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ORIGINAL ARTICLE

Hydrogeochemical and isotopic composition of a low-temperature geothermal source in northwest Turkey: case study of Kirkgecit geothermal area

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Abstract Chemical and isotopic compositions of three hot springs and one cold spring in the Kirkgecit geothermal field, located 15 km southwest of Canakkale-Biga in the northwest of Turkey, were monitored five times during 2005 and 2007. The physico-chemical characteristics of the hot springs are average discharge 3–3.5 L/s, surface temperature 45–52°C, pH 8.9–9.3, and electrical conductivity (EC) 620–698 μS/cm. The cold spring has a temperature of 12–13°C, pH 7.5–8.3, and EC 653–675 μS/cm. The hot waters are Na-SO_4 type, whereas the cold water is Ca-HCO_3 type. Chemical geothermometers suggest that the reservoir temperature is around 80–100°C. The isotopic data (oxygen-18, deuterium and tritium) indicate that the thermal waters are formed by local recharge and deep circulation of meteoric waters.

Keywords Geothermal · Hydrogeochemistry · Isotope · Kirkgecit · Turkey

Introduction

Turkey is one of the most seismically active regions in the world. Its geological and tectonic evolution has been dominated by the repeated opening and closing of the Paleozoic and Mesozoic oceans (Dewey and Sengor 1979; Jackson and McKenzie 1984; Baba and Ármannsson 2006). It is located within the Mediterranean Earthquake Belt, whose complex deformation results from the continental collision between the African and Eurasian plates (Bozkurt 2001).

The distribution of hot springs in Turkey roughly parallels the distribution of the fault systems, young volcanism, and hydrothermally altered areas (Simsek 1997; Mutlu and Gulec 1998; Baba and Ármannsson 2006) (Fig. 1a). The geothermal fields of western Turkey have high enthalpies combined with large variations in chemical compositions. The major high-enthalpy geothermal fields of Turkey are Kizildere (200–240°C), Omerbeyli–Germencik (232°C), Canakkale–Tuzla (174°C), Simav–Kutahya (165°C) and Izmir–Seferihisar (232°C) (Simsek and Gulec 1994; Gokgoz 1998; Vengosh et al. 2002). About 1,000 hot and mineral spring areas have also been identified, most associated with low or medium-enthalpy geothermal systems (MTA 1980; Simsek 1988). There is widespread use of these thermal waters in space heating, power generation, greenhouses, spas, balneotherapy, and other hot spring facilities.

The province of Canakkale, which covers almost all of the Biga Peninsula, is closely related to active tectonic zones because it is located in the western part of the North Anatolian Fault Zone (NAFZ). For this reason, there are various geothermal systems with associated hot water springs in the region (Fig. 1b). Most of these areas have been studied, e.g., by Erdogan (1966), Samilgil (1966), Urgun (1971), Ongur (1973), Karamanderesi and Ongur (1974), Karamanderesi (1986, 1994), Gevrek and Sener (1985), Mutzenberg (1990, 1997), Sener and Gevrek (2000), Pehlivan (2003), Baba (2003), Baba and

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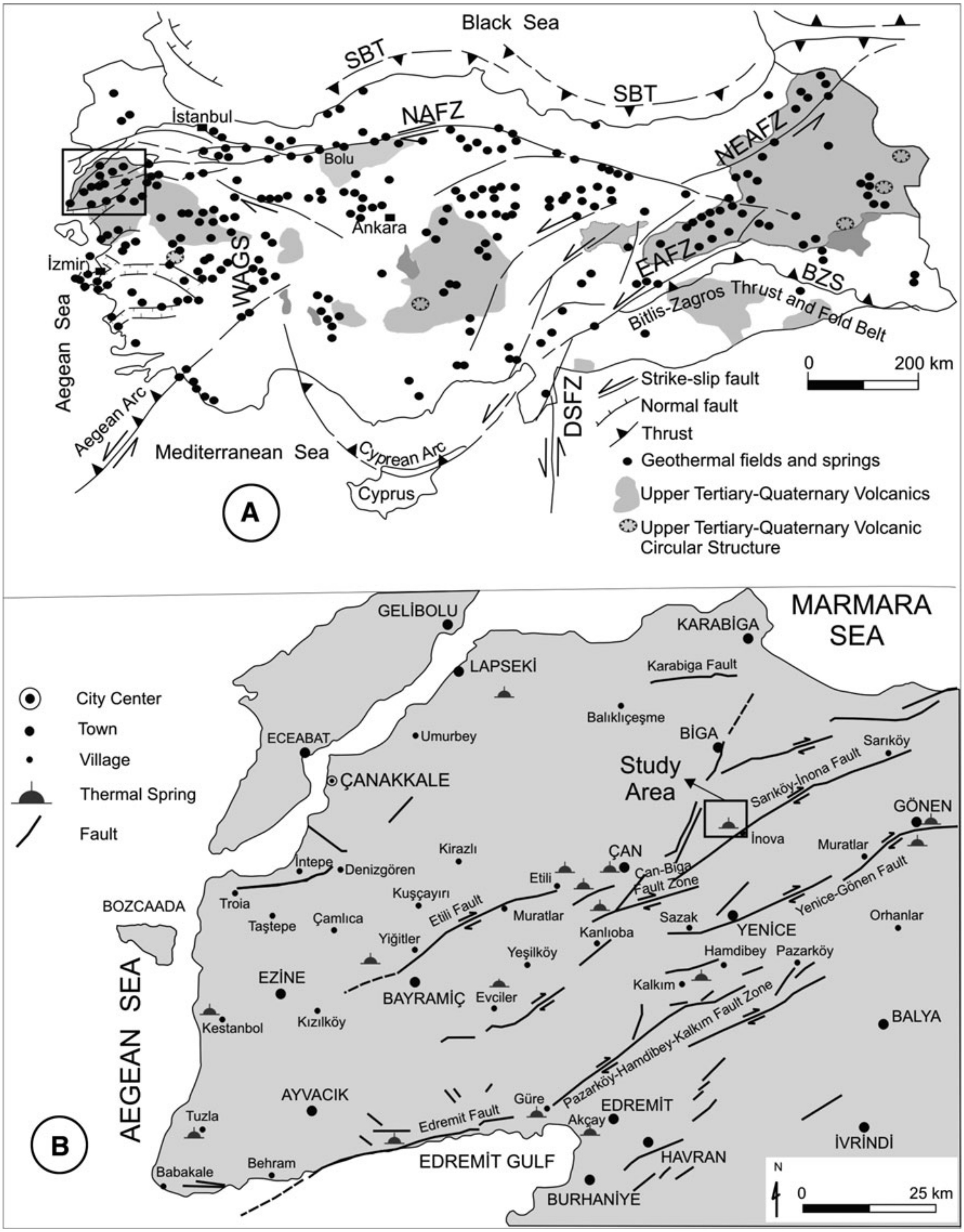

Fig. 1 **a** Tectonic map of the eastern Mediterranean region showing structures developed during the Miocene to Holocene time and distribution of hot water supplies around Turkey (compiled from; Simsek et al. 2002 and Yigitbas et al. 2004). (*SBT* Southern Black Sea Thrust, *NAFZ* North Anatolian Fault Zone, *NEAFZ* Northeast Anatolian Fault Zone, *EAFZ* Eastern Anatolian Fault Zone, *WAGS* Western Anatolian Graben System, *DSF* Dead Sea Fault Zone, *BZS* Bitlis-Zagros Suture.) **b** Tectonic and geothermal area of Biga Peninsula (modified from Saroglu et al. 1992)

Ármannsson (2006), Yalcin (2007), Sanliyuksel and Baba (2007), Baba et al. (2007), Sanliyuksel (2008) and Sanliyuksel and Baba (2008). The tectonic zones and geological units cropping out in this region have been investigated, together with the chemical composition of hot spring waters.

The present investigation was carried out to determine the hydrogeological, hydrogeochemical, and isotopic characteristics of the Kirkgecit geothermal springs. Kirkgecit geothermal area, which is affected by the North Anatolian Fault's western extensions and by the West Anatolian Graben system, is located in the Biga Peninsula. The geothermal area is approximately 15 km southwest of Biga, a town in the province of Canakkale, and is one of the most important geothermal areas in the Biga Peninsula (Fig. 1b). Thermal waters in the study area have been used for balneological purposes and bathing since the Genoese period. Nowadays this geothermal source is used for bathing, heating, and balneological purposes, and the potential of the area is high on the list of priorities for economic evaluation. Although the thermal springs have been known since historical times, only a few broad-brush studies of the Kirkgecit geothermal field are available, and there is a need for a detailed study of the hydrogeological, hydrogeochemical and isotopic characteristics of the Kirkgecit geothermal springs. The current study addresses the basic characteristics of the water chemistry.

Materials and methods

For the investigation and comparison of the hydrogeochemical characteristics, geothermal fluids from natural springs were sampled at outlet conditions on five occasions between 2005 and 2007. Three geothermal springs and one cold water spring were monitored in the study area. The concentrations of major ions, some heavy metals, oxygen-18 (^{18}O), deuterium (^{2}H), and tritium (^{3}H) were determined in the water samples.

During the field surveys, some physical parameters of the geothermal source, including temperature (°C), pH, and electrical conductivity (EC, μS/cm), were measured in-situ with a WTW Multi 340i/SETS. The pH-meter was calibrated with pH 4, pH 7, and pH 10 buffer solutions before commencing field work. In order to determine the variation in mineral content of the water samples, they were collected in unused 50, 500, and 1,000 mL hard-plastic bottles. To prevent the formation of heavy metal complexes with oxygen, samples were acidified with HNO_3 to $pH < 2$. Acidified samples were analyzed for major and trace elements with an ICP-MS (inductively coupled plasma mass spectrometer) at ACME Labs (Canada). A non-acidified sample was used for anion analyses. Chlorine and HCO_3 were determined volumetrically and SO_4 by a gravimetric method. Samples for determination of ^{2}H and ^{18}O content were analyzed at DSI-Ankara (State Water Works) Isotope and Environmental Laboratory. The tritium (^{3}H) analyses were carried out at Hacettepe University using the Liquid Scintillation Counting Method of the IAEA (International Atomic Energy Agency).

Geological and hydrogeological settings

Turkey is located within the Alpine–Himalayan orogenic belt. Seismically active regions are concentrated along high-strain zones, many of which are major strike-slip faults, such as the North Anatolian fault (Ketin 1956, 1968), East Anatolian transform fault (Dewey and Sengor 1979) and graben zones (e.g. Buyuk Menderes graben, Kucuk Menderes graben, Gediz graben, Simav, Manyas, Kizilcahamam) (Sengor et al. 1985) (Fig. 1a). The North Anatolian Fault Zone (NAFZ) splits into three branches in the Marmara Region, where it is located on the northwest part of Turkey, which is a transition zone between the strike–slip tectonics manifested by the NAFZ and the N–S directed extensional regime of western Anatolia (Gurer et al. 2003). This region is characterized by a number of approximately east–west trending, subparallel normal fault zones bordering a set of grabens and intervening horst blocks. The study area is located in the NAFZ where the high-grade metamorphic rocks of the Kazdag mountain range, termed the Kazdag group, crop out under the Karakaya complex in northwestern Turkey. Karakaya complex is the basement rock in the study area. Previous researches in the study area have identified three different lithological units in Karakaya complex. The lithological units, consisting of the Nilufer, Hodul, and Cal units (Okay et al. 1990) belonging to the Triassic Karakaya complex, are in the form of tectonic slices (Yalcin, 2007). The Nilufer unit consists mainly of metabasalts, metatuffs, phyllites, schists, and marbles. The Hodul unit overlies the Nilufer unit tectonically, is represented by arkosic gravel, sandstone, and gray colored shale. Spilite and recrystallized limestone blocks have also been identified in unit. The Cal unit which contains spilite, greywacke, shale and different sized limestone blocks of Permian age, and olistostromes with spilite blocks overlies the Hodul unit. Early-Middle Miocene-aged Biga volcanics, which consist of rhyolite, perlite, and agglomerate, rest unconformably on the Karakaya complex. Quaternary alluvium overlies all the units unconformably (Fig. 2).

Fault and fracture zones are very important for the movement and storage of water. The hydrogeological structure of the Kirkgecit hydrothermal system is largely controlled by the extension of the North Anatolian fault system. This fault has also played an important role in the morphology of the region. The Sarikoy Inova fault, of the study area in a NE–SW direction, is the most important tectonic structure the area. Water in the geothermal region flows to depth via fractures and is heated by the Biga

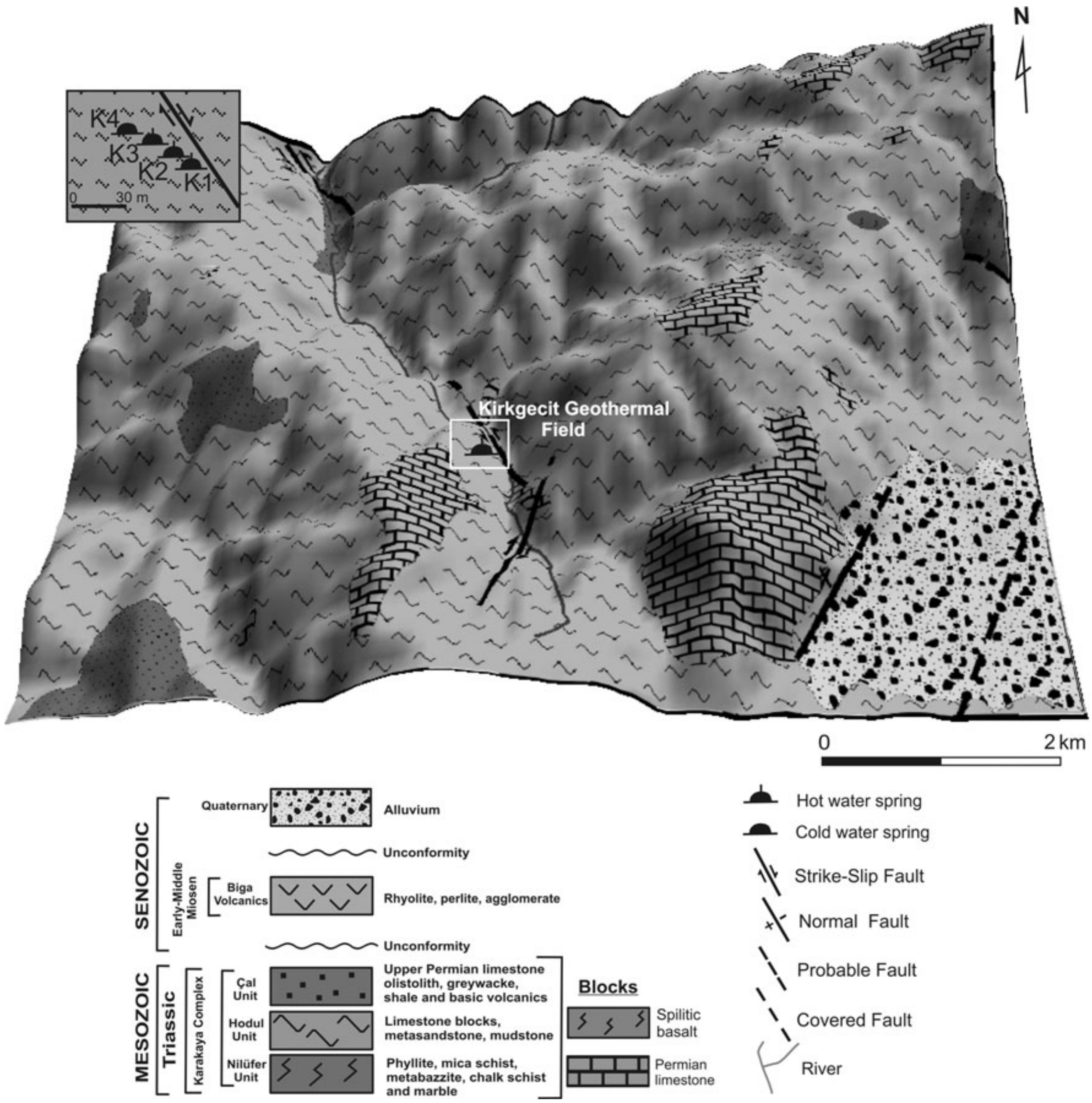

Fig. 2 Geological map of Kirkgecit geothermal area, Turkey

volcanics, which can be seen in outcrop in the northeastern part of the study area (Fig. 2). There is an intersecting fault system with two faults in the study area where also a local thermal water reservoir exists (Fig. 3). The hot waters, which are controlled by a fault with a NW–SE direction near the Kirkgecit River bed, reach the surface along the fault.

The recrystallized karstic limestone olistoliths of the Karakaya complex are permeable units. However, due to their limited size and volume, they cannot be considered as important aquifers for thermal waters (Yalcin 2007) although, in some places, they may appear as secondary reservoirs. The other units of the Karakaya complex act as a caprock owing to their aquitard and aquiclude natures (Yalcin 2007). Alluvial plains located SE of study area have water-bearing properties for cold groundwater systems.

Hydrogeochemical features of the waters

Four water sampling locations were selected in the Kirkgecit geothermal field. Three of them were thermal waters, designated K1, K2 and K3, while one of them was a cold water source, named as K4 (Fig. 2). The average discharges of Kirkgecit springs range between 3 and 3.5 L/s, surface temperatures are 45–52°C, pH values are 8.9–9.3, and electrical conductivity values are 620–

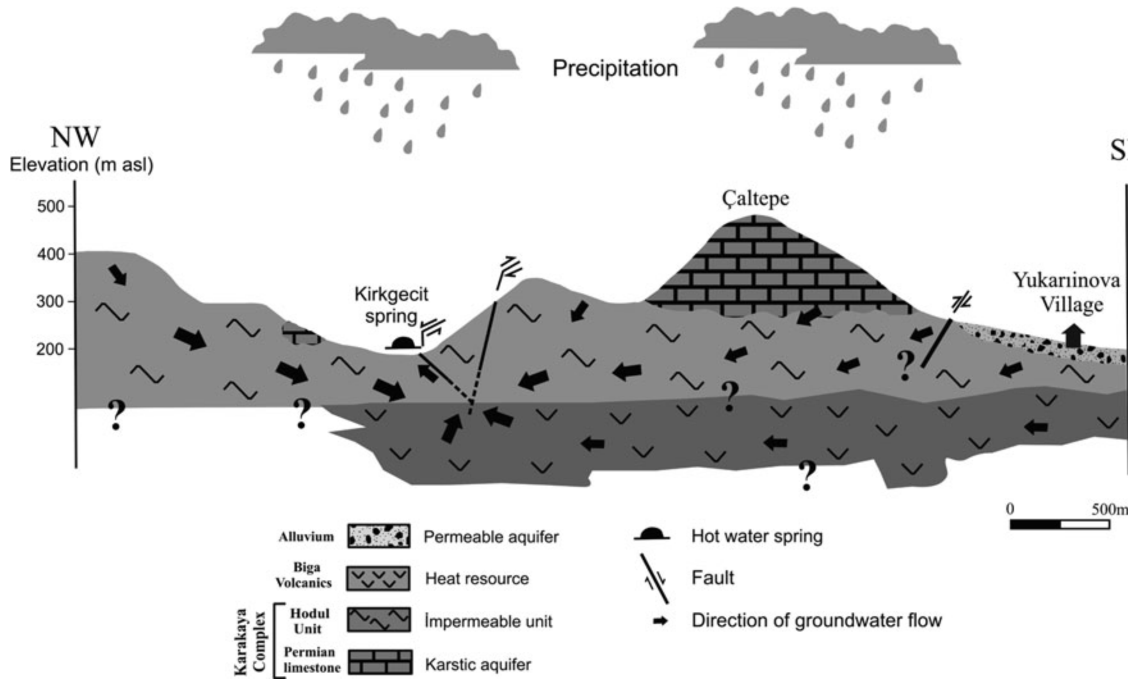

Fig. 3 Simplified geothermal model of Kirkgecit thermal waters

698 µS/cm (Table 1). The geothermal waters have a basic character and their low electrical conductivity indicates that their residence time in the aquifer is short. The surface temperature of the cold water spring (K4) ranges between 12 and 13°C, pH values are 7.5–8.3, and EC values are 653–675 µS/cm. The average discharge of cold water is 0.25 L/s.

Figures 4 and 5 show the relative concentrations in the thermal fluids to classify the water samples and water rock processes. The results of the chemical analyses of the thermal and cold waters from the study area are listed in Table 1. According to the IAH (International Association of Hydrogeologists) (1979) classification all thermal waters are of the Na-SO_4 type, which is characteristic of most of the thermal waters in NW Turkey (Fig. 4). In the Schoeller semi-logarithmic diagram, waters with similar chemistry yield similar peaks. It is clearly seen that the thermal waters have similar chemical characteristics, with $Na + K > Ca > Mg$ and $SO_4 > HCO_3 > Cl$ chemical compositions (Fig. 5). The cold water is derived from different geological units and shows different chemical characteristics from the thermal waters. The cold water samples are dominated mainly by Ca-HCO_3 ions.

We calculated the correlation coefficients for physical parameters and some of the chemical components of the hot waters in the study area (Table 2). Generally, no good correlation exists between physical and chemical parameters. Temperature does not affect the value of major ions. Among the chemical species, there is only one significant correlation, between Cl and K ($r > 0.90$).

The higher ratios of Na/Ca, Na/Mg, Na/Cl, (Na + K)/Cl, and (Na + K)/(Ca + Mg) in the samples indicate relatively prolonged water–rock interaction time (Gemici et al. 2003). High Na/Ca ratios (>50) are indicative of a direct feed from the reservoir and a smaller contribution from cold groundwater (Nicholson 1993).

Isotope hydrogeology

Environmental isotope samples were collected from the hot and cold waters in the study area at five different times during 2005–2007. Deuterium (^{2}H), oxygen-18 (^{18}O) and tritium (^{3}H) analyses were carried out on the samples. The water origin and transit time of the groundwater system were determined by evaluation of the analysis results. Results of the stable isotope analyses of waters from the study area are presented in Table 1.

The relationship between δ^{18}O and δD values is plotted in Fig. 6, which also shows the worldwide meteoric line ($\delta D = 8 \times \delta^{18}O + 10$) of Craig (1961), the Marmara meteoric water line ($\delta D = 8 \times \delta^{18}O + 15$) from Eisenlohr (1997), and the Mediterranean meteoric water line ($\delta D = 8 \times \delta^{18}O + 22$) of Gat and Carmi (1970). Positive shifts in the δ^{18}O values are related to δ^{18}O exchange between deeply circulating meteoric waters in geothermal systems. The degree of the shift depends on the reservoir

Table 1 Chemical and isotopic data of waters in Kirkgecit geothermal area

Spring	Data from	Sampling Date	T (°C)	Cond. (μS/cm)	pH	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Cl (ppm)	SO_4 (ppm)	HCO_3 (ppm)	SiO_2 (ppm)	Li (ppm)	Na / Ca	$\delta^{18}O$ (SMOW)	δD (SMOW)	T (TU)
K1	This Study	October 2005	48	620	8.9	142.57	1.7	0.05	5.29	35	185	97.6	–	0.09	26.95	−9.87	−55.2	0.1
K2			48.5	670	8.96	141.62	1.79	0.07	5.45	35	180	122	–	0.09	25.99	−9.86	−57.19	0.03
K3			49	669	8.95	140.56	1.74	0.15	5.88	35	173	122	–	0.09	23.9	−9.87	−57.78	0.44
K4			12	672	7.68	14.88	0.91	20.89	122.71	17	25	537	–	–	0.12	−9.31	−51.03	6.97
K1		February 2006	49.1	630	9.1	140.59	2.29	0.05	5.26	42	117.8	130	–	0.08	26.78	−10.12	−59.57	0.14
K2			45.1	695	9.2	140.73	2.25	0.08	5.84	43	155.7	110	–	0.09	24.09	−9.95	−60.72	0.26
K3			48.2	698	9.2	139.81	2.46	0.19	6.11	42	177.3	122	–	0.09	22.88	−9.95	−60.17	0.04
K4			12.3	675	8.3	14.11	1.51	17.42	82.22	18	21	370	–	–	0.17	−8.71	−57	7.12
K1		August 2006	51.1	640	9.3	140.56	1.75	0.05	5.32	34	157.67	96	27.61	0.08	26.42	–	–	–
K2			52.1	664	9.3	141.94	1.8	0.07	5.46	34	157.31	100	27.38	0.08	25.99	–	–	–
K3			51.1	681	9.3	142.17	1.71	0.06	5.4	34	157.64	101	27.59	0.08	26.33	–	–	–
K4			13.1	653	7.5	14.94	0.66	17.67	119.25	14	14.56	480	–	–	0.13	–	–	–
K1		March 2007	46.9	663	8.86	136.71	2.18	0.05	5.25	40	166.45	30.37	45.58	0.09	26.04	–	–	–
K2			52	655	8.75	133.91	2	0.13	5.61	40	166.81	70.88	45.94	0.09	23.87	–	–	–
K3			47.3	653	8.85	135.47	2.28	0.07	5.52	41	169.4	20.25	45.91	0.09	25.54	–	–	–
K4			13.2	686	5.92	15.15	1.47	24.33	103.76	18	43.51	360	–	–	0.15	–	–	–
K1		August 2007	48.4	663	9.07	136.42	1.79	0.05	5.96	34	157.67	72.5	–	0.08	22.89	−9.97	−63.05	0.7
K2			49.7	662	9.07	136.78	1.96	0.06	5.66	35	157.31	77.5	–	0.08	24.17	−10.11	−64.13	0.9
K3			51.4	660	9.07	139.14	1.86	0.05	5.85	34	157.64	77.5	–	0.08	23.78	−10.08	−63.6	0.4
K4			–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K3	Pehlivan	2003	52	1,900	7.4	494	30.2	15.2	102	121.7	1200.2	32.5	66.22	–	–	–	–	–
K3	Yalcin	2007	53.1	523	8.6	134	1.8	2	8.2	46	189	73.2	49	0.1	–	−9.63	−61.76	–

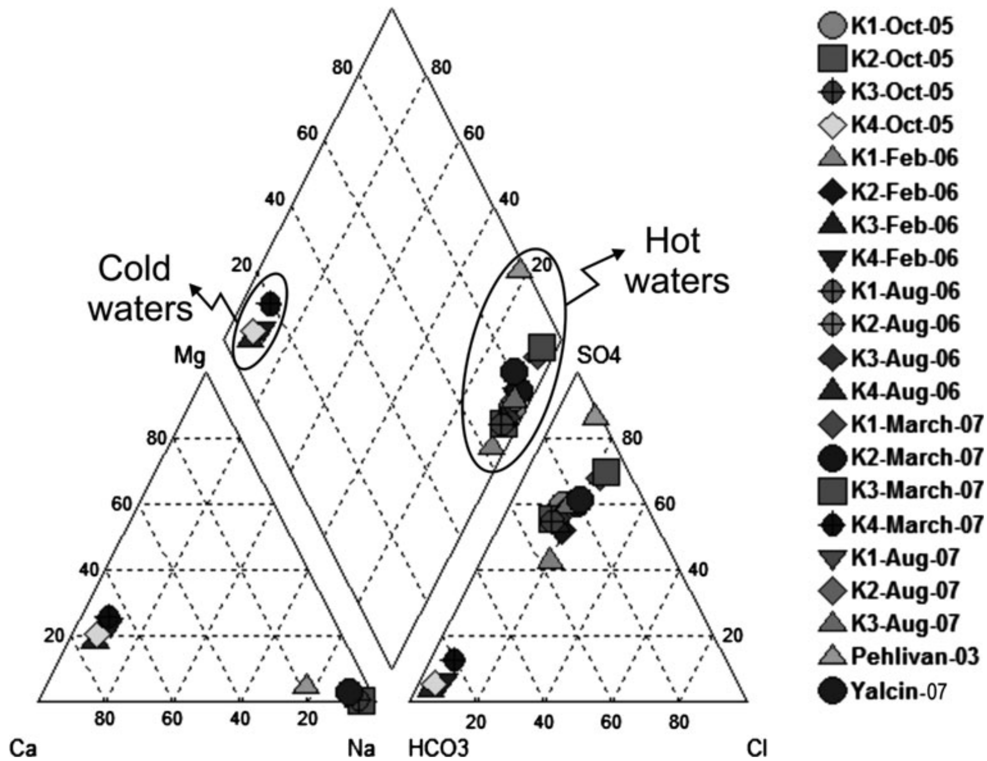

Fig. 4 Piper diagram of waters from the Kirkgecit geothermal area, Turkey

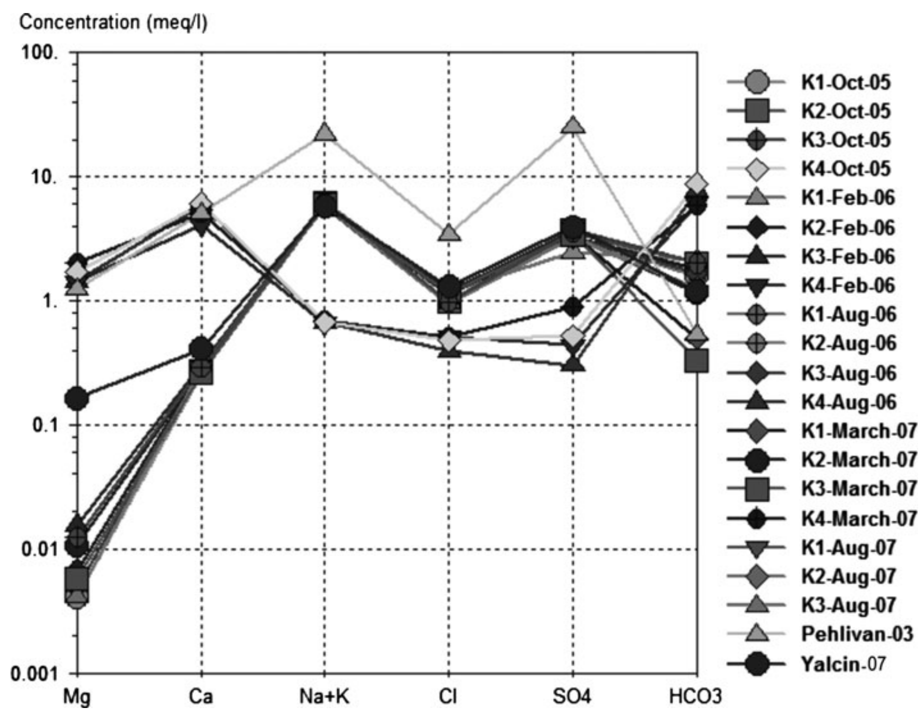

Fig. 5 Schoeller semi-logarithmic diagram of waters from Kirkgecit geothermal area, Turkey

temperature, residence time, and rock–water interaction (Truesdell and Hulston 1980). The results of water sampling from the study area showed that there is no positive oxygen shift. This indicates that geothermal system has been controlled by meteoric waters. The oxygen and hydrogen isotope compositions in this study suggest a meteoric origin for both hot and cold waters (Fig. 6).

Tritium can be used in reservoir monitoring studies since an increase in the ^{3}H of geothermal discharges can be indicative of increasing dilution or of a rapid recharge

Table 2 Coefficient correlation of some major ions for thermal waters from study area (values are in mg/l)

Correlation	T	Cond	pH	Na	K	Mg	Ca	Cl	SO_4	HCO_3
T	1									
Cond	−0.22	1								
pH	0.23	0.32	1							
Na	0.02	0.01	0.59	1						
K	−0.50	0.28	−0.10	−0.34	1					
Mg	−0.01	0.51	−0.11	−0.11	0.34	1				
Ca	−0.13	0.64	0.10	−0.20	0.20	0.61	1			
Cl	−0.56	0.21	−0.23	−0.30	0.92	0.35	0.08	1		
SO_4	−0.17	0.20	−0.37	0.01	−0.23	0.37	0.20	−0.19	1	
HCO_3	0.10	0.15	0.48	0.73	−0.14	0.29	0.15	−0.08	−0.15	1

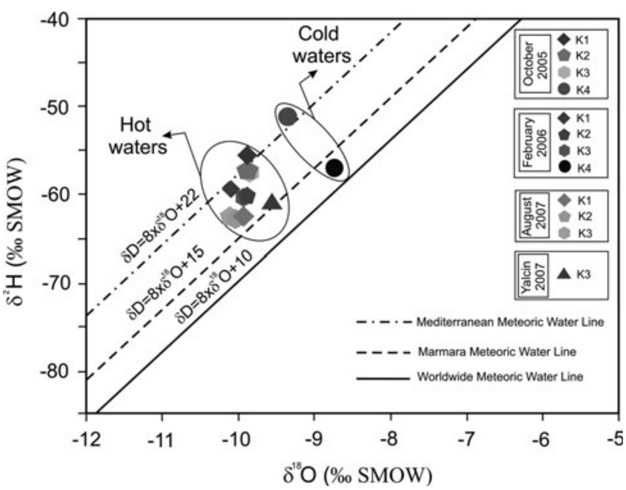

Fig. 6 Distribution of some hot and cold waters from study area in $\delta^{18}O$–$\delta^{2}H$ diagram

by meteoric waters. The activity of tritium (^{3}H, half-life 12.43 years) in thermal waters provides a useful tracer to indicate underground residence times. Tritium contents of the cold waters in this study are higher than those of the hot waters, revealing that the cold water aquifers have been recharged by more recent precipitation (<5–10 years). The low TU contents of the hot waters, on the other hand, suggest deep circulating hot waters with long residence times. However, the higher values of tritium measured in the hot waters in August 2007 may indicate the mixture of cold and hot water. This can be explained by the lag time of the rain event occurring during the wet season (spring) to reach the geothermal springs in dry period (summer).

According to a compilation by Gat (1980), the tritium content of meteoric precipitation in the northern hemisphere has fluctuated widely from values less than 25 TU prior to 1953 up to more than 2,200 TU in 1964 following the extensive testing of nuclear devices in the atmosphere. If groundwater contains 1.1 TU in groundwater indicates that it occured before the testing of nuclear activity in the atmosphere. As such it may be older than 1953 (Gulec and Mutlu 2002). Low tritium concentration levels in the hot waters (<1 TU) suggest that the thermal aquifer is recharged by groundwaters having a relatively long residence time (>55 years), indicating a deep groundwater circulation system in the area. The cold water aquifers, on the other hand, appear to have been recharged with a component of relatively younger precipitation.

Chemical geothermometer applications

Geothermometry is presently an integral part of all the geochemical investigations for the exploration and development of geothermal resources (Verma 2005). The concept of cation-exchange geothermometry violates the fundamental laws of chemical thermodynamics (Verma 2002). He asserted that the cation exchange geothermometers are merely empirical and different geothermometer equations provide different values of temperature.

In this study, to get a general idea about the geothermal reservoir system, solute geothermometry techniques were applied to the thermal waters of the Kirkgecit geothermal area. The reservoir temperatures calculated by solute geothermometers in the Kirkgecit geothermal area are shown in Table 3 (in °C). Since some results, such as those of February 2006, were lower than the measured surface temperatures, they are not reported in the Table.

The Na–K–$Mg^{1/2}$ ternary diagram was proposed by Giggenbach (1988) as a method to identify thermal waters that are suitable for the estimation of reservoir temperature by the application of solute geothermometers. Most of the water samples in this study, when shown on the Na–K–Mg triangular diagram of Giggenbach (1988), fall in the partly equilibrated waters zone (Fig. 7). This indicates that the water–rock interactions have not reached equilibrium,

Table 3 Reservoir temperatures (in °C) calculated by solute geothermometers, Kirkgecit geothermal area

Spring	Data from	Sampling Date	Na-K[a,b]		Li-Mg[c]	Na-K-Ca[d]	SiO_2[e,f]	
K1	This study	October 2005	91	84	102	74	–	–
		February 2006	105	99	102	83	–	–
		August 2006	93	86	102	74	76	76
		March 2007	104	98	102	81	94	93
		August 2007	95	89	100	72	–	–
K2		October 2005	94	87	97	74	–	–
		February 2006	[g]	[g]	95	[g]	–	–
		August 2006	94	87	97	75	76	76
		March 2007	108	102	89	82	98	98
		August 2007	99	92	98	76	–	–
K3		October 2005	93	86	90	72	–	–
		February 2006	109	103	87	82	–	–
		August 2006	91	84	102	73	76	76
		March 2007	107	101	97	82	98	98
		August 2007	96	90	97	74	–	–
K3	Pehlivan (2003)	–	180	178	–	121	116	115
K3	Yalcin (2007)	–	96	90	57	66	101	101

[a] Arnórsson et al. (1983)

[b] Fournier (1979)

[c] Kharaka and Mariner (1989)

[d] Fournier and Truesdell (1973)

[e] Fournier and Potter (1982)

[f] Fournier (1977)

[g] Below measured at spring

suggesting that silica geothermometers are of doubtful significance. The reservoir temperature of the Kirkgecit geothermal area has been estimated by silica geothermometers to be in range 76–116°C.

A different approach to geothermometry is shown in Fig. 8, where the changes in saturation indices (SI) of relevant minerals with temperature were investigated for the Kirkgecit thermal waters. Reed and Spycher (1984) have proposed that considering the changes in the SIs of several minerals with temperature for a given aqueous solution can give the best estimate of reservoir temperature. Figure 8 shows the SIs with respect to selected hydrothermal minerals versus temperature for the thermal waters of the Kirkgecit geothermal area. SIs were initially calculated by using the PHREEQCi computer code (Parkhurst and Appelo 1999) at outlet temperature and measured pH. On the mineral saturation versus temperature diagrams, some of the minerals do not converge to zero at a particular temperature, but approach zero at various temperatures. Crossing lines for several minerals below or above the zero line may indicate admixture of waters at various temperatures. It would appear that the thermal waters of the Kirkgecit geothermal area are partially equilibrated waters fed by geothermal fluids at different temperatures between 100 and 150°C.

Conclusions

Water resources from the study area can be divided into two distinct types. The hot waters are $Na\text{-}SO_4$ type, whereas the cold water is $Ca\text{-}HCO_3$ type. Geological and hydrogeochemical investigations have shown that Kirkgecit hydrothermal system is largely controlled by the extension of the North Anatolian fault system. Water in the geothermal region flows into the Karakaya complex via fractures and is heated by the upper-middle Miocene age Biga volcanics, where the heat source would be due to deep meteoric water circulation in a region of elevated heat flow and thermal gradients. Tritium values lower than 1 TU indicate that the residence times of thermal waters are greater than 55 years.

According to the results of this study, it is possible that a low/medium temperature aquifer could be found in this field. Assessment of the estimated geothermometry results

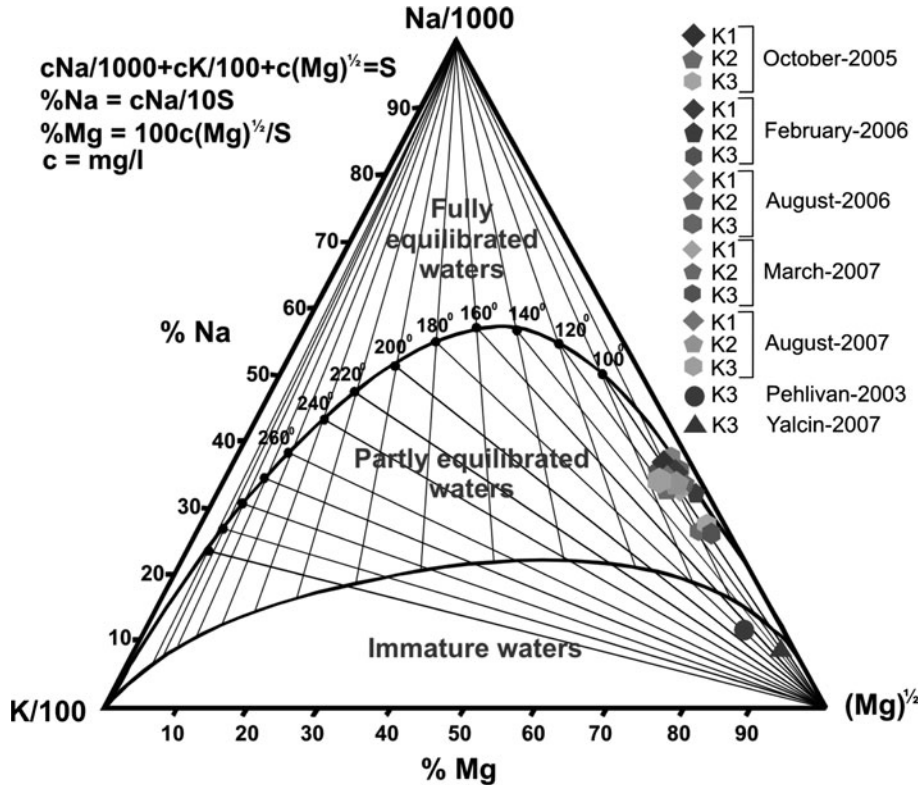

Fig. 7 Distribution of thermal waters from study area in Na–K–Mg triangular diagram (Giggenbach 1988)

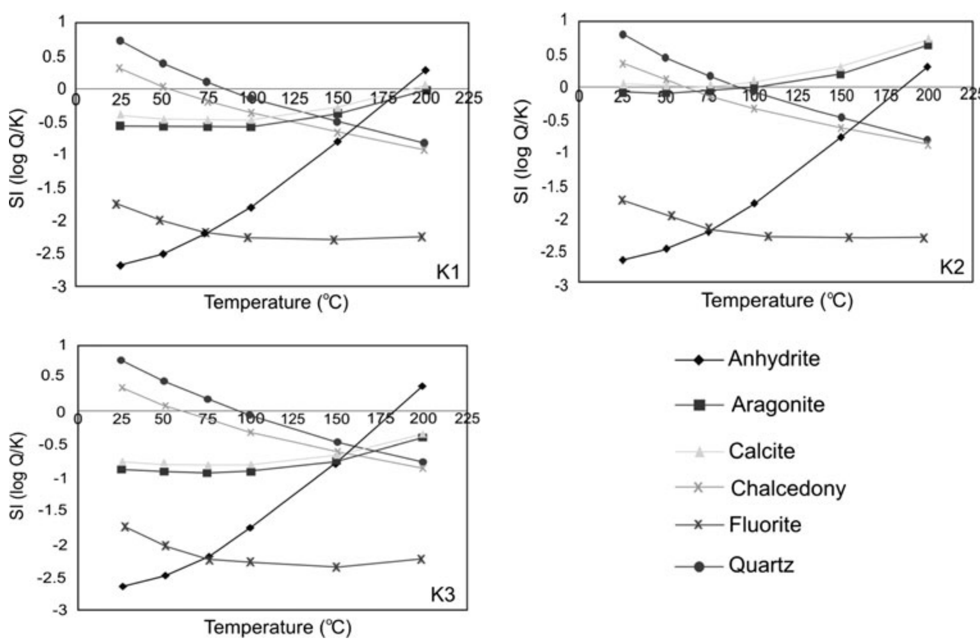

Fig. 8 Mineral equilibrium diagrams for thermal waters from Kirkgecit geothermal area, Turkey

show that the reservoir temperatures of the Kirkgecit geothermal system probably lie in the range 76 and 116°C, while SI diagrams give estimates of reservoir temperature between 100 and 150°C. No exploration boreholes or geophysical surveys have been carried out to study the subsurface structure of the area. The discharge rate is limited and exploratory drilling is needed for further development of the area.

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