

## Reinjection of the CO<sub>2</sub> into the Reservoirs of the Geothermal Waters in the Continental Rift Zones of the Menderes Massif, Western Anatolia, Turkey

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### ABSTRACT

Turkey has high potential for exploitation of geothermal waters which are distributed with high temperatures up to 287 °C within the Menderes Massif intensively. The geothermal waters are associated with the faults that strike preferentially NW-SE and NE-SW and also located diagonal to the general strike of the rift zones of the Menderes Massif in western Anatolia, Turkey. These NW-SE and NE-SW striking faults were probably generated by compressional tectonic regimes which lead to deformation of uplift between two extensional rift zones of the Menderes Massif. The active geothermal waters of Kızıldere, Bayındır and Salihli and Alaşehir in the continental rift zones of the Büyük Menderes, Küçük Menderes and Gediz represent typical examples in the study area. The meteoric waters in the drainage areas of the rift zones percolate at NE-SW and/or NW-SE trending fault zones and permeable clastic sediments into the reaction zone of the roof area of a magma chamber situated in a probable depth of up to 4-5 km where meteoric fluids are heated by the cooling magmatic melt and ascend to the surface due to their lower density caused by convection cells. The volatile components of CO<sub>2</sub>, SO<sub>2</sub>, HCl, H<sub>2</sub>S, HB, HF, and He out of the magma reach the geothermal water reservoir where an equilibrium between altered rocks, gas components, and fluids performs. Thus, the geothermal waters ascend in the tectonical zones of weakness at the continental rift zones of the Menderes Massif in terms of hot springs, gases, and steams. These fluids are characterized by high to medium CO<sub>2</sub>, H<sub>2</sub>S and NaCl contents. 2.0 percent of the production of the geothermal waters in the area of the Menderes Massif displays CO<sub>2</sub> emissions. In order to consider the geothermal waters as environmental and human friendly energy, CO<sub>2</sub> emissions must be reinjected into the reservoirs of each geothermal waters. As alternative to inhibitors, it can be taken in consideration a reinjection of the waste CO<sub>2</sub> quantities into the reservoir of the geothermal waters for adjust of pH values of geothermal fluids. Approximately 2.0 percent of CO<sub>2</sub> in the production of the geothermal waters is available for reinjection into the reservoirs. A small amount of this total mass might be attributed to a correction of pH value of 6-7 of geothermal fluids in a reinjection process. An acid reinjection pH value can decrease an arising oversaturation of calcite and aragonite by the pH effect of reinjected geothermal waters. However, there are difficulties. A superficial blow on of CO<sub>2</sub> into reinjection fluid leads to push of dissolved gases in reinjection well, because high CO<sub>2</sub> contents at high pressures can be dissolved in deeper spheres of reinjection well. Therefore, CO<sub>2</sub> gases should be conducted to the depth below the solution depth in a separate intern pipe and must be reinjected into the reservoir of geothermal waters. However, this assumes previous condensing of CO<sub>2</sub> gases, because die pressure in the total gas column must overstep die pressure in the mixing depth. The geothermal waters in the continental rift zones of the Menderes Massif have CO<sub>2</sub> contents of up to 2.0 percent which represent very important environmental problems. Therefore, these CO<sub>2</sub> emissions must be reinjected into the reservoirs at the achievement of the geothermal energy.

### 1. INTRODUCTION

The tectonic position of the eastern Mediterranean area between the Eurasian and African plates is controlled by the Anatolian and Aegean micro plates. The plate tectonic development results in the uplift of the Menderes Massif showing a dome shaped structure due to compressional tectonic features from Oligocene to Middle Miocene (Figure 1; Okay, 2001). From Early to Middle Miocene, the continental rift zones of the Büyük Menderes, the Küçük Menderes and the Gediz were formed by extensional tectonic features (Figure 2; Bozkurt, 2001), which strike E-W generally and are represented by a great number of geothermal waters, epithermal mineralizations, and volcanic rocks of Middle Miocene to recent age. The present-day geothermal waters, epithermal Hg, Sb and Au mineralizations and young volcanoes are related to faults which strike preferentially NW-SE and NE-SW and locate diagonal to general strike of the rift zones. These faults are probably generated by compressional tectonic stress which leads to the deformation of uplift between two extensional rift zones (Özgür, 1998; Özgür et al., 1998a). In addition to earthquake activities and heat flow anomalies in the continental rift zones of the Menderes Massif, the important localities of calc-alkaline towards basic towards acidic volcanic rocks were mapped which are distinguished by an Rb/Sr age of  $15,0 \pm 0,2$  Ma in Karaburç, an K/Ar age of  $16,7 \pm 0,5$  Ma in Yenişehir (Özgür et al., 1997; Özgür, 1998) and an 7,5 Ma age of 20.000ain Kula (Ercan et al., 1992, 1995) and can be classified into Middle Miocene. These volcanic rocks are considered as products of continental crust due to isotope analyses of <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd and come into consideration as heat source for the geothermal waters in the rift zones of the Menderes Massif (Özgür, 1998). Therefore, we have selected geothermal fields in the continental rift zones of the Büyük Menderes, the Küçük Menderes and the Gediz and were investigated circumstantially (Figure 1). The aim of this paper is to present the hydrogeological, hydrogeochemical and isotope geochemical features of the geothermal waters in the rift zones of the Menderes Massif in combination with the origin and evolution of these waters and to make a

hydrogeological modeling of the geothermal waters and to suggest the methods for reinjection of the CO<sub>2</sub> contents into the geothermal reservoirs in the study area.

**2. GEOLOGIC SETTING**

The present-day geothermal waters, i.e. Kızıldere, Bayındır and Alaşehir, in the rift zones of the Büyük Menderes, the Küçük Menderes and the Gediz within the Menderes Massif (Figure 1 and 2). The Menderes Massif is one of the oldest basements in Turkey and consists of (i) gneiss-core surrounded by a schist and marble envelope and (ii) an intensely deformed volcano-sedimentary sequence with incipient HP/LT metamorphism (Dora et al., 1995). The rift zones with present-day geothermal waters are the results of an extension which is believed to be closely related to the northward movement of the Arabian plate in the east pushing Anatolia westwards through the North Anatolian and East Anatolian Faults. The southerly bending of the North Anatolian Fault in the northern Aegean and Greece prevents the escape of the Anatolian plate further westwards placing the system in a locking geometry (Dewey and Şengör, 1979). This creates an E-W compression in the Menderes Massif which is relieved by N-S extension. The driving force of extension in the Aegean is believed to be subduction along Hellenic Trench (McKenzie, 1978).

**3. HYDROGEOLOGY, HYDROGEOCHEMISTRY AND ISOTOPE GEOCHEMISTRY**

**3.1 Hydrogeology**

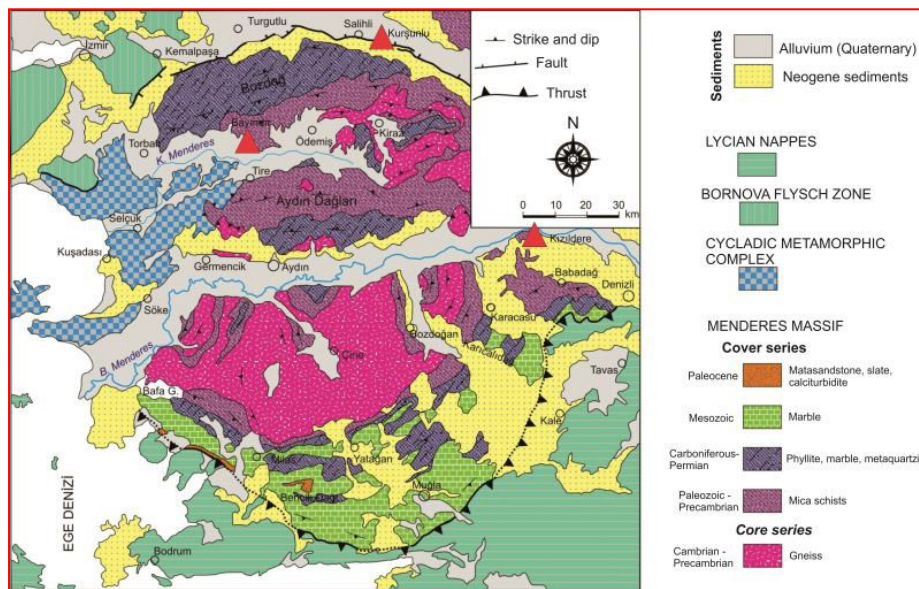


Figure 1. Geological map of the of the Menderes Massif and continental rift zones with investigated active geothermal systems (modified from Okay, 2001).

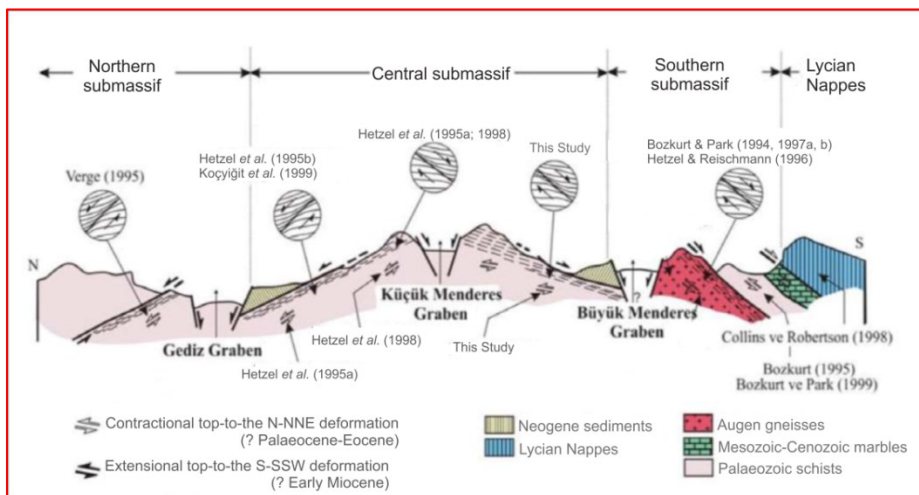


Figure 2. N-S schematic cross section through the Menderes Massif (modified from Bozkurt, 2001).

In the study area of the rift zone of the Büyük Menderes, the groundwaters flow northwards at the northern side of the continental rift zone within the Buldan Horst, where the geothermal waters are supplied immediately. The distance from the watershed to the geothermal waters is about 10 km. Consequently, the drainage area occupies an area from 100 to 150 square kilometers. The river of the Büyük Menderes is a watercourse which springs as karst spring at Dinar near Isparta, flows past by Sarayköy, Aydın and Söke and leads into Aegean Sea at Akköy. The discharge rate of river is 15-20 m<sup>3</sup>/s in winter and 2 m<sup>3</sup>/s in summer. With an annual precipitation of 430,15 mm and average annual temperature of 17,6 °C, the region of the Menderes Massif has semiarid climatic conditions. A great part of the precipitation takes place in the winter months from December to March, during aridity is predominant in the remainder of the time. The time of aridity leads to a deficit of groundwater; therefore, the surface waters play a secondary role for the feeding of geothermal waters only.

Groundwaters flow in the drainage area of the geothermal waters in Bayındır southwards on the northern part of the rift zone of the Küçük Menderes in Bozdağ Horst, where geothermal water reservoir is supplied by meteoric groundwaters; thereby, the Ilıca creek plays an important role (Özgür, 1998). The distance from the northern watershed is about 10 km. The drainage area occupies an area of 50-100square kilometers. With an average annual precipitation of 652 mm and an average annual temperature of 17,4 °C, the study area has a semiarid climatic conditions. A great part of precipitation is the result of months from December to March, during aridity of the time is predominant else. This aridity of the time leads to a groundwater deficit; therefore, the deep holes in the rift zone of the Küçük Menderes for irrigation applications. In summer time, the agricultural irrigation leads to shortage of groundwater additionally. The Küçük Menderes is watercourse which springs at Bozdağ near Kiraz, flows by Ödemiş and Bayındır and leads into Aegean Sea near Selçuk.

In Salihli and Alaşehir, groundwaters flow in the drainage area of the geothermal fields northwards on southern part of the rift zone of the Gediz; thereby, the geothermal water reservoir is supplied by groundwater dominantly in meteoric origin (Özgür, 1998; Özgür et al., 2017). The distance from the watershed in Bozdağ Horst to geothermal fields of Kurşunlu and Çamurlu is about 10 km. The drainage area of the geothermal fields occupies a total area of about 150 km<sup>2</sup>. With an average annual precipitation of 652mm and an average annual temperature of 16,6°C, the drainage area of both geothermal fields have semiarid climatic conditions. The Gediz is a watercourse which springs in the northern part of Kula, is supplied by a system of tributaries and leads into Aegean Sea in the northern part of İzmir. The discharge rate of the Gediz is at 20-25 m<sup>3</sup>/s in winter and 3-5 m<sup>3</sup>/s in summer.

### 3.2 Hydrogeochemistry

Generally, the geothermal waters in the rift zones of the Menderes massif can be classified as Na-HCO<sub>3</sub> type. In the drainage area of Kızıldere, the geothermal waters of Kızıldere, Tekkehamam and Babacık Pınarı can be classified as Na-(SO<sub>4</sub>)-HCO<sub>3</sub> type exchange waters, during the geothermal waters of Pamukkale and Karahayit show Ca-Mg-HCO<sub>3</sub> type exchange waters (Figure 3; Özgür, 1998). The origin of Na<sup>+</sup> in the geothermal waters is linked to metamorphic rocks in substratum, while carbonate rocks in the reservoirs form the origin for Ca<sup>2+</sup> and Mg<sup>2+</sup>. The high-temperature geothermal waters of Kızıldere demonstrate TDS (total dissolved solids) values from 5000 to 5500 mg/l and high mineralization rate (Özgür, 1998). Before the separator, the pH values of these waters range from 6 to 7, which correspond with the pH values of natural geothermal springs in the environs. The HS<sup>-</sup> ions in Babacık Pınarı show values up to 5 mg/l. In comparison, the geothermal waters of Kızıldere show HS<sup>-</sup> values below 0,02 mg/l. The magmatic sulfur promotes as a source for H<sub>2</sub>S, H<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> (Hattori and Cameron, 1986). The entry in sulfur compound can be assimilated and transported to the surface which could be observed in reinjection wells in Tekkehamam in depth of 2000 m and in Kızıldere in depth of 2261 m (Özgür, 1998, 2013). HS<sup>-</sup> or H<sub>2</sub>S ions in geothermal waters, which are either magmatic origin or can be dissolved from sulfides by weathering, can be oxidized and ascend to the surface and set sulfur free (Özgür, 1998, 2013). In the carbonate-bearing sediments, which are associated with geothermal springs immediately, gypsum efflorescences could be observed. The formation of gypsum stand in contrast to carbonatization thereby. It indicates thereby, that the sulfur system carries the principal responsibility; thereby, the existence of water is assumed.

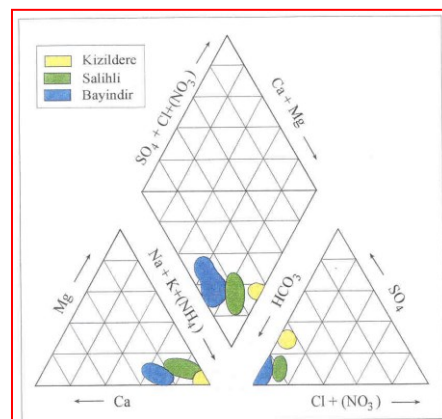


Figure 3. Geothermal waters of the thermal fields of Kızıldere, Bayındır and Salihli in the continental rift zones within the Menderes Massif.

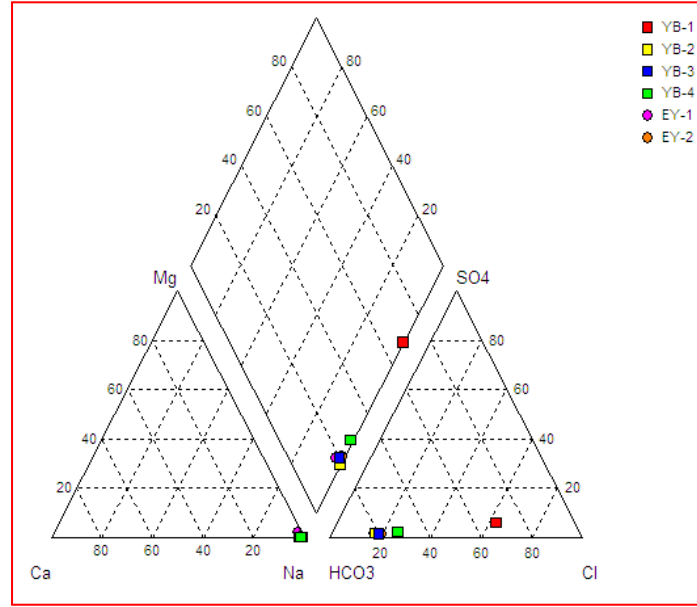


Figure 4. Piper Diagram of the geothermal waters of Alaşehir in the continental rift zone of the Gediz.

The geothermal waters of Kızıldere represent average  $\text{Si}^{4+}$  contents of 115 mg/l (Özgür, 1998) which have been leached from the silicates in reservoir at a temperature of about 200 °C by fluid-rock interactions conditionally. Solubility equilibrium of  $\text{Si}^{4+}$  depends upon the modification of amorphous silica, which allow high concentrations. The separation, where the geothermal waters are separated as steam and fluid phase, gives rises to a 25 percent water loss in terms of water steam, a  $\text{CO}_2$  leakage and a  $\text{Si}^{4+}$  enrichment in the fluid on 150 mg/l. Thereby, the  $\text{CO}_2$  leakage causes a pH increasing on 9 at a temperature of 100 °C. At a temperature of 45 °C, the geothermal waters in drainage basins represent average Si contents of 150 mg/l and a pH value of 9. The geothermal waste waters of geothermal power plant of Kızıldere are reinjected, in order to supply the geothermal water reservoir constantly and remove agricultural danger for citrus fruits in the rift zone des Büyük Menderes in view of environmental aspects. The precipitation of Si as precipitates represents a danger potential for the reinjection system as documented by thermodynamic and kinetic results (Giese, 1997). Thereby, the Si precipitates occur in the reinjection well in depending upon time with regard to ion strength of pH values and temperature (below 100 °C). The geothermal waters in Kızıldere represent As values up to 1,08 mg/l and Sb values up to 0,21 mg/l (Özgür, 1998). Die both elements of As and Sb in geothermal waters show a close correlation in depending upon temperature which is case in the rocks as well. The rocks of the geothermal field of Kızıldere have Au contents up to 6 ppb and Sb contents ranging from 194 ppb to 1373 ppb. The cap rocks which are close connected with geothermal water reservoirs represent high Ag contents of 1,21ppm; thereby, these high Ag contents in the metamorphic rocks are represented by a high background value of 0,5 ppm. It shows, that the metamorphic rocks form a formerly source for Au and Ag. The carbonate and silicate precipitates show Au contents up to 3,5 ppm and Ag contents up to 194 ppb. The base metals in the geothermal waters show distinct low contents as expected.

The geothermal waters of Bayındır are distinguished by a temperature of 46 °C, a pH value of 6,9, an Eh value of -94 mV, an average EC value of 1015  $\mu\text{S}/\text{cm}$  and an average TDS value of 1399 mg/l (Özgür, 1998) and differ from the surface waters and groundwaters in respect with hydrogeochemical composition and standardization distinctly. In comparison to Kızıldere, the geothermal waters of Bayındır show relative poor fluid-rock interaction in low- temperature spheres, how is generated a light paragenesis of alteration minerals.

In the geothermal fields of Salihli, there are five geothermal springs of Kurşunlu and Çamurlu and eight production wells (Özgür, 1998). Four of the geothermal springs are located in Kurşunlu with temperatures from 96 to 36 °C. One of them is situated in Çamurlu. The first well located near the geothermal spring has a depth of 42,5 m, a surface temperature of 96 °C, a surface pressure of 5,5 to 6,0 bar and a flow rate of 20 l/s. The second well is located in the northern part of the first well and represents a depth of 70 m, a surface temperatures of 96 °C and a flow rate of 45 l/s. Thereby, the first 20 m depth consists of alluvium, the depth between 20,00 and 68,80 m is an alternation of mica schist and marble, and the depth between 68,80 and 70,00 m consists of marble. The third well is located in the northern part of the geothermal field of Kurşunlu and shows a depth of 117 m, a surface temperature of 96 °C, a surface pressure of 5,5 to 6,0 bar and a flow rate of 80 l/s. Drill log of this third well comprises Quaternary alluvium between 0 and 5 m, Pliocene Sedimentary rocks in a thickness from 5 to 83 m, Miocene conglomerate in depth from 83 to 92 m, Paleozoic marble in depth from 92 to 104m and Paleozoic alternation of mica schist and marble in depth from 104 to 117 m. In the geothermal field of Salihli, the geothermal waters differ from the groundwaters and surface waters hydrogeochemically (Özgür, 1998). The geothermal waters of Salihli are of Na-K- $\text{HCO}_3$  type exchange water during the groundwaters show Ca- $\text{HCO}_3$  type (Figure 3). In comparison to Kızıldere, the low contents of  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{As}^{3+}$  and  $\text{Sb}^{3+}$  and the high contents  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in geothermal waters of Salihli are conspicuous distinctly. The low contents of  $\text{F}^-$  can be indicated with the increasing  $\text{Ca}^{2+}$  offer, because the both elements in fluids can be precipitated as  $\text{CaF}_2$ . The  $^3\text{H}$  isotopes in

geothermal waters of Salihli show the existence of mixing water; therefore, the components of anions and cations are diluted in comparison to Kızıldere and occur in present concentrations.

In Alaşehir within the continental rift zone of the Gediz, the samples of geothermal waters in localities of 5 geothermal production wells and 1 reinjection well can be considered as Na-HCO<sub>3</sub> hydrogeochemical type of waters ([Figure 4). There, the geothermal waters belong to the cations of Na+K>Ca>Mg and anions of HCO<sub>3</sub>>Cl>SO<sub>4</sub> facies. The ternary Na+K-Mg-Ca diagram of the study area shows that Na+K are the predominant cations (Özgür et al., 2017). This is expected because Na contents in water increase with temperatures while Ca and Mg contents decrease explaining the low values of these elements in the geothermal waters of the study area

The geochemical thermometers show reservoir temperatures of 147-170 °C (quartz), 140-160 °C (quartz with steam loss), 120-145 °C (chalcedony), 205-220 °C (Na-K), 195-215 °C (Na-K-Ca), 35-135 °C (Na-K-Ca-Mg), 240-260 °C (Na-Li), 120-155 °C (Mg-Li) and 100-120 °C (K-Mg), thereby, the thermometers of Na-K, Na-K-Ca and quartz correspond with Özgür (1998) and are more suitable. In order to re-examine the calculated reservoir temperatures, an enthalpy versus SiO<sub>2</sub> mixing model was used with respect to Fournier (Özgür, 1998; Özgür and Çalışkan, 2016). In the process, the used enthalpy values reflect surface temperatures and have been gathered from Henley et al. (1984). In this diagram, the mixing line cuts through quartz solubility curve which connects samples with meteoric groundwaters and geothermal waters at an enthalpy value at 880 kJ/kg indicating a reservoir temperature of 205 °C. This temperature estimation is based on the assumption that the steam originated by the boiling was not separated from the residual liquid phase before mixing with cold groundwaters. When the steam loss takes place before the mixing with the cold groundwaters, the enthalpy accepts the value of waters at temperatures of steam phase of 96 °C; in this process, the initial enthalpy value lies at 620J/g which corresponds to a reservoir temperature of 148 °C.

A reliable calculation of temperature of geothermal water reservoir of Kurşunlu can be realized by using enthalpy versus Cl<sup>-</sup> mixing model according to Truesdell and Fournier (1975). In this process, the boiling point of geothermal waters is connected with a temperature of 97 °C and Cl<sup>-</sup> contents of 72,2 mg/l (Özgür, 1998). In this diagram, the boiling point of geothermal waters has an enthalpy value of 2670 kJ/kg and Cl<sup>-</sup> contents of 0 ppm. Firstly, the groundwater sample with geothermal water samples from Kurşunlu was drawn in the diagram. These are Cl<sup>-</sup> contents and measured surface temperatures. There, the mixing line affects boiling line at an enthalpy value of 500 kJ/kg which corresponds a reservoir temperature of 120 °C. Finally, this leads to the reservoir temperatures of 148 to 205 °C, which corresponds to the calculated temperatures of quartz, Na-K, Na-K-Ca. The modeling indicates a pH values from 5,0 to 5,5 of the reservoirs of the geothermal waters in Kurşunlu and Çamurlu. By using indicator matters, such as Cl<sup>-</sup>, B, Li, and temperature, mixing ratio of geothermal waters and groundwaters can be calculated relatively. At Çamurlu, there is a moderate mixing ratio of 42,5 percent geothermal waters and 57,5 percent groundwaters. In comparison, 83,0 percent geothermal waters are connected with 17,0 percent groundwaters in Kurşunlu.

### 3.3 Isotope geochemistry

The geothermal waters of Kızıldere, Bayındır and Salihli can be considered meteoric water due to isotope ratio of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (Figure 5). The  $^3\text{H}$  contents in investigated geothermal waters are attributed to atmospheric and anthropogenic effects. They indicate, that the geothermal waters of Bayındır and Salihli can be considered as mixing water. The geothermal waters of Kızıldere show scarcely mixing of young groundwaters, because  $^3\text{H}$  contents are below the detection limit. The ratios of  $\delta^{13}\text{C}$  in groundwaters, mixing waters and geothermal waters reveal, that the origin of CO<sub>2</sub> can be linked to a magmatic activity by a subvolcanism in basement and to reactions with carbonate rocks. The  $\delta^3\text{He}$  surplus in geothermal waters of Kızıldere reveal interactions of these fluids with basic to intermediate still cooling volcanic rocks of mantle and the existence of a subvolcanic intrusion (Özgür, 1998). The CO<sub>2</sub> production in connection with carbonate rocks in reservoir dilutes  $^{14}\text{C}$  in geothermal waters, by which the age determination with  $^{14}\text{C}$  is impossible almost.

In Alaşehir within the continental rift zone of the Gediz, samples of the geothermal waters were analyzed for their  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$  contents (Özgür et al., 2017). The mixed groundwater and geothermal water systems lie along the meteoric water line whereas the high temperature geothermal waters deviate from the meteoric water line showing intense water-rock interaction under high temperature conditions (Figure 6]. These data are well correlated with the results of hydrogeochemical analyses which indicate high water-rock interaction and reactions with silicates. The tritium data reveal that (i) the geothermal waters in the study area do not contain any measurable tritium firstly and (ii) the sedimentary mineralized groundwaters and the low temperature geothermal waters contain atmospheric and anthropogenic tritium. Therefore, a mixing process between the fresh groundwaters and deep geothermal waters are evidenced for the geothermal waters elsewhere in the environs of the study area of Alaşehir.

## 4. GEOTHERMAL RESERVOIRS

### 4.1 Shallow reservoirs

The Sazak formation stands in particular contrast to other sediment formations due to its distinctly high carbonate contents (Özgür, 1998). It consists predominantly of limestones, which are more clayey and sandy depending upon the facies. Moreover, a small amount of marls and sandstones are also present. The limestones in the Sazak formation are ostracod-, gastropod- and lamellibranch-bearing. The total thickness of the Sazak formation varies between 150 and 400 m. Tectonically, this formation is the hardest in the geothermal field due to hydrothermal silicification and reacts brittly, forming the outermost joints. This is a reason for the accumulation of block

debris in valleys in which the tectonic and physical erosion is faster than the chemical. The Sazak formation is strongly fractured, porous to pitted, and is thereby an excellent aquifer. Therefore, it forms the first reservoir in the field of Kızıldere with a temperature of 200 °C. Due to its particular features, the Sazak formation has been located as a thermal water reservoir in the center of the continental rift zone of the Büyük Menderes, at a depth of 800 m by gravimetric and geoelectric methods (Guidi et al., 1990). In Alaşehir within the rift zone of the Gediz, the limestones in Pliocene age in a depth up to 500 m form the geothermal reservoir which can be considered as shallow reservoir.

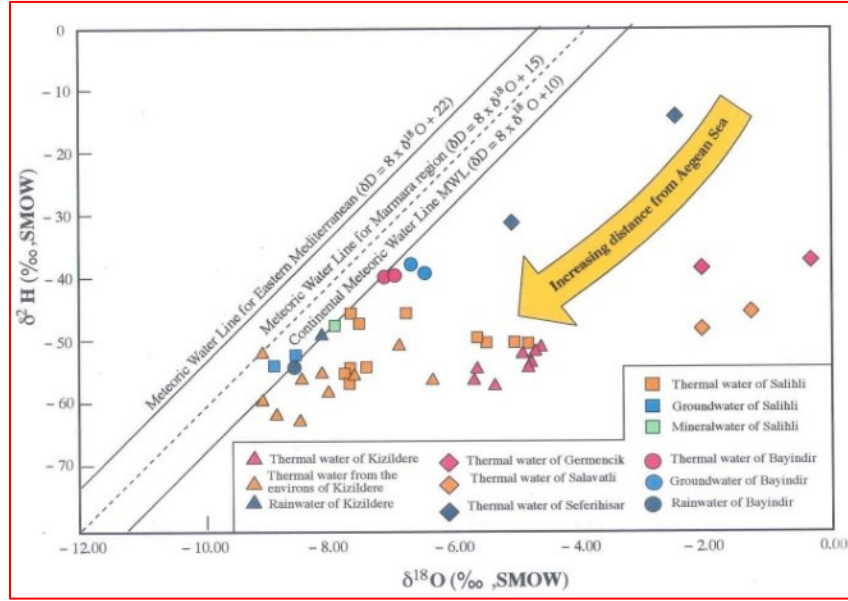


Figure 5. Plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  of thermal waters of Kızıldere, Bayındır and Salihli in the continental rift zones of the Mendere Massif.

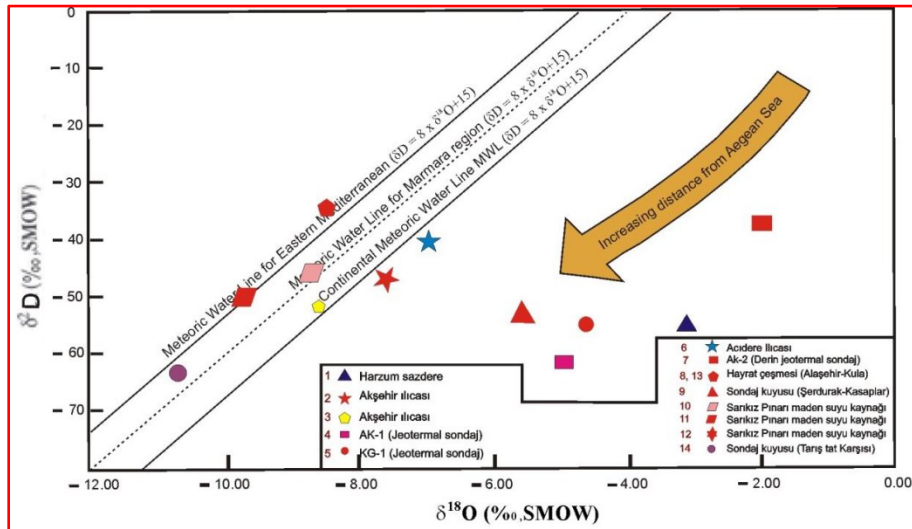


Figure 6. Plot of  $\delta^2\text{D}$  versus  $\delta^{18}\text{O}$  in the different groundwaters and geothermal waters in Alaşehir and environs in the continental rift zone of the Gediz.

## 4.2 Deep reservoirs

The thermal field of Kızıldere and environs consists of Paleozoic metamorphic rocks and Tertiary to Quaternary sediments (Özgür, 1998). The metamorphic rocks are composed of gneisses, mica schists and the İğdecik formation, which is composed of mica schists, quartzites and marbles. The gneisses are located in the NW part of the investigated area and show an immediate change with high grade metamorphic mica schists. The tourmaline content in the gneisses is remarkable, and together with the biotites plays an important role for high boron contents in thermal waters. The mica schists overlie the gneisses and are considered to be a garnet-muscovite-biotite-schist assemblage. The İğdecik formation, which forms the last upper sequence in the thermal field of Kızıldere, consists of alternating beds of mica schists, quartzites and marbles and shows light metamorphic features. It is traversed by ruptures and fissures and forms the second deep reservoir with a temperature of 240 °C (Özgür and Çalışkan, 2014). The Pliocene sediments are of continental lacustrine origin and overlie metamorphic basement. In the rift zone of the Gediz, the deep reservoir rocks consist of Paleozoic to Mesozoic alternation of metamorphic marbles, quartzites and schists with a depth up to 2.200 m in which the main production of geothermal energy is ensured.

## 5. REINJECTION OF CO<sub>2</sub> INTO THE RESERVOIRS

A lowering of the pressure of geothermal waters in the reservoir can be established due extremely production; it lies on the lack of reinjection well clearly. Moreover, there are hits for the shift of points of steam outlets from higher areas to lower located areas today. This shows disappear of the old points of steam outlets. It shows that a distinct lateral movement of the fields of steam outlets to catchment area of the geothermal power plant took place. The lowering of the steam outlet level of about 100 up to 150 m C in Tekkehamam and 96-100 °C in Kızıldere, 62-88° in Tekkehamam and Babacık, 37-55 °C in Pamukkale and Karahayıt and 40-54 °C in Yenice I and II, during Na/K thermometers (Fournier, 1979) give reservoir temperatures of 220-248 °C in Kızıldere, 211-234 °C in Tekkehamam and Babacık, 260-313 °C in Pamukkale and Karahayıt and 251-288 °C in Yenice I and II. The special development of the reservoir characteristic is understood as unfavorable pre-conditions for a reinjection. It seems to depict, that total inorganic carbon in cooler margins of this geothermal system increases clearly. Furthermore, it is intelligibly, because the solubility of CO<sub>2</sub> rises with decreasing temperature. The acidification of pH value in the margins of the system effectuates a clearly increase of saturation concentration of Ca<sup>2+</sup>, as long as the reservoir water could be saturated with calcite before. These facts create problems for a reinjection clearly. During silica precipitations in reinjection system constitute main problems, carbonate precipitations occur in the reinjection reservoir clearly which brings the process to a standstill for a short term. An approach of the injection point to the production zone may reduces this main problem indeed, but it is to approve of thermic reasons. If inhibitors will be foregone, the ones of the solutions are as follows: (i) the reinjection of HCl or better CO<sub>2</sub> for calibration of pH values at what a high expenditure must be operated against buffer capacity or (ii) drilling of a deeper injection well, in which the water is undersaturated due to calcite in enough amount. Under these certain considerations, the waste waters in Kızıldere can be reinjected into the reservoir. In Figure 7, the geothermal waters in the continental rift zone of the Büyük Menderes show a spectrum from immature to partially equilibrated waters according to Giggernbach (1988). In comparison, the geothermal waters in the rift zone considered as partially equilibrated waters (Figure 8).

In summary, Fig. 9 shows the development of saturation indexes of main scaling minerals of calcite aragonite and silica for heat exchanger and reinjection system in the area of Kızıldere and environs (Giese, 1997). The special development of the reservoir characteristic is understood as unfavorable pre-conditions for a reinjection. It seems to depict, that total inorganic carbon in cooler margins of this geothermal system increases clearly. Furthermore, it is intelligibly, because the solubility of CO<sub>2</sub> rises with decreasing temperature. The acidification of pH value in the margins of the system effectuates a clearly increase of saturation concentration of Ca<sup>2+</sup>, as long as the reservoir water could be saturated with calcite before (Giese, 1997). These facts create problems for a reinjection clearly. During silica scalings in reinjection system main problems constitute, carbonate scalings occur in the reinjection reservoir clearly which brings the process to a standstill for a short term. An approach of the injection point to the production zone may reduces this main problem indeed, but it is to approve of thermic reasons. If inhibitors will be foregone, the one of the solutions are as follows: (i) the reinjection of HCl or better CO<sub>2</sub> for calibration of pH values at what a high expenditure must be operated against buffer capacity or (ii) drilling of a deeper injection well, in which the water is undersaturated due to calcite in enough amount. Under these considerations, the waste waters in Kızıldere are reinjected into the reservoir. The geothermal waters in Alaşehir and environs in the continental rift zone of the Gediz have up to 2.0 percent CO<sub>2</sub> contents which represent very important environmental problems, because CO<sub>2</sub> emissions are naturally neither reinjected nor stored. Therefore, these CO<sub>2</sub> emissions must be reinjected into the reservoirs at the achievement of the geothermal energy.

## 6. DISCUSSION

In the geothermal fields of Kızıldere in the rift zone of the Büyük Menderes, Bayındır in the rift zone of the Küçük Menderes, and Salihli with areas of Kurşunlu and Çamurlu in the rift zone of the Gediz, there are excellent conditions for the formation of geothermal waters. Firstly, the Paleozoic marbles and quartzites and Miocene limestones in Kızıldere, the Carboniferous to Permian marbles and quartzites in Bayındır, and the Paleozoic marbles and quartzites in Salihli play an important role for the formation of geothermal reservoirs. Secondly, the Pliocene Kızılburun formation, Kolonkaya formation and Tosunlar formation in Kızıldere and the Paleozoic mica schists in Bayındır and Salihli can be considered as impermeable basement and cap rocks for the formation of geothermal reservoirs. Thirdly, the study areas of Kızıldere, Bayındır, and Salihli are of very active from the views of tectonical points.

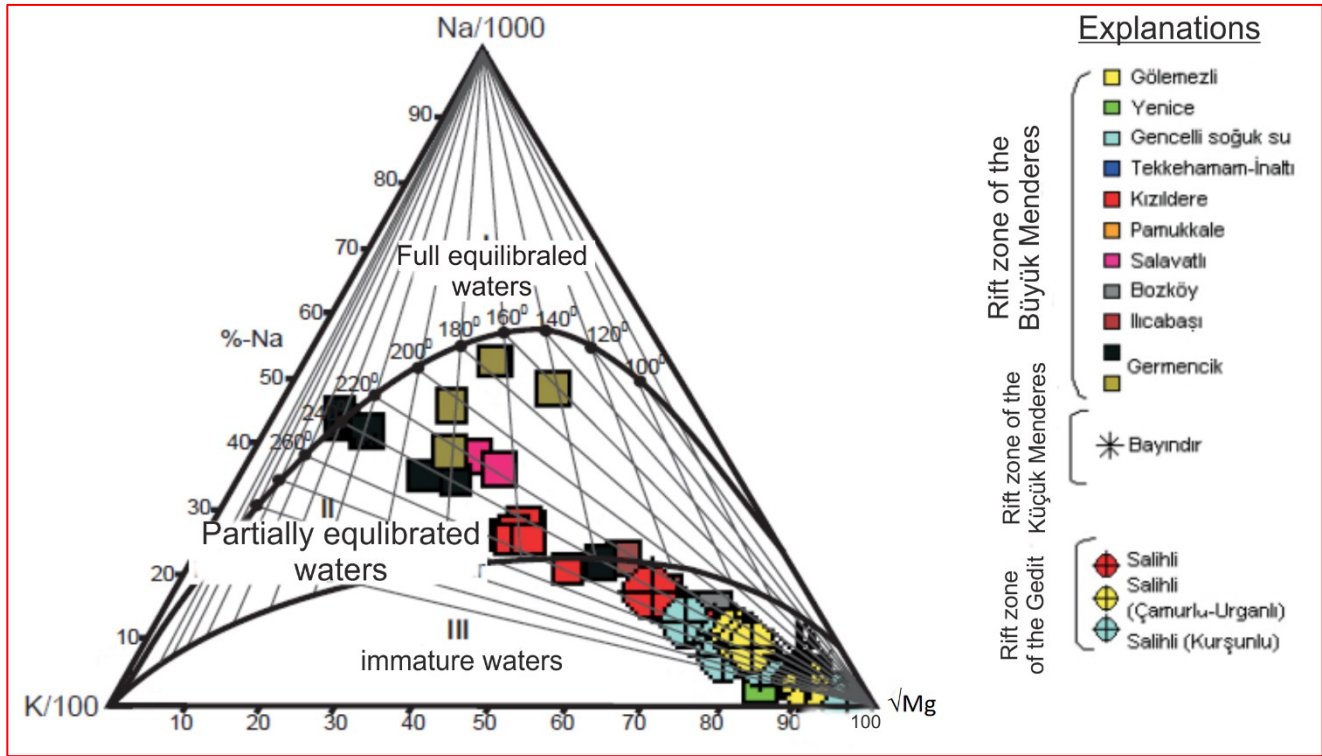


Figure 7. Distribution of the geothermal waters from the rift zone of the Büyük Menderes in the Na-K-Mg<sup>1/2</sup> ternary diagram (Yaman, 2005).

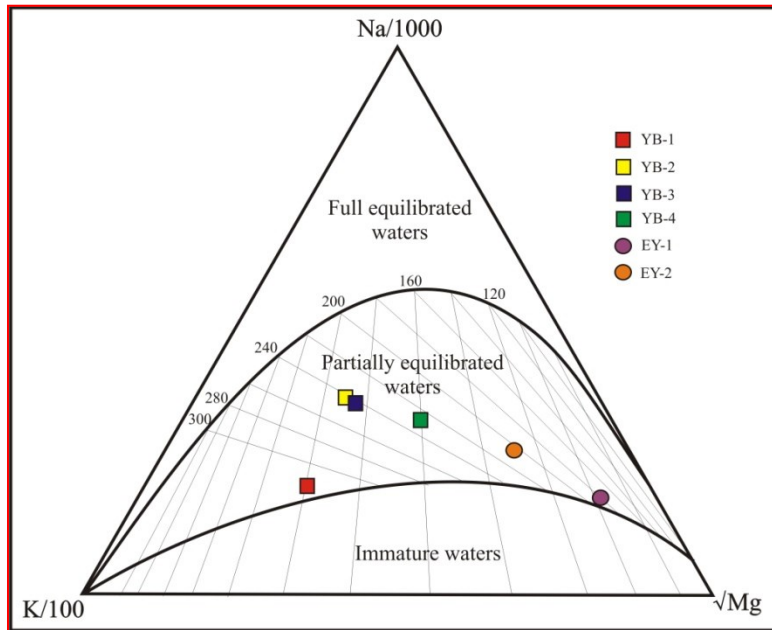


Figure 8. Distribution of the geothermal waters from the rift zone of the Gediz in the Na-K-Mg<sup>1/2</sup> ternary diagram (Özgür et al., 2017).



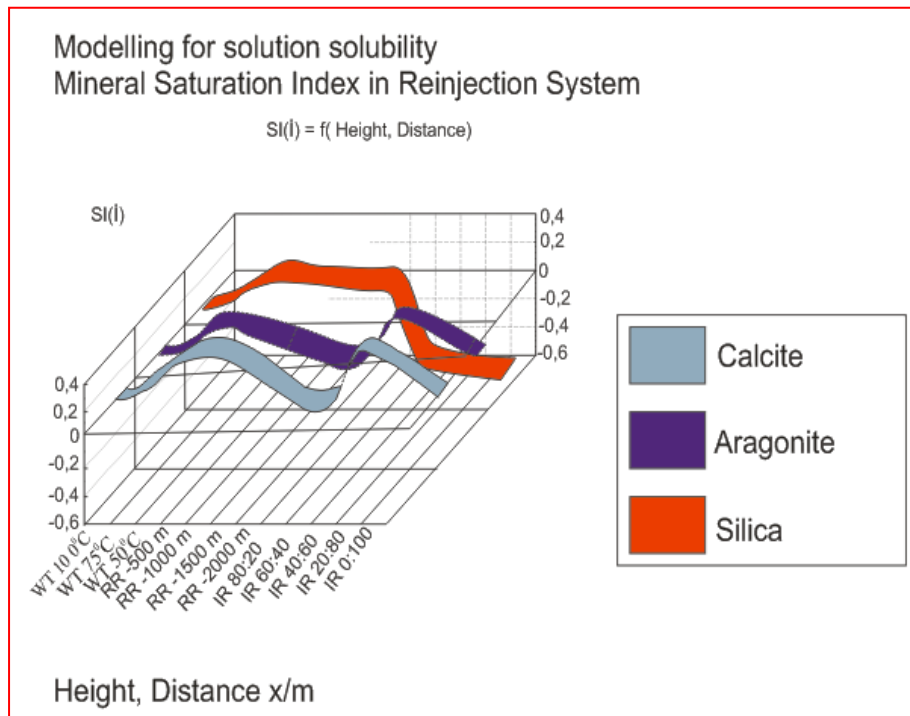


Figure 9. Development of saturation indexes of main scaling minerals calcite, aragonite and silica in heat exchanger and reinjection system (Özgür and Çalışkan, 2014).

By the plate tectonical development, the Menderes Massif showed a dome shaped structure due to compressional tectonic features from Oligocene to Middle Miocene. From Early to Middle Miocene, the continental rift zones of the Büyük Menderes, the Küçük Menderes and the Gediz were formed by extensional tectonic features, which strike E-W generally and are represented by a great number of geothermal waters, epithermal mineralizations of Hg, Sb, and Au, and volcanic rocks of Middle Miocene to recent. The geothermal waters are related to faults which strike preferentially NW-SE and NE-SW and locate diagonal to general strike of the rift zones. These faults are probably generated by compressional tectonic stress, which leads to the deformation of uplift between two extensional rift zones. This can be corroborated by the intensively earthquake activities in the study area. Lastly, some intrusive in the continental rift zones of the Menderes Massif, calcalkaline and basic to intermediate rocks exist which are generated from Middle Miocene to recent. The volcanic rocks are of products of continental crust based on isotope analyses of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{144}\text{Nd}/^{143}\text{Nd}$  and can be considered as heat source for the heating of geothermal waters in the rift zones and elsewhere. In active geothermal fields of Kızıldere, Bayındır and Salihli, groundwater flow takes place in drainage areas from higher spheres around the watershed in horst to the lower located continental rift zones where the groundwaters find the watercourse ultimately (Figure 10). These meteoric waters in the drainage area percolate at fault zones and permeable clastic sediments into the reaction zone of the roof area of a magma chamber situated in a probable depth of up to 5km where meteoric fluids are heated by the cooling magmatic melt and ascend to the surface due to their lower density caused by convection cells. The volatile components of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{HF}$ , and  $\text{He}$  out of the magma reach the geothermal water reservoir where an equilibrium between altered rocks, gas components, and fluids performs. Thus, the geothermal waters ascend in the tectonical zones of weakness at the continental rift zones of the Menderes Massif in terms of hot springs, gases, and steams. These fluids are characterized by high to medium  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NaCl}$  contents. It is very important, that the fluids indicate a reduced pH-neutral environment after equilibrium adjustment with hard rocks in the reaction zone, namely in the roof area of magma chamber (Giggenbach, 1992). In superficial areas, i.e. beneath a depth of 550 m in Kızıldere with a pressure of 50 to 100 bar, a temperature of 200 to 220 °C and a pH value of lesser than 5,0, it comes to boiling by decrease of pressure; thereby,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  rich steams are splitted off from geothermal waters which can lead to formation of sulfate rich waters after condensation and surface oxidation. The geothermal waters are exploited for various uses consequently, i.e. for geothermal energy, balneology, and green houses.

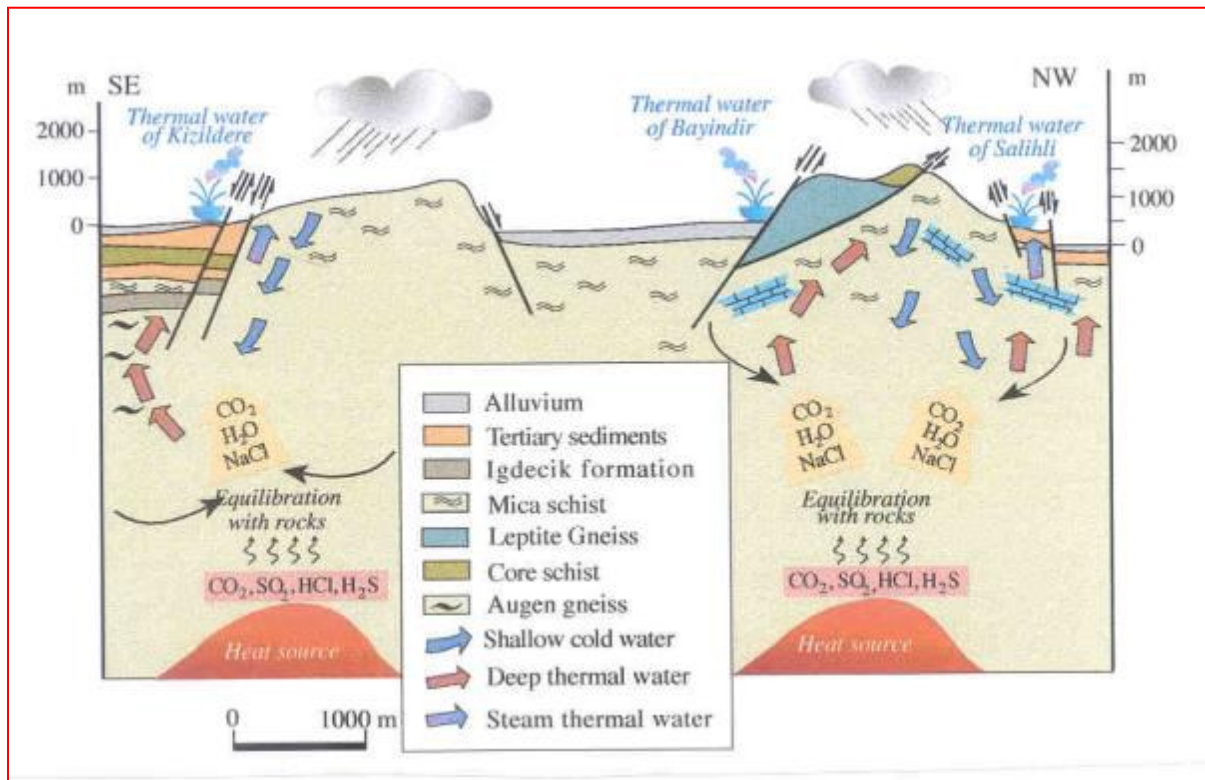


Figure 10. Simplified presentation of geothermal model of the geothermal waters in the rift zones of the Büyük Menderes, Küçük Menderes and Gediz within the Menderes Massif (Özgür, 1998).

2.0 percent of the production of the geothermal waters in the area of the Menderes Massif displays CO<sub>2</sub> emissions. In order to consider the geothermal waters as environmental and human friendly energy, CO<sub>2</sub> emissions must be reinjected into the reservoirs of each geothermal waters. As alternative to inhibitors, it can be taken in consideration a reinjection of the waste CO<sub>2</sub> quantities into the reservoir of the geothermal waters for adjust of pH values of geothermal fluids. Approximately 2.0 percent of CO<sub>2</sub> in the production of the geothermal waters is available for reinjection into the reservoirs. A small amount of this total mass might be attributed to a correction of pH value of 6-7 of geothermal fluids in a reinjection process. An acid reinjection pH value can decrease an arising oversaturation of calcite and aragonite by the pH effect of reinjected geothermal waters. However, there are difficulties. A superficial blow on of CO<sub>2</sub> into reinjection fluid leads to push of dissolved gases in reinjection well, because high CO<sub>2</sub> contents at high pressures can be dissolved in deeper spheres of reinjection well. Therefore, CO<sub>2</sub> gases should be conducted to the depth below the solution depth in a separate intern pipe and must be reinjected into the reservoir of geothermal waters. However, this assumes previous condensing of CO<sub>2</sub> gases, because die pressure in the total gas column must overstep die pressure in the mixing depth.

## REFERENCES

- Bozkurt, E. and Park, R.G.: Southern Menderes Massif: an incipient metamorphic core complex in western Anatolia, Turkey, *J. Geol. Soc. Lond.*, 151, (1994), 213-216.
- Bozkurt, E.: Deformation during main Menderes metamorphism (MMM) and its tectonic significance: evidence from southern Menderes Massif, western Turkey, *Terra*, 7, (1995), 176.
- Bozkurt, E. and Park, R.G.: Evolution of mid-Tertiary extensional shear zone in the southern Menderes Massif, western Turkey, *Soc. Geo. Fr. Bull.*, 168, (1997a), 3-14.
- Bozkurt, E. and Park, R.G.: Microstructures of deformed grains in the augen gneisses of southern Menderes Massif and their tectonic significance, *Geol. Rundsch.*, 86, (1997b), 103-119.
- Bozkurt, E. and Park, R.G.: The structure of the Paleozoic schists in the southern Menderes Massif, western Turkey: a new approach to the origin of the main Menderes metamorphism and its relation to the Lycian Nappes, *Geodinamica acta (Paris)*, 12, (1999), 25-42.
- Bozkurt, E.: Late Alpine evolution of the central Menderes Massif, western Turkey, *Int. J. Earth Sciences*, 89, (2001), 728-744.
- Collins, A.S. and Robertson, A.H.F.: Processes of Late Cretaceous to Late Miocene episodic thrust-sheet translation in the Lycian Taurides, SW Turkey, *J. Geol. Soc. Lond.*, 155, (1998), 759-772.

- Dewey, J.F. and Şengör, A.M.C.: Aegean and surrounding regions: complex multiplate and continuum tectonics in a convergent zone, *Geol. Soc. Am. Bull.*, Part I, 90, (1979), 84-92.
- Dora, O.Ö., Candan, O., Dürr, S. and Oberhänsli, R.: New evidence on the geotectonic evolution of the Menderes Massif, *Proceedings. Int. Earth Science Colloquium on Aegean Region*, 9-14 October 1995, İzmir-Güllük, Turkey, (1995), 53-72.
- Ercan, T., Türkecan, A. and Erdoğan, G.: petrochemical characteristics and genetic interpretation of the basaltic volcanism of Kula (Manisa, Turkey), *Geological Balcanica*, 22 (1992), 51-73.
- Ercan, T., Matsuda, J.-I., Nagao, K. and Kita, I.: Noble gas isotopic compositions in gas and water samples from Anatolia, *Proceedings, Int. Symp. on the Geology of the Black Sea Region*, September 7-11, 1992, Ankara, Turkey, (1995), 197-206.
- Fournier, R.O.: A revised equation for the Na/K geothermometer. *Geothermal Resources Council Transactions* 3, (1979), 221-224.
- Giese, L.: Geotechnische und umweltgeologische Aspekte bei der Bohrung und Reinjektion von Thermalfluiden zur Nutzung geothermischer Energie am Beispiel des Geothermalfeldes Kızıldere und des Umfeldes, W-Anatolien, Türkei, *Ph.D. thesis, Freie Universität Berlin*, (1997), 201 pp.
- Giggenbach, W. F., (1992), "Magma degassing and mineral deposition in hydrothermal systems along convergent plate boundaries," *Econ. Geol.* **87**, 1927-1944.
- Giggenbach, W.F.: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geothermometers. *Geochim. Cosmochim. Acta*, 52, (1988), 2749-2765.
- Guidi, M., Marini, L., and Principe, C.: Hydrogeochemistry of Kızıldere geothermal system and nearby region, *Geothermal Resources Council Transactions*, **14** (1991), 901-908.
- Hattori, K. and Cameron, E.M.: Archaean magmatic sulphate, *Nature*, 319/60842, (1986), 45-47.
- Henley, R.W., Truesdell, A.H., Barton, P.B. and Whitney, J.A., 1984, Fluid-mineral equilibria in hydrothermal systems: *Econ. Geol. Rev.* 1, (1984), 267 p.
- Hetzl, R., Passchier, C.W., Ring, U. and Dora, O.Ö.: Bivergent extension in orogenic belts: the Menderes Massif (southwestern Turkey), *Geology*, 23, (1995a), 455-458.
- Hetzl, R., Ring, U., Akal, C. and Troesch, M.: Miocene NNE-directed extensional unroofing in the Menderes Massif, southwestern Turkey, *J. Geol. Soc., London*, 152, (1995b), 1-16.
- Hetzl, R. and Reischmann, T.: Intrusion age of Pan-African augen gneisses in the southern Menderes Massif and the age of cooling after Alpine ductile extensional deformation. *Geol. Mag.*, 133, (1996), 565-572.
- Hetzl, R., Romer, R.L., Candan, O. and Passchier, C.W.: Geology of the Bozdağ area, central Menderes Massif, SW Turkey: Pan-African basement and Alpine deformation, *Geol. Rundsch.*, 87, (1998), 394-406.
- Koçyiğit, A., Yusufoglu, H. and Bozkurt, E: Evidence from the Gediz graben for episodic two-stage extension in western Turkey, *J. Geol. Soc. Lond.*, 156, (1999), 605-616.
- McKenzie, D.P.: Active tectonics of the Alpine-Himalayan belt: the Aegean and the surrounding regions, *Geophys. J. R. Astr. Soc.*, 55, (1978), 217-254.
- Okay, A.: Stratigraphic and metamorphic inversions in the central Menderes Massif: a new structural model, *Int. J. Earth Sciences*, 89, (2001), 709-727.
- Özgür, N., Halbach, P., Pekdeğer, A., Sönmez, N., Dora, O.Ö., Ma, D.-S., Wolf, M. and Stichler, W.: Epithermal antimony, mercury, and gold deposits in the rift zone of the Küçük Menderes, Western Anatolia, Turkey: preliminary studies, *Proceedings, 4th Biennial SGA Meeting, Turku, Finland, August 11-13, (1997)*, 269-273.
- Özgür, N.: Aktive und fossile Geothermalsysteme in den kontinentalen Riftzonen des Menderes-Massives, W-Anatolien, Türkei, *Freie Universität Berlin, Habilitationsschrift* (1998), 171 p.
- Özgür, N., Pekdeğer, A., Wolf, M., Stichler, W., Seiler, K. P. and Satır, M.: Hydrogeochemical and isotope geochemical features of the thermal waters of Kızıldere, Salavatlı and Germencik in the rift zone of the Büyük Menderes, Western Anatolia, Turkey, *Proceedings. 9th Internat. Symp. on Water-Rock Interaction, Taupo, New Zealand, (1998)*, 645-648.
- Özgür, N.: Hydrogeological, hydrogeochemical, and isotope geochemical modeling of the thermal waters of the Menderes Massif, western Anatolia, Turkey, *Proceedings, 38th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, February 2013, (2013)*, SGP-TR 198.
- Özgür, N. and Çalışkan, T. A.: Reservoirs and Reinjection of the Thermal Waters of Kızıldere, Western Anatolia, Turkey, *Proceedings, 39th Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 24-26, 2014, (2014)*, SGP-TR-202
- Özgür, N. and Çalışkan, T. A.: Active geothermal systems in the continental rift zones of the Menderes Massif, western Anatolia, Turkey, *Proceedings 14<sup>th</sup> Int. Congr., Bull. Geol. Soc. Greece*, 1, (2016), 885-898.

Özgür

- Özgür, N.: Conceptual model of geothermal resources of Alaşehir in the continental rift zone of the Gediz within the Menderes Massif, western Anatolia, Turkey, Proceedings, 42nd Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, February 13-15, (2017), (2017), SGP-TR-212.
- Özgür, N., Bostancı, Y. and Anılır Yürük, E.: Hydrogeological modeling of the geothermal waters of Alaşehir in the continental rift zone of the Gediz, western Anatolia, Turkey, IOP Conf. Series: Earth and Environmental Science 95, (2017), 022037.
- Truesdell, A. H. and Fournier R. O.: Calculation of deep temperatures in geothermal systems from the chemistry of boiling spring waters of mixed origin. Proceedings, Second UN Symposium on Geothermal Resources, San Francisco, (1975), 837-844.
- Verge, N.J.: Oligo-Miocene extensional exhumation of the Menderes Massif, western Anatolia, *Terra*, 7, (1995), 117.
- Yaman, D.: Origin of high boron contents in geothermal waters within continental rift zones of the Menderes Massif (in Turkish), Ph. D. Thesis, Suleyman Demirel University, (2005), 165 p.