,10 Th 8,8 11,1 15,3 12 12,75 11,2 12,15 10,95 2,65 7,91 7,54 12,3 Th 8,8 11,1 15,3 0,27 0,66 0,7 0,65 0,7 2,55 7,91 7,54 12,3 U 2,78 0,25 0,35 0,27 0,29 0,25 0,26 0,25 0,27 0,25 0,25 0,24 12,3 U 2,78 2,54 4,38 3,87 3,62 2,41 2,43 0,12 W 2 2 2 1 7 V		Та	0,5	0,6	0,8	0,6	0,7	0,6	0,6	0,8	$<\!0,1$	0,4	0,3	0,6
Th 8.8 11,1 15,3 12 12,7 12,1 13,5 12,7 12,7 13,5 14,4 13,1 14,4 13,1 14,4 20,1 13,5 14,7 13,1 14,4 13,1 14,4 13,1 14,4 13,1 14,4 13,1 14,4 14,1 14,7		Tb	0,44	0,47	0,68	0,49	0,57	0,5	0,44	0,49	0,06	0,11	0,12	0,19
TI <0,5 <0,6 <0,7 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <0,5 <		Th	8,8	11,1	15,3	12	12,75	11,2	12,15	10,95	2,65	7,91	7,54	12,3
Tim 0,21 0,25 0,35 0,27 0,29 0,26 0,26 0,01 0,05 0,04 0,12 V 2,78 2,54 4,38 3,87 3,62 2,41 2,49 3,56 0,6 2,91 2,42 4,6 V 79 67 132 71 70 68 76 68 17 93 104 136 W 2 2 2 1 2 2 1 3 3 5 W 2 2 1 2 2 1 2 2 1 3 3 3 5 W 2 2 1 2 1 2 1 3 3 5 5 Y 13,1 14,4 20,1 15,4 18,3 1,7 1,8 1,7 0,03 0,4 0,7 0,4 Y 13 124 118 134 18	185	ΤΙ	<0,5	<0,5	0,6	0,7	0,6	<0.5	0,7	2,2	<0,5	€,0>	$<\!0,5$	<0,5
H U 2.78 2.54 4.38 3.87 3.62 2.41 2.49 3.56 0.6 2.91 2.42 4.6 V 79 67 132 71 70 68 76 68 17 93 104 136 W 2 2 2 1 2 2 1 3 3 3 5 W 2 2 2 1 2 2 1 3 3 5 5 5 Y 131 14,4 20,1 15,4 18,3 16 11,8 15,5 0,5 2 1,9 4,2 Y 1,1 1,4 2,16 1,85 1,89 1,73 0,03 0,48 0,37 0,94 Zr 131 124 118 118 118 118 124 143 4 90 72 126 X 131 1,3 1,3	SM-	Tm	0,21	0,25	0,35	0,27	0,29	0,26	0,25	0,26	<0,01	0,05	0,04	0,12
V 79 67 132 71 70 68 76 68 17 93 104 136 W 2 2 2 1 2 2 1 2 3 3 3 5 Y 13,1 14,4 20,1 15,4 18,3 16 11,8 15,5 0,5 2 1,9 3 3 5	ME	U	2,78	2,54	4,38	3,87	3,62	2,41	2,49	3,56	0,6	2,91	2,42	4,6
W 2 2 1 2 2 1 2 2 1 3 3 3 5 Y 13,1 14,4 20,1 15,4 18,3 16 11,8 15,5 0,5 2 1,9 4,2 Yb 1,4 1,61 2,16 1,85 1,89 1,72 1,8 1,73 0,03 0,48 0,37 0,94 Yb 1,1 11 3,6 1,18 11,8 124 143 4 90 72 126 Xb 2,8 1,1 11 3,6 1,1 1,3 17,9 47,2 44 25,5 213 45,4 Hg 0,05 0,07 0,02 0,03 0,06 72 45,4 7,4 Hg 0,16 0,33 0,03 0,06 20,05 0,03 0,69 72 126 73 Hg 0,16 0,27 0,19 0,27 4,99 <td></td> <td>Λ</td> <td>62</td> <td>67</td> <td>132</td> <td>71</td> <td>70</td> <td>68</td> <td>76</td> <td>89</td> <td>17</td> <td>63</td> <td>104</td> <td>136</td>		Λ	62	67	132	71	70	68	76	89	17	63	104	136
Y 13,1 14,4 20,1 15,4 18,3 16 11,8 15,5 0,5 2 1,9 4,2 Yb 1,4 1,61 2,16 1,85 1,89 1,72 1,8 1,73 0,03 0,48 0,37 0,94 Zr 131 124 118 134 118 134 118 72 143 0,7 0,94 0,37 0,94 As 2,8 1,1 11 3,6 1,1 1,3 1,1 1,3 1,7 44 22,5 213 45,4 Bi 0,16 0,33 0,07 0,03 0,06 6,003 6,003 6,004 6,03 0,01 0,07 0,07 0,072 0,379 Hg 0,22 0,11 0,32 0,14 0,27 4,99 4,76 31,8 2,83 Hg 0,22 0,14 0,27 0,05 0,062 0,379 0,379 0,379		M	2	2	2	1	2	2	2	2	1	3	3	2
Yb 1,4 1,61 2,16 1,85 1,89 1,72 1,8 1,73 0,03 0,48 0,37 0,94 Zr 131 124 134 118 134 118 134 118 124 143 4 90 72 126 As 2,8 1,1 11 3,6 1,1 1,3 17,9 47,2 44 22,5 213 45,4 Ka 0,016 0,33 0,07 0,02 0,03 0,06 0,27 4,99 4,76 31,8 2,83 Hg <0,05		Υ	13,1	14,4	20,1	15,4	18,3	16	11,8	15,5	0,5	2	1,9	4,2
Zr 131 124 118 134 118 134 118 124 134 118 124 134 134 134 134 134 134 134 134 134 134 136 134 136 134 136 134 136 134 136 134 136		ЧY	1,4	1,61	2,16	1,85	1,89	1,72	1,8	1,73	0,03	0,48	0,37	0,94
As 2,8 1,1 11 3,6 1,1 1,3 17,9 47,2 44 22,5 213 45,4 Bi 0,16 0,33 0,13 0,07 0,02 0,03 0,06 0,27 4,99 4,76 31,8 2,83 Hg <0,005	_	Zr	131	124	134	118	134	118	124	143	4	06	72	126
QBi0,160,330,130,070,020,030,060,060,274,994,7631,82,83Hg<0,005		As	2,8	1,1	11	3,6	1, 1	1,3	17,9	47,2	44	22,5	213	45,4
Hg <0,005 <0,005 0,006 <0,005 <0,005 <0,005 <0,005 <0,005 <0,005 <0,005 <0,005 <0,011 <0,062 <0,379 No Sb 0,22 0,11 0,32 0,25 0,14 0,27 0,65 1,74 3,42 6,65 24,2 12,9 Se 0,3 0,3 0,3 0,3 0,3 0,3 12,9	242	Bi	0,16	0,33	0,13	0,07	0,02	0,03	0,06	0,27	4,99	4,76	31,8	2,83
Sb 0,22 0,11 0,32 0,25 0,14 0,27 0,65 1,74 3,42 6,65 24,2 12,9 Se 0,3 0,3 0,3 0,3 0,3 0,3 0,4 1,1 22,1 6,8 71,9 12,3	SM-3	Hg	<0,005	<0,005	0,005	0,006	<0,005	<0,005	0,011	0,009	1,18	0,072	0,062	0,379
Se 0,3 0,3 0,5 0,3 0,3 0,4 1,1 22,1 6,8 71,9 12,3	ME	Sb	0,22	0,11	0,32	0,25	0,14	0,27	0,65	1,74	3,42	6,65	24,2	12,9
		Se	0,3	0,3	0,3	0,5	0,3	0,3	0,4	1, 1	22,1	6,8	71,9	12,3

Table 6.1 (cont.)

*see Chapter 1 for details ** Samples KD18: dacite porphyry, KD19-a: granodiorite, KD25: granodiorite, KD26: altered granodiorite

	Alteration	Least	t altered m:	agmatic 1	rocks	Prop	ylitic alter	ation	Quartz- Kaolin	Qua	rtz – Alu yrophyllit	nite te	Massive silicification
*Method	**Sample	KD18	KD19-a	KD25	KD26	KD1-a	KD1-c	KD2	KD3-d	KD5-a	KD5-c	KD8-c	KD9
	Те	0,02	0,03	0,03	0,04	0,03	0,04	0,05	0,17	2,45	1,06	4,81	2,6
C-IR07	С	0,72	1,14	0,12	0,87	0,3	1,18	<0.01	<0.01	<0.01	<0.01	<0.01	0,01
C-IR08	S	0,02	0,01	0,05	0,01	<0.01	<0.01	0,02	0,01	0,32	7,93	16,25	0,16
	Ag	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	10,1	1,5	5,3	13,3
	Cd	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<i>2</i> ,05	<0,5	<0,5
180	Co	8	9	12	9	7	8	10	1	3	16	25	\leq 1
/CD	Cu	1	10	21	11	6	L	15	9	22	270	737	26
74-5	Мо	\sim	\leq	\leq	$\stackrel{\scriptstyle \sim}{\sim}$	≤ 1	<1	$\overline{\vee}$	<1	2	<1	≤ 1	\leq 1
W	Ni	7	3	3	1	5	4	25	<1	7	32	80	\leq
	Pb	17	18	19	16	16	13	14	11	859	428	1120	555
	Zn	55	51	62	57	63	55	85	8	4	9	6	<2
*see Chapte	r 1 for details												

Table 6.1 (cont.)

** Samples KD18: dacite porphyry, KD19-a: granodiorite, KD25: granodiorite, KD26: altered granodiorite
6.1.1.1 Element Mobility during Propylitic Alteration of Dacite Porphyry

Based on their petrographic properties, three samples were selected as the representative samples of the propylitic zone (sample no. KD1-a, KD1-c, KD2). The element mobility is examined via the isocon diagrams (Fig.6.2) and the gains and losses of the elements are summarized in Table 6.2.

Regarding the isocon diagrams, a value of about 93%-98% for the slope implies almost no total mass change in the rock. The feature most apparent from the isocon diagrams (Fig. 6.2) and Table 6.2 is the enrichment of all the samples in K₂O and MnO, and in Ba and Rb which are the trace elements associated with K (due to their similar ionic properties). The K-enrichment seems to correlate with the presence of illite in these samples (as revealed by alteration petrography studies-Chapter 5) and is likely to reflect the influence of illite dominated argillic alteration zone neighboring the propylitic zone. Regarding the MgO, FeOt, CaO and NaO, which are supposed to be typically increasing for propylitic alteration, the observations from Fig. 6.2 and their relevant interpretations are as follows:

i) MgO shows slight enrichment in samples KD1-c and KD2, but depletion in sample KD-1a. FeOt, like MgO, show enrichment in two samples (KD1-a and KD2). The increase in MgO in sample KD2, accompanied by an increase in FeOt, seems to correlate with the presence of chlorite-smectite mixed layered clay mineral in this sample as detected by XRD studies (see Chapter 5).

ii) CaO is enriched in KD1-c, while depleted in KD2. Enrichment in KD1-c seems to be conformable with the mineral assemblage of propylitic zone (Chapter 5) and is also likely to have been caused by late calcite formation (commonly in the form of veining) overprinting the propylitic alteration, as observed petrographically in this sample, while the depletion in KD2 might be the result of leaching of Ca from the breakdown of the Ca-rich minerals like hornblende in the protolith. iii) Na_2O displays slight increase in KD1-a, but decrease in KD1-c and KD2. The decrease in Na_2O is opposite to the expectations from the XRD studies which revealed the presence of albite in sample KD2.



Figure 6.2 Isocon diagrams showing the oxide and trace element variations between the propylitic samples and least altered dacite porphyry sample (dashed lines are the isocons, s is the slope)

Samples	Oxides (wt%) and Trace elements (ppm)	G/L wt%/ppm(avg)
	SiO ₂	2.92
-	TiO ₂	0.00
-	Al ₂ O ₃	0,90
-	FeOtt	0,34
-	MnO	0,02
-	MgO	-0,29
-	CaO	-0,06
~	Na ₂ O	0,28
DI	K ₂ O	0,81
S K	P_2O_5	-0,03
ns.	Rb	22,60
vei	Sr	224,29
-3	Cs	6,13
ē	Ba	348,73
×	Nb	2,57
_	La	8,42
_	Sm	0,95
_	Yb	0,53
_	Zr	5,98
_	Hf	0,08
_	Th	4,23
	U	0,92
	SiO ₂	0,51
	TiO ₂	0,00
	Al_2O_3	0,47
-	FeOtt	0,25
-	MnO	0,08
-	MgO	0,19
KD1-c versus KD18	CaO	3,98
	Na ₂ O	-0,55
	K ₂ O	0,29
	P_2O_5	-0,05
	Rb	17,05
	Sr	205,65
	Cs	13,14
	Ba	219,79
	Nb	2,51
-	La	8,25
-	Sm	0,86
-	Yb	0,44
-		-4,77
-		-0,19
-	Th	3,18
	U	-0,20

Table 6.2 Gains (G) and losses (L) of the elements during propylitic alteration

Samples	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
	elements (ppm)	
	SiO ₂	4,56
	TiO ₂	0,00
	Al_2O_3	1,67
	FeOtt	0,13
	MnO	0,06
	MgO	0,14
	CaO	-3,09
	Na ₂ O	-1,00
8	K ₂ O	0,84
DI	P_2O_5	-0,06
S K	Rb	40,29
ns.	Sr	19,84
vei	Cs	2,87
02	Ba	144,29
X	Nb	2,57
	La	2,08
	Sm	0,29
	Yb	0,44
	Zr	-4,24
	Hf	-0,23
	Th	3,62
	U	-0,23

Table 6.2 (cont.)

6.1.1.2 Element Mobility during Quartz - Kaolin and Quartz -Alunite-Pyrophyllite Alterations

Quartz-kaolin zone is represented by sample KD3-d and quartz -alunite- pyrophyllite zone by KD-5a, KD-5c and KD-8c (Table 6.1). According to the isocon (KD3-d versus KD18) diagram (Fig. 6.3, A) constructed for the quartz-kaolin zone, a slope about 1, 07 suggest a slight increase in the total mass of the rock. It is clearly seen that the SiO₂ and K₂O are the oxides enriched in the altered sample conformable with the findings (quartz and illite) from XRD and EDX studies. Since gained oxides suggest the presence of the alteration minerals like illite (K₂O) and quartz (SiO₂), mostly, "quartz-kaolin" term used for this alteration may be changed into the quartzkaolin-illite zone. Depletion in MnO, P₂O₅, MgO, FeOt, CaO, and Na₂O, compared with the least altered sample (KD-18), confirms the replacement of the minerals of plagioclase and hornblende by the clay minerals. In the case of the trace element distributions, Rb, Cs, Nd, La, and Th are the gained elements, whereas Sr and Ba comprise the depleted elements during the quartz-kaolin alteration.

Regarding the quartz -alunite- pyrophyllite alteration, the slopes of isocons (Fig. 6.3 B, C, and D), ranging between 4 % and 63 %, point to significant loss in the total mass of the rock during alteration. Enrichment in SiO₂, P₂O₅, FeOt, and Al₂O₃, along with Sr and Ba, suggests that the the zone of alteration is dominated by quartz and aluminum silicates (e.g. kaolinite and pyrophyllite). Furthermore, the considerably high S content in sample KD5-c and KD-8c (Table 6.1), is in conformity with the presence of alunite (as well as pyrite, covellite and sphalerite) as determined by petrographic studies. The comparatively higher S, Cu, FeOt and Al₂O₃ concentrations in sample KD-5c and KD-8c (compared to KD-5a) can be attributed to the relatively higher amounts of covellite (CuS), pyrite (FeS₂), kaolin (mostly kaolinite) and the sulfates (e.g. alunite) in these samples.

A summary of the gains and losses of the elements during these alterations (quartz - alunite- pyrophyllite and kaolin) is given in Table 6.3.



Figure 6.3 Isocon diagrams showing the oxide and trace element variations of the samples from (A) quartz- kaolin (Sample no. KD3-d) and (B, C, and D) pyrophyllite-alunite-quartz zone (Sample no. KD5-a, KD5-c, and KD8-c) (dashed lines are the isocons, s is the slope)

Table 6.3 Gain (G) and losses (L) of the elements during Quartz-Kaolin (sample no.KD3-d) and Pyrophyllite-Alunite-Quartz (samples no. KD5-a, 5-c, and 8-c)alterations

Samples	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
	elements (ppm)	
_	SiO ₂	6.59
-	TiO ₂	0.00
-	Al_2O_3	-0.56
-	FeOtt	-3.10
-	MnO	NA
-	MgO	-1.06
-	CaO	-3.52
<u>8</u>	Na ₂ O	-2.96
Ē.	K ₂ O	2.68
s k	P_2O_5	-0.26
rsu	Rb	162.93
ve	Sr	-285.80
3- d	Cs	4.04
ë.	Ba	-31.41
<u> </u>	Nb	2.68
-	La	7.50
-	Sm	0.07
-	Yb	0.22
-	Zr	3.24
-	Hf	NA
-	Th	1.48
	U	0.56
-	SiO ₂	2134.00
-	TiO ₂	0.00
-	Al ₂ O ₃	17.23
-	FeOtt	26.85
-	MnO	NA
-	MgO	-1.57
5-a versus KD18	CaO	-2.40
	Na ₂ O	-2.32
	K ₂ O	-0.16
	P_2O_5	4.52
	Rb	-35.10
	Sr	12930.00
	Cs	-1.20
ë.	Ba	6962.00
<u> </u>	Nb	1.60
-	La	76.50
-	Sm	76.50
-	Yb	-0.71
-	Zr	-39.00
-	Hf	NA
-	Th	52.15
	U	11.02

Samplas	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
Samples	elements (ppm)	
	SiO ₂	43.62
	TiO ₂	0.00
	Al_2O_3	1.38
	FeOtt	8.60
	MnO	NA
_	MgO	-1.78
_	CaO	-3.52
×	Na ₂ O	-2.77
D1	K ₂ O	-0.57
s K	P_2O_5	-0.01
nsı	Rb	-53.74
vei	Sr	407.69
2-6	Cs	-4.02
Ŭ,	Ba	53.28
¥	Nb	2.31
	La	5.91
	Sm	0.04
	Yb	-0.64
	Zr	11.76
	Hf	NA
	Th	3.75
	U	1.84
_	SiO ₂	39.54
_	TiO ₂	0.00
-	Al ₂ O ₃	8.43
_	FeOtt	27.08
-	MnO	NA
-	MgO	-1.78
_	CaO	-3.49
D8-c versus KD18	Na ₂ O	-2.47
	K ₂ O	1.45
	P_2O_5	0.17
	Rb	-52.04
	Sr	1200.00
	Cs	-4.04
	Ba	883.73
¥ -	Nb	03.06
-	La	16.07
-	Sm	0.63
-	Yb	-0.63
-	Zr	19.55
-	Hf	NA
-	Th	6.97
-	U	2.28

Table 6.3 (cont.)

6.1.2 Alteration Geochemistry of Madendağ Deposit

In the Madendağ district, altered rocks can be broadly grouped into two as silicified and argillized (illite dominated) rocks. Almost fresh and least altered host rocks of the Madendağ mineralization are listed in the Table 6.4 with their altered counterparts. To estimate the element mobility during the argillization and silicification of the host rock -calc-micaschist (sample no. MD9-1) -representative samples for the related alteration zones were selected and their relationship was discussed by using isocon diagrams as in the case of Kartaldağ. Especially the samples of the Vein # 1 (sample no. MD6-1, 6-4, 6-8, and 6-14) and of the Vein #2 (MD12 and MD13) were presumed to be the precursor samples for the isocon analyses to gather the elemental transition from the argillized micaschist to the quartz veins truncating micaschist.

Table 6.4 Representative chemical analyses of almost fresh and altered samples from Madendag Mine District (oxides and S and C ii	wt %, trace and rare earth elements in ppm) (bold values were used to construct isocon diagrams)
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	Alteration		Least altere	ed rocks		AI	rgillic (illi	ite domin:	ated)	M	assive silicifica	ıtion
*Method	**Sample	MD3	MD6-Ust	MD7	MD9-1	MD18	MD6-1	MD6-4	MD6-14	MD6-8 (Vein #1)	MD12 (Vein #2)	MD13 (Vein #2)
	SiO_2	46	64,7	64	51,1	57,5	75,7	80	92,5	95,5	94,8	96,7
	Al_2O_3	10,6	20,2	16,25	8,84	10,1	10,7	9,4	2,13	0,56	3,24	1,12
	$\mathrm{Fe}_{2}\mathrm{O}_{3}$	7,48	5,46	4,61	4,47	5,02	4,73	2,14	1,47	0,94	0,54	0,6
	CaO	11,8	0,25	4,17	14,35	10,6	0,11	0,16	0,08	0,05	0,04	0,1
	MgO	5,83	0,12	1,45	2,53	2,51	0,75	0,5	0,04	0,03	0,02	0,04
900	Na_2O	0,04	0,02	4,04	0,07	0,07	0,04	0,01	0,05	0,02	0,03	0,03
-ICI	K_2O	0,18	0,08	1,87	1,96	2,35	2,9	2	0,45	0,07	0,11	0,12
ME	Cr_2O_3	0,03	<0,01	<0,01	0,03	0,02	0,01	0,01	0,01	0,01	<0,01	<0,01
	TiO_2	0,48	0,49	0,49	0,52	0,52	0,46	0,41	0,09	0,02	0,01	0,02
	MnO	0,09	0,02	0,09	0,12	0,1	0,01	0,01	<0,01	0,01	<0,01	0,01
	P_2O_5	0,08	0,25	0,24	0,19	0,12	0,18	0,08	0,05	0,11	0,07	0,09
	SrO	0,01	<0,01	0,05	0,03	0,01	0,03	0,05	0,02	0,01	<0,01	<0,01
	BaO	<0.01	<0,01	0,05	0,03	0,03	0,03	0,02	<0,01	<0,01	<0,01	$<\!0,01$
	LOI	15,65	7,75	2,89	14,45	9,93	3,12	3,38	1,71	0,96	1, 7	0,78
	TOTAL	98,3	99,3	100	98,7	98,9	98,8	98,2	98,6	98,3	100,5	99,6
	;											

*see chapter 1 for details ** Samples MD3: mafic volcanic rock, MD6-Ust: dacite, MD7: dacite, MD9-1: calc-micaschist

	Alteration		Least altered	d rocks		Arg	gillic (illite	e dominat	ed)	M	assive silicifi	cation
*Method	**Sample	MD3	MD6-Ust	MD7	MD9-1	MD18	MD6-1	MD6-4	MD6-14	MD6-8 (Vein #1)	MD12 (Vein #2)	MD13 (Vein #2)
	Ba	23,2	12,3	403	248	287	221	135,5	43,3	29,1	16,6	12,6
	Ce	16,4	20,4	40,5	46,5	47	42,1	50,5	11,5	1,4	1,5	6,7
	Cr	180	30	20	190	150	70	80	50	50	20	20
	C_S	1,5	1,21	2,45	6,64	6,68	15,75	13,4	2,76	4,77	4,47	4,71
	Dy	2,31	1,58	2,58	3,63	3,2	2,76	2,81	1,12	0,11	0,2	0,26
	Er	1,39	0,93	1,51	2,09	1,8	1,73	1,88	0,59	0,08	0,13	0,13
	Eu	0,64	0,37	0,96	0,98	0,97	0,86	0,69	0,23	0,06	0,05	0,19
I	Ga	6	19,5	16	11,8	13,5	16	12	2,4	1,2	1,8	1,2
8SV	Gd	2,23	1,62	3,07	4,11	4,16	3,34	3,15	1,03	0,1	0,13	0,57
IE-I	Ηf	1,2	4,5	3,2	2,6	2,6	3,5	3,3	0,6	<0.2	<0.2	0,2
N	Но	0,51	0,32	0,54	0,76	0,64	0,59	0,62	0,21	0,02	0,04	0,04
	La	7,7	7,8	21,4	24,4	25,4	21,3	26,8	5	0,7	0,8	3,4
	Lu	0,2	0,18	0,25	0,3	0,3	0,26	0,27	0,07	0,01	0,02	0,01
	Nb	2,4	7,1	5,6	9,4	9,3	10,5	9,8	2	1,5	0,3	0,4
	Nd	8,6	8,3	15,8	20,3	21,1	19	18,1	5,8	0,6	0,6	3
	Pr	2,1	2,26	4,55	5,59	5,7	4,87	5,37	1,57	0,18	0,16	0,82
	Rb	6,8	2,9	60,9	86,4	99,3	171,5	111	10,6	4,7	5,9	7,9
	Sm	2,06	1,65	3,05	4,24	4,17	3,75	3,25	1,04	0,11	0,16	0,64
*see chapte ** Samples	r 1 for details MD3: mafic v	olcanic roc	k, MD6-Ust: d	acite, ML	07: dacite, M	ID9-1: calc-	micaschist					

Table 6.4 (cont.)

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	Alteration		Least alte	red rocks		Ar	gillic (illit	e dominat	ed)	M	assive silicific	ation
*Method	**Sample	MD3	MD6-Ust	MD7	MD9-1	MD18	MD6-1	MD6-4	MD6-14	MD6-8 (Vein #1)	MD12 (Vein #2)	MD13 (Vein #2)
	Sn	1	1	1	2	2	2	2	2	<1	<1	<1
	Sr	57,1	11,9	388	240	42,8	252	438	141,5	45,1	17,6	8,1
	Та	0,2	0,6	0,5	0,7	0,8	0,8	0,7	0,1	0,1	<0.1	<0.1
	ЧЪ	0,38	0,28	0,47	0,63	0,59	0,51	0,49	0,19	0,02	0,03	0,07
	ЦЦ	1,91	7,91	9,39	7,46	8,08	4,61	7,55	3,16	0,18	0,25	0,36
185	Τl	<0,5	<0,5	<0,5	0,6	0,6	1,6	1,3	0,8	<0,5	<0,5	<0,5
SM-	Tm	0,2	0,14	0,23	0,33	0,28	0,27	0,27	0,07	0,01	0,01	<0,01
ME	U	0,88	1,59	2,71	1,28	1,21	1,64	1,36	0,41	0,09	0,07	0,3
	Λ	148	58	75	99	77	72	49	14	<5	5	8
	M	4	4	1	2	1	28	7	1	2	<1	1
	Υ	11,6	8,4	13,3	19,9	16,9	15,2	16,2	5,4	0,6	1,3	1,2
	Чł	1,25	1,04	1,52	1,86	1,85	1,71	1,68	0,43	0,07	0,12	0,09
	Zr	42	177	130	66	98	138	133	25	9	4	6
	As	59,1	14,1	4,7	55,6	69,5	88,7	9,9	141	140	25,5	11,6
2.	Bi	0,03	0,15	0,03	0,3	0,25	0,37	0,11	1,38	0,18	0,23	0,11
tsv	Hg	0,152	0,007	<0,005	0,005	0,005	0,065	0,029	0,152	0,975	0,062	0,023
IE-I	Sb	0,93	9,04	0,51	76,0	0,85	22,2	5,67	44,9	22,3	16,5	2,99
M	Se	2,4	<0.2	0,4	0,4	0,4	3,5	0,6	7,1	4,7	0,2	0,2
	Te	0,99	<0.01	0,05	0,16	0,11	0,21	0,1	0,65	1,6	3,1	2,21
*see chante	r 1 for dataile											

Table 6.4 (cont.)

*see chapter 1 for details ** Samples MD3: mafic volcanic rock, MD6-Ust: dacite, MD7: dacite, MD9-1: calc-micaschist

	Alteration		Least altere	d rocks		Ar	gillic (illite	e dominate	ed)	Ma	ssive silicifica	ıtion
*Method	**Sample	MD3	MD6-Ust	MD7	MD9-1	MD18	MD6-1	MD6-4	MD6-14	MD6-8 (Vein #1)	MD12 (Vein #2)	MD13 (Vein #2)
C-IR07	С	4,43	0,01	<0.01	3,37	2,41	0,02	0,05	0,02	0,01	0,01	0,05
C-IR08	S	3,64	0,02	<0,01	0,01	<0,01	0,02	0,05	0,49	0,13	<0,01	$<\!0,01$
	Ag	<0,5	<0,5	<0,5	<0,5	<0,5	1,9	<0,5	3	8	1,6	0,8
	Cd	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5
180	Co	25	3	6	18	20	1	1	3	1	1	1
VCD	Cu	45	6	16	41	46	17	24	33	8	14	4
74-5	Mo	\leq	1	$\stackrel{\scriptstyle \wedge}{\sim}$	\sim	\leq	24	2	237	13	5	3
W	Ni	63	8	10	163	116	10	6	9	5	4	4
	Pb	<2	6	17	7	12	56	53	776	8	7	7
	Zn	29	26	60	82	76	12	19	8	11	8	6
•	:											

Table 6.4 (cont.)

*see chapter 1 for details ** Samples MD3: mafic volcanic rock, MD6-Ust: dacite, MD7: dacite, MD9-1: calc-micaschist

6.1.2.1 Element Mobility during Argillic (Illite Dominated) Alteration of the Micaschist

Sample no. MD6-1, MD6-4, MD18 and MD6-14 are used as the representative samples of the argillized zone to construct the isocon diagrams (Fig. 6.4) against the least altered (host) micaschist, MD9-1. In the sample MD6-1, there is depletion in Na₂O, MnO, MgO, CaO with Th, and enrichment in SiO₂, K₂O, Al₂O₃, FeOt, and all other trace elements, which in turn represent the enrichment in illite, quartz, and pyrite, while the leaching of the depleted elements (Ca, Mg, Na, Mn, P) as a result of breakdown of the respective mineral phases (calcite, chlorite, plagioclase) in the micaschist. In the sample MD6-4 in addition to the depleted elements in MD6-1, P₂O₅, FeOt, and Ba contents are also decreasing. The relative concentration similarity (slope = 1) between the sample MD18 and MD9-1 is because MD18 is least altered compared to other samples; it is slightly enriched in K₂O, FeOt, Al₂O₃, SiO₂, Ba, and Rb and depleted in P₂O₅, CaO, and Sr. In the sample MD6-14, in which silicification is more abundant, SiO₂ constituent is more enriched compared with other oxides. It is depleted only in MgO and CaO suggesting the leaching of these elements due to the breakdown of the schist composition (biotite, chlorite, and calcite).

A summary of the gains and losses of the elements during argillic alteration is presented in Table 6.5.



Figure 6.4 Isocon diagrams showing the oxide and trace element variations of argillized (illite dominated) samples with respect to calc-micaschist host rock (dashed lines are the isocons, s is the slope)

Samples	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
	elements (ppm)	
_	SiO ₂	34.47
_	TiO ₂	0.00
_	Al ₂ O ₃	3.26
-	FeOt	0.79
-	MnO	-0.11
-	MgO	-1.68
-	CaO	-14.23
-1	Na ₂ O	-0.02
Ď,	K ₂ O	1.32
N N	P_2O_5	0.01
ins.	Rb	107.47
ver	Sr	44.87
-	Cs	11.16
D6	Ba	1.83
M	Nb	2.47
_	La	-0.32
_	Sm	0.00
_	Yb	0.07
	Zr	57.00
	Hf	1.36
_	Th	-2.25
	U	0.57
· .	SiO ₂	50.36
-	TiO ₂	0.00
-	Al ₂ O ₃	3.08
_	FeOt	-1.58
_	MnO	-0.11
_	MgO	-1.90
-	CaO	-14.15
-1	Na ₂ O	-0.06
versus MD9.	K ₂ O	0.58
	P_2O_5	-0.09
	Rb	54.38
	Sr	315.51
4	Cs	10.36
Dé	Ba	-76.15
Σ	Nb	3.03
_	La	9.59
_	Sm	-0.12
_	Yb	0.27
	Zr	69.68
_	Hf	1.59
-	Th	2.12
-	U	0.44

Table 6.5 Gain (G) and losses (L) of the elements during argillic alteration (sample no. MD6-1, MD18, MD6-4, and MD6-14)

~	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
Samples	elements (ppm)	0,2 ((0,0) PP(0,8)
	SiO ₂	6.40
-	TiO ₂	0.00
-	Al ₂ O ₃	1.26
-	FeOt	0.49
_	MnO	NA
	MgO	-0.02
	CaO	-3.75
.	Na ₂ O	0.00
60 -	K ₂ O	0.39
M _	P_2O_5	-0.07
sns	Rb	12.90
ver	Sr	-197.20
18	Cs	0.04
Â.	Ba	39.00
2	Nb	-0.10
_	La	1.00
_	Sm	-0.07
_	Yb	-0.01
-	Zr	-1.00
-	Hf	NA
-	Th	0.62
	U	-0.07
-	SiO ₂	483.34
-	TiO ₂	0.00
-	Al_2O_3	3.47
-	FeOt	3.62
-	MnO	NA
-	MgO	-2.30
		-13.89
-60	Na ₂ O	0.22
- WE		0.64
[sn	P ₂ O ₅	0.10
ersi	<u>Rb</u>	-25.16
- - -	<u>Sr</u>	577.56
- 1,		9.31
- De		2.18
E_		2.16
-		4.49
-	Sm XI-	1.//
-	<u>YD</u> 7	0.02
-		43.44 NLA
-		10 90
-		10.80
	U	1.09

Table 6.5 (cont.)

6.1.2.2 Element Mobility during Silicic Alteration (Silicification) of the Micaschist

Silicified samples in the Vein #1 (sample no. MD6-8) and Vein #2 (MD12 and MD13) were used to plot the isocon diagrams (Fig. 6.5) against the micaschist host. The considerably small values of the isocon slopes suggest significant loss in the total mass of the rock (see Table 6.6 for gains and losses of elements). SiO_2 is the most enriched constituent in all samples (MD6-8, 12, and 13) as predictable. With the exception of a slight depletion in CaO, all the other oxides and trace elements are enriched in the silicified zone.





Samples	Oxides (wt%) and Trace	G/L wt%/ppm(avg)
	elements (ppm)	
-	SiO ₂	2431.90
_	TiO ₂	0.00
_	Al_2O_3	5.72
_	FeOt	17.97
_	MnO	NA
_	MgO	-1.75
_	CaO	-13.05
-1	Na ₂ O	0.45
D6	K ₂ O	-0.14
N S	P_2O_5	2.67
sins.	Rb	35.80
ver	Sr	932.60
8	Cs	117.38
D6	Ba	508.60
M	Nb	29.60
_	La	-6.20
_	Sm	-1.38
_	Yb	-0.04
_	Zr	57.00
_	Hf	NA
_	Th	-2.78
	U	1.06
	SiO ₂	4878.50
-	TiO ₂	0.00
-	Al_2O_3	159.64
-	FeOt	21.24
-	MnO	NA
-	MgO	-1.49
-	CaO	-12.27
MD12 versus MD9-1	Na ₂ O	1.49
	K ₂ O	3.76
	P_2O_5	3.45
	Rb	220.40
	Sr	675.20
	Cs	225.80
	Ba	615.20
	Nb	6.20
-	La	17.20
-	Sm	4.08
-	Yb	4.38
-	Zr	109.00
-	Hf	NA
-	Th	5.54
-	U	2.36

Table 6.6 Gain (G) and losses (L) of the elements during silicic alteration (sample no. MD6-8, MD12, and MD13)

Samples	Oxides (wt%) and Trace	G/L wt%/ppm(avg)	
	elements (ppm)		
	SiO ₂	2463.10	
	TiO ₂	0.00	
	Al_2O_3	20.28	
	FeOt	10.01	
	MnO	NA	
	MgO	-1.49	
	CaO	-11.75	
-	Na ₂ O	0.71	
D9	K ₂ O	1.16	
Μ	P_2O_5	2.15	
sns	Rb	119.00	
/er:	Sr	-29.40	
31	Cs	115.82	
[D]	Ba	79.60	
M	Nb	1.00	
	La	64.00	
	Sm	12.40	
	Yb	0.48	
	Zr	135.00	
	Hf	NA	
	Th	1.90	
	U	6.52	

Table 6.6 (cont.)

6.2 Stable Isotope Compositions

Stable isotope studies in the epithermal deposits commonly focus on the oxygen (O), hydrogen (H), and sulfur (S) isotopes because of the abundance of these constituents in such systems. Based on the compositions, the hydrothermal activities affecting the development of the related deposits are traced and modeled. To determine the source regions of aqueous and gaseous constituents in the mineralizing fluid and to estimate the paleohydrology, S and C isotopes, which are consistent with the magmatic origin, and H and O isotopes are used to interpret the water compositions, so the source characteristics (Cooke and Simmons, 2000). Commonly, oxygen in quartz, adularia, alunite, sericite,

calcite, and clay minerals, S in pyrite and related sulfosalts and sulfides, and C in carbonates are chosen as the main concern for the stable isotope studies.

In this study, the oxygen isotope analyses were conducted on quartz separates collected from silicified zones for both areas. The sulfur isotopic composition is limited to a single composite (pyrite) sample representing mixture of KD5-c and KD8-b from Kartaldağ area. In Madendağ area, since all the pyrite separates (hand-picked under the microscope) were including and/or turned totally to goethite, suitable sample could not be found for S-isotope analysis. Table 6.7 summarizes the results of stable isotope analyses for both areas.

District	<u>Sample</u>	Mineral	<u>δ¹⁸O (*SMOW)</u>	Silicification stage	$\frac{\delta^{34}S (**V-}{CDT)}$
044	MD6-2	Quartz	9,55	Early	-
ndağ	MD10	Quartz	13,00	Early	-
Made	MD8	Quartz	18,19	Late	-
~	MD6-1	Pyrite (?)			***N
Kartaldag	KD9	Quartz	7,93	Early	-
	KD11	Quartz	8,33	Early	-
	KD6	Quartz	8,95	Late	-
	KD5-c & KD8-c	Pyrite	-	-	-4.8

 Table 6.7 Representative oxygen and sulfur isotope analyses results of the silicified samples from Madendağ and Kartaldağ mine districts

*Standard Mean Ocean Water

V-CDT: Vienna - Canyon Diablo Troilite *N: Negligible

6.2.1 Oxygen Isotope Compositions of Kartaldağ and Madendağ Districts

In order to obtain information about the silicification stages and source characteristics of the fluids that formed alteration and mineralization in both districts, quartz crystals were used. The samples were selected on the basis of relative time of formation of silicification phases at each district. Therefore, a special care was given to sample early and late silicification phases that formed the main quartz veins and/or silicified ridges at both districts. In the Kartaldağ deposit, quartz separates from the samples KD9, KD11, and KD6 were analyzed for their oxygen isotope compositions. The first two of these separates are from veins formed during early silicification phase, and yielded δ^{18} O values of 7.93 and 8.33 per mil, respectively, whereas sample KD6, which is obtained from a vein of the late silicification phase, has a δ^{18} O value of 8.95 per mil (Table 6.7). The composition of the Kartaldağ samples is compared in Fig. 6.5 with those characteristic for various rocks and water sources. As can be seen from Fig. 6.6 Kartaldağ samples are within the range defined by magmatic rocks and waters, and hence suggest an essentially magmatic origin for the hydrothermal fluid responsible for silicification. Although there is a small increase in the δ^{18} O value from early to late stage silicification in the Kartaldağ samples, it is rather difficult (with the limited amount of data) to comment on the possible contribution from other (sedimentary) sources towards the later stages of the silicification process.

Similar to the Kartaldağ district, for the characterization of the silicification stages and source characteristics of the fluids, three samples (MD6-2, MD10, and MD8) were selected in the Madendağ district. Oxygen isotopes of quartz separate from veins of the early silicification phase (MD6-2 and MD10) yielded δ^{18} O values of 9.55 and 13.00 per mils, whereas separates from veins of late silicification phase (MD8) returned δ^{18} O value of 18.19 per mil. Based on the source regions shown in Figure 6.6 and regarding the host rock characteristics, the ore bearing fluid in Madendağ appears to have been affected by a metamorphic source, at least towards the late stages of silicification. It should also be noted, however, that the difference in the early and late silicification may

be the result of a possible boiling process which is common to most of the low sulfidation type epithermal deposits. Such boiling processes are evidenced indirectly by brecciation via hydraulic fracturing. In fact, the sample representing the late stage in Madendağ is a brecciated sample (MD-8). The proposed boiling process could have enriched the heavy oxygen isotopes in the late stage hydrothermal solution due to separation of a gas phase from the original fluid.



Figure 6.6 Comparison of the δ^{18} O values of Kartaldağ and Madendağ samples with those from various rocks and water sources (KD: Kartaldağ, MD: Madendağ) (Rollinson, 1993)

6.2.2 Sulphur Isotope Compositions of Kartaldağ and Madendağ Deposits

As explained above, S-isotope analyses could be performed only for a single (composite) pyrite sample separated from sample no. KD5-c & KD8-c from Kartaldağ mine area. In the Madendağ area, sample MD6-1 from the Vein #1 area was selected as the representative samples but since all the pyrite separates (hand-picked under the microscope) were including and/or turned totally to goethite no data could be obtained for that sample. (All trials on these separates yielded with negligible sulfur isotope compositions).

Regarding the Kartaldağ sample the δ^{34} S value (relative to V-CDT) is -4.8 per mil. This value is compared in Figure 6.7 with the ranges characteristic for various sulphur reservoirs. As appears from Fig. 6.7, the S-isotope composition of the Kartaldağ sample is within the range defined by volcanic and granitic rocks, but the possibility of contribution from sedimentary sources (characterized essentially by negative δ^{34} S values) can not be ruled out.



Figure 6.7 δ^{34} S value of Kartaldağ samples and various rocks and water sources (KD: Kartaldağ) (Rollinson, 1993)

CHAPTER 7

FLUID INCLUSIONS

7.1. Fluid Inclusion Analyses

For the fluid inclusion analyses, samples MD9-2 from the Madendağ, and KD6 and KD7 from the Kartaldağ mine areas were selected. Samples from the Madendağ area represent a hydrothermally brecciated sample from Dump # 2, whereas samples of Kartaldağ area are from the main silicified core (main gallery). All fluid inclusion information was gathered from the quartz minerals within the quartz veins and pervasively silicified rocks. Homogenization temperatures and salinities belonging to these aqueous inclusions were determined and presented in *Fluid Inclusion Microthermometry* part of this chapter.

Fluid inclusions are basically defined as the fluids (liquid, gas) trapped in the minerals when they form. Fluid inclusions are the key solutions to gather information about the ancient temperatures, pressures, and fluid compositions on the basis of salinity, homogenization temperatures, freezing temperatures, and isotopic ratios such as oxygen and hydrogen. Similar to the stable isotope studies performed for the identification of the ore-bearing fluid' characteristics, fluid inclusion analyses provide valuable information about the origin and evolution of an ore-bearing fluid and, consequently, deposition mechanisms (i.e. chemical and physical environments) of the mineralization system. Especially in studies focused on epithermal systems and their hydrothermal evolution, quartz crystals bearing millions of fluid inclusions play important role to obtain information about the precious and base metal bearing fluids. At the room temperature, epithermal inclusions typically contain only two phases as liquid, generally low salinity H₂O liquid and a vapor bubble (Bodnar et al., 1985). In the epithermal environments,

calcite, quartz, sphalerite, and fluorite minerals are studied mostly because of their abundance in such systems and their handiness to study inclusions trapped in them.

Roedder (1984) first described the trapping mechanisms of the fluid inclusions within minerals and some of them are explained as i) fluid inclusions in the irregularities formed during growing of a mineral or ii) fluid inclusions formed in a crack developed after growth of a mineral grain. Basically, fluid inclusions are classified into three as primary, secondary, and pseudosecondary inclusions in which primary inclusions (Fig. 6.1) form generally on the growth zones of the minerals or as an isolated occurrence, secondary inclusions form within the microstructures (after the crystal growth is complete) (Goldstein and Reynolds, 1994). Pseudosecondary inclusions, on the other hand, are trapped during the crystal growth which may be enveloped by an additional growth zone. The visual representation of these three types of inclusions is given in Figure 6.2. They can involve sometimes only one phase (generally liquid water, methane, air etc.), sometimes two phases (generally, water and vapor H_2O , CO_2 etc.), and sometimes three phases such as halite, gaseous water and liquid water.



Figure 7.1 Primary fluid inclusion textures trapped within quartz crystals (Goldstein and Reynolds, 1994)



Figure 7.2 Representative mineral grain displaying the types of the fluid inclusions among the growth zones (defined by the distribution of primary fluid inclusions). s: secondary fluid inclusions, ps: pseudosecondary fluid inclusions, p: primary fluid inclusions (Goldstein and Reynolds, 1994)

7.2 Fluid Inclusion Petrography

In order to understand the paragenetic relation between the quartz crystals and the aqueous fluid inclusions, six quartz polished-thin sections were examined under both plane light and UV illumination. Fluid inclusion assemblages were identified according to their presence, relationship to the host, consistency of visual parameters (e.g., apparent liquid/vapor ratio) and applicability for determining the microthermometric information. Studied fluid inclusion assemblages revealed three types of fluid inclusions in the selected three quartz samples (sample no. MD9-2, KD6, and KD7): primary (p), secondary (s), and pseudosecondary (ps). Petrographical features of the fluid inclusion populations (FIP) within the representative quartz crystals in the samples are presented in Table 7.1, 7.2, and 7.3.

FI Population	n (# of FI)	Description
1	4	Primary fluid inclusions in early silicification phase
2	7	Primary fluid inclusions in early silicification phase
3	20	Secondary and pseudosecondary fluid inclusions in early silicification phase
4	5	Secondary and pseudosecondary fluid inclusions in early silicification phase
5	1	Secondary fluid inclusions in early silicification phase
6	3	Secondary fluid inclusions in early silicification phase
7	1	Secondary fluid inclusions in late silicification phase
8	1	Secondary fluid inclusions in late silicification phase

 Table 7.1 Fluid inclusion petrography of sample MD9-2

FI Population	n (# of FI)	Description	
1	6	Primary fluid inclusions in late silicification phase	
2	5	Primary fluid inclusions in late silicification phase	
3	3	Primary fluid inclusions in late silicification phase	
4	3	Primary fluid inclusions in late silicification phase on the core of a zoned quartz crystal	
5	9	Primary fluid inclusions in late silicification phase on the middle of a zoned quartz crystal	
6	4	Primary fluid inclusions in late silicification phase on the rim of a zoned quartz crystal	
7	2	Primary fluid inclusions in late silicification phase on the rim of a zoned quartz crystal	
8	2	Secondary and pseudosecondary fluid inclusions late silicification phase within the rim of a zoned quartz crystal	
9	2	Secondary fluid inclusions in late silicification phase	
10	8	Secondary fluid inclusions in late silicification phase	
11	1	Secondary fluid inclusions late silicification phase	

 Table 7.2 Fluid inclusion petrography of sample KD6

 Table 7.3 Fluid inclusion petrography of sample KD7

FI Population	n (# of FI)	Description	
1	5	Primary fluid inclusions in late silicification phase	
2	5	Primary fluid inclusions in late silicification phase	
3	6	Primary fluid inclusions in late silicification phase	
4	3	Primary fluid inclusions in late silicification phase	
5	8	Secondary fluid inclusions in late silicification phase	
6	6	Secondary fluid inclusions in late silicification phase	
7	7	Secondary fluid inclusions in late silicification phase	
8	1	Secondary fluid inclusions in late silicification phase	
9	1	Secondary fluid inclusions in late silicification phase	
10	1	Secondary fluid inclusions in late silicification phase	

In sample MD9-2, which is hydrothermally brecciated quartz, six fluid inclusion (FI) populations are found in early silicification phase and two FI populations in the late silicification phase (Table 7.1). Generally two phases (a gaseous state bubble within a liquid phase) are observed with a commonly consistent vapor/liquid (V/L) ratio. Photomicrograph identifying a representative inclusion population in the sample MD9-2 is presented herein along with a low power photograph for general rock identification (Fig. 7.3).

In the samples KD6 and KD7, eleven and ten fluid inclusion populations were found respectively (Table 7.2 and 7.3). Since sample KD6 includes coarse grained, zoned quartz crystals, fluid inclusion studies were performed so as to represent those on the rim, core and middle of the crystal. While in KD6 seven populations are displaying the primary inclusions, in KD7 four populations are primary. The fluid inclusions in KD6 are relatively bigger (3-7 μ m in size) and irregularly shaped (Fig. 7.4) with variable V/L ratio, whereas KD7 includes FI populations that have more consistent V/L ratio (Fig. 7.5).All populations for both samples represent late stage silicification observed for Kartaldağ mineralization.



Figure 7.3 Sample photomicroscopy for the sample MD9-2



Figure 7.4 Sample Photomicroscopy for the sample KD6



Figure 7.5 Sample photomicroscopy for the sample KD7

7.3 Fluid Inclusion Microthermometry

Microthermometric analyses were carried out for each population to determine the, homogenization temperatures (Th $_{aq}$), final (ice) melting temperatures (Tm $_{aq}$), and salinity values (wt %). Salinities were interpreted from the table prepared by Bodnar et al. (1992) in NaCl – H₂O system.

Analyses performed for sample MD9-2 (Table 7.4) show that primary and high temperature secondary/pseudo-secondary inclusions in early phase quartz have homogenization temperatures (Th) of 235-285°C; with most in the 240-255°C range for the Madendağ district (Fig. 7.6). Salinities are low at 0.0-0.7 weight percent (i.e. wt % NaCl eqv.).

Low temperature secondary aqueous inclusions both in early and late phase quartz from the silicified rocks in the Madendağ have Th in the range 90-130°C, with somewhat bimodal distribution at 90-98°C and 128-130°C (Fig. 7.6). Salinities could not be measured, due to metastable phase behavior, but are inferred to be quite low. These secondary inclusions may represent external conditions attending waning stages of a cooling system.

*Population #	Th aq (°C)	Tm aq (°C)	Salinity (wt %)
1 (p, early)	250-255 (4)	metastable	N/A
2 (p, early)	235-255 (7)	0 to -0.2	0.0-0.4
3 (s/ ps, early)	265-285 (20)	0 to -0.2	0.0-0.4
4(s/ ps, early)	240-250 (5)	0 to -0.4	0.0-0.7
5 (sec, early)	130 (1)	metastable	N/A

 Table 7.4 Microthermometric analysis results of the fluid inclusion populations the

 Madendag district in sample MD9-2 (number in parentheses indicates the number of inclusions measured, N/A is not available)

*p: primary, ps: pseudo-secondary, s: secondary inclusions; early-late: phases of silicification

*Population #	Th aq (°C)	Tm aq (°C)	Salinity (wt %)
6 (sec, early)	90-95 (3)	N/A	N/A
7 (sec, late)	128 (1)	N/A	N/A
8 (sec, late)	98 (1)	metastable	N/A

Table 7.4 (cont.)

*p: primary, ps: pseudo-secondary, s: secondary inclusions; early-late: phases of silicification



Figure 7.6 Homogenization temperature (Th °C) ranges determined for the fluid inclusion populations (FIP) found in sample MD9-2

Primary and high temperature secondary/pseudo-secondary inclusions in the late phase, growth-zoned euhedral quartz from the Kartaldağ district in sample KD6 have Th dominantly in the range of 245-285°C, although values as low as 135°C were measured (Table 7.5 and Fig. 7.7). A transect from core to rim did not reveal any drastic temperature changes, although there is some evidence of oscillatory high temperature (Fig. 7.7). Salinities are low at 0.0-1.7 wt % salt. Salinity appears to decrease slightly from core (c) to rim (r) (1.1-1.7 vs. 0.0-1.4 wt % NaCl eqv.).

Secondary aqueous inclusions in late phase quartz cement have bimodal measured Th of 110-140°C and 215-220°C (Fig. 7.7). Salinities are 0.0-1.4 weight percent salt.

*Population #	Th aq (°C)	Tm aq (°C)	Salinity (wt %)
1 (p, late)	275-285 (6)	0 to -1.0	0.0-1.7
2 (p, late)	185-200 (5)	metastable	N/A
3 (p, late)	135-140 (3)	metastable to -0.6	1.1
4 (p, c, late)	260-275 (3)	-0.6 to -1.0	1.1-1.7
5 (p, m, late)	245-255 (9)	-0.6 to -1.0	1.1-1.7
6 (p, r, late)	255-267 (4)	0 to -0.8	0.0-1.4
7 (p, r, late)	270-277 (2)	0 to -0.8	0.0-1.4
8 (s/ps, late)	270-279 (2)	0 to -0.8	0.0-1.4
9 (s, late)	110-120 (2)	metastable	N/A
10 (s, late)	215-220 (8)	metastable to 0.0	0,0
11 (s, late)	140 (1)	-0,8	1.4

Table 7.5 Microthermometric analysis results of the fluid inclusion populations for

 the Kartaldag district in sample KD6 (number in parentheses indicates the number of inclusions measured, N/A is not available)

*p: primary, ps: pseudo-secondary, s: secondary inclusions; early-late: phase of silicification, c: core, m: middle, r: rim of the crystal


Figure 7.7 Homogenization temperature (Th °C) ranges determined for the fluid inclusion populations (FIPs) in sample KD6

Although KD7 sample includes both early and late phase quartz crystals, only late phase coarse grained quartz could be used for the microthermometry as early phase quartz crystals did not yield adequate fluid inclusion populations (FIP) to be analyzed. According to the results (Table. 7.6), primary inclusions in late phase quartz have Th of 250-270°C (Fig. 7.8). Salinities are found in the range of 0.0-1.7 weight percent salt.

Secondary aqueous inclusions in late phase quartz have bimodal measured Th of 93-105°C and 185-260°C (Fig. 7.8). The low temperature mode may represent conditions attending waning stages of a cooling system. Salinities could only be determined for the high temperature mode, and were found to be 0.9-1.1 weight percent salt.

*Population #	Th aq (°C)	Tm aq (°C)	Salinity (wt %)
1 (p, late)	250-267 (5)	-0.7 to -1.0	1.2-1.7
2 (p, late)	250-265 (5)	-0.4 to -0.8	0.7-1.4
3 (p, late)	255-270 (6)	-0.4 to -1.0	0.7-1.7
4 (p, late)	260-270 (3)	0 to -0.4	0.0-0.7
5 (s, late)	250-260 (8)	metastable	N/A
6 (s, late)	185-200 (6)	metastable to -0.6	1,1
7 (s, late)	235-245 (7)	metastable to -0.5	0,9
8 (s, late)	95 (1)	N/A	N/A
9 (s, late)	93 (1)	N/A	N/A
10 (s, late)	105 (1)	N/A	N/A

 Table 7.6
 Microthermometric analyze results of the fluid inclusion populations

 found in sample KD7 (number in parentheses indicates the number of inclusions measured, N/A is Not Available)

*p: primary, s: secondary inclusions; early-late: phases of silicification



Figure 7.8 Homogenization temperature (Th °C) ranges determined for the fluid inclusion populations (FIPs) in sample KD7

CHAPTER 8

DISCUSSION AND CONCLUSIONS

8.1 Kartaldağ Deposit

Kartaldağ gold deposit is hosted by dacite porphyry (known as the Yeniköy volcanics, Dönmez et al., 2008) observed to the southern part of the study area. Main structural features presumed to act as channel for the fluids are normal faults (Kartaldağ fault) and a small-scale thrust fault. Dacite porphyry is assumed to be volcanic equivalent of the granodiorite plugs observed in the area because of their i) geographic closeness, ii) geochemical similarities, and iii) age relations in which dacite porphyry (sample no. KD-18) and granodiorite (sample no. KD-25) are both determined to be Middle Eocene (42.19 ± 0.45 and 40.8 ± 0.45 Ma, respectively) in age. These ages are likely to fall into the age interval during which post-collisional Middle-Late Eocene magmatism was pronounced in the Biga Peninsula.

Main alteration styles formed in the Kartaldağ mineralization area consist of (from wall rocks towards the center of epithermal vein) 1) propylitic alteration, 2) quartz-kaolin, 3) quartz-alunite-pyrophyllite and 4) vuggy quartz (pervasive or massive silicification) zone. An Ar/Ar biotite age of 42.27 ± 0.96 Ma found for weakly altered (argillized) dacite porphyry sample (sample no. KD-1a) suggests that the dacitic volcanism and the wall rock alteration which in turn associated with the gold mineralization should be genetically and temporally related to each other.

Propylitic alteration refers to assemblage of albite, chlorite-smectite mixed layer, epidote, illite, α -quartz ± calcite. The assemblage of quartz-kaolin is characterized by the kaolin (dominantly kaolinite), illite, pyrite, α -quartz, chlorite, and zunyite (?).Quartz-alunite-pyrophyllite alteration, which could also be termed as the advanced argillic alteration, is accompanied by pyrite, covellite and sphalerite.

Pervasive or massive silicification is composed of fine to medium grained quartz crystals displaying mostly vuggy quartz textures typical for the high sulfidation epithermal systems. Euhedral pseudomorphs of the parental grains such as plagioclase and hornblende minerals appear to form the vugs during pervasive leaching of the dacite porphyry. Based on relative cross-cutting relationships of quartz textures, dacitic host rock is noticed to have experienced at least two phases of silicification as early and late silicification, which are likely to have formed by (adiabatic) boiling process throughout the hydrothermal evolution. The textural characteristics of the quartz crystals formed at each phase is different such that early silicification exhibits the vuggy quartz texture with fine grained quartz crystals, whereas late phase silicification is characterized by colloform, banded, growthzoned, commonly euhedral coarse grained quartz crystals, and occurs as an overprint on the vuggy quartz. Concerning the depth where these textures were observed, banded, colloform, coarse grained zoned quartz formations (late phase silicification) might indicate the level above the boiling zone, whereas vuggy quartz formations (and possible brecciation at depth) with base metal deposition might specify the presence of rapidly cooling boiling zone.

Isocon plots constructed for Kartaldağ alterations suggest the followings:

- In the propylitic alteration, enrichment in K₂O and MnO, and in Ba and Rb which are the trace elements associated with K are most striking features.
- In Quartz Kaolin zone, the enrichment in SiO₂ and K₂O in the altered sample is conformable with the findings (quartz and illite) from the XRD and SEM/EDX studies. Depletion in MnO, P₂O₅, MgO, FeOt, CaO, and Na₂O, compared with the least altered sample (KD-18), confirms the replacement of the minerals of plagioclase and hornblende by the clay minerals.
- In quartz-alunite- pyrophyllite alteration, enrichment in SiO₂, P₂O₅, FeOt, and Al₂O₃, along with Sr and Ba, suggests that the zone of alteration is dominated by quartz and aluminum silicates (e.g. kaolinite and pyrophyllite).

Furthermore, higher S, Cu, FeOt and Al_2O_3 concentrations seem to be associated with the dominance of covellite (CuS), pyrite (FeS₂), kaolin (mostly kaolinite) and the sulfates (e.g. alunite).

Oxygen isotope analysis performed on the quartz separates representing early and late silicification phases yield δ^{18} O (relative to SMOW) values of 7.93 and 8.33 per mil, and of 8.95 per mil, respectively. Since these values plot within the range of magmatic-water dominated area, Kartaldağ mineralization might have been formed by essentially magmatic waters, but increasing δ^{18} O value from early to late silicification points to a possible contribution from other (e.g. sedimentary) sources as well. Additionally, the sulfur isotope analysis performed on a composite pyrite sample (separated from two different specimens) yield δ^{34} S value (relative to V-CDT) of -4.8 per mil, which in turn gives the idea of a possible magmatic origin for sulfur.

Fluid inclusion petrography, at room temperature, reveal the presence of two phases as liquid and vapor (both probably H₂O). Vapor phase in the inclusions do not generally display necking morphology, suggesting that the vapor was not introduced during a healing process but was trapped during the formation of the inclusion. Furthermore, in some samples, liquid-rich inclusions are also observed together with vapor-rich inclusions in a single quartz crystal, which is stated in the literature (Bodnar et al., 1985) to be an evidence of the contemporaneous formation of those two types via the boiling fluid. Microthermometric analysis show that the primary fluid inclusion populations determined in the late silicification samples have the homogenization temperature range of 135-285°C (dominantly of 250-285°C) and generally low salinity values at 0.0-1.7 wt % NaCl eqv. Therefore, it can be said that the late stage silicification seems to have formed mostly at moderate temperatures and from low salinity fluids. Since there is no FIP data representing the early stage silicification, fluid genesis for this stage is unknown. Given that the late silicification probably represents the level above the boiling zone, the mineralization at/below the boiling level might have occurred at even higher temperatures (>285°C).

The Kuşçayırı Au-Cu deposit (Bayramiç, Çanakkale), a high sulfidation epithermal type mineralization, hosted by calc-alkaline Miocene volcanics (Yılmaz, 2003) to the south of the Kartaldağ deposit has nearly the same structural control, and a similar alteration petrography as the Kartaldağ deposit. Although there is not enough information locating the Au distribution both laterally and vertically in Kartaldağ deposit, geological closeness and similar alteration styles may suggest they might be part of a magmatic-hydrothermal system or in a broader sense they might have a similar fluid genesis and nature. However, relatively higher salinity (35–50 wt% NaCl eqv.) values and temperature range (330–450 °C) found for the fluid inclusions in quartz samples in Kuşçayırı deposit strongly disagree with the same fluid genesis or hydrothermal evolution with the Kartaldag with a moderate temperature of 250-285°C and a very low salinity of 0.0-1.7 wt% NaCl eqv.

8.2 Madendağ Deposit

Madendağ gold deposit is located nearly 20 km northwest to the Kartaldağ mine, is hosted by micaschist units mainly observed western part of the study area. Micaschist units outcropping in this area are known as the Çamlıca micaschist (or Çamlıca metamorphics) (Okay et al., 1991) in the literature. Two veins and two dump areas were identified as the representative sampling locations where the brecciation lenses seem to act as main structural features. An Ar/Ar (sericite) age of 55 Ma on a mica-schist sample (sample no. MD1-a) possibly points to a metamorphism age during that time interval.

Alteration types for Madendağ mineralization is defined basically as argillic and silicic alterations. Argillic alteration observed on the micaschist is classified into two groups as i) kaolin-rich argillic alteration with chlorite and ii) illite-rich argillic alteration, and is dominantly characterized by hydrothermal α -quartz, illite, kaolin and pyrite. Silicification, on the other hand, is observed as two distinct phases of quartz formations, which are grouped as early and late phases of silicification. While early silicification phase is identified by its crosscutting relation with foliation planes

of the schist with coarse to medium grained, colloform, comb and banded quartz textures (typical for the low sulfidation epithermal systems), late silicification phase is characterized by the hydrothermally brecciated samples showing occasionally the typical brecciation texture of jig-saw puzzle. Similar to Kartaldağ mineralization, the observation of certain quartz textures at different places/levels (early phase textures in the surface outcrops, and late phase textures in the dump areas) may be related with the presence of a possible boiling zone.

According to the isocon plots of illite-dominated argillic alteration, commonly Na₂O, MnO, MgO, CaO, and Th are the depleted, and SiO₂, K₂O, Al₂O₃, FeOt oxides and nearly all trace elements are the enriched constituents, which are in turn related with the formations of illite, quartz, and pyrite in this zone. In the silicification zone, as expected, SiO₂ is the most enriched constituent along with significant loss of the total rock mass. The base metal enrichment seems to be associated with early silicification phase, especially in the sample MD6-14.

The oxygen isotope analyses performed to distinguish the source region of the mineralizing fluid show that the quartz separates of early silicification yield δ^{18} O values (relative to SMOW) of 9.55 and 13.00 per mils, whereas those of late silicification show δ^{18} O value of 18.19 per mil. Regarding both the host rock nature and the source regions defined for these values, ore bearing fluid in Madendağ deposit is thought to have been affected mostly by a possible metamorphic source and the increase in δ^{18} O values suggest the expected boiling process at depth.

The petrographic features of FI populations show that the inclusions are dominantly liquid-rich (probably liquid H₂O), and occasionally one-phase (liquid), and are irregularly shaped with medium to small sizes (5-15 μ m). In two-phase inclusions, the vapor phase seems to be primary (not necking) which may point to a possible boiling origin as in the case of Kartaldağ mineralization. Microthermometric analysis carried out on a brecciated sample (including both early and late phase silicification stages) of the Madendağ mineralization, primary fluid inclusion populations found in early silicification phase show the homogenization temperature (Th) range of 235-

255 °C, with the data gathered from those of secondary and pseudosecondary FI populations, the range may extend to 235-285 °C. Salinity values determined for this sample yield the range of 0.0-0.7 wt % (NaCl eqv.). The homogenization temperatures and the salinity values suggest moderate temperatures and low salinity fluids for the early silicification and the possibly associated ore bearing stage.

If Madendağ deposit is compared with the Şahili/Teşpih Dere intermediate style epithermal deposits (Y1lmaz et al., 2010) hosted by the Upper Oligocene volcanics in Lapseki, Canakkale region (to the northeast of the Madendağ (or Akbaba) mineralization), it is observable that the base metal content and fluid evolution in terms of the temperature and salinity ranges (average: 276 °C on quartz and 259 °C on sphalerite, < 7 wt % NaCl eqv.) are different compared to the findings in this study (235-255 °C temperature range on quartz and 0.0-0.7 wt % NaCl eqv.). This show both a similarity in fluid nature and a significant difference in salinity which is in turn related with the metal bearing and transport capacity of the fluids in these hydrothermal systems. While in the Şahinli and Teşbih Dere mineralization, polymetallic deposition with a variety of clay minerals sensitive to a wide range of temperature and pH conditions is stated to be formed, in the Madendağ deposit, limited base metal content is associated with limited alteration styles. Besides, the vein textures and temporal association of vein and breccia facies defined in Sahinli are lacking in the Madendag, and this suggests that these two deposits have different fluid evolution and genesis.

8.3 Concluding Remarks

Major concluding remarks figured out from this thesis study are summarized as follows:

In the Kartaldağ mine district, the advanced argillic alteration (quartz alunite- pyrophyllite alteration) covers and/or envelopes the pervasively silicified zone (core of residual part of the system), and wall rock (Middle-Late Eocene dacite porphyry) alteration can be traced from propylitic at the margins to massive silicification at the center of the mineralized system. This may be stated as evidence that fluid (ore bearing) was channel through a single conduit close to or within the massive-vuggy quartz zone.

- The temporal and spatial association of alterations, zoning patterns, predominant clay mineral compositions being pyrophyllite, kaolinite and alunite, vuggy quartz texture, and covellite, pyrite, sphalerite ore minerals can be taken as the key minerals supportive of an argument that the Kartaldağ epithermal gold mineralization is formed by a low pH-oxidizing fluid.
- > In addition to the alteration petrography in the Kartaldağ epithermal system, stable isotope compositions (i.e., δ^{18} O and δ^{34} S values) and the temperature range (dominantly 250-285°C) suggest a magmatic origin for a possible ore bearing (Au?, Ag, Cu, Pd, Mo, Zn) fluid which is recently accepted to be associated with the high sulfidation epithermal systems (Hedenquist and Lowenstern, 1994).
- Regarding the quartz textures and the associated base metal concentrations, early silicification phase (in the Kartaldağ mine) containing mostly fined grained vuggy quartz can be stated to have controlled the mineralization possibly through a boiling process.
- In the Madendağ mine district, the limited types of wall rock (dominantly micaschist) alterations (argillic and silicic) may refer to a simple mineralizing system encompassing boiling process which may be evidenced with hydrothermal breccia samples in dump areas.
- > Being formed at a near-neutral pH condition, illite, kaolin, chlorite, calcite, and α -quartz may suggest that the argillic alteration in the Madendağ mineralization is formed in a low sulfidation epithermal environment.
- > The presence of the colloform, comb and banded quartz formations in early

phase silicification reflects the low temperature conditions in Madendağ mineralizing system. The temperature range (235-255 °C) estimated from the primary FIP in comb, banded and brecciated quartz samples can be regarded as a support for this argument. The occurrence of banded quartz along with comb quartz and bladed calcite-ghost blades may be indicative of boiling in the system.

- Although the oxygen isotope compositions of Madendağ samples suggest a metamorphic contribution (conformable with the composition of the host rock), the ore forming fluid is thought to be related with the Kartaldağ system (i.e. an essentially magmatic origin overprinted by meteoric fluids) because of the geographic closeness of, and nearly the same temperature ranges obtained from the primary fluid inclusion populations in both mineralizing systems.
- The absence of advanced argillic zone (particularly alunite), vuggy quartz, and limited base metal content suggest that Madendağ mineralization is not a high-sulfidation type epithermal system defined in the literature. Additionally, the difference in salinity values of Kartaldağ (0.0 to 1.7 wt %) and Madendağ (0.0 to 0.7 wt %) systems reflect both low salinity fluids, but with a slight decrease in the latter. In this respect, Madendağ gold mine appears to reflect a mineralizing system that can be regarded as a low-sulfidation type epithermal deposit.
- For further studies, more sulfur isotope studies will be carried out for genesis for the Madendağ sulfide deposition This will help to solve genetic link between Kartaldağ and Madendağ epithermal systems. The evolutionary relation along with the fluid origins between two deposits may be further understood with oxygen and hydrogen analyses on the fluid inclusions in quartz generations obtained petrographically. Clay minerals which are observed abundant in both deposits can be used to strengthen the understanding of the source regions for the oxygen isotope compositions,

particularly in the Madendağ deposit. In addition, the temporal and spatial distribution of Au deposition in both deposits should be determined in by means of further chemical and petrographical analyses. It is recommended further studies on the ore microscopy to identify the distribution of Au with related base metals and relation between Au and possible Au bearing quartz generations. Recommended studies would also be used in interpreting the possible genetic relation with other epithermal deposits (e.g. Kuşçayırı and Şahinli mineralization) in Biga Peninsula.

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