Extinct Geothermal Systems in the Continental Rift Zones of the Menderes Massif, Western Anatolia, Turkey

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ABSTRACT
The Hg, Sb and Au deposits of Haliköy, Emirli and Küre are related to faults which strike preferentially NE-SW and NW-SE and are located diagonal to the general strike of the rift zone of the Küçük Menderes within the Menderes Massif. The calcalkaline volcanics of Middle Miocene age, which occur in the E and NE part of the investigated ore fields, indicate basic towards acidic features and crustal origin and seem to be closely related with tectonic features, ore deposits and active geothermal systems. The Hg, Sb and Au deposits of Haliköy, Emirli and Küre can be considered as fossil equivalents of formerly active geothermal systems due to various similarities of parameters. The metals originated in the host rocks were transported in a hydrothermal system as (HS)–complexes. The precipitation of metals depended upon T, P, pH and redox potential as well as total sulfur concentration. Due to ore microscopical observations and fluid inclusion studies of the epithermal ore field of Küre, it can be concluded that Au was precipitated by a relatively low low fO2 and temperature from 210 to 300 °C accompanied by arsenopyrite as oldest mineralization in connection with Miocene volcanism. The antimony mineralization of Emirli was generated in a temperature interval between 180 to 220 °C as second mineralization in connection with cooling Miocene volcanism. The Hg mineralization of Haliköy seems to be youngest mineralization of the epithermal deposits due to low temperatures from 128 to 200 °C in connection with cooling Miocene volcanism. Finally, the Hg, Sb and Au deposits of Haliköy, Emirli and Küre can be assigned to an epithermal type in connection with an calcalkaline volcanism in Middle Miocene age, comparable to other Hg, Sb and mineralizations in the rift zones of the Menderes Massif, similar to the epithermal Sb and Au deposits in the metallotect of Jiangnan, PR China and active and extinct geothermal systems of New Zealand, and considered as fossil equivalents of active geothermal systems.

1 INTRODUCTION
The Anatolian and Aegean micro plates control the plate tectonic position of the Eastern Mediterranean area between the Eurasian and African plates. This plate tectonic development results in the lifting of the Menderes Massif in Western Anatolia, Turkey showing a dome structure due to compressional tectonic features from Oligocene to Miocene (Özgür 1998, 1999). From Early Miocene to Middle Miocene, the continental rift zones of the Büyük Menderes, Küçük Menderes, and Gediz were formed by extensional tectonic features, which strike E-W generally and are represented by a great number of Hg, Sb, and Au mineralizations and thermal waters in connection with volcanic rocks from Middle Miocene to recent (Fig. 1; Özgür 1999, 2019).

The Hg, Sb and Au mineralizations and thermal waters are related to faults, which strike preferentially NW-SE and NE-SW, diagonal to the general strike of the continental rift zones. These faults, representing a multitude of Hg, Sb and Au mineralizations and thermal waters, are probably generated by compressional tectonic stress, which leads to the deformation of uplift between two extensional continental rift zones. The investigated Hg, Sb and Au deposits of Haliköy, Emirli and Küre (Fig. 1) represent typical examples of epithermal mineralizations. The aim of this paper is to introduce Hg, Sb and Au deposits in the continental rift zone of the Küçük Menderes within the Menderes Massif and to compare them geneticaly to each other with regard to (i) relationship between Hg, Sb and Au deposits as fossil geothermal systems, active geothermal systems, tectonic features and volcanism, (ii) fluid-rock interactions, (iii) geochemical, hydrogeochemical and isotope geochemical features, (iv) fluid inclusion studies in ore and gangue minerals and (v) source, transport and deposition of Hg, Sb and Au deposits.

2 GEOLOGIC SETTING
The Hg, Sb and Au mineralizations of Haliköy, Emirli and Küre occur 25 km S and SE of the town of Ödemiş in SE part of the rift zone of the Küçük Menderes. The metamorphic rocks of the Massif are (i) Precambrian to Cambrian core series consisting of high-grade schists, gneisses, granites and metagabbros and (ii) Ordovician to Paleocene cover series composed of mica schists, phyllites, metaquartzites and metagabbros (Fig. 1; Dora et al. 1995). In Cambrian, the first metamorphism in the massif took place under amphibolite to granulite facies conditions affecting the core series. The late phase of the Variscan orogenesis affected the massif for a second time, which may be postdated by the Early to Middle Triassic granites.

In Eocene, high-pressure metamorphism was generated under epidote-blue schist to eclogite facies conditions, and the late main metamorphism developed in Late Eocene to Early Oligocene (Dora et al. 1995) and is overprinted by the Barrowian-type metamorphism. The metamorphic rocks in the massif are overlain by Neogene to Quaternary thick sedimentary rocks. From Middle Miocene to recent, an intense volcanism was generated in connection with the evolution of the continental rift zones in the Menderes
Massif (Ercan & Güny 1981; Ercan et al. 1983, 1992; Özgür 1998). The volcanic rocks in the NE part of the Hg, Sb and Au deposits of Hahköy, Emirli and Küre in the rift zone of the Küçük Menderes are distinguished by Rb/Sr age of 15,0± 0,2 Ma in Karaburç and a K/Ar age of 16,7 ± 0,5 Ma in Yenişehir and can be classified into Middle Miocene (Özgür et al. 1997; Özgür 1998). These volcanic rocks may be considered as products of continental crust due to isotope analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. The youngest volcanism in the Menderes Massif is characterized by the Late Pliocene volcanic rocks of Denizli (Ercan et al. 1983) and the volcanics of Kula with an age ranging from 7,5 Ma to 7,5 Ma to 18.000a (Ercan et al. 1992). Finally, the volcanic rocks can be considered as heat source for the heating of thermal fluids in the continental rift zones in addition to earthquake activity and heat flow anomalies.

3 MERCURY, ANTIMONY AND GOLD DEPOSITS

The strongly altered mica schists and quartzites form the host rocks of Hg, Sb and Au deposits of Haliköy, Emirli and Küre. The Hg deposit of Haliköy consists of ore formations in terms of veins and veinlets, which contain cinnabar, metacinnabarite, pyrite, marcasite, chalcopyrite and quartz and calcite as gangue minerals (Fig. 2). The Emirli Sb deposit is distinguished by veins and veinlets and consists of pyrite, arsenopyrite, stibnite, sphalerite, chalcopyrite, tetraedrite, marcasite, orpiment, realgar, cinnabar and gangue minerals of quartz, adularia and calcite. As mineral assemblage in the Au deposit of Küre representing ore types of veins and veinlets, there are arsenopyrite, gold, pyrite, marcasite, fahlore and gangue minerals of quartz and calcite.

In the abandoned Haliköy Hg mine, there are measured ore reserves of 56.000 metric tonnes with a Hg mean value of 0,30 percent, indicated ore reserves of 210.000 metric tonnes with a Hg mean value of 0,25 percent and possible ore reserves of 210.000 metric tonnes with Hg mean value of 0,23 percent (Özgür, 1998). The recoverable ore reserves of the Sb deposit of Emirli are estimated at 400.000 tonnes with an average content of 5,5 percent Sb. The Au deposit of Küre consists of three occurrences and shows Au contents up to 30 ppm.

Fig. 1. Geologic setting of the Menderes massif with some locations of active geothermal waters and some locations of epithermal mineralizations as extinct geothermal systems (1: Hg deposit; 2: Sb deposit; 3: Au deposit; Özgür, 1998).
4 FLUID INCLUSION STUDY AND FLUID GEOCHEMISTRY

For the fluid inclusion studies of the Hg, Sb and Au deposits of Haliköy, Emirli and Küre, we have collected about 50 quartz samples (stage 2), which were compared with quartz samples of the crystalline massif (stage 1) and stibnite crystals. The fluid inclusion measurements were made in the Freie Universität Berlin, Germany using a Linkam THMSG 600 programmable freezing-heating stage attached to a Leitz Ortholux transmitted-light microscope. This used stage has a dynamic range from -180 to 600 °C. The measurements in stibnite crystals were used in GeoForschungsZentrum Potsdam, Germany by a FLUID.INC SYSTEM gasflow freezing-heating stage attached to an Olympus IR transmitted-light microscope. Three types of primary fluid inclusions were recognized in quartz and stibnite crystals. The type (i) is an inclusion (H₂O-NaCl), which can be observed in quartz stage (1) as well as in stibnite crystals and shows two phases (liquid and vapor) at room temperature (Özgür 1998). The type (ii) is a system of H₂O-NaCl-CO₂ ± CH₄ of which inclusions show three phases of CO₂ (CH₄)-liquid, CO₂ (CH₄)-gas and aqueous solutions at room temperature and an increase in salinity. The type (iii) is a system of aqueous vapor, which is associated with Sb deposit of Emirli and indicates boiling conditions in the system. The quartz samples of stage (2) which are associated with ore deposits show homogenization temperatures from 180 to 300 °C and salinity ranging from 3.75 to 9.0 NaCl (eq wt %), which correspond with each other (Özgür et al. 1997). The quartz samples of the Haliköy indicate average homogenization temperature of 128 °C and salinity of 3.4 NaCl (eq wt %) (Gökçe & Spiro 1995). The quartz samples of the Au deposit of Küre (Fig. 3) is distinguished by the homogenization temperatures from 210 to 300°C and a salinity between 1.60 and 10.0 NaCl (eq wt %).
In order to understand the composition of hydrothermal ore-forming fluids we have analyzed the fluid inclusions in the quartz samples to $\delta^{18}$O and $\delta^2$H by mass spectrometer, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, Al$^{3+}$ by ICP emission spectrometer, F$^-$ by anion-selective electrode, Cl$^-$ by mercury thiocyanate colorimetric analysis, SO$_4^{2-}$ by barium sulfate turbimetric analysis, and HCO$_3^-$ by acid-base capacity titration in the State Key Laboratory for Research of Mineral Deposits, Nanjing University, PR China. The stable isotopes of $\delta^{18}$O and $\delta^2$H in fluid inclusions of quartz samples from the investigated Hg, Sb and Au deposits show a connection with them of active geothermal systems (Özgür et al. 1997; Özgür 1998). The strongly deviation of the $\delta^{18}$O from the global meteoric water line proves the intensively fluid-rock interaction in the hydrothermally environment during the differences in the degree of isotope shift from the active geothermal systems to investigated Hg, Sb and Au deposits indicate a relationship between the both systems in meteoric origin (Özgür et al. 1997; Özgür 1998; Fig. 4). The fluid inclusion studies show that the fluids in quartz and stibnite crystals from the ore fields of Haliköy, Emirli and Küre are of Na-HCO$_3^-$ type similar to those of active geothermal systems in the rift zones of the Menderes Massif, whereas the analyses of anions and cations in fluid inclusions of quartz crystals show Ca-(Cl)-(SO$_4$)-HCO$_3^-$ type exchange fluids which form a sharp contrast with them of active geothermal systems and fluid inclusion studies (Fig. 5). In one respect, this may relate to the process of albitization by Na metasomatism in the investigated area and its environs in which Ca contents dominate during Na contents decrease due to the same process (Nebert & Ronner, 1956).
**5 DISCUSSION**

The Hg, Sb and Au deposits of Haliköy, Emirli and Küre are related to faults which strike preferentially NE-SW and NW-SE and are located diagonal to the general strike of the rift zone of the Küçük Menderes (Fig. 1). The calcalkaline volcanics of Middle Miocene age, which occur in the E and NE part of the investigated ore fields, indicate basic towards acidic features and crustal origin (Özgür, 1998) and seem to be closely related with tectonic features, ore deposits and active geothermal systems (Özgür & Pekdeger 1995). The intensively altered mica schists and quartzites, which form the host rocks for Hg, Sb and Au deposits, can be considered as source rocks...
for the metals, as supported by leaching tests (Özgür 1998). The hydrothermal alteration is distinguished by phyllic, argillie and silicie + hematization alteration zones which are comparable with those of active geothermal systems in the continental rift zones of the Menderes Massif. This type of alteration is comparable with adularia-sericite-type-mineralization due to presence of adularia and bladed calcite crystals. The homogenization temperatures of quartz and stibnite crystals range from 150 to 300 °C (Özgür et al. 1997), which can be compared with geochemical temperatures of thermal water reservoirs from 220 to 260 (Özgür & Pekdeger 1995). The ore-forming fluids of Haliköy, Emirli and Küre show a mean value of 6 NaCl eq wt %; it is comparable with the salinity of active geothermal fluids. The isotope ratios of δ18O and δ2H in fluid inclusions of quartz crystals of Haliköy, Emirli and Küre show a similarity with those of active geothermal fluids. The strong deviation of the δ18O values from the meteoric water line shows the intensive fluidrock interaction in the hydrothermal environment. The trend of deviation increases linearly from the active geothermal field to the epithermal ore fields indicating a relationship between the two. Finally, it might be concluded that (i) the fluids of Hg, Sb and Au mineralizations of Haliköy, Emirli and Kure can be attributed to a meteoric origin due to stable isotopes of δ18O and δ2H, (ii) the metamorphic rocks act as the source of metals of Hg, Sb, As and Au which are forming ore deposits in the rift zones and leached from the metamorphic rocks by fluid-rock interaction and transported as bisulfide complexes with circulating geothermal fluids to the subsurface environment between 500 to 1500 m in depth at temperature below 350 °C. Ultimately, with the cooling of magma chamber, the Au mineralization of Kure was formed at temperatures below 300 °C. Arsenopyrite is present in the ore mineral assemblages of investigated Hg, Sb and Au mineralizations. In connection with further cooling of magma chamber, the Sb mineralization of Emirli took place at temperatures from 180 to 250 °C. The Hg deposit of Haliköy is generated as the last mineralization at temperatures from 128 to 200 °C.

Fig. 6. Simplified genetical modeling of Hg, Sb and Au mineralizations of Haliköy, Emirli and Kure in the continental rift zone of the Küçük Menderes within the Menderes Massif (Özgür, 1998, 2019).

Fig. 7. Microscopical observation of rhomboidal, triclinic adularia crystals in strong silicified host rocks of Sb mineralization of Kuşunlu in the continental rift zone of the Gediz within the Menderes Massif. 500 X and // N (Özgür, 1998, 2019).
The meteoric fluids percolate above permeable clastic sediments in the reaction zone of the roof area of magma chamber in depth of 2–3 km where the fluids are heated and ascend to the surface because low density. The volatile components of CO₂, SO₂, H₂S and HCl from magma reached the geothermal water reservoir as ascending gas phases where an equilibrium reactions between altered rocks, gas components and fluids took place. The ascending fluids contain CO₂, H₂S and HCl particularly. Hydrothermal convection cells press the heated fluids toward the surface because of their lower density. Thus, geothermal waters ascend in tectonic zones of weakness. As geochemical pH-neutral fluids, the waters outlet at the surface as hot springs, gas and steam. The fluids indicate a reduced pH-neutral sphere in the reaction zone after equilibrium with host rocks. At the subsurface spheres, the ore deposits are generated in terms of stockwork mineralizations (veins, veinlets) and gangue minerals represented by quartz, calcite and adularia (Özgür 1998). The Hg, Sb and Au deposits of Haliköy, Emirli and Kure can be assigned to an epithermal type in connection with an alkali-alkaline volcanism in Middle Miocene age, comparable to other Hg, Sb and mineralizations in the rift zones of the Menderes Massif, similar to the epithermal Sb and Au deposits in the metuallotet of Jiangnan, PR China and active and extinct geothermal systems of New Zealand, and considered as fossil equivalents of active geothermal systems.

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REFERENCES


