Conceptual hydrodynamic model of the Pamukkale hydrothermal field, southwestern Turkey, based on hydrochemical and isotopic data

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Abstract The results of study on the hydrochemical and isotope characteristics of shallow and deep waters at Pamukkale hydrothermal field Turkey are described in order to obtain a better understanding of the hydrological circulation. The field can be grouped into two groundwater sub-systems; cold water springs of $Ca–HCO_3$ type (10–12 °C), and CO_2-rich thermal waters of $Ca–HCO_3–SO_4$ type (25–58 °C). The occurrence of these water types is closely related to the morphology of the region, where intense tectonism formed horst and graben structures. Hence, two hydrogeological systems were defined: a deep geothermal system which is related to extensive and deep circulation of meteoric water in the regional flow system, and a shallow system which is related to local groundwater flow through sedimentary strata. The meteoric water falling at higher elevations percolates to the local groundwater system at a shallow level and flows to the deep geothermal system. During a deep convection cycle from a recharge to discharge area, the cold water attains heat from the asthenospheric intrusions, causing it to ascend. Variations of chemical and isotopic composition of thermal waters result from their mixing with cool groundwater in a shallow aquifer during their ascent to the surface.

Résumé Les résultats d'une étude portant sur les caractéristiques hydrochimiques et isotopiques de puits phréatiques et profonds situés dans le champ hydrothermal de Pamukkale, sont décrits de telle manière à éclairer le fonctionnement des circulations hydrologiques. Le champ peut étre divisé en deux sous-systèmes d'eaux souterraines, l'un avec des eaux de sources froides (10–12 °C) de type $Ca–HCO_3$, et les eaux thermales (25–58 °C) riches en CO_2 et de type $Ca–HCO_3–SO_4$. L'occurrence de ces types d'eaux est fermement liée à la morphologie de la région, oùne tectonique intense a engendré des structures en horsts et en grabens. Dés lors deux systèmes hydrogéologiques ont été définis : un système profond, qui est lié à la circulation extensive et profonde des eaux météoritiques dans le système régional d'écoulement, et un système phréatique lié aux écoulements locaux des eaux souterraines à travers les strates sédimentaires. Les eaux météoritiques aux altitudes élevées, percolent jusqu'aux systèmes locaux phréatiques, puis coulent jusqu'aux systèmes géothermaux plus profonds. Durant le cycle de convection profond des zones de recharge jusqu'aux zones de décharge, l'eau froide atteint les zones chaudes liées aux intrusions athenosphériques, provoquant la remontée. Les variations de la composition chimique et isotopique des eaux thermales résultent dans leurs mélanges avec des eaux souterraines froides dans les aquifères phréatiques durant leur remontée jusqu'à la surface.

Resumen Se describen los resultados del estudio de las características isotópicas e hidroquímicas de las aguas someras y profundas para obtener un mejor entendimiento de la circulación hidrológica del campo hidrotermal Pamukkale. El campo puede agruparse en dos sub-sistemas de agua subterránea: manantiales de agua fría del tipo $Ca–HCO_3$ (10–12°C) y aguas termales ricas en CO_2 del tipo $Ca–HCO_3–SO_4$ (25–58°C). El ambiente de estos tipos de aguas se relaciona estrechamente con la morfología de la región donde el tectonismo intenso ha formado estructuras extensionales tipo graben y horst. Se definieron dos sistemas hidrogeológicos: un sistema geotermal profundo que se relaciona con la circulación profunda y extensa de agua meteórica en el sistema regional de flujo y un sistema somero el cual se relaciona con flujo local de agua subterránea a través de estratos sedimentarios. El agua meteórica que cae en altas elevaciones percola al sistema local de agua subterránea en un nivel somero y fluye hacia el sistema geotermal profundo. Durante un ciclo de convección del área de recarga hacia la zona de descarga, el agua fría se calienta a partir de los intrusivos astenosféricos lo que ocasiona que asciendan. Como resultado de la mezcla de las aguas recalentadas, con agua subterránea fría en un acuífero somero durante el ascenso hacia la superficie, se derivan variaciones en la composición química e isotópica de las aguas termales.

Keywords Hydrodynamic · Hydrochemistry · Isotope · Hydrothermal · Turkey

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Introduction

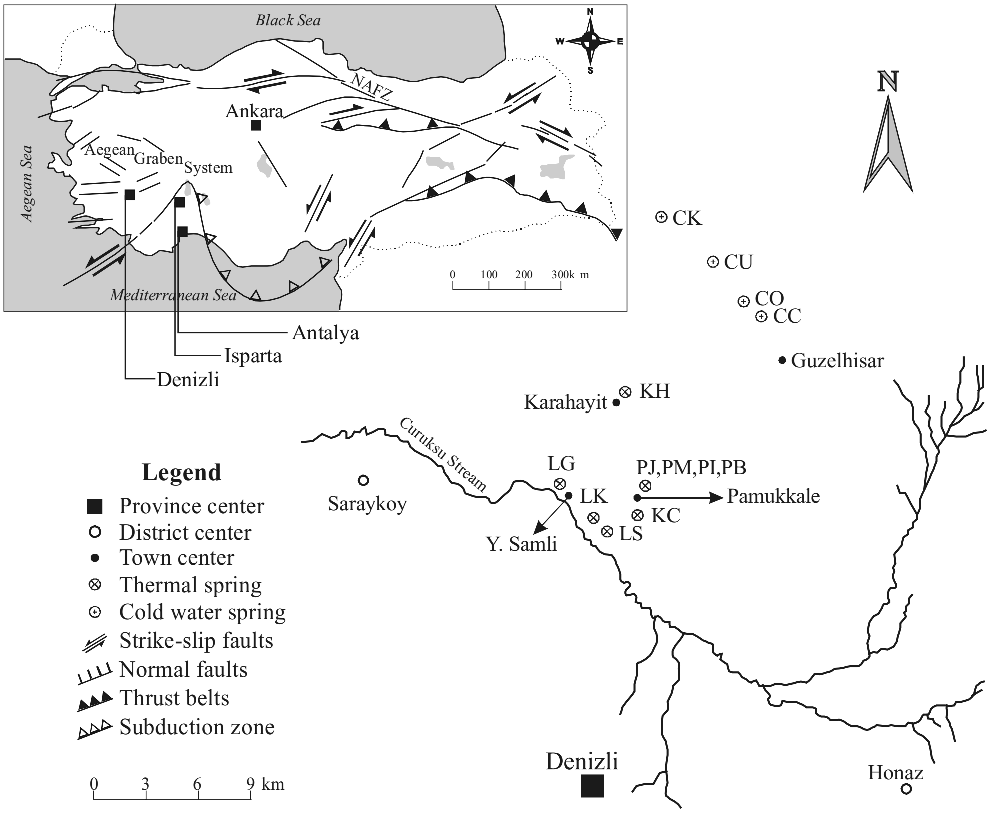
Pamukkale hydrothermal field (PHF) is located on a plateau at a distance of 20 km from the provincial center of Denizli (37° 42′ N, 29° 2′ E) in southwestern Turkey, at an elevation of 350 m a.s.l. (Fig. 1). The field is characterized by numerous thermal and cold springs at different altitudes, the source of which is precipitation. Since the altitude is the dominant control over the precipitation distribution in and around the study area, it varies with the different climatic types that occur in Denizli. The physiography of the region is responsible for a transition in climate which is influenced by Mediterranean, Aegean and inner Anatolian climatic characteristics (Denizli Governorship Ministry et al. 1992). The area is located at the confluence of two main grabens (see Fig. 1) which have an important effect as they act as a corridor which conveys moist westerly winds. The mean annual rainfall of the area is about 837 mm based on the observed rainfall-altitude relationship method for a 20-year record of the closest climate stations (I. Simmers and E. Seyhan, 2002, personal communication). The maximum and minimum monthly rainfall records are ca. 90 mm in December and January and 7 mm in August, respectively. The mean annual temperature is about 16 °C with minimum values of 5.5–7 °C in December and January, and maximum values of 26–27 °C in July and August (I. Simmers and E. Seyhan, 2002, personal communication).

From a hydrological point of view, there is no specific reference to previous work examining the chemical and isotopic characteristics of the water resources at the PHF. Although some studies were carried out in the field (Gokalp 1971; Kocak 1976; Simsek 1985; Esder and Yilmazer 1991; Filiz et al. 1992; Ekmekci et al. 1995; Gunay et al. 1997; Ozler 2000), they do not give information on the characteristics of the underground flow systems, as is detailed as in this study. In order to propose a conceptual model of the underground flow systems at the PHF, the current report discusses the location and the functioning of thermal and cold springs based on chemical and isotopic data. Various graphical and analytical techniques have been used to interpret water–rock interaction processes and the interrelationship between the groundwater systems of different groups of springs that discharge through fault lines and are fed from different recharge areas.

Structural and geological setting

The regional tectonic movements in the Upper Miocene, resulting from the northward movement of the Arabian Plate in the east, created E–W compression and N–S extension regimes in western Anatolia because the North Anatolian Fault Zone (NAFZ) prevented any westward movement of the Anatolian Plate. Simultaneous subduction of the East Mediterranean lithosphere under the Anatolian Plate caused uplift of the Menderes Massif and the intrusion of asthenospheric mantle into the Massif, leading to the formation of the Aegean graben systems, with the Menderes Massif in their center (see Fig. 1). These graben systems are also seen farther to the west in the Aegean Sea area

Fig. 1 Location map of the PHF (simplified tectonic map modified from Altunel and Hancock 1993; Ozpinar 1994). Bordering countries not named on the map: Bulgaria, Greece, Georgia, Armenia, Iran, Iraq, and Syria



(Dewey and Sengor 1979; Jackson and McKenzie 1988; Westaway 1990; Jackson 1994). Further detailed information about the structural geology of western Turkey can be obtained from the references mentioned above along with Kocyigit et al. (1999), Bozkurt (2000), Yilmaz et al. (2000) and Robertson (2000).

Stratigraphically, the oldest rocks in the area are Paleozoic gneisses, gneiss schists, quartzites, mica schists, and marbles of the Menderes Massif. Mesozoic crystalline limestone, whose outcrops are not seen in the field generally, has been superimposed on the Paleozoic material by an allochthonous process. These units are overlain by continental and lacustrine Pliocene sediments divided distinctively into two periods. The Lower Pliocene has three main formations: the Pl1 formation, which consists of red and brown conglomerates, sandstones, and claystones with a total thickness of ca. 250 m; the Pl2 formation, which consists of gray limestones, marls, and siltstones with a total thickness of ca. 270 m; and the Pl3 formation, which is composed of marls, siltstones and sandstones with a total thickness of ca. 200 m. The Upper Pliocene is represented by the Pl4 formation (Plio-Quaternary), which consists of poorly consolidated conglomerates, sandstones, and mudstones with a total thickness of ca. 200 m. The Quaternary formations are characterized by alluvium, slope debris, alluvial fans, and travertines. Alluvium forms agricultural fields in the plain (Esder and Yilmazer 1991; Ozpinar 1994). The travertine deposits, which rise about 200 m higher in elevation than the Lower Curuksu Plain, are about 6 km long, extending between the villages of Pamukkale and Karahayit (Fig. 2).

Pamukkale hydrothermal system

The heat source of the Pamukkale thermal system is asthenospheric intrusions, and the development of these intrusions is related to the intrusion of a granitic pluton in the Aegean region, particularly beneath the Menderes Massif (Sengor and Yilmaz 1981; Bozkurt and Park 1999; Gulec et al. 2002).

There is more than one reservoir in the system because tectonic movements have modified the fracture patterns and created regions of enhanced permeability. The deepest reservoir supplying thermal water is fractured Paleozoic marble and Mesozoic crystalline limestone. These units generally crop out at higher altitudes where they would be recharged by meteoric water. A significant thickness of the limestone with high permeability in Pl2 formation hosts another reservoir. However, the lateral and vertical facies variations with siltstone, claystone, and marl restrict the hydraulic continuity and result in this reservoir containing poor quality water. Units made up of claystone, marl, and sandstone, belonging to the Pl3 and Pl4 formations, cover the Pl2 reservoir and act as an impermeable caprock. The Pl1 formation comprising units of consolidated conglomerates, sandstone and claystone is also a very efficient caprock. The travertine deposits of Quaternary age, with karstic features and a thickness of 75–85 m, contains the youngest reservoir. Data from shallow drillholes in travertine deposits in the Karahayit area indicate that the temperature of the produced water is 55–60 °C (Simsek 1985; Esder and Yilmazer 1991; Filiz et al. 1992; International Research and Application Center for Karst Water Resources, Report on Conservation and Development of Pamukkale Travertines, Phases I Final Reports. Hacettepe University, Ankara, 1994 (unpublished).

The fluid circulation between the reservoir and the surface within the thermal system is largely controlled by a fault and fracture system which is orientated mainly E–W, WNW–ESE and NW–SE (Ozpinar 1994). Tectonic fracturing has enhanced the anisotropic permeability in the Quaternary and Tertiary formations with the important consequence that the thermal springs in the area under consideration represent mixed waters of different ages. During deep percolation from horst to graben through fault zones, driven by the hydraulic gradient, the water becomes heated and then convects upwards within the graben, where permeable structures divert the regional groundwater flow. As it flows upward it mixes with increasing amounts of shallow cool groundwater close to the surface (see Fig. 2).

Sampling procedures

The hydrochemical studies were carried out under varying meteorological conditions to determine the hydrodynamic and chemical response of the hydrothermal system. Water samples were collected and analyzed for physical, chemical, and isotopic parameters in February 1995, representing a wet period, and in September 1995, representing a dry period. Thermal springs are differentiated into three groups including (1) Pamukkale (PJ, PM, PI and PB), (2) Karahayit (KH and KC), and (3) Lower Curuksu Plain (LK, LG and LS). Cold springs are named as CK, CU, CO and CC (see Fig. 1). All water samples were filtered in the field through 0.45-µm filters.

The physical and chemical data used in this study were obtained using conventional in situ measurements and laboratory analysis of the water samples as appropriate. Field measurements of pH, electrical conductivity (EC), temperature (T), free CO_2 (fCO_2) and alkalinity were measured at sampling sites. The concentrations of HCO_3^- and CO_3^{2-} together comprise carbonate alkalinity, and were determined at the laboratory within 24 h. For the remaining analyses, samples were collected and preserved in the field. The concentration of certain dissolved constituents may change between the time of field collection and the time of laboratory analysis owing to loss of gases, temperature changes, and precipitation of solids, e.g., $CaCO_3$. Since the intent of analyses was to represent the real chemistry of water as closely as possible, the samples were treated before being sent to the laboratory to prevent changes before analysis. Samples for cation analysis were acidified to $pH<2$ with 2 ml 65% HNO_3. Samples for anion analysis were untreated and stored at ca. 5 °C to avoid secondary reactions. All analyses were performed in the Water Chemistry Laboratory of the International Research and Application Center for Karst Water Resources at Hacettepe University

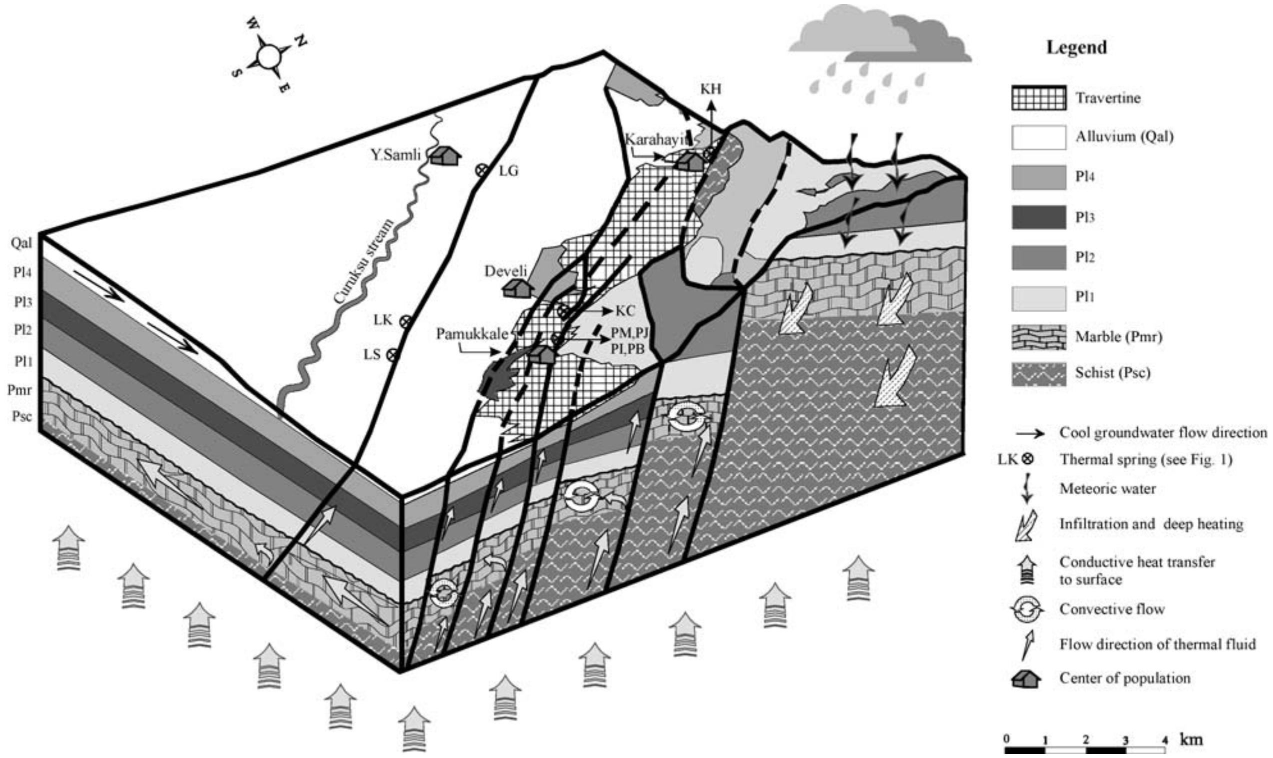


Fig. 2 Three-dimensional schematic hydrogeological model of the PHF (vertical scale is not realistic)

in Ankara. The results of hydrochemical analysis for major constituents of thermal and cold waters in meq l^{-1} have an accuracy better than 5%. The unit used in this report is mmol l^{-1}. Stable isotope compositions of the waters sampled, as discussed in Mozar (1991), are expressed using the usual δ notation reported in units of parts per thousand (denoted as ‰ or permil) relative to a standard of known composition. The standard for $\delta^{18}O$ and δD is V-SMOW, which stands for Vienna Standard Mean Ocean Water.

Results

Hydrochemical aspects

Composite chemical data for thermal and cold spring discharges are presented in Table 1. Based on the chemical composition of the springs, Ca^{2+} and HCO_3^- ions dominate the waters. There are also significant concentrations of Mg^{2+} and SO_4^{2-} (Fig. 3). Chloride, however, is not a major component in thermal and cold springs, in the range between 0.3–1.2 and 0.2–0.7 mmol l^{-1} respectively, and its presence could likely derive from both rainfall itself and anthropogenic pollution, i.e., agriculture, with deposition from fertilizers and animals. Sulfate is probably formed by oxidation of the H_2S gas component in thermal waters because no lithological source was identified in previous studies which would make this ion dominant in the system. In field observations, a rotten egg smell can be detected in the thermal springs and groundwater abstraction wells in the Curuksu Plain which contain sulfide. Sulfide can be removed from the aqueous phase by degassing of H_2S. The boundary between H_2S and SO_4^{2-} is;

$$SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S + 4H_2O \tag{1}$$

Another removal mechanism could be the precipitation of metal sulfide solids that have very low solubilities, i.e., if ferrous iron is available then it will precipitate with sulfide at low temperatures as FeS, and this solid can be converted to crystalline pyrite (Albu et al. 1997; Preda and Cox 2000). The redox reaction is;

$$FeS_2 + 2H_2O + 7O_2 \leftrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{2}$$

Ca–HCO_3–SO_4 type groundwater from Pamukkale thermal springs discharges mainly from four outlets (PJ, PM, PI and PB) at an altitude of 350 m. They exhibit characteristic temperature, pH, and electrical conductivity values with annual variations of 34–36 °C, 5.5–6.0 standard units and 2,700–2,800 μS cm^{-1}, respectively. At the outlets, these thermal waters possess calculated pCO_2 values of the order $10^{0.07}$–$10^{0.5}$ atm, being significantly higher than that of the atmosphere ($10^{-3.5}$ atm). The flow measurements were performed monthly between 1993 and 1998 by International Research and Application Center for Karst Water Resources at Hacettepe University in Ankara, Turkey, for each thermal spring outlet. The total annual average discharge of Pamukkale thermal springs varies between 365 and 385 l s^{-1}. Karahayit thermal waters, emerging from KH and KC springs at elevations of 330 and 300 m respectively,

Table 1 Major ion composition of waters collected from springs (T in °C; fCO_2 in mg l^{-1}; EC in µS cm^{-1}; concentrations in mmol l^{-1}; pCO_2 in atm; *ND* stands for not detected)

Code	Period	T	pH	fCO_2	EC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	CO_3^{2-}	Accuracy (%)	pCO_2
KC	Wet	55.5	6.32	260.0	4,700	11.41	4.01	4.57	0.83	1.20	7.95	23.53	ND	5.72	$10^{-0.07}$
KH		48.0	5.75	225.0	3,900	12.16	4.01	3.26	0.90	1.00	8.31	21.81	ND	3.87	$10^{0.44}$
PM		36.0	5.66	380.0	2,810	10.48	3.50	2.94	0.38	0.50	6.35	18.98	ND	1.46	$10^{0.41}$
PJ		36.0	5.61	330.0	2,800	9.98	3.29	2.50	0.70	0.50	5.52	19.18	ND	1.62	$10^{0.47}$
PI		36.0	5.62	325.0	2,800	9.92	3.09	1.63	0.58	0.60	5.64	19.08	ND	4.67	$10^{0.46}$
PB		35.0	5.55	365.0	2,810	9.61	3.09	2.94	0.45	0.40	6.09	18.98	ND	4.64	$10^{0.52}$
LK		28.0	5.84	115.0	2,310	9.61	3.78	1.70	0.26	0.70	7.33	13.03	ND	0.59	$10^{0.02}$
LG		23.0	5.66	145.0	2,110	9.61	3.46	1.57	0.18	0.70	7.05	14.95	ND	3.26	$10^{0.22}$
CK		12.0	7.2	5.0	260	1.75	0.10	0.48	0.19	0.30	0.05	3.23	0.20	4.08	$10^{-2.00}$
CO		12.0	6.52	5.0	510	2.38	0.25	0.28	0.06	0.60	0.12	4.85	0.20	4.10	$10^{-1.16}$
CC		12.0	6.63	5.0	360	2.21	0.23	0.20	0.03	0.55	0.05	4.65	0.20	5.62	$10^{-1.29}$
CU		12.0	6.79	5.0	378	2.11	0.12	0.39	0.10	0.70	0.09	3.94	0.20	2.60	$10^{-1.51}$
KC	Dry	55.5	6.49	230.0	4,500	11.48	4.32	5.10	1.47	0.90	7.65	21.74	ND	0.28	$10^{-0.28}$
KH		51.0	6.1	350.0	3,990	10.35	4.42	4.76	0.77	0.80	7.74	18.63	ND	0.23	$10^{0.03}$
PJ		34.8	5.95	455.0	2,730	10.23	3.13	1.67	0.13	0.40	5.91	18.63	ND	3.96	$10^{0.11}$
PM		34.7	5.95	480.0	2,700	9.78	3.09	1.68	0.18	0.30	6.05	17.66	ND	4.30	$10^{0.09}$
PB		34.2	5.97	445.0	2,790	10.00	3.13	1.68	0.18	0.40	6.16	17.95	ND	4.34	$10^{0.07}$
LK		30.0	6.27	110.0	2,280	8.01	3.33	2.24	0.18	0.80	6.17	13.30	ND	2.62	$10^{-0.38}$
LS		29.0	6.33	205.0	2,290	8.01	3.46	2.21	0.33	0.50	6.65	12.62	ND	1.86	$10^{-0.47}$
LG		26.0	6.37	220.0	2,510	8.93	4.03	2.91	0.31	0.80	7.69	14.37	ND	2.35	$10^{-0.49}$
CK		12.5	7.5	5.0	260	1.32	0.16	0.08	0.18	0.20	0.05	2.62	0.40	6.92	$10^{-2.31}$
CO		12.0	7.35	5.0	400	2.57	0.33	0.26	0.18	0.40	0.12	4.37	0.50	1.87	$10^{-1.99}$
CC		12.0	7.33	5.0	350	2.25	0.29	0.17	0.18	0.20	0.06	4.18	0.25	3.97	$10^{-2.02}$
CU		13.0	7.41	5.0	370	2.00	0.16	0.26	0.13	0.70	0.10	4.08	0.10	4.72	$10^{-2.13}$

are also Ca–HCO_3–SO_4 type waters but exhibit different chemical concentrations from those of Pamukkale. The groundwater from Karahayit thermal springs is characterized by temperature, pH, and electrical conductivity values with annual variations of 50–56 °C, 6.0–6.5 standard units and 4,000–4,700 µS cm^{-1}, respectively. The measured average total flow rate for both springs is about 2–3 l s^{-1} and the rapid spreading of waters from those thermal springs results in accelerated CO_2-loss as indicated by travertine deposition. Compared with Pamukkale, Karahayit thermal springs deposit travertine in red-brown-yellow color due to relatively higher concentrations of iron and manganese ions. Calculated pCO_2 values at the outlets of KH and KC are in the range $10^{-0.28}$–$10^{0.44}$ atm. Ca–HCO_3–SO_4 type thermal waters from the Lower Curuksu Plain are derived from LG, LK, and LS springs at an altitude of 160 m, and the long-term temperature, pH, and electrical conductivity values have annual variation of 25–30 °C, 5.8–6.4 standard units and 2,100–2,300 µS cm^{-1}, respectively. These groundwaters are characterized by calculated pCO_2 of $10^{-0.49}$–$10^{0.22}$ atm. The measured content of fCO_2 of thermal waters from Pamukkale is up to 480 mg l^{-1}, up to 350 mg l^{-1} from Karahayit, and up to 220 mg^{-1} from the Lower Curuksu Plain. Cold waters that circulate at shallow depths are of the Ca–HCO_3 type and are characterized by the average temperature, pH, and electrical conductivity values of 10–12 °C, 6.5–7.5 standard units and 250–500 µS cm^{-1}, respectively. The emergence altitudes of sampled cold springs vary from 1,000 m to a maximum of 1,100 m. CU, CO and CC cold springs have a flow rate of 6–8, 4–5 and 2–3 l s^{-1}, respectively. The estimated flow rate of CK is of 1–2 l s^{-1} (International Research and Application Center for Karst Water Resources, Report on Conservation and Development of Pamukkale Travertines, Phases II Final Reports. Hacettepe University, Ankara (unpublished) 1995).

The highest values of CO_2 are in the thermal fluids at the PHF; water vapor samples from Pamukkale and Karahayit thermal springs have 69–86 and 66–90% CO_2, and in water samples there is 69–85 and 67–84% CO_2, respectively (Selcuk 1996). The considerable source of CO_2 has been suggested by Simsek et al. (2000) and Ozler (2000) as coming from the decomposition of carbonate rocks, releasing CO_2 as a result of thermometamorphic or hydrolysis reactions in the Paleozoic marbles and Mesozoic limestone, while, as mentioned in Vengosh et al. (2002), another source suggested by Filiz (1984) and Ercan et al. (1994) are magmatic emanations. However, due to a study by Gulec et al. (2002), the $^3He/^4He$ ratio in gas samples in Pamukkale thermal springs is about 5.05×10^{-6}, referring to an air-corrected R/R_A sample ratio of 3.63 (where R = sample $^3He/^4He$ and R_A = air $^3He/^4He$). This value is higher than that for crustal production (ca. 0.05), revealing the presence of mantle-derived gas. Consequently, considering the above-cited scientific studies, both decomposition of carbonate rocks and magmatic emanations are the main sources of carbon dioxide in relative ratios.

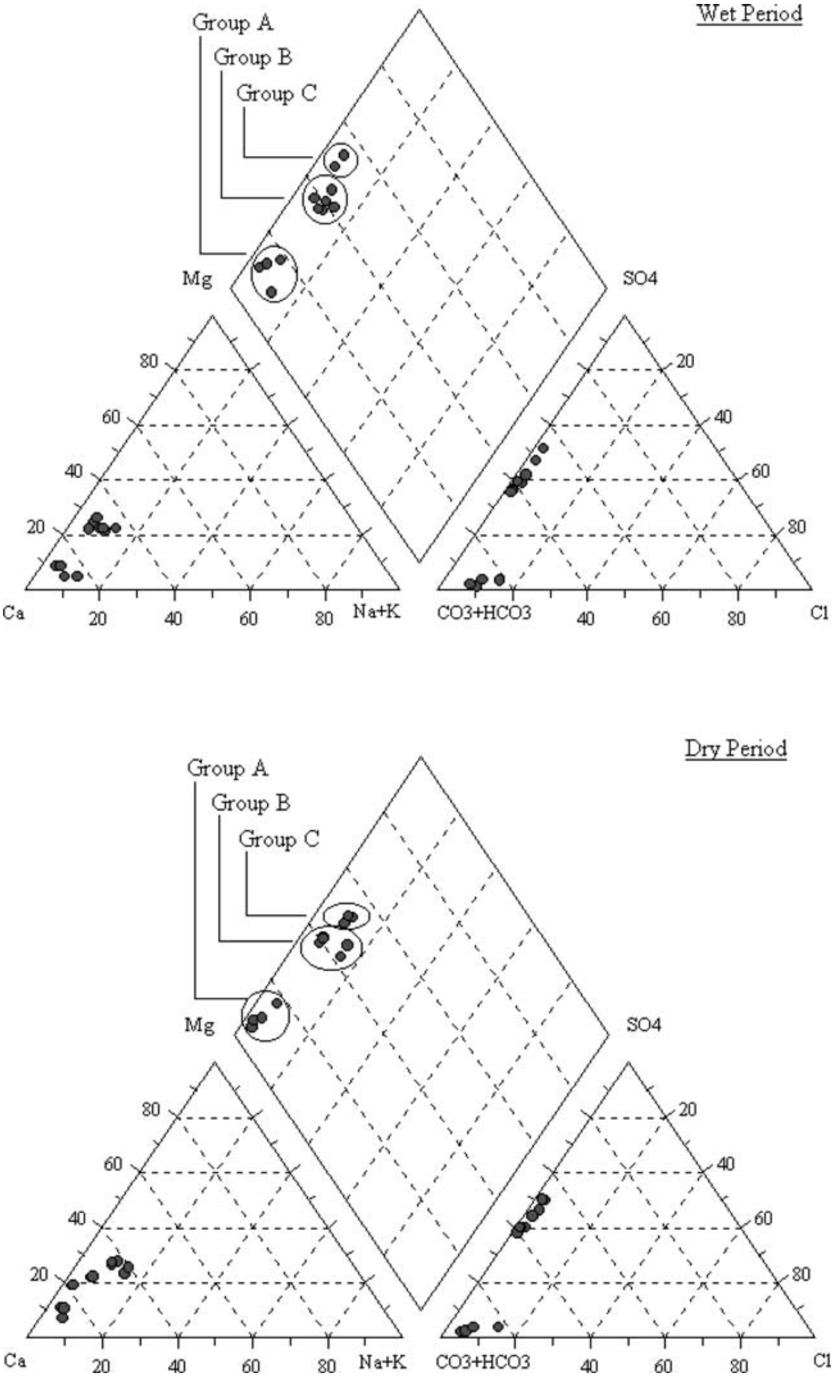


Fig. 3 Piper diagrams representing wet and dry periods (*Group A* Cold Springs; *Group B* Pamukkale and Karahayit thermal springs; *Group C* Plain thermal springs)

Saturation index (SI) and CO_2 partial pressure (pCO_2)

Major ion activities and saturation index values with respect to the minerals anhydrite, aragonite, calcite, dolomite and gypsum were calculated for all water samples by using the PHREEQC-2 computer program (Parkhurst and Appelo 1999), and they pertain only to the location where the samples were collected. The program calculates the saturation state of the water with respect to solid mineral phases and the resulting values indicate whether the solution is undersaturated (negative SI value), supersaturated (positive SI value), or at equilibrium (SI=0) with respect to the mineral in question.

The SI calculations paradoxically reveal that the thermal waters, except Karahayit thermal springs (KH and KC), are undersaturated with anhydrite, aragonite, calcite, dolomite, and gypsum minerals (Fig. 4). The precipitation of travertine depends on the abundance of Ca^{2+} and HCO_3^- ions, and consequently solutions must be supersaturated with respect to calcite. The fluids probably are in chemical equilibrium or supersaturated with respect to calcite, and possibly also aragonite and dolomite deep underground.

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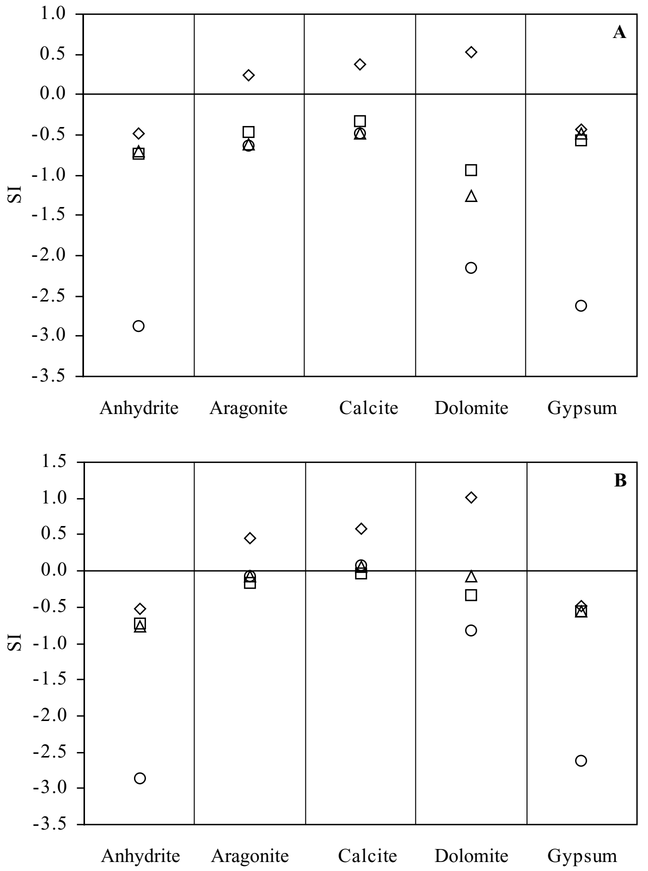

Fig. 4 Saturation Index (SI) variations with respect to minerals for spring samples (**A** wet period; **B** dry period; ☐ Pamukkale thermal springs; ◊ Karahayit thermal springs; △ Plain thermal springs; ○ Cold springs)

It is important to know at what depth the upflow channels attain super-saturation, but this cannot be specified due to lack of in situ data from wells because drilling activities are strictly forbidden. At the point of discharge of Pamukkale and Curuksu Plain thermal springs, the high artesian head (ca. 2−>10 m), evidence of the impermeable character of the caprock, could hinder the rapid outgassing of CO_2 into the atmosphere. The acidity of thermal waters is, therefore, increased by the dissolved CO_2 and that means the saturation of mineral species diminishes. Owing to the extensive discharge area of groundwater outflow from Karahayit thermal springs along with low discharge rates, CO_2 is rapidly outgassing into the atmosphere. In this respect, precipitation of travertine takes place near the outlet of these thermal springs and saturation indexes exhibit the highest values with respect to carbonate minerals.

The thermal springs must have already started to nucleate and precipitate carbonate minerals at the subsurface. As all the thermal springs appear to emit bubbles of CO_2 at the point of emergence from the ground, the calculated pCO_2 values in the upward flowing water are much greater (as high as ca. 3 atm) than the local atmospheric pressure. When the CO_2-saturated thermal water flows upward, the dissolved CO_2 effervesces. This separation into the gas phase increases the pH of the solution and leads to a supersaturated condition with respect to carbonate minerals, which then precipitate at some depth tending to seal the fracture system. However, the accumulation of extensive travertine deposits at Pamukkale has been progressing over a very long period of time, ca. since Late Pleistocene. During this period, the climatic and hydrological variations in the region must have played a significant role as to where the $CaCO_3$ precipitates more progressively. For example, the boiling process causes supersaturation at depth while further boiling causes an increase in calcite solubility because of further decrease of the temperature, leading to carbonate precipitation at the surface as white travertine. The SI for anhydrite and gypsum shows that the waters are undersaturated with sulfate minerals, though they are generally considered to be reactive minerals. Sulfate minerals have no significant response in wet and dry periods in Fig. 4 because no lithological unit exists in the aquifers to supply these minerals.

Cold springs that are located near the recharge area where total dissolved ions are low and exhibit non-saturation conditions. Reactions between rainfall and aquifer material during percolation give the groundwater its essential mineral character. The extent of reaction in the aquifer will be controlled by the residence times of the water and the primary mineralogy of the aquifer (Edmunds and Smedley 1996). Hence, negative values of the SI may represent the initial stage of the groundwater circulation within the aquifer because they may not had sufficient time to proceed to equilibrium conditions with the carbonate minerals.

Geothermometry

This section is specifically intended to clarify the application of cation geothermometers to Pamukkale thermal waters because many authors previously suggested different reservoir temperatures which were estimated by inappropriate geothermometers.

Geothermometers are based on the equilibrium of temperature-dependent reactions that occur in the reservoir (Fournier 1992). These reactions become slower as temperature decreases allowing the temperature at which they occur to be estimated. Geothermometers can re-equilibrate and provide erroneous temperatures if water mixing occurs after equilibrium (Portugal et al. 2000). As shown in Fig. 5, all thermal waters in the PHF are immature, which represents dissolution of rock without reaching chemical equilibrium. The reservoir temperature estimations using K^2/Mg or Na/K geothermometers (Giggenbach 1988) could produce doubtful results. However, the assumptions required in using the Giggenbach ternary diagram, i.e., Na and K fixed by exchange of cations between feldspars, and pH fixed by hydrolysis reactions involving feldspars and clay (Fournier 1992), are not likely to be valid for the thermal waters in the PHF.

The deep waters in the PHF have long reaction times to equilibrate in the deepest reservoirs, and the apparent immaturity of thermal waters may be due mostly to the mixing, but also may be due in part to a different mineral suite controlling cations and to pH being controlled

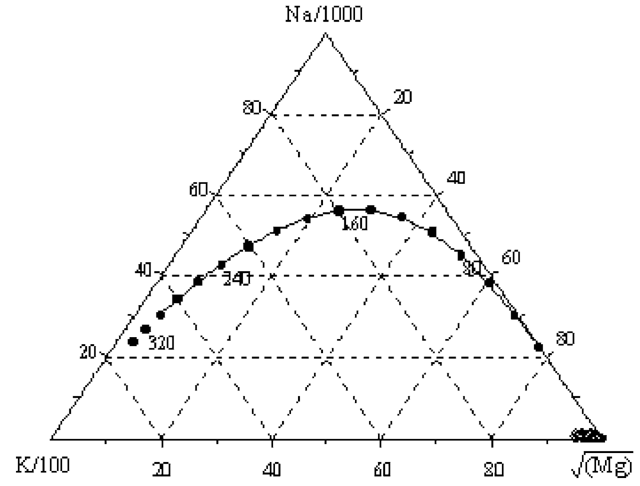

Fig. 5 Water-rock equilibration for thermal springs (Na, K and Mg concentrations in mg kg^{-1})

by CO_2. Therefore, the thermal waters, which are a mixture of waters, are not appropriate for the usual application of chemical geothermometers. The dissolved silica concentration of the mixed water and enthalpy-silica diagram might be used to determine the temperature of the thermal water component (Fournier 1992). The range of SiO_2 concentrations for thermal waters is 114–230 mg l^{-1}, and the value for cold waters is 20 mg l^{-1} (Ozler 2000). The application of the enthalpy-silica mixing model using the chalcedony solubility curve, to which the thermal waters plot very closely, gives a reservoir temperature between 60 and 90 °C. Filiz et al. (1992) and Caglar (1994) calculated the reservoir temperature of Pamukkale and Karahayit thermal springs using silica (chalcedony) geothermometry in the ranges 63–93 and 76–82 °C, respectively. The chart in Fig. 5 also provides evidence that the chemical evolution of thermal springs is controlled by simple crustal dissolution processes at a temperature below 100 °C.

Isotopic composition

Environmental isotope data (^{18}O and ^{2}H stable isotopes, and ^{3}H radioactive isotope) were measured at representative sampling points to provide useful information on sources of water and processes in the area. Figure 6 shows that the $\delta^{18}O$ and δD values of samples vary in the range of >−9.4 to >−8.5‰ and −57.1 to >−61‰, respectively, for thermal springs. For cold springs, the values vary from −8.1 to −8.45‰ and −55.50 to −56.0‰, respectively (Table 2). Nearly all water samples plot between $\delta D = 8\delta^{18}O + 10$ of the Global Meteoric Water Line (GMWL) defined by Craig (1961) and $\delta D = 8\delta^{18}O + 14.6$ of the Lake District (LD), which contains several lakes around Isparta province (see Fig. 1 for location). The meteoric water line of LDMWL is from the State Water Works (1989). This suggests that the springs in and adjacent to PHF are fed from meteoric water whose isotopic composition is different from the composition of meteoric water from the Antalya area (see Fig. 1 for location), which is characterized by $\delta D = 8\delta^{18}O + 18.6$ of the Antalya Meteoric Water Line (AMWL).

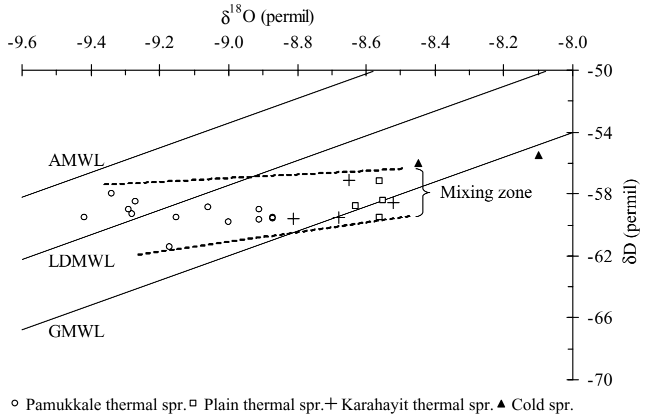

Fig. 6 $\delta^{18}O$ and δD relationship of water samples

The main noteworthy observation regarding the stable isotope composition of the water samples collected in the field is the absence of the evaporation effect on the isotopic composition, which means that the recharge of the reservoir is quite rapid and the recharging meteoric water does not occupy the soil zone of the recharge area for a long time. Only the cold and the Curuksu Plain thermal springs show a proximity to GMWL.

Table 2 Isotopic composition of thermal and cold springs

Code	Date (mm/yy)	$\delta^{18}O$ (‰)	δD (‰)	^{3}H (TU)
PM	11/93	−9.42	−59.50	3.30
PB	11/93	−9.28	−59.30	3.70
PJ	11/93	−9.29	−59.00	4.10
PI	11/93	−9.27	−58.50	4.20
PM	11/94	−9.10	−80.20	3.60
PB	11/94	−9.08	−63.40	4.20
PJ	11/94	−9.00	−59.80	4.00
PI	11/94	−9.17	−61.40	4.20
KC	11/94	−8.81	−59.60	0.80
KH	11/94	−8.65	−57.10	0.80
LK	11/94	−8.56	−57.20	4.00
LG	11/94	−8.56	−59.50	3.20
PM	12/94	−8.87	−59.50	4.30
PB	12/94	−9.34	−58.00	3.90
PJ	12/94	−8.91	−59.00	4.00
PM	02/95	−9.06	−58.90	4.10
PB	02/95	−8.91	−59.70	4.50
PJ	02/95	−8.87	−59.60	4.50
PI	02/95	−9.15	−59.50	3.60
KC	02/95	−8.52	−58.60	0.30
KH	02/95	−8.68	−59.50	0.90
LK	02/95	−8.55	−58.40	3.10
LG	02/95	−8.63	−58.80	2.90
CK	02/95	−8.45	−56.00	17.40
COr[a]	02/95	−8.10	−55.50	14.80

[a] *COr* Ca–HCO_3 type cold spring (T=10 °C): not shown in Fig. 1 (located ~2 km NE from the town of Pamukkale)

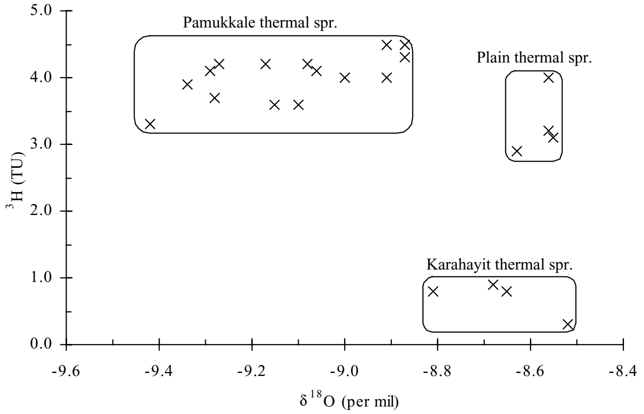

Fig. 7 $\delta^{18}O$ and ^3H relationship of water samples (cold water springs are not on the figure because their tritium concentrations are higher than those of thermal waters)

The waters with the same or a similar origin, i.e., thermal waters characteristic of deep regional origin or the cold waters characteristic of shallow origin, plot clustered together on the $\delta^{18}O$ and ^3H chart (Fig. 7). Since tritium is a radioactive isotope, the evaluation of $\delta^{18}O$ and ^3H together provides considerable support for estimating the relative elevations of recharge area and the residence time of water in a reservoir.

More negative values of ^{18}O are considered to indicate a relatively high elevation recharge area, and low tritium values represent a relatively long travel time. It can be concluded from Fig. 7 that Pamukkale thermal springs are fed from higher elevations than the source of Karahayit thermal springs. In addition, however, the source of Karahayit springs is also relatively high but they have a longer residence time. Cold springs have the highest ^3H values indicating the shortest time of underground circulation. The existing distinct correlation between $\delta^{18}O$ values and the elevation of the source of the cold springs presented by the International Research and Application Center for Karst Water Resources (Report on Conservation and Development of Pamukkale Travertines, Phases III Final Reports, 1996. Hacettepe University, Ankara (unpublished) 1996), defines the depletion for $\delta^{18}O$ of about $-0.5‰$ per 100 m rise in altitude and this result agrees with the upper part of the overall range for altitude effect in $\delta^{18}O$ (-0.15 to $-0.5‰$ per 100 m rise) stated by Clark and Fritz (1997). The isotopic gradient of $\delta^{18}O$ indicates that the Pamukkale, Karahayit and Curuksu Plain thermal springs are recharged from meteoric waters at altitudes of ca. 750, 600, and 550 m, respectively. These estimations are interpreted as average recharge elevations and they correspond to the natural topographic situation in the study area. Within the Karahayit thermal system, the transmissivity of the aquifer is relatively low (International Research and Application Center for Karst Water Resources (unpublished) 1996), so that there is a longer traveling time of thermal water through that aquifer. Because of the extensive fracture network around Pamukkale, thermal groundwater rises easily towards shallow depths where it mixes with cooler groundwater. The similarity in ^3H contents of the Pamukkale and Curuksu Plain thermal springs suggests that the groundwater system is well mixed.

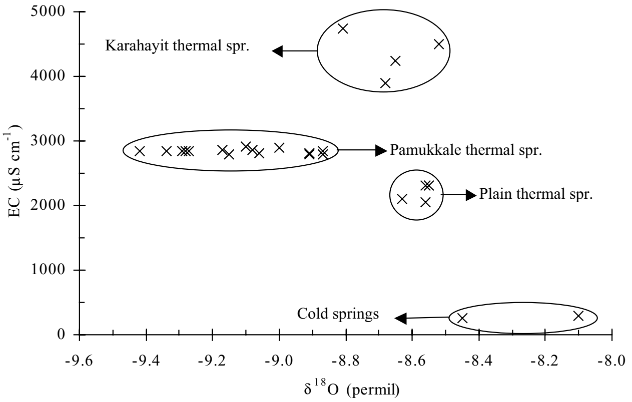

Fig. 8 $\delta^{18}O$ and EC relationship of water samples

The conductivity and total dissolved solid values provide a good indication of the interaction time between the water and reservoir rock. In Fig. 8, the ion concentrations increase from cold springs towards Karahayit thermal springs. Whereas Karahayit thermal springs are represented with high EC values, cold springs are represented with high $\delta^{18}O$ values. It must be emphasized that, although Pamukkale thermal springs originate in higher recharge areas, their ion concentrations are lower than those of Karahayit because of mixing with shallow cool groundwater.

The relationship between ^3H and EC gives valuable information about the circulation between recharge (represented by cold springs) and discharge points (Fig. 9). The presence of ^3H in thermal springs indicates a possible intermixing between deep and shallow groundwaters. The mixing process may result from direct infiltration of local meteoric water for thermal springs at the PHF, but lateral inflow of river water is another considerable mechanism for the Curuksu Plain thermal springs. Generally, the ^3H content of the fluids decreases as the salinity increases and the lowest values of ^3H represent a long circulation period (e.g., Aranyossy 1985; Mozar 1991; Shevenell and Goff 1995; Stimson et al. 1996). Karahayit thermal springs, with the highest EC and lowest ^3H values, have a greater depth of

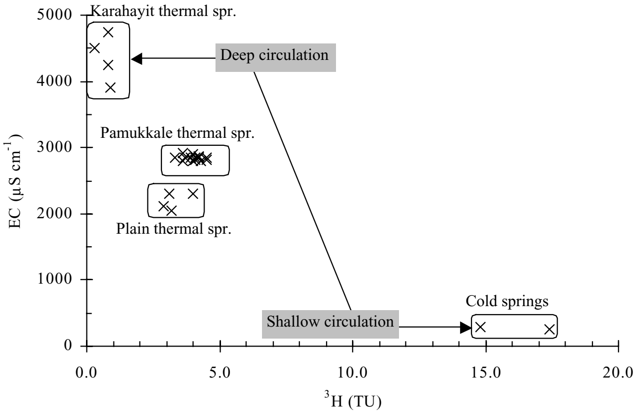

Fig. 9 ^3H and EC relationship of water samples

circulation and hence a much longer time of residence. The Pamukkale and Curuksu Plain thermal springs plot between deep and shallow circulation on the chart, but close to the Karahayit spring group. Cold springs represent shallow and fast circulation since they are affected very rapidly by recent rainfall events. The ^{3}H contents of Pamukkale thermal springs are higher than those of Karahayit, which are the most mineralized and better characterize the hydrothermal system in the field. The less mineralized springs involved in the mixing therefore should be the younger ones, and their deuterium values can be very negative if their Cl^- content is relatively low. From this observation, it seems a reasonable assumption that the deeper (and oldest) water must be the more mineralized end member.

Conclusion

In the present study, the sampled thermal springs (Pamukkale, Karahayit and Curuksu Plain) and cold springs in the Pamukkale hydrothermal field were characterized in terms of chemical and isotopic compositions and the conceptual underground flow systems were proposed. Cold water springs with temperatures of 10–12 °C, characterizing groundwater circulation at shallow depths, are of the Ca–HCO_3 type. In contrast to the shallow environment, the CO_2-rich, deeper thermal waters with temperatures of 25–58 °C are of the Ca–HCO_3–SO_4 type, and undergo significant changes in the baseline chemistry along flow lines with increasing residence time. Chloride is not a major component in thermal and cold springs and its presence could likely be derived from both rainfall and anthropogenic pollution. Sulfate is possibly formed by oxidation of the H_2S gas component in thermal waters. The considerable source of CO_2 is thought to be derived from magmatic emanations.

Two hydrogeological systems were defined in the study area: (1) a deep thermal system, which is related to extensive and deep circulation of meteoric water in the regional flow system where the influence of shallow waters is relatively small, and (2) a shallow system, which is related to shallow circulation, and is affected very rapidly by recent rainfall events. The Pamukkale and Curuksu Plain thermal springs are controlled both by the regional and local flow systems, and their chemical and isotopic compositions are the result of mixing processes with cool groundwater. The Karahayit thermal springs, as a thermal end member, characterizes the hydrothermal system better at the field. The vertical communication between aquifers is facilitated by a series of mainly NW-SE trending normal faults, forming the horst and graben structures of the Curuksu Plain and is restricted by the low permeability of the geological formations.

The hydrochemical evidence indicates that thermal waters issuing from the Pamukkale and Karahayit springs flow through separate geothermal systems or systems that are not hydrologically connected. This interpretation suggests that the apparent lack of hydrologic connection between these two thermal systems results from either a lack of permeable pathways or the presence of structural barriers.

The fluids, except for the Karahayit thermal springs, are undersaturated or almost at equilibrium with respect to carbonate minerals. A possibility could be that the waters have already started to nucleate and precipitate in the subsurface. However, many processes have been acting to perturb the systems—i.e., variable mixing, recharge, rock dissolution, rock alteration, and other water-rock interactions—and these processes occur to varying degrees in different locations. The saturation index (SI) for sulfate minerals shows the waters to be undersaturated because these minerals are not present in the aquifer.

All the underground flow systems are fed by meteoric water. The Pamukkale thermal springs are fed from recharge at the highest elevations and the Karahayit thermal springs have a relatively more distant and lower recharge elevation. Although the Pamukkale thermal springs are derived from a higher recharge area, they have lower ion concentrations than those of the Karahayit springs because the Pamukkale thermal waters are diluted by cool shallow groundwater prior to discharge to the surface. The presence of ^{3}H in thermal springs also indicates the possible intermixing of deep thermal fluid with shallow water that had been recently recharged. The mixing mechanism may result from direct infiltration of local meteoric water for thermal springs at the PHF, but lateral inflow of river water is another major source for the Curuksu Plain thermal springs.

The Karahayit thermal springs, with the highest electrical conductivity (EC) and the lowest ^{3}H values on a graph showing the relationship of these variables, have the greatest depth of circulation as confirmed by the outlet temperatures of the springs, and hence a much longer time of residence in the reservoir. On the same graph, the Pamukkale and Curuksu Plain thermal springs are plotted between deep and shallow circulation, but close to the Karahayit spring group. Cold springs represent shallow and fast circulation since they are affected very rapidly by recent rainfalls.

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