Geothermal Waters in Pamukkale as an Hydrogeological Model within the Menderes Massif, Turkey

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Abstract: The area is located in the northern shoulder of the eastern part of the E-W trending continental rift zone of the Büyük Menderes and consists of Paleozoic rocks, Mesozoic limestones and sedimentary rocks in age of Eocene, Pliocene and Quaternary. The marbles, quartzites and carbonate rocks, limestones, sedimentary rocks, alluvium and travertine deposits are of passable rocks for geothermal waters. Geothermal waters of Pamukkale show outlet temperatures ranging from 35 to 48 °C and reservoir temperatures of between 150 and 180 °C and are of Mg-Ca-SO₄-HCO₃ type waters. Geothermal waters in Pamukkale are distinguished by Mg>Ca>Na+K as dominant cations and HCO₃>SO₄>Cl as dominant anions. The diagram of Na₁/1000-K₁/100-√Mg shows that the samples of Pamukkale are of immature waters. Finally, the geothermal waters in Pamukkale were represented as a hydrogeological model.

1. Introduction
The area of Pamukkale is located in the northern shoulder within the eastern part of the rift zone of the Büyük Menderes (20 km NW of the province capital of Denizli) within the Menderes Massif [Figure 1]. The aims of this study are (i) to update the data hydrogeologically, hydrogeochemically and isotope geochemically and (ii) to represent an hydrogeological model of geothermal waters of Pamukkale.

2. Material and methods
During the field works in Pamukkale, we have collected 3 samples [2; 3; Table 1]. At the same time, we have carried out in-situ measurements [Table 1]. By using ICP-OES methods, the elements of Na⁺, K⁺, Ca²⁺, Mg²⁺, Si⁴⁺ and B³⁺ were analyzed. For the analyses of F⁻, SO₄²⁻, NO₃⁻ and Cl⁻, IC methods were used [Table 1]. In addition, alkalinity measurements were applied in the field for determination of HCO₃⁻ and CO₃²⁻ values. The evaluation of the obtained data and representation of graphics were carried out using geochemical software program Aqua Chem 3.7 [4].

3. Results
3.1. Geological setting
The area is located in the northern shoulder of the eastern part within the rift zone of the Büyük Menderes within the Menderes Massif. At the location of the study area, the rift zone of the Büyük Menderes in E-W direction and the rift zone of the Gediz in NW-SE direction convergent [Figure 2; 2; 3; 5]. Paleozoic rocks form impermeable basement underlying limestones in Mesozoic age, sedimentary rocks in Eocene to Pliocene age and Quaternary alluviums and travertine deposits in the
area. The travertine precipitations can be observed on some parts of the Pamukkale fault. Moreover, the travertine deposits can be observed somewhere else.

![Geological sketch map of the Menderes Massif and the area of Pamukkale](image)

**Figure 1.** Geological sketch map of the Menderes Massif and the area of Pamukkale [1; 3]. For sample location see [1].

3.2. Hydrogeology

Besides Paleozoic marbles and Mesozoic limestones, sedimentary rocks in age of Pliocene and Miocene and alluviums and travertine deposits in Quaternary age occur in the study area as permeable rocks. Paleozoic marbles are located in the N and NE parts of geothermal outlets of Pamukkale and form the deep reservoir. In comparison, Mesozoic limestones occur also in the N Pamukkale and form the shallow reservoir. Sedimentary rocks in Pliocene age are situated in the surrounding area of geothermal outlets of Pamukkale indicating a shallow reservoir in the area. In the area, the Kolonkaya and the Tosunlar formations a thickness between 350 and 600 m are composed of claystones, marls and sandstones and may be considered as cap rocks for shallow reservoir.

3.3. Hydrogeochemistry

In the piper diagram, geothermal waters of Pamukkale are to assign to of Ca-Mg-(SO$_4$)-HCO$_3$ type, waters [Figure 3]. With dominant cations of Ca>Mg>Na+K and dominant anions of HCO$_3$>SO$_4$>Cl geothermal waters are represented in the area respectively. Geothermal waters contain high sulfate concentrations indicating the existence of pyrite and gypsum minerals in reservoir and different cap rocks [1]. In the ternary diagram of Na/1000-K/100-√Mg [Figure 4; 6], geothermal waters of Pamukkale are of immature waters. In addition, geochemical waters show reservoir temperatures between 150 and 180 °C in the area calculated by cation thermometers of Na-K and Na-K-Ca [2; 3].
Figure 2. Geological map of Pamukkale with sample locations [modified from 5]. DK-1, DK-2 and DK-3 are sample locations.
Table 1. In-situ measurements and hydrogeochemical analyses of geothermal waters in Pamukkale and environs [2; 3; DK-1: Pamukkale; DK-2: Pamukkale; DK-3: Karahayıt].

| Sample | T (°C) | pH  | Eh (mV) | EC (µS/cm) | Na⁺ (mg/l) | K⁺ (mg/l) | Ca²⁺ (mg/l) | Mg²⁺ (mg/l) | Si⁴⁺ (mg/l) | B³⁺ (mg/l) |
|--------|--------|-----|---------|------------|------------|---------|------------|------------|------------|--------|
| DK-1   | 35     | 6.56| 259.9   | 2430       | 44.2       | 5.45    | 99.4       | 401        | 15.8       | 1.0    |
| DK-2   | 35.1   | 6.44| 282.1   | 2400       | 40.1       | 5.08    | 95.4       | 479        | 15.2       | 0.9    |
| DK-3   | 46.6   | 6.52| 63      | 2680       | 107        | 21.1    | 124        | 414        | 26.8       | 1.6    |

| Sample | F⁻ (mg/l) | SO₄²⁻ (mg/l) | Cl⁻ (mg/l) | NO₃⁻ (mg/l) | HCO₃⁻ (mg/l) |
|--------|------------|--------------|------------|-------------|--------------|
| DK-1   | 0.8        | 649          | 13         | 1.56        | 1098         |
| DK-2   | 1.8        | 642          | 14.1       | 1.88        | 1079.7       |
| DK-3   | 2.2        | 905          | 31.8       | 0.65        | 927.2        |

Figure 3. Geothermal waters of Pamukkale in Piper diagram.

3.4. Isotope geochemistry
In the area, the ratio of δ¹⁸O versus δ²H of geothermal waters is plotted [Figure 5]. Stable isotope data of geothermal waters of Pamukkale are distinguished by δ²H values ranging from -61.9 and -51.8 ‰ and δ¹⁸O values between -9.24 to -5.85 ‰. The tritium contents are between 0.7 and 3.3 TU. In the diagram of δ¹⁸O versus δ²H, samples of geothermal waters from study area lie along GMWL (Global Meteoric Water Line). In comparison, samples of geothermal waters of Kızıldere [1; 7] show a strong shift from GMWL which indicates intense water-rock interaction under high temperature conditions in the area of Kızıldere. ³H values of up to 3.3 TU can be attributed to an atmospheric an/or
anthropogenic origin. Therefore, it can be assumed that there is a mixing process between groundwater and geothermal waters in the area of Pamukkale which are evidenced for geothermal waters.

**Figure 4.** Geothermal waters of Pamukkale in diagram of Na/1000-K-100-√Mg.

**Figure 5.** Ratio of $\delta^{18}$O versus $\delta^2$H of geothermal waters of Pamukkale. In comparison, values of stable isotopes were entered in this diagram. For the data of stable isotopes see [1; 2; 3; 7].
4. Discussion
Geothermal waters of Pamukkale was represented as an hydrogeological model in [Figure 6] which has been described comprehensively by [1; 3; 8]. In this process, meteoric waters flow in catchment area through faults, fractures and fissures and by permeable rocks into reservoir rocks in the reaction zone of a magma chamber in a depth of up to 5-6 km firstly. These meteoric waters in the reservoir are heated by cooling magmatic melt, for which the Middle Miocene to recent volcanics such as Middle Miocene Denizli and Kiraz volcanics and recent Kula volcanics with a youngest age of up to 18.000 a in the Menderes Massif are responsible. The geothermal waters ascend to the surface because of the lower density lastly which is caused by plate tectonical convection cells. In this late phase, the volatiles reach the reservoir of geothermal waters: there, an equilibrium between rocks, gases, and geothermal waters take place. Finally, geothermal waters ascend along the structures of faults, fractures, fissures and permeable rocks at the rift zones of the Büyük Menderes and the Gediz in terms of steams, gases and hot springs.

Figure 6. Schematic representation of a conceptual model of geothermal waters in Pamukkale and environs[modified from 8]. For legends of rock formations see [2; 8].

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