Hydrogeochemistry of the thermal waters from the Pamukkale and Karahayıt Geothermal Fields (Denizli Basin, Southwestern Anatolia, Turkey)

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ABSTRACT

The chemical and isotopic properties of thermal waters (Pamukkale and Karahayıt) and cold springs from the Pamukkale and Karahayıt geothermal fields (PGF and KGF, Southwestern Anatolia, Turkey) are investigated in order to establish a conceptual hydrogeochemical-hydrogeological model. These thermal waters derive from metamorphics of Menderes Massif and carbonates of Lycian Nappes and emerge along northern normal faults in the Denizli Basin; they are commonly used for heating of greenhouses and bathing facilities. Discharge temperatures of thermal waters are mean of 33°C for Pamukkale and 53°C for Karahayıt, whereas cold groundwaters are mean of 13°C. Pamukkale and Karahayıt thermal waters are mostly of Ca-Mg-HCO_3-SO_4 type, whereas cold groundwaters are mainly Ca-HCO_3 types.

In the reservoir of the geothermal system, dissolution of host rock and ion-exchange reactions change thermal water types. High correlation in some ionic ratios (e.g., Na vs. Cl, Mg vs. Cl, K vs. Cl, HCO_3 vs. Cl, SO_4 vs. Cl) and high concentrations of some minor elements (e.g., Sr, B, Cl, F) in thermal waters likely originate from enhanced water-rock interaction. Pamukkale and Karahayıt thermal waters are oversaturated at discharge temperatures for carbonate and silica minerals allowing increase to a carbonate- and silica-rich scale and correspond to travertine/tufa precipitation in the discharge area. Water samples from PGF and KGF have not reached complete chemical re-equilibrium, possibly as a result mixing with groundwater during upward flow. Geothermal reservoir temperatures are calculated as 57-61°C (mean 59°C) for Pamukkale and 41-73°C (mean 57°C) for Karahayıt fields, based on the chalcedony geothermometry.

Very negative $\delta^{18}O$ and $\delta^{2}H$ isotopic ratios (~-9 ‰ and ~-58 ‰) and high tritium values (3-10 TU) of the Pamukkale thermal waters are indicative of a shallow circulation and a meteoric origin, and radioactive decay with a mixture of pre-modern (old) water mixed with modern (new) water recharge or recent additions. The other hand, negative $\delta^{18}O$ and $\delta^{2}H$ isotopic ratios (~-8 ‰ and ~-51 ‰) and low tritium values (1 TU) of the Karahayıt thermal waters reflect a deep circulation pathway and a meteoric origin. These waters likely derived from the infiltration of rainwater through fractures and faults to the deep hot reservoir. Subsequent heating by conduction in the high geothermal gradient setting (resulting from regional crustal thinning) controls geothermal waters upwards along faults and fractures that act as hydrothermal pathways. The CO_2 gases of Pamukkale field have negative $\delta^{13}C$ values with ~-4 ‰, probably indicating mantle-derived magmatic origin. This study was sponsored by the Scientific and Technical Research Council of Turkey (TÜBİTAK research grants ÇAYDAG113Y551).

1. INTRODUCTION

Low-moderate- (<150°C) to high- (>150°C) enthalpy geothermal fields are widely known throughout the western Turkey (Fig. 1A). The Denizli Basin of southwestern Anatolia (Turkey) (Fig. 1B) characterized by an array of low- to high-temperature geothermal fields along NW-SE trending normal faults that are related to ongoing N–S directed crustal extension in the region. The basin is prominent for its thermal springs long before realized for its geothermal potential. The utility of geothermal sources in the basin are attractive during last decades after their properties have been studied since 1967 (e.g., Şimşek, 1981, 1984, 1985; Gökgöz, 1998; Vengosh et al., 2002; Şimşek, 2003a, b; Şimşek et al., 2005; Alçiçek et al., 2016 and references therein). The information on the low- to moderate- enthalpy geothermal resources have commonly been incomplete due to their low temperatures has enabled them unsuitable for electricity generation and thus uneconomical for exploitation. Since these resources are more abundant than their high temperature counterparts, they have been efficiently developed in recent years to gain a source of thermal water for a diversity of industrial, commercial and residential purposes. Understand of the source and nature of the resource is very important for enhancing reservoir exploitation and longevity.

The Pamukkale (PGF) and Karahayıt (KGF) geothermal fields are one of the low-to moderate enthalpy geothermal fields located in the northern margin of the Denizli Basin (Fig. 1B). These fields and their surroundings (e.g. Gölemezli, Yenice geothermal fields; Fig. 1B) are well known for their spectacular travertine formations having a major tourist attraction. These geothermal fields show well-developed hydrothermal activities as a result of many mineralized thermal springs. The Pamukkale and Karahayıt geothermal fields are also characterized by some fossil fissure ridges built around the active travertines which are using for a variety of purposes (including spa, greenhouse heating, etc.) as well as used during ancient times (Altunel & Hancock 1993a,b, 1996; Brogi et al., 2014, 2016).

The aims of the present study included: (i) to determine the geological, hydrogeological and hydrogeochemical properties of the thermal and cold waters of the PFG and KGF; (ii) to calculate maximum reservoir temperatures by application of chemical geothermometers based on previous and new data obtained from springs and wells; (iii) to reconstruct a conceptual hydrogeochemical-hydrogeological model of the PGF and KGF geothermal systems using different proxies; and (iv) to understand the aquifer fluid composition and fluid-mineral equilibria for exploration and evaluation of the geothermal resources in these fields.

2. GEOLOGICAL SETTING

Western Anatolia (Turkey) (Fig. 1A) is one of the well-known extensional setting in the World (Şengör and Yılmaz, 1981; Bozkurt, 2003; ten Veen et al., 2009), which is represented by moderate- to high-enthalpy geothermal fields located along the major graben bounding faults (Fig. 1B; Vengosh et al., 2002; Güleç et al., 2002). All thermal springs (50-100°C) are closely concerned with young Neogene-Quaternary volcanic activity and block faulting which have been responsible for heating up the geothermal fields in the western Anatolia (Vengosh et al., 2002; Güleç and Hilton, 2006). The presence of more than 600 hot springs with outlet temperatures (up to 100°C) reflects a significant geothermal potential in Turkey that has been supported by drilling studies implemented by the General Directorate of Mineral Research and Exploration of Turkey (MTA) since the 1960s (Çağlar, 1961; MTA, 2005). In the Denizli Basin, the geothermal exploration studies began with the Kızıldere Geothermal Field by the MTA-UNDP project cooperation during 1968 (Şimşek, 2003a, b).

The Denizli Basin is one of the extensional basins of western Anatolia where crustal extension lasting from late early Miocene onward. The basin is 50 km wide and 70 km long delimited by NW- and SE-faults and located at the junction of the E-trending Büyük Menderes and the NW-trending Gediz basins (Fig. 1B; Şimşek, 1984; Sun 1990; Koçyiğit, 2005; Kaymakçı, 2006; Alçiçek et al., 2007). The Neogene to Quaternary sedimentary succession of the basin is up to 1300 m thick, overlies unconformably the metamorphic rocks of the Menderes Massif and consists of alluvial-fan, fluvial, and lacustrine deposits (Alçiçek et al., 2007). The lithostratigraphical subdivision of Denizli Basin has been determined by Şimşek (1984) as Denizli Group consisted of Kızılburun, Sazak, Kolankaya and Tosunlar formations. The Denizli Group is subdivided into four lithostratigraphic units consisted by the alluvial fan to fluvial Kızılburun (Early-early Middle Miocene), lacustrine Sazak (middle Middle-early Late Miocene), lacustrine to fluvio-lacustrine Kolankaya (middle Late Miocene-Early Pleistocene), and alluvial fan to fluvial Tosunlar (Late Pleistocene) formations (Fig. 2). The basin was initially a half graben during the late early Miocene subsiding along NW-SE directed Babadağ fault to the south (Alçiçek et al., 2007). The Neogene half graben turned into a full graben by the early Quaternary due to activity associated with the Pamukkale and Tripolis (Yenice) faults to the north, which gave rise of hot springs that caused to the formation of major travertine/tufa precipitation (Altunel and Hancock, 1993a,b; Hancock et al., 1999; Alçiçek et al., 2007; Brogi et al., 2014, 2016; Alçiçek et al., 2016). It is suggested that the travertine masses in the basin have formed where dip-slip normal fault segments display step-over zones along the fault-strikes (e.g. Çakır, 1999; Brogi et al., 2014; 2016).

The pre-Neogene bedrock of the basin is exposed at its northwestern and southwestern margin, contain Palaeozoic-Mesozoic metamorphic rocks of the autochthonous Menderes Massif and allochthonous Lycian Nappes constituting westernmost part of the Tauride orogen (Fig. 2; Okay, 1989; Sun, 1990; Alçiçek et al., 2007). The Menderes Massif includes a crystalline core and metamorphic cover rocks with the core comprising augen gneisses surrounded by schists, quartzite, marbles, and carbonates forming a dome-like structure (Okay, 1989; Sun, 1990; Bozkurt, 2001; ten Veen et al., 2009; van Hinsbergen and Schmid, 2012). Lycian allocthon units are composed of Mesozoic recrystallized dolomitic limestones, marbles, and turbiditic sandstones which are tectonically overlain by ophiolitic mélange (Okay, 1989; Sun, 1990). A recrystallized dolomitic limestone succession in the nappes is intercalated with Triassic evaporitic units in the easternmost part of Denizli Basin (Alçiçek et al., 2007). The bedrock units represent the closure of the Neotethyan oceanic basin during the Mesozoic-early Cenozoic with the emplacement of large-scale platform carbonate and ophiolitic rocks (Collins and Robertson, 1998).

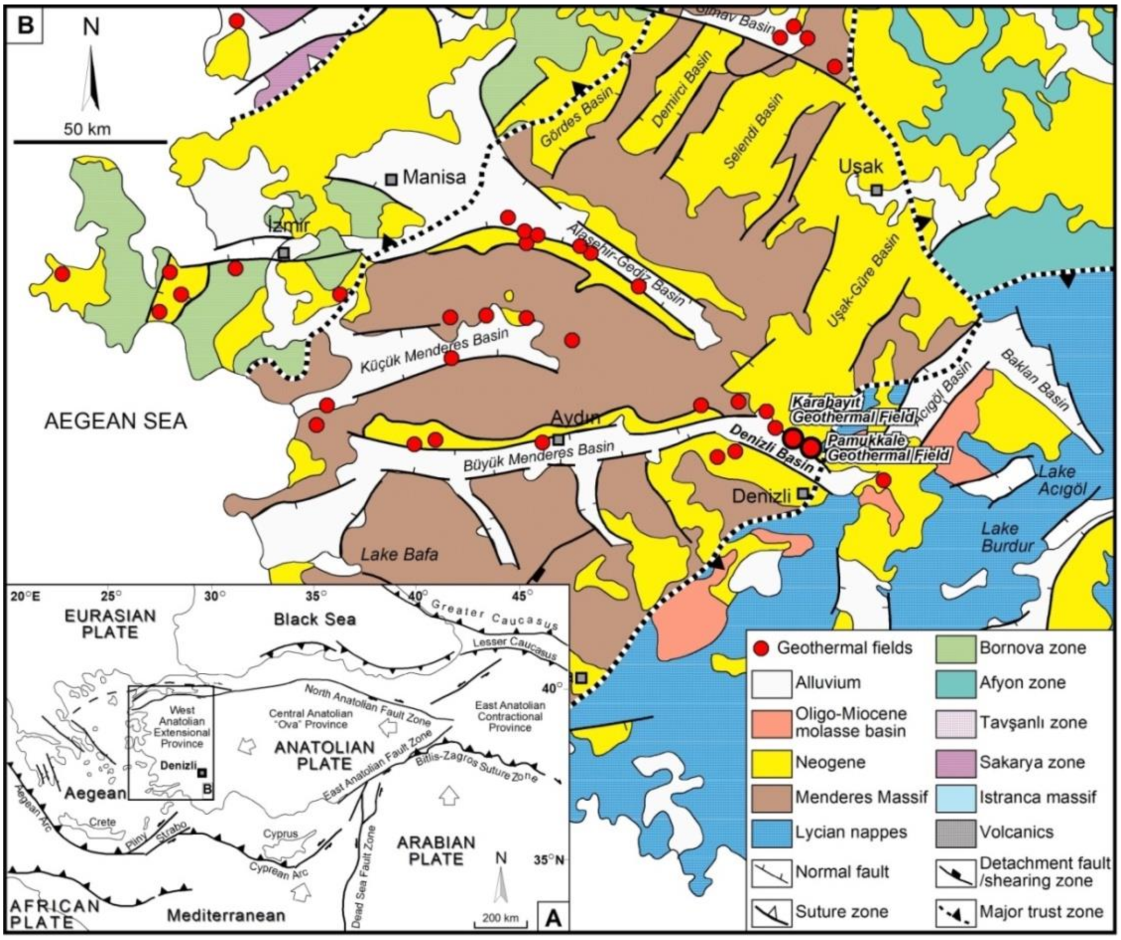

Figure 1: (A) Location map of the Denizli Basin, SW Turkey (Bozkurt, 2003); (B) Overview of the prominent extensional basins of western Anatolia surrounding the Denizli Basin and location of geothermal fields (modified from Sözbilir et al., 2001; Baba and Sözbilir, 2012)

3. HYDROGEOLOGICAL SETTING

The Denizli Basin is characterized by many low- to high-temperature geothermal fields. Low-temperature geothermal fields commonly occur at the eastern part (Karahayıt, Pamukkale, Kokarpınar, Ilıcapınar-Beylerli), whereas high-temperature geothermal fields (Kızıldere, Bölmekaya, Tosunlar, Yenice, Gölemezli, Babacık, Demirtaş, Karataş, Tekkehamam, Uyuz and İnaltı) are generally found on the western part of the basin (Fig. 1B). The Pamukkale and Karahayıt geothermal fields are such low-temperature geothermal fields, which are located at the northwestern margin in the Denizli Basin (Fig. 1B).

The Pamukkale geothermal field is represented by six thermal springs and one well which are situated on the NW-trending Pamukkale fault footwall (Şimşek, 1984). Four thermal springs (Jandarma, Beltes, İnciraltı and Antik-Havuz) are located at above the terraced slope-travertine, whereas Kocagöz and Küçükgöz thermal springs and Yenitimar well are situated at the foot of the terraced slope on the plain. These springs have a temperature range of 31-35°C with discharge rates of 30-130 lt/sn (MTA, 2005). The Karahayıt geothermal field contains one spring and numerous thermal wells drilled by MTA (KH-1, -2 and -3) and private sector. The spring, named as "red water thermal spring", discharged 2.5 l/s of water at 51°C and dried up due to the well exploration in 1996. The four, deep exploration wells (KH1-3; respectively) were in 2007, reaching depths of 468 m (flow 12 l/s, T 58°C, KH-1 well), 452 m (22 l/s, 58.5°C, KH-2 well), 570 m (58 l/s, 61.5°C, KH-3 well). Also, shallow exploration wells of the private sector have a depth range of 5 to 140 m with discharge rates of 0.5-75 lt/sn. These wells are commonly used for spa and greenhouse facilities. Two reservoir and three cap rock units were identified in the PGF and KGF based on lithological, structural, and hydrogeological characteristics (Fig. 2; Şimşek, 1984; 2003b; Şimşek et al., 2005).

First (shallow) reservoir unit contain the Sazak Formation (up to 300 m thick) and subdivided into three units from bottom to top: (i) lake-margin unit: bioclastic limestone, green marl, laminated mudstone, and clayey limestone alternations; (ii) shallow lake unit: including cherty limestones and dolostones; and (iii) playa/saline lake unit containing gypsarenite, selenite, shale, gypsiferous mudstone alternations. This formation is a good aquifer for the thermal waters, and thus it represent first (shallow) reservoir due to primary permeability and intensely faulted and fractured. In the study area, this reservoir unit exhibits a wide lateral continuity and is up to 150 m thick. Second (deep-main) reservoir corresponds to the Paleozoic İğdecik Formation which are composed of quartzite, marble, and schist alternations and Mesozoic carbonates. Similar to the first reservoir, this unit is broadly widespread in the subsurface and represented by a relatively high secondary porosity and permeability due to faults and fractures. Thus, this reservoir unit is main reservoir rock, and reaches up to 300 m thick in the study area. There is a positive temperature gradient among three exploration wells (48.5°C at 452 m, 58°C at 468 m and 61.5°C m at 570 m).

In the study area, first cap rock is composed of the Tosunlar and Kolankaya formations which cover the first reservoir Sazak Formation. The Tosunlar Formation (up to 150 m thick) is unconformably overlain by previous formations. This formation includes two units from bottom to top: (i) proximal and medial alluvial-fan unit: conglomerate, sandstone, siltstone and mudstones alternations, and (ii) fluvial unit: sandstone, siltstone, mudstones and marl alternations. The Kolankaya Formation (up to 500 m thick), rests conformably on the Sazak Formation and overlies unconformably the metamorphic bedrock in the northern part of the basin. This formation consists of four units from bottom to top: (i) shallow lake unit: laminated mudstone-siltstone and marl alternations, (ii) sublittoral to profundal lake unit: alternating marl-claystone, sandstone, and clayey limestone, (iii) littoral unit: conglomerate, sandstone, siltstone alternations, and (iv) alluvial fan deposits: conglomerate, sandstone, siltstone and mudstone alternations. The second cap rock Kızılburun Formation is situated below the first upper reservoir of Sazak Formation acting as the second cap rock in the field for the second and main reservoir of İğdecik Formation as a result of its well-consolidated properties. This formation (up to 450 m thick), overlies the bedrock unconformably and passes upwards into the first reservoir Sazak Formation. It is composed of two units from bottom to top: (i) proximal-medial alluvial-fan including conglomerate, sandstone, siltstone and mudstones alternations, and (ii) distal alluvial-fan containing sandstone, siltstone, mudstones, coal and clayey limestone alternations.

4. MATERIAL AND METHODS

Twelve thermal and seven cold water samples were collected in 2015 in the study area for analyses in order to identify their chemical properties. A further 21 thermal and 5 cold waters datasets were compiled from previous studies. Samples were stored in two polyethylene bottles. One of the bottles was acidified with suprapure HNO_3 for determination of cations and SiO_2 analyses and the other was kept unacidified for anion analyses. EC (electrical conductivity), pH and temperature were measured in the field, while alkalinity as HCO_3 was defined by titration with HNO_3 (0.1 M) when pH value reaches 4.2 (for HCO_3) on the day of sampling. Major ion and trace element contents in the water samples were determined at the Acme Laboratories (Ankara, Turkey) using inductively coupled plasma mass spectrometry (ICP-MS). The $\delta^{18}O$ and $\delta^{2}H$ ratios of 12 thermal and 7 cold water samples were analyzed at SIRFER Laboratory (Utah, USA) and $\delta^{13}C$ ratios were analyzed at Iso-Analytical laboratory (UK). The precision of the analyses is ±0.15 for $\delta^{18}O$, ±2 for $\delta^{2}H$ and ±0.2 for $\delta^{13}C$. Tritium isotope analyses of (8 thermal and cold waters) were conducted at the Water Chemistry Laboratory of the Hacettepe University (Ankara, Turkey).

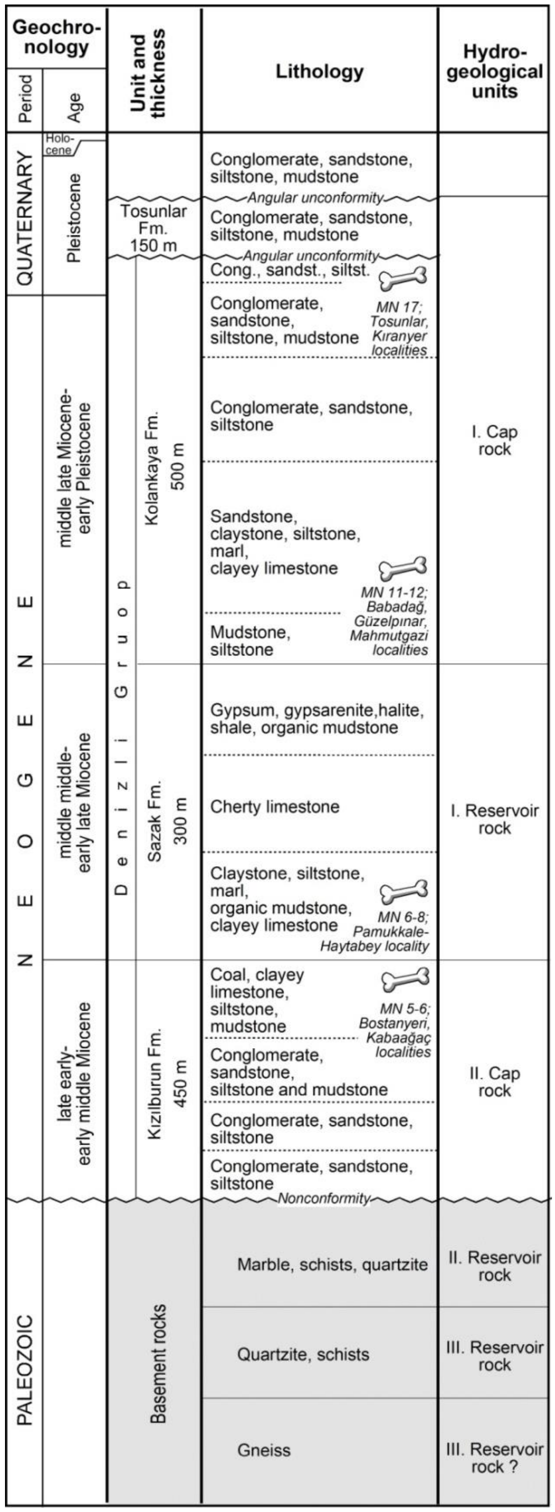

Figure 2: Composed stratigraphy of the Denizli Basin (Sun, 1990; Alçiçek et al., 2007)

5. WATER CHEMISTRY

5.1. Hydrogeochemical characteristics

The hydrochemical properties of the thermal and cold waters from the study area are shown on the basis of physico-chemical data. According to classification in the Piper diagram, the Pamukkale and Karahayıt thermal waters and cold waters plot in different fields (Fig. 3). Both thermal waters are mostly of Ca-Mg-HCO_3-SO_4 type, whereas cold groundwaters are mainly Ca-HCO_3 types.

Pamukkale and Karahayıt thermal waters include HCO_3 (mean 1119 mg/l and 1304 mg/l, respectively) and SO_4 (mean 723 mg/l and 1013 mg/l, respectively) as dominant anions and Cl (mean 12,3 mg/l and 27,8 mg/l, respectively) as minor anions, and Na (mean 49 mg/l and 132 mg/l, respectively) and Ca (mean 431 mg/l and 498 mg/l, respectively) as dominant cations and K (mean 6,4 mg/l and 27 mg/l, respectively) and Mg (mean 104 mg/l and 147 mg/l, respectively) as minor cations. However, anion (HCO_3, SO_4 and Cl) and cation (Na, Ca, K and Mg) concentrations in Pamukkale samples are commonly lower than Karahayıt samples. Similar to the samples collected from Pamukkale and Karahayıt, predominant anions of cold waters are HCO_3 (mean 345 mg/l) and SO_4 (mean 49 mg/l) and minor anions are Cl (mean 14 mg/l), whereas predominant cations are Ca (mean 81 mg/l) and Na (mean 14 mg/l) and minor cations are K (mean 2 mg/l) and Mg (mean 23 mg/l). But, anion and cation contents are higher in the thermal waters compared to cold waters. Pamukkale and Karahayıt thermal waters as well as the cold waters have very similar isotopic compositions and have a similar origin.

Thermal waters from Pamukkale and Karahayıt have distinct discharge temperatures and electrical conductivities (EC). Electrical conductivity and temperatures are lower in Pamukkale (mean 2288 μS/cm and 32,5°C, respectively) compared to Karahayıt (mean 2840 μS/cm and 52°C, respectively). This reflects that thermal waters from Karahayıt have longer circulation and residence times compared to Pamukkale. EC and temperature values of cold waters are much lower than both thermal waters (mean 528 μS/cm and 13°C, respectively), whereas pH values are higher (7,5).

5.2. Minor elements

Mean As, Sr, Cl, B, F, Li and F concentrations of Pamukkale thermal samples are lower than those of Karahayıt, and concentrations in the measured cold waters are lower than both, likely resulting from water-rock interaction. The abundance of minor elements in thermal waters in comparison to cold waters implies that thermal waters have a higher reactivity leading to increased leaching of the minor elements from the host rock during deep circulation (Ma et al., 2011). Moreover, the contrast in concentrations is probably accelerated by the shorter residence times of colder waters and their dilution by phreatic or river waters (Ma et al., 2011). The high Sr concentrations in the studied thermal waters indicate exchange between rising thermal waters and the Miocene Sazak Formation sediments. Boron in thermal waters may have derived from interaction with the various geological formations and degassing of magma intrusions (Gemici and Tarcan, 2002). Cl and B concentrations are higher in thermal waters than cold waters. Relatively high B and Cl contents of thermal waters probably reflect relatively deep circulation paths and interaction with and leach host rocks. B and Cl are commonly considered as conservative elements, using for a main tool for following the groundwater flow paths and mixing processes of different waters (Motyka et al., 1993). There is a moderate correlation of B and Cl concentrations. The Pamukkale and Karahayıt thermal waters have high F contents. This implies the ascending thermal waters interacted with amorphous fluorite present in the carbonates and clastic clays and conglomerate of Sazak Formation. High Li contents result exchange with clays from the Sazak formation that are common in these parts of the basin's subsurface.

Base Exchange Indices (bei) are commonly used to identify hydrochemical facies of the waters (Schoeller, 1965). Pamukkale and Karahayıt have very negative bei values, whereas cold waters have slightly negative to positive values. The negative values are typical for waters deriving from metamorphic and sedimentary rocks with alkaline ions released by alteration of silicate minerals. This supports that Pamukkale and Karahayıt thermal waters circulated through Paleozoic metamorphic rocks and Miocene lacustrine deposits of the Sazak Formation.

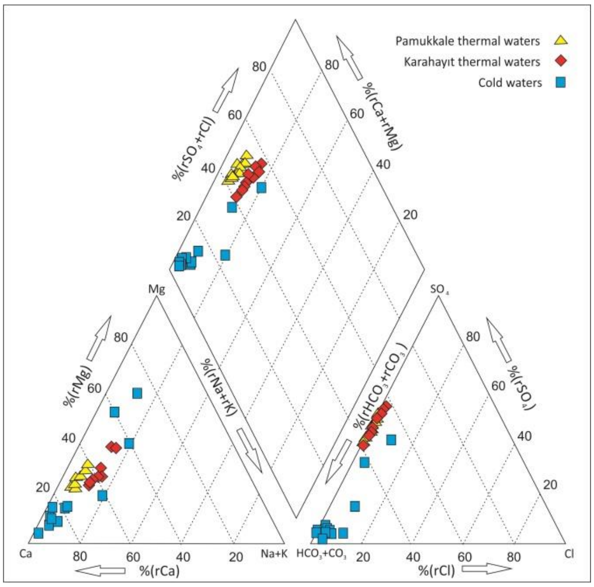

Figure 3: Piper diagram for the studied water samples from the PGF and KGF

5.3. Stable isotopes

The $\delta^{18}O$-$\delta^{2}H$ composition of the thermal and cold waters from PGF and KGF is compared to the Local Meteoric Water Line (LMW;

$\delta^2H = 8\delta^{18}O + 16$; Şimşek, 2003a), the Global Meteoric Water Line (GMWL; $\delta^2H = 8\delta^{18}O + 10$; Craig, 1961) and the Eastern Mediterranean Meteoric Water line (EMMWL; $\delta^2H = 8\delta^{18}O + 22$; Gat and Carmi, 1970) (Fig. 4A). All of the studied waters reflect a common meteoric origin on the GMWL and the LMWL showing that they initiated as meteoric waters. The $\delta^{18}O$ and δ^2H values of Pamukkale thermal water (mean of -9,03 ‰ and -59,28 ‰, respectively) are slightly lower than those of Karahayıt thermal water (mean of -8,53 ‰ and -55,39 ‰, respectively); values of cold waters (mean of -8,20 ‰ and -53,11 ‰, respectively) are slightly higher. Possibly this reflects a higher altitudinal origin for the thermal waters recharge. The combination of relatively high $\delta^{18}O$ values and low EC and HCO_3 values for the cold waters (Fig. 4B and 4C) implies a low elevation recharge and a shallow circulation path.

5.3.2. Tritium (^3H) isotopes

Tritium contents can distinguish a modern (less than about 50 years in age) or ancient (older than about 50 years in age) origin of groundwaters (Clark et al., 1997). Tritium contents below 1 TU are generally considered to represent ages older than 50 years and values above 1 TU are considered to represent modern groundwater. The tritium values varying from 1 to 8 TU is interpreted as an admixture of recent water with old groundwater and groundwater having been subjected to radioactive decay (Ravikumar and Somashekar, 2011). Therefore, the tritium values of the cold waters in the study area (between 1 and 8 TU) indicate radioactive decay (1-8 TU) with a mixture of pre-modern (old) water mixed with modern (new) water recharge or recent additions. Tritium-Cl and tritium-EC relationships have been separated shallow from deep circulating waters (Ravikumar and Somashekar, 2011). The combination of low tritium values with high EC and Cl values in the Pamukkale and Karahayıt thermal waters reflects deep circulation. Likewise, high tritium values and low EC and Cl contents of the cold waters reflect young and shallow circulation and short residence times.

The $\delta^{13}C$ isotopes were used to determine the source of carbon in water samples. The main sources of carbon contributing to DIC in the natural waters are CO_2 deriving from decaying organic matter in soils and from the dissolution of carbonate, whereas the contribution of atmospheric CO_2 can usually be neglected (Mook and Tan, 1991). The $\delta^{13}C$ ratios of the Pamukkale and Karahayıt thermal waters have positive values (mean +7,48 ‰ and +7,76 ‰, respectively), whereas the cold waters contain negative ratios (-8,68 ‰). The positive $\delta^{13}C$ values (0 to +5 ‰) of thermal waters suggest that the source of carbon can be admixture of metamorphic CO_2 and marine carbonates, whereas the low $\delta^{13}C$ ratios (-12 to +2 ‰) of cold waters is organic in origin (Clark and Fritz, 1997). The $\delta^{13}C$ ratios in Pamukkale travertines are between +5 to +11‰ (Kele et al., 2011), indicating a thermogene type origin (Pentecost, 2005). The geochemistry and isotopic composition of the studied thermal waters and travertines could reflect the importance of diverse processes such as evaporation and deposition rates, and separation/escape of gases in parallel with morphology (Pasvanoğlu and Gültekin, 2012). Pentecost (2005) suggested that the thermogenic travertines with relatively high $\delta^{13}C$ values (-3 to +8 ‰) precipitate quickly from high-temperature waters during cooling and exhibit a minor amount of organic material and a massive structure, and are commonly related with tectonic and volcanic activities.

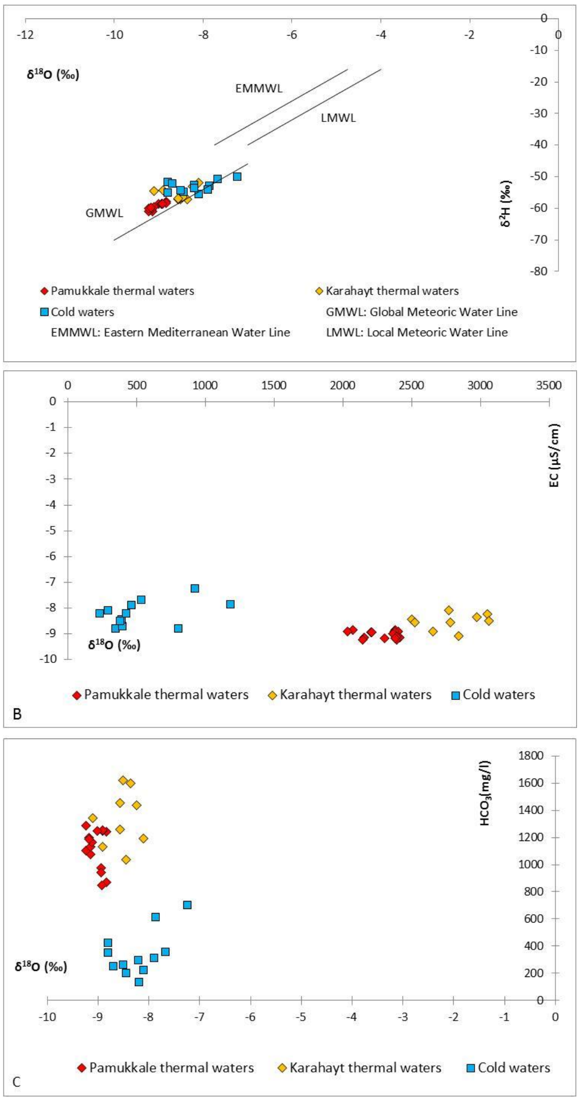

Figure 4: (A) Plot of $\delta^{18}O$-δ^2H for some waters in the PGF and KGF; (B) $\delta^{18}O$-EC diagram; (C) $\delta^{18}O$-HCO_3^- diagram

6. ESTIMATION OF AQUIFER TEMPERATURE

6.1. Mineral saturation states (SI)

Mineral saturation indices for the Pamukkale and Karahayıt thermal waters were calculated using the “Aquachem-Phreeqc” software (Parkhurst and Appelo 1999). The results show that samples from Pamukkale thermal waters are undersaturated with respect to are undersaturated with respect to anhydrite, aragonite, chalcedony, chrysotile, dolomite, fluorite, gypsum, strontianite; and oversaturated with respect to calcite, quartz. The samples from Karahayıt thermal waters are undersaturated with respect to anhydrite, chalcedony, chrysotile, gypsum, strontianite; and oversaturated with respect to aragonite, calcite, dolomite, fluorite, quartz. As a consequence, it should generally predict a scale for the deposition of calcite, and quartz for the Pamukkale and Karahayıt fields.

The equilibrium state between waters and specific minerals are temperature-dependent and therefore provide temperature estimates in the flow path (Reed and Spycher, 1984). Saturation indices of Pamukkale and Karahayıt were calculated at discharge temperatures and measured pH values. The hydrogen mass-balance causes changing of temperatures (Kharaka and Mariner, 1988) and then saturation indices were recalculated to assess the equilibrium states of some hydrothermal minerals at different temperatures. If the equilibrium lines of a group of estimated minerals converge, this reflects a temperature corresponding to the most likely reservoir temperature (Tole et al., 1993). For example, the samples P16 from Pamukkale (Fig. 5), saturation indices with respect to chalcedony and aragonite minerals tend to get closer to the zero (SI=0) around the temperature of 29°C at which temperature these minerals are presumed to be in equilibrium with water giving rise the estimated reservoir temperature. The sample P12 from Pamukkale (Fig. 5), aragonite and quartz minerals are saturated at temperature of 61°C.

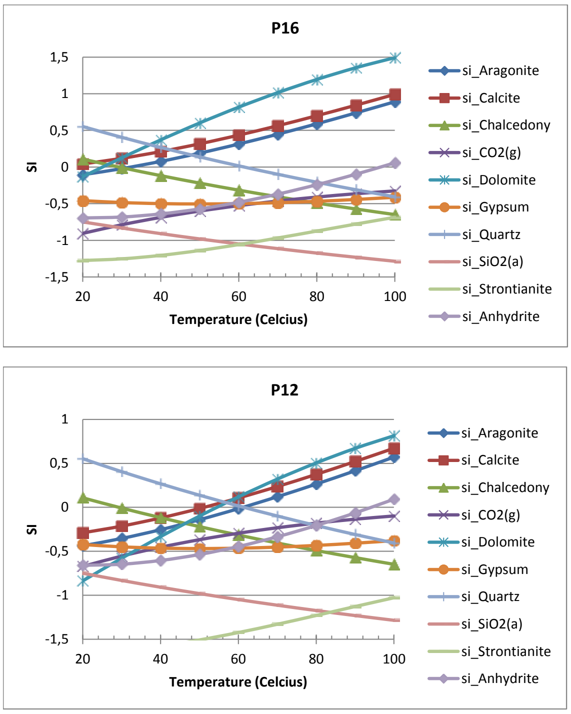

Figure 5: Mineral equilibrium diagrams for PGF thermal waters

Fig. 6 shows the variation of saturation indices of Karahayıt thermal waters. In sample K13, chalcedony and aragonite minerals tend to be near to zero (SI=0) around the temperature of 40°C. The sample K17, aragonite and quartz minerals are saturated at temperatures of 58°C. Consequently the assessment of the saturation indices of the minerals presented in Figs. 5 and 6 give a reservoir temperature between 29°C to 61°C for the Pamukkale and 40°C to 58°C for the Karahayıt geothermal fields.

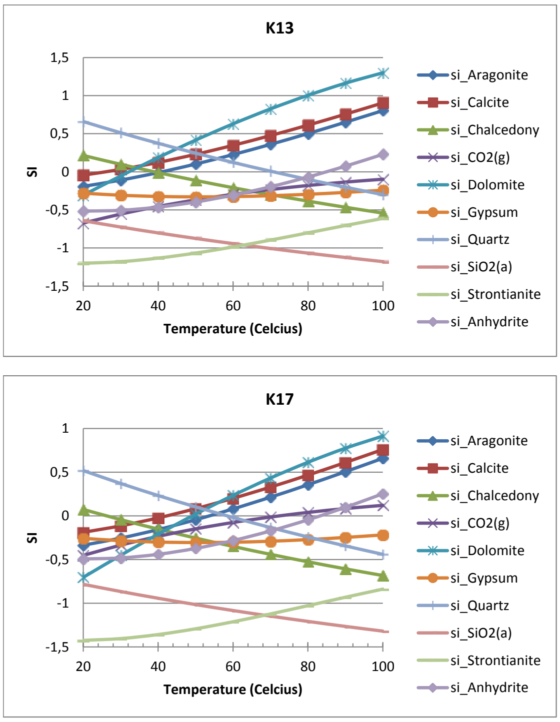

Figure 6: Mineral equilibrium diagrams for KGF thermal waters

6.2. Geothermometry

In this study, silica (quartz and chalcedony) and cation (Na-K and K-Mg) geothermometers were used to estimate reservoir temperatures of the Pamukkale and Karahayıt geothermal systems. However, chemical processes (e.g., mixing and evaporation) affect reservoir temperature estimates. The reservoir temperatures in the Pamukkale and Karahayıt fields were calculated using silica geothermometers (Fournier, 1977), Na-K geothermometer (Fournier, 1979), and K-Mg geothermometer (Giggenbach et al., 1983). The results of the quartz geothermometer give reservoir temperatures varying from 88 to 92°C (mean 90°C) for Pamukkale and 73 to 103°C (mean 88°C) for Karahayıt. Temperatures estimated by the chalcedony geothermometers are 57 to 61°C (mean 59°C) for Pamukkale and 41 to 73°C (mean 57°C) for Karahayıt which are lower than quartz results. Na-K geothermometers give results in a wide range between 251 and 261°C (mean 254°C) for Pamukkale and 296 to 298°C (mean 297°C) for Karahayıt. It is observed that the Na-K temperatures of Pamukkale and Karahayıt thermal waters are higher than those of quartz and chalcedony temperatures. For the K-Mg geothermometer (Giggenbach et al., 1983) all of the estimated temperatures are lower than outlet temperature so the method is not useful for these thermal waters to estimate reservoir temperature. The calculated temperatures from geothermometers are commonly higher than the temperatures of samples analyzed. Therefore, quartz and/or Na-K geothermometer are indicative for reservoir temperatures. The K-Mg geothermometer reflects intermediate temperatures between the reservoir and the spring outlet temperatures values as the geothermal waters re-equilibrate upon conductive cooling or mixing with cooler Mg-rich waters (e.g., Gou and Wang, 2012). The Na-K geothermometer temperatures (Fournier, 1979) are very high, resulting from high Ca^{+2} concentrations of the waters (Fournier and Truesdell, 1973). The Pamukkale and Karahayıt thermal waters may lose some heat due to possible mixing with cold waters along the fracture zones during their ascend to the surface. Thus, estimating Na-K temperatures may be incorrect for mixing waters because leaching processes rather than the chemical equilibrium between minerals and Na–K mainly controlled cation contents in these waters. Temperatures calculated by K–Mg geothermometer in Giggenbach et al. (1983) are lower than outlet temperatures of waters and those of Na–K geothermometer. Mg represents equilibrium at shallower levels, and therefore K–Mg geothermometer is not a good indicator of deep temperatures (Mutlu and Güleç, 1998). At temperatures of less than 180°C, the silica solubility is commonly controlled by chalcedony rather than quartz, as suggested by Fournier (1991). Low SiO_2 concentrations of the studied thermal waters indicate that these waters ascend to the surface without equilibration due to rapid circulation. These waters can undergo silica precipitation or mix with dilute cold waters returning to the surface. Accordingly, the temperatures estimated by the chalcedony geothermometers may correspond closely the reservoir temperatures. Therefore, chalcedony geothermometers appear to reflect reservoir temperatures more accurately than quartz geothermometers (Mutlu, 1998). When plotted in a Na-K-$Mg^{1/2}$ diagram (Giggenbach, 1988; Fig. 7) the disequilibrium nature of Pamukkale and Karahayıt thermal waters as well as cold waters, all samples fall within the immature field (shallow or mixed waters). Thus, cation geothermometers do not likely to yield realistic equilibration temperatures. We therefore think that the most reliable estimate of the aquifer temperature lies in the range 57 to 61°C (mean 59°C) for Pamukkale and 41 to 73°C (mean 57°C) for Karahayıt thermal waters based on chalcedony geothermometry.

7. CONCLUSIONS

Pamukkale thermal waters are mean of 33°C, whereas Karahayıt thermal waters are mean 53°C) locations. The cold waters are mean of 13°C. Pamukkale and Karahayıt thermal waters are mostly of Na-Ca-HCO_3-SO_4 type, whereas cold waters are Ca-HCO_3 types. High correlation in some ionic ratios and high contents of some minor elements in the studied thermal waters indicate enhanced water–rock interaction. Pamukkale and Karahayıt thermal waters are oversaturated at discharge temperatures for carbonate (calcite) and silica minerals (quartz) allowing increase to a carbonate- and silica-rich scale and correspond to travertine/tufa precipitation in the discharge area. According to Giggenbach's method, all studied samples from PGF and KGF are far from the full equilibrium, probably reflecting mixing with colder metoric waters during the rise towards the springs. Geothermal reservoir temperatures are estimated as 57 to 61°C (mean 59°C) for Pamukkale and 41 to 73°C (mean 57°C) for Karahayıt thermal waters according to chalcedony geothermometry method.

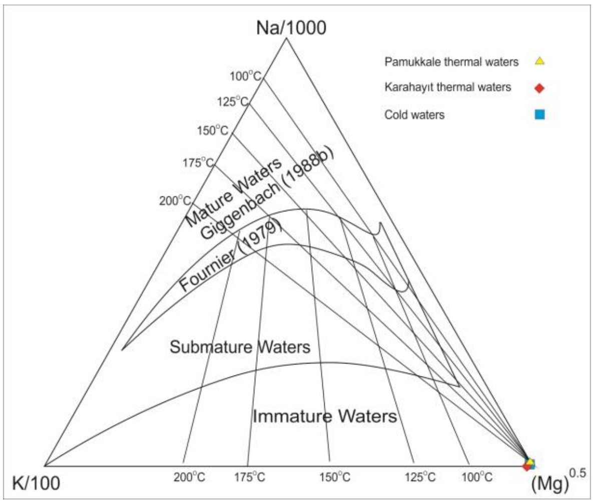

Figure 7: Distribution of the thermal and cold waters from the PGF and KGF in a Na–K–$Mg^{1/2}$ triangular diagram (modified from Giggenbach, 1988)

This study reconstructed main chemical and isotopic compositions of the PGF and KGF to establish a conceptual hydrogeochemical framework. The $\delta^{18}O$, $\delta^{2}H$ and tritium values of Pamukkale and Karahayıt thermal waters indicate their deep-circulating meteoric origin. These waters likely originated from the infiltration of rainwater through fractures and faults to the deep hot reservoir. Subsequent heating occurred by conduction the presence of the high geothermal gradient related to thinning of the continental crust. Subsequently, the waters ascend to the surface along faults and fractures that act as hydrothermal pathways. High $\delta^{13}C$ values (mean of +7,48 ‰ for Pamukkale and +7,76 ‰ for the Karahayıt thermal waters) reflect that the carbon in the thermal waters originated from metamorphic CO_2, whereas cold waters (-8,68 ‰) indicate freshwater carbonate origin.

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