Hydrogeological, Hydrogeochemical and Isotope Geochemical Features of the Geothermal Waters in Seferihisar and Environs, Western Anatolia, Turkey

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Abstract: The study area of Seferihisar is located within the Izmir-Ankara suture in the NW of the Menderes Massif in western Anatolia, Turkey. The Paleozoic metamorphic rocks of the Menderes Massif form the basement rocks in the area which are over lain by 760 m thick Izmir-flysch series consisting of metamorphic rocks, limestones and ultrabas i c rocks tectonically. The Pliocene Bahçecik formation which consists of an alternation of conglomerates, sandstones, claystones, lignite and limestones and shows a thickness of 300 m overlies the (İzmir) flysch series discordantly. This is overlain by 430 m thick Yeniköy formation composed of conglomerates, sandstones, claystones and clayey limestones discordantly. The Miocene volcanic rocks of Cumaovası overlie the Yeniköy formation concordantly which are overlain by alluvium and travertine deposits. Geothermal waters which are observed in the localities of Tuzla, Cumalı, Doğanbey and Karakoç are associated with NE-SW trending faults in the area. The geothermal waters in the area are considered as Na-Cl or Na-Cl-HCO3 type waters. The geothermal waters of Seferihisar and environs are identified to be Na+K>Ca>Mg dominant cations and Cl>HCO3>SO4 dominant anions. According to the diagram of Na/100-K/100-\sqrt{Mg}, a certainly part of the thermal waters can be considered as equilibrated thermal waters during some waters are of immature waters. According to the results of geochemical thermometers, the reservoir temperatures of thermal waters range from 150 to 240°C. The $\delta^2$H values of thermal waters are between -13.3 to -31.9, while $\delta^{18}$O values range from -2.55 to -5.70. The tritium contents of thermal waters are between 13 to 64±10 TU.

1. Introduction
The economic development of a country is right proportional with the energy consuming per person. This fact brings essentiality of increase of energy production herewith. The earth crust has too large and various energy resources. The widespread using areas of the geothermal energy, which can be considered as not consumable and renewable and does not cause environmental problems, are investigated. Geothermal energy is used in the areas of electricity production, space heating and agricultural activities. Besides, the investigations on the geothermal energy focused on the balneological effects of the geothermal waters due to healthy life of human bodies.
Figure 1. Geological map of western Anatolia with location of Seferihisar and environs within Izmir-Ankara suture [1, 2]

Geothermal areas are located in the world in connection with tectonic events and geological formations and can be considered as increasing energy resources. Each one of different types of geothermal systems has particular features and present these features in hydrogeochemical composition and application of geothermal potential spontaneously. Geothermal energy, which has a heat source in a depth of a few kilometers within the convection cells in the upper part of the earth crust, can be considered as present water accumulations.

In western Anatolia, the tectonic formation of Seferihisar ascension was developed by motion of Anatolia plate to the west and drag on the African plate. In study area, E-W trending depressions limited by tension tectonics in N-W directions and NE-SW trending strike-slip faults were developed. In connection with these fault systems, depression and ascension areas, of which rims are limited by Neotectonic faults, in the region were developed. From the west to the south, Karaburun ascension,
Urla depression, Seferihisar ascension, Cumaovası depression and Değirmendere ascension form the more important morphotectonic structures of the region (Figure 1) [1,2]. The aims of this study are (I) to update geological mapping of Seferihisar and environs, (ii) to describe fluid-rock interaction by mineralogical, petrographical and geochemical methods, (iii) to investigate the origin and development of the geothermal waters by hydrogeological, hydrogeochemical and isotope geochemical methods and (iv) to exhibit hydrogeological modeling of the formation of the geothermal waters within the fluid-rock interaction.

2. Geologic setting
The Paleozoic metamorphic rocks of the Menderes Massif form the basement (Figure 2; 3). These rocks locate in a large spheres in the SE part of the study area and consist of micaschists, quartzschists, chloriteschists and albiteschists, [4]. The Upper Cretaceous Izmir flysch-series consisting of pelitic schist, sandstone and limestone and having a thickness of 700-800 m overlies these Paleozoic metamorphic rocks. Ultrabasic rocks in the lower levels of Izmir flysch-series are pushed upwards in the upper levels and outcrop in NE-SW direction generally [4]. In the middle part of the study area, there is a Miocene NE-SW trending ÇubukluDağ depression [5]. These Miocene sediments overlie Upper Cretaceous Izmir flysch-series discordantly. Miocene sediments consist of (i) 300 m thick Bahçekecik formation, (ii) 400-450 m thick Yeniköy formation and (iii) 350-400 m thick Cumaovası volcanic rocks and are overlain by Quaternary alluvium and cover of debris discordantly. The borders between Neogene sediments and Menderes Massif are cut by high angle normal faults which play a first grade role for the formation of graben structure and geothermal waters [Figure 2]. Quaternary alluvium, travertine deposits around the geothermal water springs, vegetative soils, sodium bicarbonates and sediments with NaCl are the present-day formations.

2.1 Locations of geothermal waters

2.1.1 Geothermal waters of Cumalı
Geothermal waters of Cumalı are located in the SW part of the study area and in the end of Çubukludağ depression [Figures 1 and 2]. The area located between Seferihisar and Karakoç ascensions and grasps at Cumalı overthrust parallel. In the NW, Izmir flysch-series overlies by Yeniköy formation rushes into Cumalı overthrust in accordance with (structural) stratigraphy of reservoir rocks as limestones and gets thinner between shales in the E. The temperatures of the geothermal waters located near Kavakdere Köyü, which consist of hot springs located in a distance of a few 100 meters from each other range from 70 to 80.5 °C.

2.1.2 Geothermal waters of Tuzla
The geothermal field of Tuzla has a fault which splits into two subsections to the west from Tuzla. The fault zone between two subsections and topographic ascension outstretched in the same direction correspond to a pressure ridge in a great dimension. The faults in the W of pressure ridge cut flysch-series. Along the faults, hydrothermal alteration can be observed widespread. The hot spring of Tuzla contain sea waters generally and has surface temperatures up to 82 °C [Figure 2].

2.1.3 Geothermal waters of Doğanbey and Karakoç
The geothermal fields of Doğanbey and Karakoç are the center of tectonic activities located in SE elongation of Seferihisar ascension. In this part of Çubukludağ depression, there are the ascension of Doğanbey İlçesi and the ascension of Karakoç which cut the Yeniköy formation. There are the second-high temperature geothermal waters in the province capital of Izmir in the geothermal fields of Doğanbey and Karakoç. These both geothermal waters have reservoir temperatures of 90 and 153 °C.
3. Material and methods
During the field campaign from March 5-8, 2016, 6 samples from the geothermal waters in the study area of Seferihisar and environs were collected, for hydrogeochemical, stable isotope and tritium analyses. In this study, in-situ measurements such as coordinates, temperatures, pH, Eh, dissolved oxygen, electrical conductivity and alkalinity for calculation of HCO$_3^-$ and CO$_3^{2-}$ values were realized [6; 7; Figures 1 and 2; Table 1]. The water samples for cation analyses were shrouded in a pH interval between 2 and 3 by using pure HNO$_3$. The cation and anion analyses in the geothermal waters were realized by using ICP-OES and IC in the credential Water Laboratories of the General Directorate of the Mineral Research and Exploration in Ankara, Turkey [Table 1]. For stable isotopes (δ$^{18}$O and δ$^2$H) and tritium (³H) analyses, we collected two samples which have been analyzed credential isotope laboratory of the GSF-Institute of Hydrology, Neuherberg, Germany [8]. The Hydrogeochemical data from Seferihisar and environs were evaluated by using software program AQUACHEM version 3.7 [9]. The analyses of stable isotopes of the study area were compared with the former analyses of [3].

4. Results

4.1 Hydrogeology
Sandstones, limestones, spilitic volcanic rocks and serpentines in Upper Cretaceous to Paleocene rock series of Izmir-Ankara suture, which can be considered as impermeable rocks generally, are of reservoir rocks due to the secondary permeability caused by tectonic deformations. In comparison, the shales are of impermeable rocks in the area. In contacts between limestone’s in terms of veins and
olistolithes and shales, hot springs with low flow rates can be observed sporadically. In some geothermal wells within the Izmir flysch series realized by private persons, there are geothermal waters in a depth between 80 and 100 m with a flow rate of 1-2 l/s. Izmir flysch series consisting of serpentines, limestone, sandstone and shale forms the reservoir rocks. Conglomerates, which are observed in Neogene continental sediments, are cemented and have lower permeability due to intercalations of clayey sediments. In this rock sequence, there is a secondary permeability due to tectonic deformations. Moreover, the clayey intercalations in the sequence are of impermeable cap rocks. The alluvium located in the middle part of the study area and in the valleys near the sea is of aquifer for the groundwater potential in the area.

4.2 Hydrogeochemistry

The geothermal waters of Seferihisar and environs can be considered as Na-Cl and/or Na-Cl-HCO₃ type waters in Piper diagram [Figure 3, 6, 7]. In the geothermal waters of the study area, the cation order is Na+K>Ca>Mg, during the anion order is Cl>SO₄>HCO₃. In comparison, the cation order of the samples from Çeşme and environs is Na+K>Ca>Mg, during anion order is Cl>HCO₃>SO₄ [7, Table 1]. The high SO₄ contents of the geothermal waters are associated with the intrusion of the seawaters. Geochemical thermometers indicate reservoir temperatures between 150 and 240 °C for geothermal waters of Seferihisar and environs [6]. In comparison, the SiO₂ thermometers show reservoir temperatures of 150 °C for Cumali, 100 °C for Karakoç, 100-110 °C for Doğanbey. In the Na-K-Mg¹/₂ diagram Figure 4, the geothermal water of Karakoç[EB-2; Table 1] is of immature waters, during the samples of EB-1 and EB-3 from Cumali and Doğanbey show origin of partially maturated waters [6]. In comparison, the geothermal waters [SD- 1 and SD-2; 7] of Çeşme and environs are of origin of partially maturated waters according to [10].

5. Isotope geochemistry

In Seferihisar and environs, δ²H values of geothermal waters range from -30,9 to -14,2 during δ¹⁸O values are of an interval between -5,10 and -2,56 [Figure 5]. The values of δ¹⁸O and δ²H correspond with values of SMOW. ¹H values of the geothermal waters lie between 0,7 and 1,3 TU. According to [3], the δ¹⁸O values in geothermal waters are of (‰) -2,88 in Cumaltı, (‰) -2,55 in Tuzla, (‰) -5,04 in Doğanbey and (‰) -5,70. For the same geothermal waters, the same authors give for δ²H values of (‰) -16,3 in Cumaltı, (‰) -13,3 in Tuzla, (‰) -30,9 in Doğanbey and (‰) -31,9 in Karakoç. [3] give in their study ³H values ranging from 13 to 64 TU. According to the authors, the origin of the geothermal waters can be attributed to the meteoric waters with a supply by the intrusion of sea waters. In Seferihisar and environs, there is an enrichment of δ¹⁸O values, which point to intensive water-rock interactions in the study area. In addition, the enrichment of δ²H values can be related with high evaporation rate in the area.
Table 1. In-situ measurements and hydrogeochemical analyses of the geothermal waters in Seferihisar and environs.

| Sample | T (°C) | pH  | Eh (mV) | EC (µS/cm) | Na⁺ (mg/l) | K⁺ (mg/l) | Ca²⁺ (mg/l) | Mg²⁺ (mg/l) |
|--------|--------|-----|---------|------------|------------|-----------|-------------|-------------|
| EB-1   | 61.4   | 7.12| -57.8   | 29200      | 5858       | 754.0     | 546         | 56.3        |
| EB-2   | 55.1   | 7.27| 92.4    | 6710       | 1236       | 93.9      | 160         | 52.5        |
| EB-3   | 76.1   | 7.58| 112.0   | 10330      | 1985       | 4.22      | 195         | 59.3        |
| SD-1   | 39.2   | 7.31| 101.3   | 20700      | 6052       | 206.0     | 590         | 408.0       |
| SD-2   | 40.0   | 7.46| 73.0    | 57100      | 13400      | 437.0     | 855         | 1187.0      |

| Sample | Al³⁺ (mg/l) | B³⁺ (mg/l) | SiO₂ (mg/l) | SO₄²⁻ (mg/l) | Cl⁻ (mg/l) | NO₃⁻ (mg/l) | HCO₃⁻ (mg/l) |
|--------|-------------|------------|-------------|--------------|------------|-------------|--------------|
| EB-1   | 0.2         | 14.0       | 142.0       | 170          | 10231      | 0.10        | 427.0        |
| EB-2   | 0.2         | 8.0        | 53.5        | 187          | 1765       | 1.15        | 847.9        |
| EB-3   | 0.2         | 9.4        | 68.5        | 267          | 3075       | 0.56        | 640.5        |
| SD-1   | 0.2         | 3.1        | 19.6        | 1418         | 10287      | 5.20        | 329.4        |
| SD-2   | 0.2         | 4.9        | 13.2        | 2987         | 21566      | 0.10        | 317.2        |

Figure 3. Geothermal waters of Seferihisar and Çeşme in Piper Diagram
Figure 4. Na/1000-K/100-Mg1/2 diagram of the geothermal waters of Seferihisar and Çeşme

Figure 5. $\delta^{18}$O versus $\delta^2$H in the geothermal waters of Seferihisar and environs
6. Discussion

The geothermal waters of Seferihisar and environs are of meteoric origin with intrusion of sea waters. These meteoric waters in the drainage area percolate at fault zones and permeable clastic sediments into the reaction zone of roof area of a magma chamber located at a probable depth up to 4-5 km where the meteoric waters are heated by the cooling magmatic belt and ascend to the surface due to their lower density caused by convection cells [Figure 6]. The volatile components such as CO₂, SO₂, HCl, H₂S, HB⁻, HF⁻, and He out of magma reach the geothermal waters where an equilibrium between altered rocks, geothermal waters and gas components is performed. Thus, the geothermal waters ascend in the faults of the continental rift zone of the Gediz as hot springs, steams, and gases.

In the study area of Seferihisar and environs, marble intercalations in metamorphic schists in basement rocks, sandstones with secondary permeability in Izmir flysch-series, spilitic volcanic rocks, olistolithes of limestones and serpentinites form the reservoir rocks in study area. Geothermal waters of Cumalı and Tuzla are of meteoric origin with a supply by intrusions of seawaters and can be considered as high salinity and high enthalpy waters. In comparison, the geothermal waters of Doğanbey and Karakoç are of meteoric origin with moderate supply by intrusion of seawaters and can be considered as moderate salinity and high enthalpy waters. The reservoir temperatures of geothermal waters increase from Doğanbey and Karakoç to Cumalı and Tuzla. The volcanic rocks in the area can be considered as heat source for geothermal waters in Seferihisar and environs. The faults of Cumalı and Doğanbey are of more important for the formation of the geothermal waters.

![Figure 6. Hydrogeological modelling of the geothermal waters of Seferihisar](image)

The geothermal waters in the study area of Seferihisar and environs can be considered as Na-Cl and/Na-Cl-HCO₃ type waters with a cation order of Na+K>Mg>K and an anion order of Cl>HCO₃>SO₄.
The high sulphate contents of the geothermal waters might be attributed to the intrusion of seawaters. According to Na-K-Ca$_{1/2}$ diagram of[10], a particular part of the geothermal waters can be considered as partially equilibrated mature waters during a particular part of these waters are of immature waters. Geochemical silica geothermometers indicate reservoir temperatures of 143-149°C for Cumalı [sample number: EB-1], 99-100°C for Karakoç [sample number: EB-2] and 110°C for Doğanbey [sample number: EB-3]. Geochemical Na/K geothermometers give temperatures ranging from 140 to 180°C, which correspond with the results of geochemical silica thermometers.

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