Epithermal antimony, mercury, and gold deposits in the continental rift zone of the Küçük Menderes, western Anatolia, Turkey: Preliminary studies

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ABSTRACT: The present-day Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre in the rift zone of the Küçük Menderes within the Menderes Massif, Western Turkey can be considered as extinct deposits of formerly active geothermal systems due to various similarities of parameter with the active geothermal systems. The ore metals originated from the host rocks are transported in a fluid environment in which (HS)\textsuperscript{2-} complexes dominate. The precipitation of metals depends upon T, P, pH, and redox potential of the system as well as sulfur concentration.

1. INTRODUCTION

The Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre are located 20-30 km Sand SE of the town of Ödemiş in the SE part of rift zone of the Küçük Menderes within the Menderes Massif which was generated in terms of lifting due to compressional tectonic features in Middle Miocene (Fig 1). Subsequently, the rift zones were formed by extensional tectonic features one of which is the rift zone of the Küçük Menderes. There, the epithermal ore deposits are related to faults which strike preferentially NW-SE and NE-SW and locate diagonal to general strike of the rift zone. It is probably generated by the compressional tectonic stress, which leads to deformation of uplift between two extentional rift zones. In addition to earthquake activity and heat flow anomalies in the rift zone of the Küçük Menderes, we have mapped localities of a great number of calcalkaline basic towards acidic volcanics which are distinguished by an Rb/Sr age of 15,0 ± 0,2 Ma in Karaburç and an K/Ar age of 16,7 ± 0,5 Ma in Yenişehir and can be classified into Middle Miocene. These volcanics are considered as products of continental crust due to isotope analyses of $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd. Moreover, there are volcanics in Kula with an age up to 20,000 a. They can be considered as heat source for the heating of thermal fluids in the rift zones. The aim of this paper is to give an overview and to elucidate the genesis of the Hg, Sb, and Au deposits of...
Haliköy, Emirli, and Küre in rift zone of Küçük Menderes.

2. GEOLOGIC SETTING

The Hg deposit of Haliköy is situated near the village of Haliköy and occurs in intensively altered mica schists in connection with the Haliköy overthrust in which the Precambrian to Cambrian gneisses overlie the Paleozoic altered mica schist. The Emirli antimony deposit is located 20 km southeast of the town of Ödemiş and very close to the village of Emirli. It is associated with altered mica schist and quartzite in terms of veins and veinlets and depends upon the diagonal faults (Özgür, 1997). The Au deposit of Küre is located 30 km south of the town Ödemiş and associated with altered mica schist. The ores are linked to diagonal faults.

3. HYDROTHERMAL ALTERATION AND MINERALIZATION

At the surface, the rocks in the ore fields are intensively altered by interaction with the circulation of geothermal fluids. Therefore, these fields can be recognized by a distinct color change of the rocks. The hydrothermal alteration is noticeable at the surface which is distinguished by phyllic, argillic, and silicic±haematitization alteration zones and comparable with the fields of active geothermal systems (Özgür & Pekdeğer 1995; Özgür 1997). The intensity of the different alteration zones can be controlled by the abundance and fractionation of rare earth elements. The enrichment of ore metals such as Sb, As, and Hg show that phyllic and silicic alteration zones are associated with the ore formations. The Haliköy Hg deposits consist of ore formations in terms of veins and veinlets which show the following mineral assemblage: cinnabar, metacinnabarite, pyrite, marcasite, chalcopyrite, and quartz and calcite as gangue minerals. The Emirli antimony deposit consist of pyrite, arsenopyrite, stibnite, sphalerite, chalcopyrite, tetraedrite, marcasite, orpiment, realgar, cinnabar, and gangue mineral (quartz and calcite). As mineral assemblage in the Au deposit of Küre, there are arsenopyrite, gold, pyrite, marcasite, fahlore, and quartz and calcite as gangue minerals.
Fig. 1: Epithermal ore fields in the of the Küçük Menderes within the Menderes Massif. 1: Hg deposit of Haliköy; 2: Sb deposit of Emirli; 3: Au deposit of Küre; triangle active geothermal systems.

4. FLUID INCLUSION STUDY

For the fluid inclusion investigations, we have collected 50 quartz samples (stage 2) in the ore fields of Haliköy, Emirli, and Küre which were compared with quartz samples of the crystalline massif (stage 1). Additionally, we have collected stibnite crystals for the same study. The microthermometric measurements were made in the Free University of Berlin 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 have been used by a FLUID INC. SYSTEM gas-flow freezing-heating stage attached to an Olympus IR transmitted-light microscope. Three types of primary inclusions were recognized in quartz and stibnite minerals. The type (i) is an aqueous inclusion (H₂O-NaCl) which can be observed in quartz stage (1) and stage (2) as well as in stibnite crystals and shows two phases (liquid and vapor) at the room temperature (Özgür, 1997). 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 the increase of salinity. The type (iii) is a system of aqueous vapor which is associated with antimony ore deposits of Emirli and indicates boiling conditions in the system. The quartz samples (stage 2) which are associated with ore deposits show homogenization temperatures from 170 to 250 °C and salinity from 175 to 90 NaCl (eq wt %) during the stibnite crystals have homogenization temperatures ranging from 180 to 210°C and
salinity with a range from 375 to 90 NaCl (eq wt %) which correspond with each other (Fig. 2). Beside a salinity from 8.30 to 12.70 NaCl (eq wt %), the quartz samples of the Haliköy Hg deposit indicate a homogenization temperature from 150 to 227 °C. The high salinity in connection with low temperature is debatable. For the case of sampling, we could not take enough quartz samples because an abandoned Hg mine in Haliköy is present and there is no access to the mine adit. The quartz samples of the Au deposit of Küre is distinguished by the homogenization temperatures from 210 to 298 °C and a salinity between 1.60 and 10.0 NaCl (eq wt %) comparable with the temperature of quartz samples of the Menderes Massif.

5. FLUID GEOCHEMISTRY

In order to know the composition of hydrothermal ore-forming fluids we have analyzed the fluids in the quartz samples to $\delta^{18}$O and $\delta$D by mass spectrometer, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, and Al$^{3+}$ by ICP emission spectrometer (JY38S), F$^-$ by anion-selective electrode, Cl$^-$ by mercury thiocyanide colorimetric analysis, SO$_4^{2-}$ barium sulfate turbimetric analysis, and HCO$_3^-$ by acid-basic capacity titration in the State Key Laboratory for Research of Mineral Deposits, Nanjing University. The gas composition was also analyzed by gas chromatography there. The stable isotopes of $\delta^{18}$O and $\delta$D in fluid inclusions of quartz samples from the epithermal Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre show a connection with them of the active geothermal waters (Fig. 3). The strongly deviation of the $\delta^{18}$O from the global meteoric water line (MWL) 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 epithermal deposits indicate a relationship between the both systems in meteoric origin.

According to fluid inclusion study, the hydrothermal fluids in the quartz and stibnite crystal samples from the ore fields of Haliköy, Emirli, and Küre show Na-HCO$_3$ type corresponding with them of active geothermal systems in the rift zones of the Menderes Massif whereas the analyses of anions and cations in fluid inclusions of quartz samples show Ca-(Cl)(SO$_4$)-HCO$_3$, type exchange fluid which form a sharp contrast with them of active geothermal systems and fluid inclusion study. In one respect, it might be attributed to analytical error of Ca$^{2+}$ and Na$^+$ in the fluid inclusions of quartz samples. On the other hand, Ca contents dominate during the Na contents decrease due to the process of albitization by Na
metasomatism in the investigated area and its environs (Nebert & Ronner 1956). Therefore, the formerly active hydrothermal fluids which are responsible for the formation of the above

![Fig. 2: Homogenization temperatures, salinity and Tm_{ice} in quartz and stibnite samples of the Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre.](image)

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![Fig. 3: Plot of δ^{18}O vs. δD in quartz samples from the Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre. In comparison, the stable isotope data of active geothermal waters in the Menderes Massif were plotted in the diagram.](image)

Fig. 3: Plot of δ^{18}O vs. δD in quartz samples from the Hg, Sb, and Au deposits of Haliköy, Emirli, and Küre. In comparison, the stable isotope data of active geothermal waters in the Menderes Massif were plotted in the diagram.

mentioned Hg, Sb, and Au deposits might be considered as Na-HCO₃ type originally which are comparable with the hydrogeochemistry of the present-day geothermal systems in the continental rift zones of the Menderes Massif (Özgür & Pekdeğer, 1995). The differences between fluid inclusion study and analytical methods will be under consideration by the
further hydrogeochemical analyses of quartz samples from the investigated fields.

6. CONCLUSIONS

The epithermal Hg, Sb, and Au ore deposits of Haliköy, Emirli, and Küre are related to faults which strike preferentially NE-SW and NW-SE and are located diagonal to general striking of the rift zone of the Küçük Menderes (Fig. 1). In the eastern and northeastern part of these ore fields the calcalkaline volcanics of Middle Miocene occur which indicate basic towards acidic features and crustal origin. These volcanics seems to be closely related with these ore deposits as extinct geothermal systems. There is also a relationship between tectonical features, magmatic activity, and geothermal systems in the continental rift zones of the Menderes Massif.

The intensively altered mica schists and quartzites form the host rocks for the Hg, Sb, and Au ore minerals and can be considered as source rocks for these metals supported by leaching tests. The hydrothermal alteration is distinguished by phyllic, argillic, and silicic±haematitization alteration zones which are comparable with active geothermal systems in rift zones of the Menderes Massif. Alteration stages of these deposits together with accompanying alteration minerals are investigated now.

The homogenization temperatures of quartz samples and stibnite crystals indicate a range from 150 to 300 °C (Fig. 2) which can be compared with the geochemical temperatures of the thermal water reservoirs from 220 to 260 °C. The ore-forming fluids from Haliköy, Emirli, and Küre show a mean value of salinity of 6 NaCl eq wt %; it is comparable with the salinity of the active geothermal fluids.

With regard to albitization process by Na metasomatism in the central part of the investigated area in Menderes Massif (Nebert & Ronner, 1956) the hyrothermal ore-forming fluids might be considered as Na-(Cl)-(SO₄)-HCO₃, type which can be closely correlated with active geothermal systems in the region and established by the fluid inclusion studies in the quartz samples. In correlation with the Na metasomatism the Ca contents increase which are comparable with hydrothermal solutions of several important gold deposits in Jiangnan gold
metallogenic belt, China (Ma & Liu, 1992).

According to stable isotopes of $\delta^{18}$O vs. $\delta$D the extinct hydrothermal ore-forming fluids are related to active geothermal systems in meteoric origin which can be corroborated by the differences in the degree of isotope shift from active geothermal systems to ore-forming fluids in the investigated area.

At the surface, the hydrothermal ore fields are distinguished by an enrichment of the metals Hg, Sb, As, Tl, Au, and Ag in connection with the intensity of the hydrothermal alteration which geochemically can be compared with the geothermal fields. In comparison, the base metals are enriched at depth supported by analyses of drill cores. As reason for that preferential mobilization of the metals Hg, Sb, As, Tl, Au, and Ag by hydrothermal fluids of the continental crust and low salinity of fluids due to transport of base metals (Liu, 1989).

The ore formations are of hot-springs sub-type epithermal deposits in which the origin of the metals are attributed to leached host rocks in the geothermal reservoir. The meteoric fluids percolate above permeable clastic sediments in the reaction zone of the roof area of the magma chamber in depth of 2-3 km where the meteoric fluids are heated due to cooling of magmatic melt and ascend to the surface because of low density. The volatile components of CO$_2$, SO$_2$, H$_2$S, and HCl from the magma reach the geothermal water reservoir as ascending gas phases where an equilibrium between altered rocks, gas components, and fluids are performed. The ascending fluids contain CO$_2$, H$_2$S, and HCl particularly. The sulfur isotope of ore minerals suggest that the sulfur reservoir is sulfide dominated with isotopic values of -3.8 per mill for stibnite and -0.3 per mill for cinnabar which corresponds to that of sulfide with magmatic origin (Gökçe & Spiro, 1995). Hydrothermal convection press the heated water to the surface because of their low density. Thus, the geothermal waters ascend in tectonical zones of weakness. As geochemical pH-neutral fluids, the waters outlet at the surface as hot springs, gas, and steam. The hydrothermal 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 as stockwork mineralisations (veins, veinlets) and gangue minerals represented by quartz, calcite, and adular (?) (Özgür, 1997). By the ascending fluids, CO$_2$ and H$_2$S$^-$ rich fluids are generated in the shallow spheres which condense at the subsurface, i.e. in the permeable zone, and form sulfate-rich fluids by the oxidation of H$_2$S in which the fluids
indicate pH values of 2 to 3 and temperature of 100 °C. At the surface, the silica and carbonate precipitations are generated.

REFERENCES