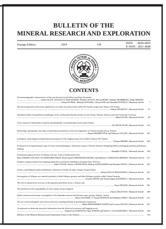
Bull. Min. Res. Exp. (2019) 158: 311-325

Bulletin of the Mineral
Research and Exploration

http://bulletin.mta.gov.tr



Hydro-chemical and isotopic investigation of the Ispendere mineral and thermal water springs, Malatya, Turkey

Murat ÇELIKER[a*] O. Faruk DURSUN[b] and Mahmut FIRAT[c]

[a] *General Directory of State Hydraulics Works, 9th Regional Directory, Elazig, Turkey orcid.org/0000-0003-1211-5561*
[b] *Department of Civil Engineering, Faculty of Engineering, Inonu University, Malatya, Turkey orcid.org/ 0000-0003-3923-5205*
[c] *Department of Civil Engineering, Faculty of Engineering, Inonu University, Malatya, Turkey orcid.org/0000-0002-8010-9289*

Research Article

Keywords:
Environmental isotopes, İspendere, mineral and thermal waters, geochemistry.

ABSTRACT

The objective of this study is to determine the source, chemical characteristics and isotopic components of the İspendere mineral and thermal waters, Malatya, Turkey. There are many mineral and thermal water springs in the area with flow rates ranging between 0.01 – 0.4 l/s. Geochemical and isotope chemistry studies were carried out at three different thermal springs in the region as well as three different cold water springs during May-October 2011. The temperature of mineral and thermal waters were measured as between 21.1°C – 23.6°C in May 2011 and as 20.8°C in October 2011. The region was determined as a low geothermal area and the reason for this is thought to be cold water mixing. The pH values of mineral and thermal spring waters were measured to be between 6.19 –6.69, EC values were measured to be between 1420 µS/cm and 2720 µS/cm, pH values of shallow and deep wells ranged between 6.04 and 7.82, whereas EC values were measured approximately between 275 µS/cm and 3300 µS/cm. The $MgHCO_3$ water type dominates the chemistry of mineral and thermal water in study area. The results of ^{18}O and ^{2}H isotope analysis yield that the springs of mineral and thermal waters as well as cold waters are fed by meteoric rains. It was determined that the İspendere mineral and thermal waters have low tritium (^{3}H), low Cl and high EC values. Reservoir rock temperatures have been estimated to be between 95 -132° C as a result of the quartz geo-thermometer calculations.

Received Date: 04.04.2018
Accepted Date: 08.10.2018

1. Introduction

Thermal springs are benefited for a variety of purposes, such as the generation of power, direct space heating, industrial processes, agriculture, aquaculture, bottled water and the extraction of rare elements (Hellman and Ramsey, 2004; Petraccia et al., 2005). With the increasing demand of spas and the growing importance attached to the 'natural' health sector, mineral and thermal springs are becoming centers of hydrotherapy (Bojadgieva et al., 2002; Harvey, 2007; Olivier et. al. 2008). The optimal use of a mineral and thermal spring is largely dependent upon its physical and chemical contents.

The aims of geochemical studies in geothermal systems are to estimate the subsurface temperatures, to understand the circulation of the thermal fluids and to have information on their origin (Battistel et al. 2014). Hydrogeochemistry, including isotope geochemistry, has significantly contributed to the understanding of geothermal systems (Chenaker et al. 2017). The chemical and isotopic composition of the geothermal water provides information about their origin, recharge areas and flow paths. Also, the major ion chemistry was used in the estimation of the sub-surface reservoir temperatures of thermal waters (Anees et al., 2015).

---

* *Corresponding author: Murat ÇELİKER, mceliker23@gmail.com*
https://dx.doi.org/10.19111/bulletinofmre.494681.

Oxygen is the most abundant element in the earth's crust. Contrary to ^{18}O, ^{2}H is generally found in waters more than mineral and rocks. This contradictory structure of these two isotopes is very important for the isotopic evaluation of water in high temperature systems (Clark and Fritz, 1997). The $\delta^{18}O$ contents of magmatic waters vary between ‰ +5.5 and +13, whereas the $\delta^{18}O$ contents of metamorphic waters vary between ‰ +3 and +25 (Hugh and Taylor, 1974; Sheppard, 1981). No significant change is observed in the ^{2}H content of mineral and thermal waters as a result of water-rock interaction, because ^{2}H is not commonly observed in rock forming minerals. In addition, it has been put forth that the value of ^{2}H can be enriched and that it increases in direct proportion with ^{18}O in many geothermal and volcanic systems that are located at convergent plate boundaries (Arnorsson et. al., 2000). The radioactive isotope that is most commonly used in hydrogeology is tritium (^{3}H).Tritium is generally used in geothermal systems to estimate the mixing ratio of water and underground residence times (Panichi and Gonfiantini, 1978). Although prior to 1952, the tritium amount in groundwater was zero (<0.5 TU in practice), it has reached significant amounts after 1952 (>10TU in practice). For some regions, measurable tritium (0.5–10 TU) represents to be a mixture of pre-1952 and post-1952 water (Mazor, 2004). Many studies have been carried out until today to determine the chemical and isotopic properties of low, moderate and high temperature mineral waters. Pasvanoğlu and Chandrasekharam (2011) carried out the hydrochemical and isotopic analyses of mineral and thermal waters at the Kozaklı district of Nevşehir (Turkey). Hydrochemical and isotopic analyses of natural spring waters of the same area were investigated and evaluated by Afşin and Canik (2013). Pasvanoğlu (2013) constructed a hydrogeochemical model for the mineral and thermal water springs in the Diyadin district located 70 km east of Ağrı (Turkey). Chandrajith et al. (2013) investigated the geochemical and isotope characterization of geothermal spring waters in Sri Lanka. Ersoy and Sonmez (2014) examined the hydrochemical and isotopic characteristics of geothermal springs in Ilıca (Erzurum, Turkey) and they determined that these geothermal springs located along the main fault zone are fed by groundwater with varying chemical and isotopic structures. Baba and Şanlıyüksel (2011) examined the hydrochemical and isotopic properties of the low temperature geothermal springs in Kırkgeçit (Northwest Turkey).

The objective of this study is to determine the source and underground transportation process of the İspendere mineral and thermal waters (Malatya, Turkey) by using physical-chemical parameters and environmental isotopes. For this purpose, analyses were carried out on samples collected from three different thermal springs that discharge in the same area as well as three different cold water springs that discharge close to the study area.

2. Study Area

The study area is located in the Eastern Anatolia region of Turkey between the cities of Elazığ – Malatya and about 20 km southeastof the Malatya city (Figure 1). This region was studied by various researchers

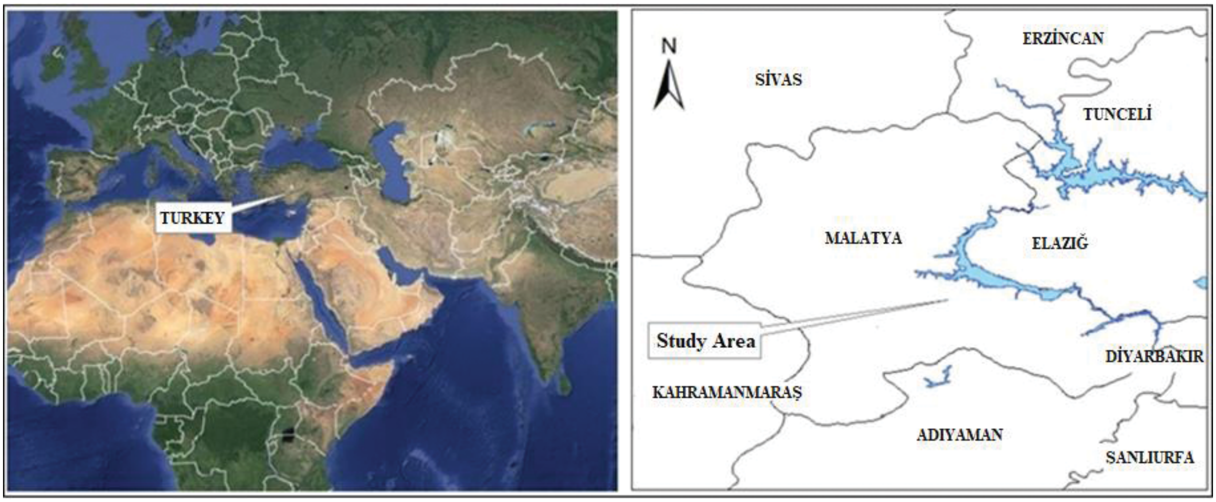


Figure 1- Study area.

in terms of geological, tectonic, petrographical, petrological and hydrogeochemical aspects (Yazgan et al., 1987; Beyarslan, 1991; Dumanlılar, 1993; Çetindağ et al., 1993; Dumanlılar et al., 1999; Gürocak and Alemdağ, 2002, Beyarslan and Bingöl, 2010; Parlak et al., 2010). The İspendere mineral and thermal springs discharge along the fault line in the N-S direction at the contact of İspendere ophiolite and Elazığ magmatics (Figure 2). They have outlet temperatures between 20.8°–23.9°C and their discharges are between 0.01-0.04 l/s. These springs are used for medical purposes and a geothermal well (well/521) with a depth of 292 m was drilled by the local administration in order to use the thermal properties of the waters in the region. However, desired temperature has not been obtained in geothermal well (well/521).

2.1. Climate

The İspendere, Malatya region has a continental climate with an average annual precipitation of 378.1 mm (1929 – 2010). The highest amount of monthly rainfalls were received in March, April and May and the averages are reported as 49.71, 56.33, and 46.2 mm, respectively. The maximum monthly air temperature (42.2°C) occurs in July, and the minimum monthly air temperature (–14.6°C) in January (DMI, 2010).

2.2. Regional Geology

The geological map of the study was prepared by Beyarslan and Bingöl (2010) (Figure 2). Geological units in the study area have tectonic and intrusive relations. These units are İspendere ophiolites, Elazığ Magmatics, Maden complex and Kırkgeçit formation (Beyarslan and Bingöl, 2010). İspendere ophiolite thrusts over the Mid Eocene aged volcano-sedimentary Maden group towards the south and is overlain by the Mid Eocene-Oligocene aged Kırkgeçit formation

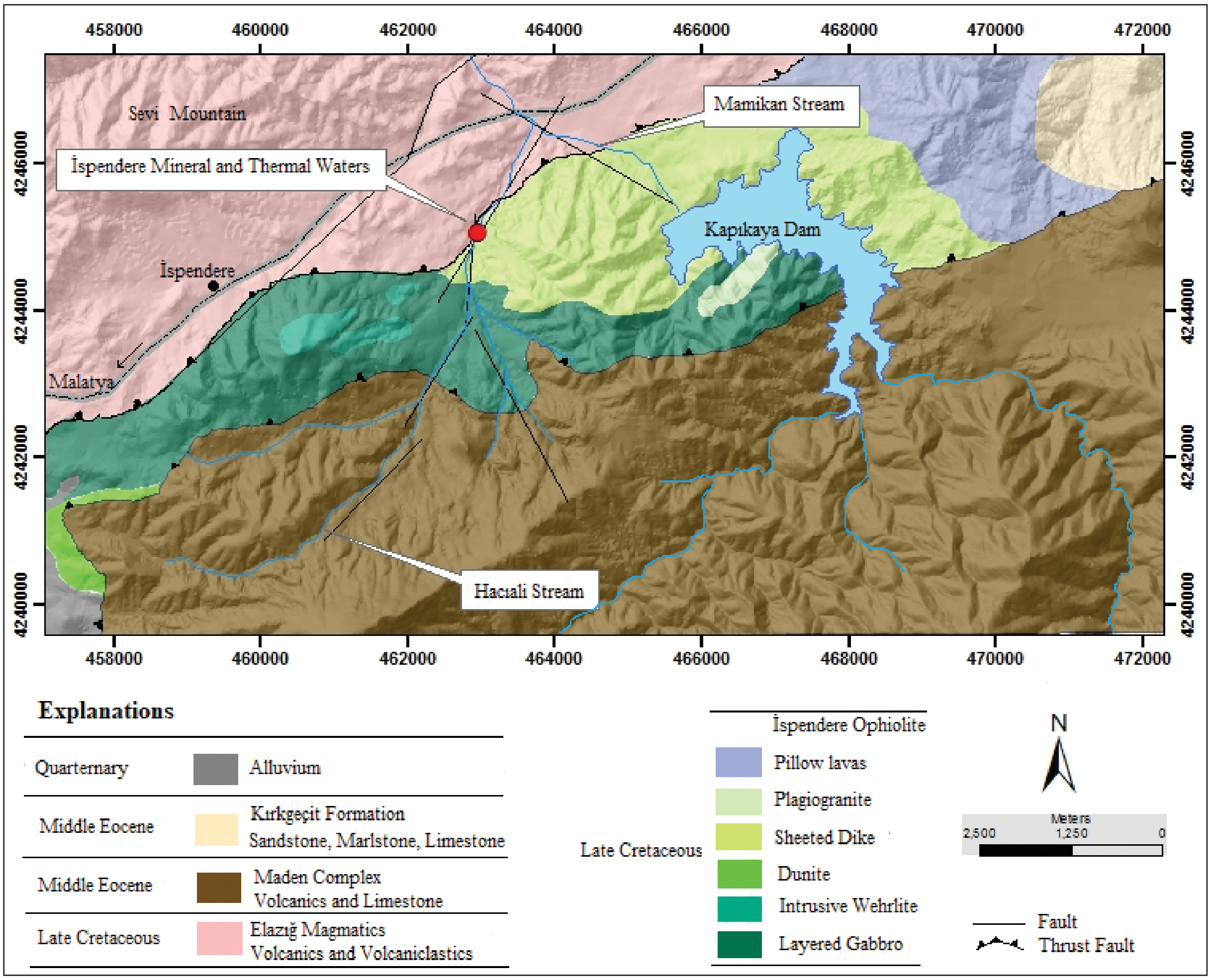


Figure 2- The Geological map of study area from Beyarslan and Bingöl (2010).

(Parlak et al., 2010). Upper Cretaceous aged İspendere ophiolites put forth a complete oceanic lithosphere crosssection and are parts of the Southeastern Anatolia ophiolite band between the Arabian and Taurus (Anatolia) Platforms. İspendere ophiolites are made up of dunite, layered and isotrope gabbro, plagiogranite, plate dyke complex, pillow and massive basaltic and andesitic lava and volcano-sedimentary rocks. Mantle rocks are harzburgitic. Ultramafic-mafic cumulate rocks are represented by verlite, dunite, troctolite, olivine gabbro and gabbro. Whereas dyke complex forms the thickest unit of the Ispendere ophiolite at the top regions of which radiolarites, micritic limestone and tuffites are observed (Beyarslan, 1991; Çetindağ et al., 1993; Dumanlılar et al., 1999; Beyarslan and Bingöl, 2010; Parlak et al., 2010). Elazığ magmatics in contact with İspendere ophiolites contain andesite and dacite dykes, agglomerate, pillow lava and tuff units (Yazgan et al., 1987; Çetindağ et al., 1993).

2.3. Hydrogeology

The main drainages of the study area are the Mamikan Stream and the Hacıali Creek and they discharge to the Karakaya Dam lake. Kapıkaya Dam has been built over the Mamikan Stream by DSI (State Hydraulic Works). İspendere mineral and thermal water springs emerge from the bed of the Hacıali Creek. The fault systems formed between Elazığ Magmatics and İspendere Ophiolites are primary cause of discharge of the mineral and thermal water springs. Secondary porosity was also developed in the Elazığ magmatics and İspendere ophiolites due to tectonic activity (Çetindağ et al., 1993). The marln and clayey levels that surface around the mineral and thermal water springs are impermeable whereas the sandstone, limestone and alluvial levels are permeable. The impermeable ophiolites act as cap rock of the geothermal reservoirs. The heat source of the geothermal system is likely the combination effect of the volcanic and tectonic activities. Limestones, sandstones, alluvial levels and structural features in magmatic rocks (faults, fractures and contacts) act as reservoir rocks in region. Many mineral and thermal water springs were determined in the study area with flow rates varying between 0.01 – 0.4 l/s. A 292 m deep geothermal well (well/541) was drilled by the local administration for benefit from the mineral and thermal waters. The flow rate of the water acquired at the end of the well was measured as 40 l/s whereas the well base temperature was measured as 25°C. The units belonging to alluvial, sandstone, limestone, marln, dacite, agglomerate, tuff, basalt, serpentine, diabase, gabbro, diabase sheets were cut through during drilling. The static level of the geothermal well was water determined as 13 m, whereas the dynamic level was determined as 33 m. Intensive water leakage was observed at 64 m and partial water leakage was observed at 176 m during drilling (Geothermal management report, 2010). It was observed as a result of the examination of the basic borehole logs of the Kapıkaya Dam built over the ophiolites about 3 km east of the İspendere mineral and thermal waters that the ophiolite unit has cracked and fractured structure due to tectonic movements and that these cracks and fractures have been covered with clay and calcite filling (DSİ. 1991). Browne (1991) has explained the calcite filling formation by stating that calcite is the main substance precipitated by geothermal fluids containing high amounts of bicarbonate and dissolved CO_2 because they are at very low temperatures below their boiling points at regions near the surface where they mix with cold water at high elevations near high temperature geothermal areas or during the rising of these systems.

3. Sampling and Analytical Methods

The groundwater level and chemistry are governed by various factors. Parallel to global climate change, climate change in study area, as reflected in precipitation and evaporation rates, influences the groundwater level fluctuation and chemistry. For this reason, sampling studies have been carried out in rainy and dry seasons. Two water samples were collected from 6 different locations in May and October 2011 in the study area in order to determine the major and minor ion chemistry of the mineral and thermal waters as well as cold waters and their oxygen-18, deuterium and tritium contents (Figure 3). The samples, which had been taken for isotope analyses as well as physicochemical analyses, were put in 1000 ml closed bottles without filtration. The water temperature, pH and electrical conductivity were measured during sample collection by using a WTW Cond 720 measuring instrument. The analyses of the major and minor elements in the waters were carried out at the Malatya Provincial Administration laboratories whereas isotopic analyses were carried out at the General Directorate of State Hydraulic Works (Ankara) laboratories.

Water samples have been analyzed for chemical constituents such as major ions in the laboratory using

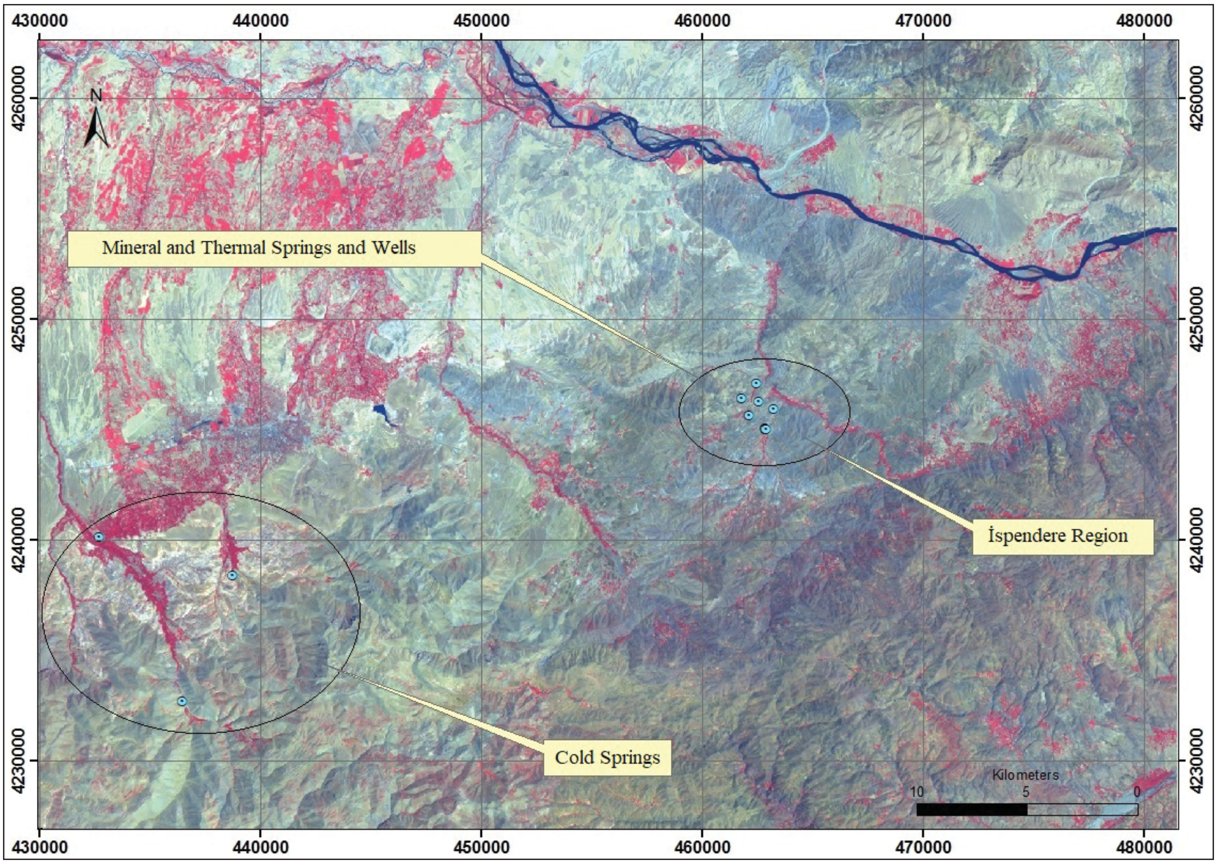


Figure 3- Sampling location (Lansat 4: 3: 1 satellite image).

the standard methods as recommended by the APHA (2005). The major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) of water samples were analyzed by ICP-OES (inductively coupled plasma optical emission spectrometry). Bicarbonate (HCO_3^-), were measured by acidimetric titration method while chloride (Cl^-) was measured by argent metric titration method. Spectrophotometer was used for determination of sulfate (SO_4^{2-}). The oxygen-18 and deuterium isotope ratios were analyzed via mass spectrometric methods by an IsoPrime dual inlet isotope-ratio mass spectrometer. Tritium values were determined by counting its radioactive decay, using liquid scintillation spectrometers (IAEA, 2010). In addition, to the data obtained in this study, chemical analyses results obtained in previous studies (Çetindağ et al., 1993) have also been used.

4. Results and Discussion

4.1. Hydrogeochemistry

The main elements of mineral and thermal waters are silica (SiO_2), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate (CO_3^{2-} and HCO_3^-), hydrogensulphide (H_2S), sulphate (SO_4^{2-}), chlorid(Cl^-) and fluoride (F^-). Cold water components are important for the calculation of mixing during operation. These elements provide valuable information for the chemical monitoring of the operated geothermal area (Gunnlaugsson, 2008). In general, mineral and geothermal waters contain dissolved minerals such as sodium, calcium, sulphate, chloride, silica at concentrations that are greater than those of local cold waters (Kipng'ok and Kanda, 2011).

Analysis results of the groundwater samples obtained from different locations at the study area as well as the analysis results of previous studies were given in table 1.

The temperatures of mineral and thermal waters were measured to be between 21.1°C – 23.6°C in May 2011 and as 20.8°C in October 2011. The temperatures of cold waters were measured in the interval of 10.5°C - 17°C. The maximum temperature at well base was

Table 1- Physical,chemical and isotope analyses results of water samples.

Sample Date	Location Type	T°C	pH	EC µS/cm	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	SiO_2 (mg/l)	$\delta^{18}O$ (‰)	δD (‰)	T (TU)	Water Type (IAH, 1979)
05.05.2011	Hot Spring 1	23.6	6.47	2710	209.4±3.44	243.5±3.98	60.21±3.44	0.018±0.002	7.26±1.44	41.3±2.44	1994.7±15.54		-9.23±0.32	-64.8±1.70	0.15±0.70	Mg-Ca-HCO_3
05.05.2011	Hot Spring 2	21.1	6.61	1460	174.7±3.42	196.5±4.01	50.85±3.09	0.001±0.001	7.96±1.41	43.9±2.45	1555.5±11.44		-8.09±0.44	-60.5±1.60	1.1±0.90	Mg-Ca-HCO_3
05.05.2011	Hot Spring 3	21.9	6.32	2015	165.3±.3.48	177.9±4.43	41.25±2.98	0.001±0.001	5.93±1.34	13.4±1.35	1464±10.54		-8.72±0.44	-61.9±1.70	0	Mg-Ca-HCO3
04.05.2011	Cold Spring 1	11.5	7.85	278	46.98±2.28	5.00±2.44	0.62±0.02	0.16±0.11	3.59±1.29	0.001±0.001	158.6±11.49		-8.73±0.43	-53.2±1.40	4.45±2.30	Ca- HCO_3
04.05.2011	Cold Spring 7	14.6	7.67	420	69.72±2.29	6.96±2.02	3.36±0.80	0.92±0.23	5.57±1.36	6.79±0.94	213.5±11.48		-9.34±0.36	-58.8±1.70	5.8±1.15	Ca- HCO_3
04.05.2011	ColdSpring 8	10.5	8.01	228	38.57±2.28	3.39±2.23	0.32±0.10	0.19±0.09	1.53±0.44	0.001±0.001	125.05±9.44		-10.4±0.35	-64.4±1.60	5.95±1.15	Ca- HCO_3
27.10.2011	Hot Spring 1	20.8	6.38	2720	216.5±3.56	282.9±3.48	64.11±3.49	3.27±1.47	8.59±1.74	44.5±2.38	1958±16.47		-8.99±0.21	-68.3±0.90	0.41±0.70	Mg-Ca-HCO_3
27.10.2011	Hot Spring 2	20.9	6.69	1420	108.3±3.04	125.5±4.08	29.74±2.28	3.35±1.54	6.1±1.32	12.7±2.44	969.9±9.08		-9.12±0.21	-61.2±0.90	0.21±0.68	Mg-Ca-HCO_3
27.10.2011	Hot Spring 3	20.9	6.19	2015	158.7±3.34	191.8±4.45	38.68±2.36	3.6±1.61	7.41±1.47	19.3±2.44	1421±10.49		-9.2±0.19	-65.4±0.90	0	Mg-Ca-HCO_3
14.10.2011	Cold Spring 1	12.1	7.69	275	47.26±2.20	6.63±1.77	0.51±0.12	0.53±0.12	2.83±0.89	0.001±0.001	170.8±9.48		-9.07±0.28	-54.2±0.80	5.11±0.81	Ca- HCO_3
14.10.2011	Cold Spring 7	16.3	7.43	435	76.90±2.21	10.03±2.03	3.60±0.34	1.98±0.23	7.14±1.39	0.01±0.01	256.2±10.14		-9.03±0.21	-53.4±0.90	5.59±0.84	Ca- HCO_3
14.10.2011	Cold Spring 8	13.5	7.89	251	41.07±2.19	6.32±1.98	0.42±0.11	1.98±0.22	3.42±1.18	0.01±0.01	152.5±9.64		-10.8±0.21	-68.6±0.90	6.19±0.86	Ca-Mg-HCO_3
02.06.2010	Well / 521*	25	6.04	3300	243.9±3.44	316.5±5.06	86.46±4.24	5.11±0.86	9.23±1.89	92.8±2.84	2724.9±19..98	146,9±2.33				Mg-Ca-HCO_3
21.10.2011	Well /1901**	12.1	7.5	293	47.26±2.14	6.63±1.23	0.52±0.18	0.53±0.12	2.83±0.43	0.001±0.001	170.8±9.44					Ca- HCO_3
21.10.2011	Well / 1903**	16.2	7.27	577	95.83±2.67	15.50±2.33	0.69±0.20	1.72±0.36	4.82±1.46	4.2±0.49	335.5±10.12					Ca- HCO_3
21.10.2011	Well / 1905**	15.9	7.82	333	60.09±2.23	4.95±1.17	0.29±0.08	1.42±0.32	3.29±1.40	0.01±0.01	219.6±3.44					Ca- HCO_3
21.10.2011	Well / 1909**	14.6	7.38	469	76,90±2.63	10.03±2.03	3.61±0.44	1.98±0.37	7.14±1.34	0.01±0.01	256.2±10.17					Ca- HCO_3
21.10.2011	Well / 1910**	14.8	7.55	275	41.07±2.14	6.32±1.97	0.42±0.11	1.98±0.36	3.42±1.45	0.01±0.01	152.5±9.78					Ca-Mg-HCO_3
10.12.2010	Well / 2244**	16.2	6.74	256	28.00±2.01	9.60±1.96	14.95±1.44	0.39±0.11	3.76±1.45	3.01±0.97	146.4±9.55					Ca-Mg-HCO_3
Çetindağ. (1992)	Hot Spring 1	19-22	6.4	2900	216	331	65	0.2	11.10	28	2410	78				Mg-Ca-HCO_3

* Physical-chemical analysis results of the geothermal drilled by local administration,

** Physical-chemical analysis of the personal wells were analyzed by Public health organization.

measured as 25°C during the geothermal water drilling (well/541; 292 m). The change in the temperature of the drill sludge during drilling was given in figure 4. It showed a slight increase due to the geothermal gradient and significant changes were observed after 104 meters (Geothermal Prossesing Report, 2010). The pH values of mineral and thermal springs are close to neutral. The lowest pH value was measured in the spring numbered 3 in October 2011 (6.19) whereas the pH value of the same spring was measured as 6.32 in November 2011. Carbon dioxide is the major cause of acidity and low pH values in mineral and thermal spring waters. The EC values of thermal springs vary seasonally and between 1420 µS/cm and 2720 µS/cm. These values do not show significant changes in both seasons. The EC values of wells drilled in the region have been determined between 275 µS/cm and 3300 µS/cm. Groundwater conductance is an indirect measurement of present ions and of dissolved constituents, and it is temperature dependent (Boyed, 2000; Hem, 1985). A number of studies on EC-temperature relations important in terms of the water chemistry are presented in the literature. Sorensen et al. (1987) have reported that the relationship between EC and temperature for natural waters is generally nonlinear. However, they stated that the degree of nonlinearity is relatively small between 0˚C - 30˚C. In 2004, Hayashi published another study of the EC and temperature relation of natural waters. In this study, it is nonlinear in a temperature range 0–30°C, but the linear equation approximated the relation reasonably well. In our study similar results also were obtained.

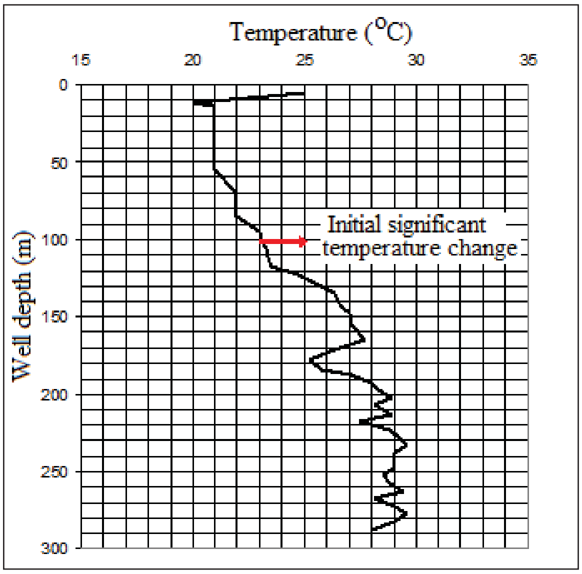


Figure 4- Well depth-temperature variation of geothermal well.

As the temperature increases, the concentrations of dissolved ions increase as shown by the upward trend in the graph (Figure 5).

Cold waters signify low ion concentration groundwater that circulates fast at shallow zone. The high bicarbonate concentration of mineral and thermal waters (969.9–2724.87 mg/l) is due to the reaction of CO_2 rich groundwaters with carbonated rocks (Giggenbach and Glover, 1992). The Mg^{2+} concentration of İspendere mineral and thermal waters have been measured between 125.5–316.5 mg/l, Ca^{2+} concentration is between 108 – 243 mg/l and Na^+ concentration is between 29.74–86.46 mg/l. In general, the mineralization of geothermal waters is characterized by an increase in Mg^{2+} content. High Mg^{2+} concentration signifies the washing of Mg^{2+} from rocks near the surface (Nicholson, 1993). The increase in magnesium mineralization can be due to the magnesium containing olivine mineral. Cl is a parameter suited for the determination of the mixture since the chemistry of the thermal waters is different from that of cold waters. Cold waters yield a chloride concentration that is lower than geothermal waters. It is generally difficult to detect cold fresh water input to a geothermal system at an early period (Kipng'ok and Kanda, 2011). The decrease in chloride concentration and the increase in bicarbonate concentration might indicate water – rock interaction in thermal waters (Giggenbach and Glover 1992). The chloride value of the geothermal waters at the region was measured between 5.93–7.96 mg/l in May 2011 sampling period and between 6.1–8.59 in October 2011. The chloride value of cold waters varies at lower intervals (generally 2.83–3.76 mg/l). The fact that the chloride value (9.23 mg/l) of the geothermal well (well/521) is higher that the chloride value (on average 7.2 mg/l**)** of mineral

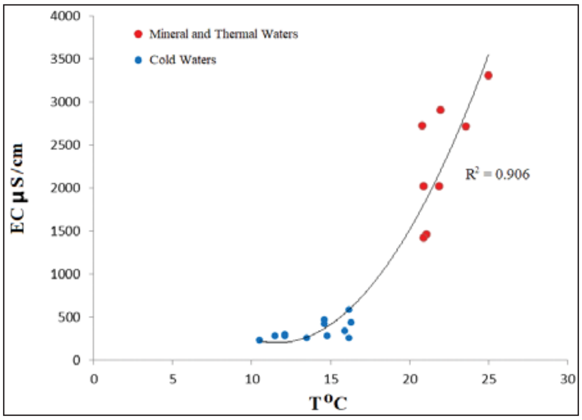


Figure 5- Temperature - EC chart.

and thermal water springs verify the cold water mixing during the rising up of thermal waters to the surface. Sulfate (SO_4^{2-}) concentrations have been measured between 12.7–92.8 mg/l in mineral and thermal waters and between 0.001–3.01 mg/l in cold waters. Prophyry copper-pyrite and/or stokwork type mineralization were observed in the study area according to the studies based on geotectonic environment. The main sulfurous minerals are pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) while sphalerite [$(Zn,Cu)S$], galenite (PbS), pyrotite (Fe_7S_8), and bornite (Cu_5FeS_4) are less. Marcasite (FeS_2), chalcocite(Cu_2S) and covellite (CuS) are detected as secondary sulfurous minerals (Dumanlılar et al., 1999). The fact that the SO_4^{2-} concentrations of mineral and thermal waters are greater in comparison to cold waters can be explained by the reaction of H_2S with oxygen at different levels and the increase of SO_4^{2-} concentrations as a result of the dissolution of sulfurous minerals (Pasvanoğlu et al., 2005). The fact that Na^+/K^+ ratio is high in thermal waters is seen as an indication of the existence of lateral flow reactions close to the surface and the conductive cooling in geothermal waters (Nicholson, 1993). The solubility of silicon is quite low at normal groundwater temperatures but high in geothermal waters (Truesdell, 1984). The fact that silicon dioxide values are measured differently in geothermal well (well/541;146.9 mg/l) and in the mineral and thermal spring (mineral and thermal spring 1(1992); 78 mg/l) is another verification of cold water mixing.

According to IAH (1979) the classification of waters is given in table 1. Total equivalents of cations and anions were considered as 100% and ions with more than 20% (meq/l) were calculated for the classification. It has been observed that İspendere mineral and thermal waters are in general at the Mg-Ca-HCO_3 and Ca–Mg–HCO_3 mixing interval and that the cold waters are generally at the Ca-Mg-HCO_3 and $CaCO_3$ mixing interval.

Piper diagram is another classification method used in the classification of water samples and enables to define the dominant geochemical process of aqua-chemistry in a more precise manner (Piper, 1944). To define composition class, Back and Hanshaw (1965) suggested subdivisions of the tri-linear diagram (Figure 6). The chemical data of the water samples collected from different locations in the study area have been marked on the Piper diagram and the chemical data have been grouped in the 5th region. From the analysis of the Piper diagram, HCO_3^- is the dominant anion whereas Ca^{2+} and Mg^{2+} are the most dominant cations. According to the Piper diagram, mineral and thermal waters in the study area have been classified as Mg-HCO_3 facies, cold waters have been classified as Ca-HCO_3 facies. From the plot it is observed the water samples exhibit that the alkaline earth metals (Ca^{2+}, Mg^{2+}) significantly exceed the alkalis (Na^+, K) and weak acid (CO_3^{2-}, HCO_3^-) exceed the strong acid (Cl^-, SO_4^{2-}) (Figure 6). The Ca–HCO_3 water type indicates dissolution of calcite, whereas the Mg–HCO_3 water type indicates dissolution of ophiolites and dolomites containing magnesium.

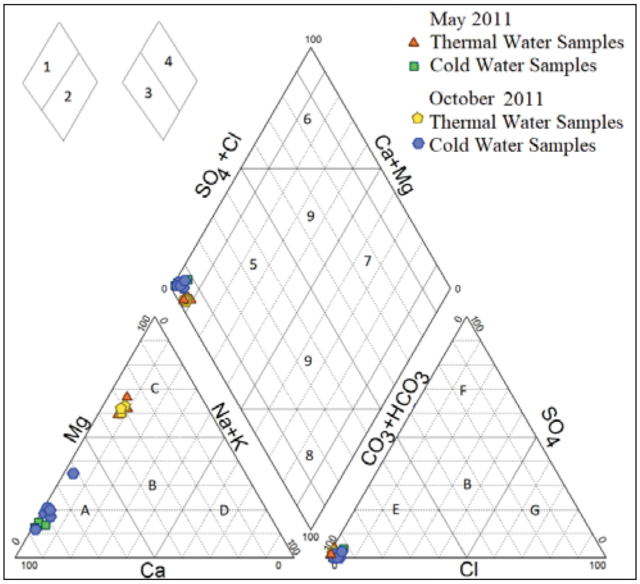


Figure 6- Piper diagram.

Schoeller (1962) diagram has been drawn in order to compare the chemical parameters of water samples taken from different locations and to determine some of the chemical properties (Figure 7). The element distributions of thermal and cold waters have yielded similar reflections on the semi-logarithmic Schoeller diagram. Cations have been ordered in mineral and thermal waters as $rMg^{2+} > rCa^{2+} > rNa^{+} + rK^{+}$ and anions as $rHCO_3^{-} > rSO_4^{2-} > rCl^{-}$ whereas cations in cold water have been ordered as $rCa^{2+} > rMg^{2+} > rNa^{+} + rK^{+}$ and anions as $rHCO_3^{-} > rSO_4^{2-} > rCl^{-}$.

Another diagram used in the classification of geothermal waters is Giggenbach (1991) triangular diagram. In this diagram, the geothermal waters are classified according to the concentration of chloride (Cl^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) ions (in mg/kg). Accordingly, it has been observed that all waters are in shallow or mixture waters region (Figure 8).

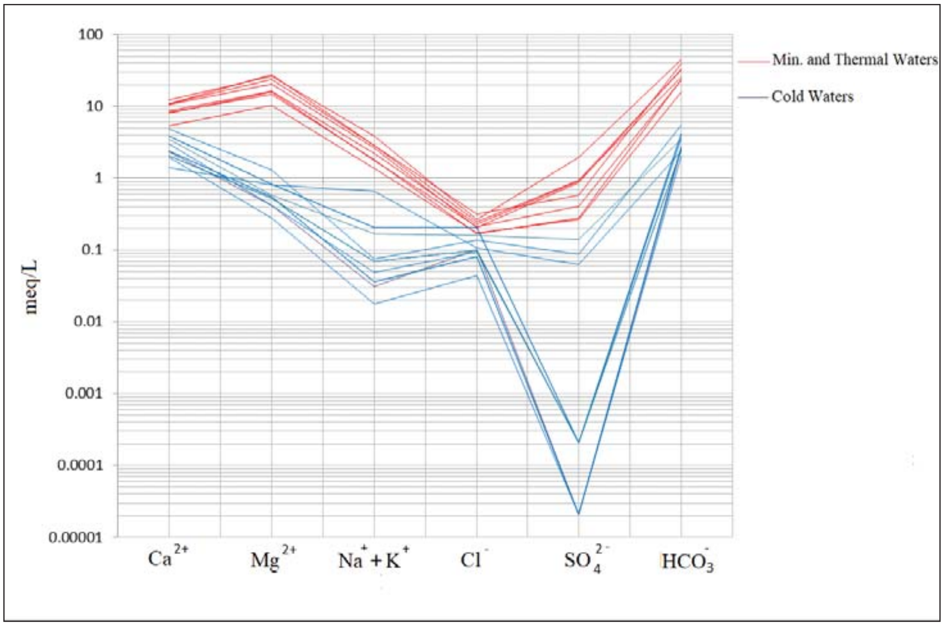


Figure 7- Schoeller diagram.

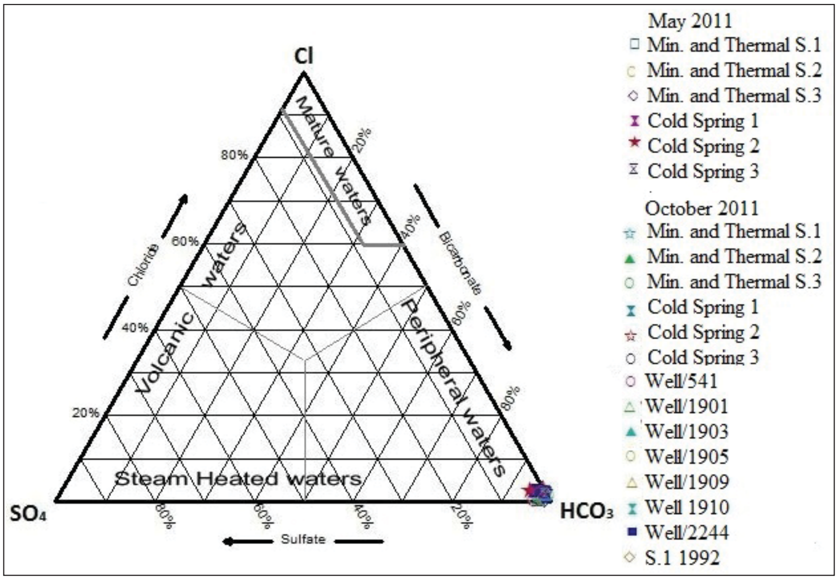


Figure 8- The triangular diagram for waters at study area (Giggenbach, 1991).

In addition, the İspendere thermal and cold waters are included in the immature waters group according to the Giggenbach equilibrium diagram (Figure 9). Hence, cation geothermometers have not be used in estimated aquifer temperature calculations since they will not yield results that are close to the actual values (Giggenbach, 1988). The reservoir rock temperatures calculated by quartz geothermometer are estimated between 95-132° C (Table 2).

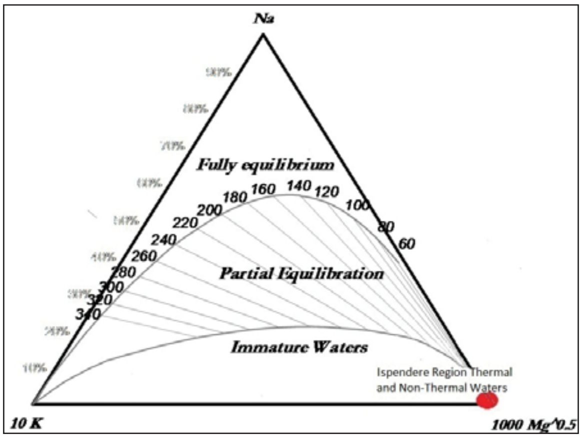


Figure 9- Giggenbach equilibrium diagram.

4.2. Isotope Geochemistry

Negative values that characterize water according to standards in isotope analyses indicate isotope depletion (light in terms of isotopes), whereas positive values indicate isotope enrichment (heavy in terms of isotopes) (IAEA, 1998; Demer, 2008). The oxygen-18 versus deuterium values ($\delta^{18}O$ – $\delta^{2}H$) of the world rainfall stations in the world generally intensify on a linear line defined as the Global Meteoric Water Line. The equation of this line (1) defines the relationship between ^{18}O and ^{2}H in the rain waters collected around the world (Craig, 1961*b*).

$$\delta^{2}H=8\delta^{18}O+d \text{ (‰ SMOW)} \qquad (1)$$

The value of *d* in this equation is known as "deuterium excess" and is defined as the indicator of the evaporation amount of sea water that is the source of rain. The *d* value of the Global Meteoric Water Line is 10 and it is a function of the relative humidity in the atmosphere over the oceans. The value of d reaches more positive values at places where evaporation is higher and varies locally according to the climate conditions that are dominant in geological epochs. This value for the Mediterranean climate that is dominant in our country is +22 ‰ (Gat, 1971; IAEA, 1981; 1983).

In this chapter, the oxygen-18 ($\delta^{18}O$), deuterium ($\delta^{2}H$), and tritium (^{3}H) content of the water samples evaluated to understand the water-rock relationship as well as the thermal water cycle. The oxygen-18 values varied between; –8.09‰ and –9.23‰ (SMOW), deuterium values between –60.5‰ and –64.8‰ (SMOW) in mineral and thermal water springs in May 2011 and between –8.99‰ and –9.20‰ (SMOW) in October 2011, whereas the deuterium values varied between –61.2‰ and –68.3‰ (SMOW). In cold water springs, the oxygen-18 values varied between;–8.73‰ and –10.4‰ (SMOW) in May 2011, deuterium values between –53.2 ‰ and –64.4‰ (SMOW), in October 2011 the variations were between –9.03‰ and –10.8‰ (SMOW) and for deuterium between –53.4‰ and –68.6‰ (SMOW) (Table 2). The oxygen-18-deuterium relationship of the waters between May 2011 and October 2011 was given in figure 10. Several local meteoric water lines have been determined for İspendere region, Malatya. The Local Meteoric Water Line (LMWL) closest to our study sites is given by the water samples collected at the Kırkgöze Sub-basin ($\delta^{2}H=8\ \delta^{18}O + 14.87$) of Pekkan et al. (2008). According to the oxygen-18 and deuterium isotope data acquired periodically, mineral and thermal water springs are located close to the Global Meteoric Water Line (Craig, 1961*a*), whereas cold water springs are

Table 2- Some geothermometric equations and calculated reservoir temperatures of the thermal waters in İspendere Region, Malatya.

Geothermometer	Equation	Thermal Spring	Thermal Well
T measured (˚C)		19 -22	25
T Qz – no st. Loss (Fournier, 1973)	$=\frac{1309}{5,19-\log S_iO_2}-273,15$	123,7	159,86
T Qz – max. st. loss at 100 ˚C (Fournier, 1973)	$=\frac{1522}{5,75-\log S_iO_2}-273,15$	121,36	151,63
T chalcedony, no steam loss (Fournier, 1977)	$=\frac{1032}{4,69-\log S_iO_2}-273,15$	95,69	135,89
T chalcedony - max. st. loss at 100 ˚C (Fournier, 1977)	$=\frac{1182}{5,09-\log S_iO_2}-273,15$	96,46	131,23
T chalcedony, no steam loss (Arnorsson ve ark., 1983	$=\frac{1112}{4,91-\log S_iO_2}-273,15$	95,31	132,24

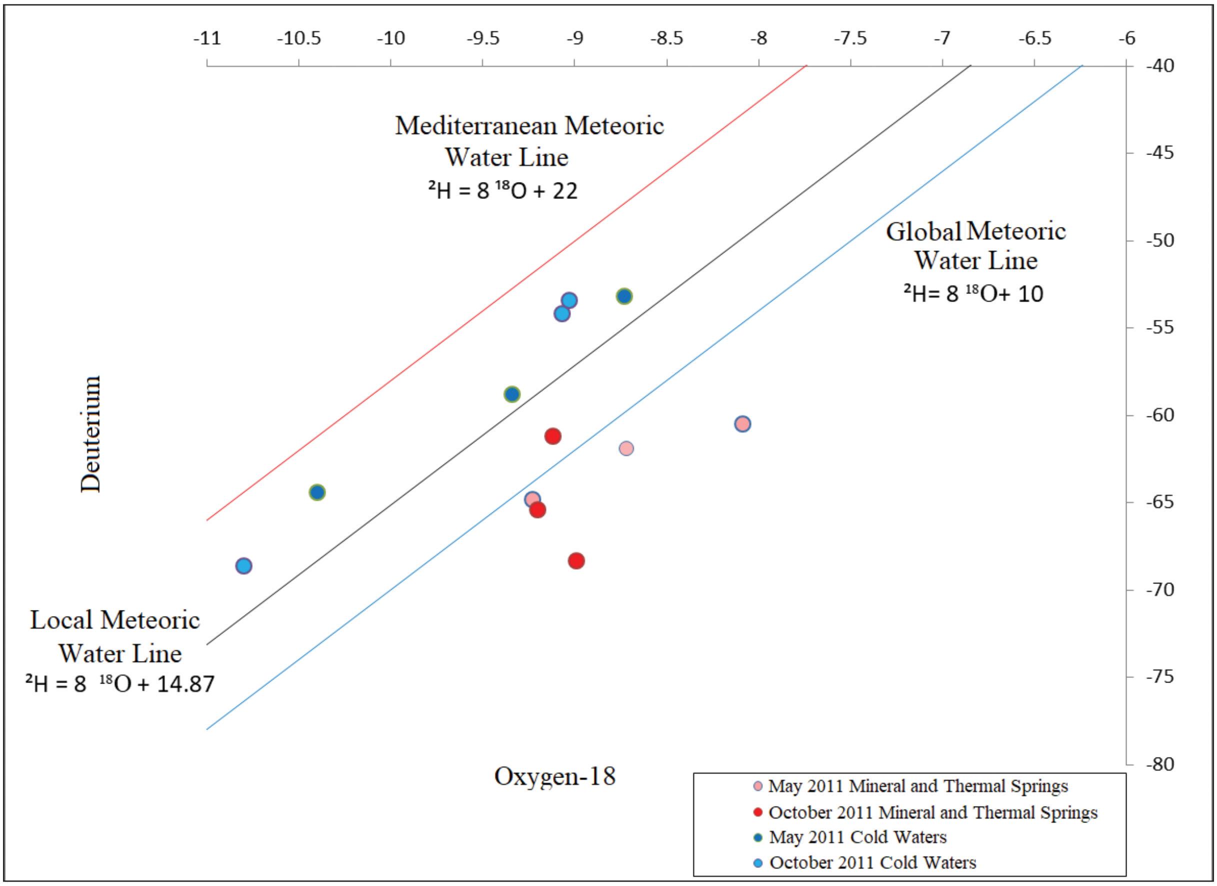


Figure 10- Oxygen-18-deuterium plots of water resources in the study area.

located between the Global Meteoric Water Line and the Mediterranean Meteoric Water Line (Dansgaard, 1964) (Figure 10). Thermal and cold water springs have similarities among themselves and it has been determined that they are of meteoric origin. The $\delta^{18}O$ and $\delta^{2}H$ values of the springs aren't significant observed shift from the GMAIL in both seasons. Only mineral and thermal springs in wet season were light affected by evaporation factors.

The tritium value in mineral and thermal waters was between 0 – 1.1 TU in May 2011 and between 0–0.41 TU in October 2011. These values are close to detection limits in both seasons. The tritium value in the same period was between 4.45–5.95 TU in May 2011 and between 5.11–6.19 TU in October 2011 for cold water springs (Table 1). It is thought as a result of the tritium values of the İspendere mineral and thermal waters, <0,5 [excluding the May 2011 analysis result of thermal spring number 2 (1.1 ± 0.9 TU)] it displayed deep circulation for about 50 years and above (Figure 11). The relationship between tritium-electrical conductivity in the waters was given in figure 12. The decrease in tritium content and the increase in electrical conductivity show a correlation between the long residence time and slow rate of regeneration of the groundwater system. Cold waters have comparatively low electrical conductivity (EC $\leq$ 435) and high tritium ($\geq$4.45 TU) values corresponding to rainfall, indicating fast recharge and short flow path. Mineral and Thermal water samples with no seasonal variation (Table 1) in tritium contents show relatively longer residence time with slow movement and that is also evident by low tritium values (< 1.1 TU). These waters have been in contact with geological units for a longer period and dissolves salts increasing its EC.

5. Conclusion

In this study, geothermal and hydrochemical characteristics of mineral and thermal waters in the İspendere geothermal fields are described. The results and interpretations that have been obtained from this study and the geothermal borehole data (292 m depth, maximum temperature of 25°C) were listed below:

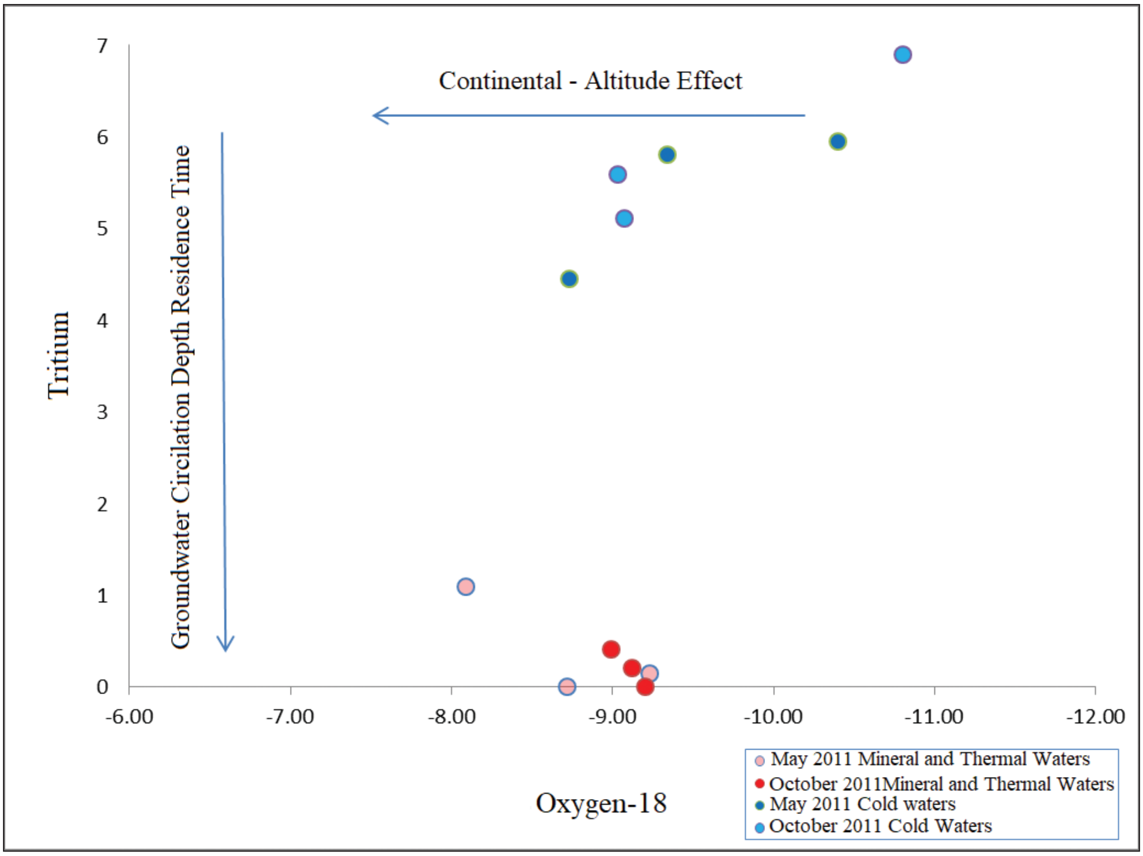


Figure 11- Tritium - Oxygen-18 chart.

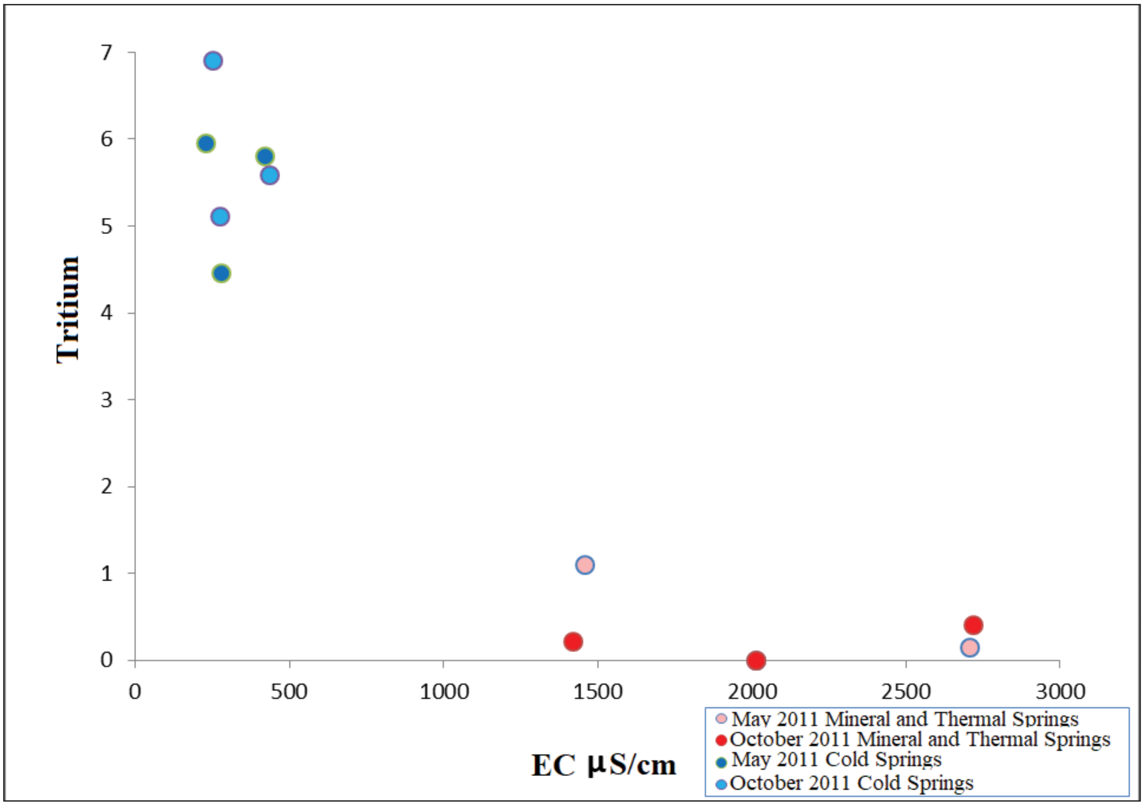


Figure 12- Tritium - EC chart.

1. It has been determined that the İspendere region has low geothermal potential because of intensive cold water mixing. Mineral and thermal waters in the study area have been classified as Mg-HCO_3 water type, cold waters have been classified as Ca-HCO_3 water type.

2. The cations in the mineral and thermal waters have been listed as $rMg^{2+}>rCa^{2+}>rNa^{+}+rK^{+}$ and the anions as $rHCO_3^{-}>rSO_4^{2-}>rCl^{-}$, whereas the cations in the cold waters have been listed as $rCa^{2+}>rMg^{2+}>rNa^{+}+rK^{+}$ and the anions as $rHCO_3^{-}>rSO_4^{2-}>rCl^{-}$. It has been determined that the mineral, thermal waters and cold waters are of meteoric origin and they have been defined as about 50 years and above waters because of their low tritium content.

3. The İspendere thermal and cold waters have been evaluated within the scope of shallow and peripheral flow immature mixture waters according to the Giggenbach diagrams.

4 Based on the quartz geothermometers, reservoir rock temperatures were calculated as 95-132° C for İspendere thermal well and springs.

5. The light $\delta^{18}O$ values of the cold springs from which samples were taken within the scope of this study as well as the high tritium and low chloride and EC values in comparison with the thermal waters indicates that these springs are fed by rains at high altitude and that they surface in a short time. That is why; these cold waters have been classified as young waters with shallow circulation.

Acknowledgement

This research was supported by IUBAP (Inonu University Scientific Projects Unit) under the project number of IUBAP 2011/46. The authors are grateful for Editor and anonymous reviewers for their helpful and constructive comments on an earlier draft of this paper.

References

Afşin, M., Canik, B. 2013. Orta Anadolu'daki bazı jeotermal sularda su kimyası ve izotopik değişimlerin anlamı, Aksaray Üniversitesi Jeoloji Müh. Bölümü Baki Canik Su Medeniyeti Semp. s.24.

APHA. 2005. Standard methods for examination of water and wastewater 21st ed. American Public Health Association, Washington D.C.

Arnórsson, S., D'Amore, F., Gerardo-Abaya, J. 2000. Isotopic and Geochemical Techniques in Geothermal Exploration, Development and Use: Sampling Methods, Data Handling, Interpretation (ed. Arnórsson S), International Atomic Energy Agency Publication, Vienna.

Arnorsson, S., Gunnlaugsson, E., Svavarsson, H. 1983. The chemistry of geothermal waters in Iceland III., chemical geothermometry in geothermal investigations. Geochim Cosmochim Acta. 47, 567–577

Anees, M., Shah, M.M. Qureshi, A.A. 2015. Proc. Earth Planet. Sci. 13, 291–295.

Baba, A., Sanliyuksel D. 2011. Hydrogeochemical and isotopic composition of a low-temperature geothermal source in northwest Turkey: case study of Kirkgecit geothermal area. Environ Earth Sciences. 62, 529–540.

Back, W., Hanshaw, B.B. 1965. Advances in hydroscience. In chemical Geohydrology, Academic Press, New York, Vol. 11, p-49.

Battistel, M., Hurwitz, S., Evans, W., Barbieri, M. 2014. Energy Proc. 59, 359–365.

Beyarslan, M. 1991. Petrographic Properties of the ophiolite of İspendere (Kale-Malatya). Firat University, Institute of Science. M.Sc. Thesis, pp 57.

Beyarslan, M., Bingo,l A.F. 2010. Ultramafics and Mafic Bodies in Cumulates of Ispendere and Kömürhan Ophiolites (SE Anatolian Belt, Turkey). Turkish Journal of Science and Technology. 5(1), 19- 36.

Boyed, C.E. 2000. Water Quality: An Introduction. Kluwer Academic Publisher, New York, 330 p.

Browne, P.R.L. 1991. Mineralogical guides to interpreting the shallow paleohydrology of epithermal mineral depositing environments. Proc 13 th NZ Geothermal work – shop, Auckland. 263-270.

Bojadgieva, K., Dipchikova, S., Benderev, A., Koseva, J. 2002. Thermal Waters and Balneolody in Bulgaria. GHC Bulletin, March, 18-25

Chenaker, H., Houha, B., Valles, V. 2017. Isotope studies and chemical investigations of hot springs from North-Eastern Algeria, J. Mater. Environ. Sci, 8 (12), pp. 4253-4263.

Clark, I.D., Fritz, P. 1997. Environmental Isotopes in Hydrogeology, Lewis Publication. Pp 328. New York.

Craig, H. 1961*a*. Isotopic variations in meteoric waters. Science. 133, 1702–8.

Craig, H. 1961*b*. Standard for reporting concentration of deuterium and oxygen-18 in natural waters. Science. 113, 1833–34.

Çetindağ, B., Afşin, M., Canik, B. 1993. Hydrogeological investigation of mineral and thermal water of İspendere (Malatya). Suat Erk Symposium Ankara, Turkey. 403-410. (In Turkish).

Chandrajith, R., Barth, J.A.C., Subasinghe, N.D., Merten, D., Dissanayake, C.B. 2013. Geochemical and isotope characterization of geothermal spring waters in Sri Lanka: Evidence for steeper than expected geothermal gradients. Journal of Hydrology.476, 360-369.

Dansgaard, W. 1964. STab. isotopes in precipitation. Tellus. 16, 436–438.

Demer, S. 2008. Hydrogeological, hydro-geochemical and isotope geochemical investigations of the groundwater in Isparta and its nearly environs and monitoring of the drink water quality. Suleyman Demirel University, Institute of Science, 182 p. PhD. Thesis, Isparta, Turkey. (In Turkish).

DMI. 2010. General Directorate of State Meteorological Service, in Turkish.

DSİ. 1991. Kapıkaya Dam planning report. the General Directorate of State Hydraulic Works. Ankara, Turkey. (In Turkish).

Dumanlılar, Ö. 1993. Geology and petrography of magmatites of İspendere (Malatya) region: A.U. Institute of Science, M.Sc. Thesis, Ankara, Turkey. pp 62. (In Turkish).

Dumanlılar, H., Aydal, D., Dumanlılar, Ö. 1999. Geology, Mineralogy and Geochemistry of Sulphide mineralization of İspendere (Malatya) Region. Bulletin of Mineral Research and Exploration. 121, 225-250. (In Turkish).

Ersoy, A.F., Sönmez, S.Ç. 2014. Hydrogeochemical and isotopic characteristics of the Ilica geothermal system (Erzurum, Turkey). Environ Earth Sci, 72: 4451-4462.

Fournier, R.O. 1973. Silica in lhermal waters laboratory and field investigations. Proceedings of the International Symposium on Hydrogeochemistry and Biochemistry, Tokyo, Vol 1, Clark Co, Washington DC. 122–139.

Fournier, R.O. 1977. Chemical geothermometers and mixing models for geothermal systems. Geothermics. 5, 41–50.

Gat, J.R. 1971. Comments on the STab. Isotope Method in Regional Groundwater Investigations. Water Resources Research. 7, 980-993.

Giggenbach, W.F. 1988. Geothermal solute equilibrium. Derivation of Na- K- Mg- Ca geoindicators. Geochim Cosmochim Acta. 52, 2749–2765.

Giggenbach, W.F. 1991. Chemical techniques in geothermal exploration. In: D’Amore, F. (coordinator), Applications of geochemistry in geothermal reservoir development. UNITAR/UNDP publication, Rome, 119-142.

Giggenbach, W.F., Glover, R. 1992. Tectonic regime and major processes govering the chemistry of water and gas discharges from the Rotorua geothermal field. Geothermics, 21, 121–140.

Gunnlaugsson, E. 2008. Importance Of Chemıstry In Geothermal Exploratıon And Utılızatıon Presented at the Workshop for Decision Makers on Direct Heating Use of Geothermal Resources in Asia, organized by UNU-GTP, TBLRREM and TBGMED, in Tianjin, China,

Gürocak, Z., Alemdağ, S. 2002. Kinematical Assessments on Rock Slopes at The Kapıkaya (Malatya) Dam Site. Bulletin of Faculty of Engineering of Cumhuriyet University, Serie A-Earth Sciences. 19(2), 151-164.

Harvey, K. 2007. Healing Touch. Sawubona, 75-76.

Hayashi, M. 2004. Temperature-electrical conductivity relation of water for environmental monitoring and geophysical data inversion. Environmental Monitoring and Assessment 96:119–128.

Hellman, M.J. Ramsey, M.S. 2004. Analysis of hot mineral springs and associated deposits in Yellowstone National Park using ASTER and AVIRIS remote sensing. J. Volcanol. Geotherm. Res. 134 (1-2) 195-219.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. 3rd Edition, US Geological Survey Water-Supply Paper 2254, 246 p.

Hugh, P., Taylor, H. P. Jr. 1974. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Economic Geology. 69, 843-883.

IAH (International Association of Hydrogeologists). 1979. Map of Mineral and Thermal Water of Europe, Scale 1: 500,000. International Association of Hydrogeologists, London.

IAEA. 1981. Stable. isotope in hydrology, IAEA. Tech., Rep. International Atomic Energy Agency - Ser., No 210, pp 339.

IAEA. 1983. International Atomic Energy Agency, Guidebook on Nuclear Techniques in Hydrology, IAEA. Tech. Rep. Ser., No 91, pp 439.

IAEA. 1998. Analytical quality in the IAEA isotope hydrology laboratory: Some recent improvements. Water and environment news, IAEA, No.3, pp 5-7.

IAEA. 2010. Overview of Laboratory Isotope Analyses Methods for Water Resources Studies. International Atomic Energy Agency, Vienna.

Geothermal Prossesing Report. 2010. İspendere mineral and thermal water processing report, Special Provincial Administration General Secretary (Unpublished, In Turkish). Malatya, Turkey.

Kipng'ok, J., Kanda, I. 2011. Introductıon To Geochemıcal Mappıng Presented at Short Course VI on Exploration for Geothermal Resources, organized by UNU-GTP, GDC and Ken Gen, at Lake Bogoria and Lake Naivasha, Kenya, Oct. 27 – Nov. 18.

Mazor, E. 2004. Chemical And Isotopic Groundwater Hydrology. Marcel Dekker Inc., New York, pp 453.

Nicholson, K. 1993. Geothermal Fluids, Chemistryand Exploration Techniques.Springer-Verlag, Berlin.

Olivier, J., Van Niekerk, H.J., Van der Walt, I.J. 2008. Physical and chemical characteristics of thermal springs in the Waterberg area in Limpopo Province, South Africa. Water SA Vol. 34 No. 2.

Panichi, C., Gonfiantini R. 1978. Environmental isotopes in geothermal studies. Geothermics. 6, 143 – 161.

Parlak, O., Nurlu, N., Rızaoğlu, T., Karaoğlan, F., Bağcı, U., Önal, A., Kürüm, S. 2010. Tectonic Setting and Significance of İspendere (Malatya) Ophiolite within the SE Anatolian Orogenic Belt, IV. National Geochemistry Symposium. 45 – 46. (In Turkish).

Pasvanoğlu, S. 2013. Hydrogeochemistry of mineral and thermalized waters in the Diyadin(Ağri) area, Eastern Turkey, Applied Geochemistry. 38, 70-81.

Pasvanoğlu, S., Canik, B., Arıgün, Z. 2005. Hydrochemical Investigation of Banaz-Hamamboğazı Mineral and thermal Water, II. Isotope Techniques in Hydrology Symposium, İzmir, Turkey. 209-225. (In Turkish).

Pasvanoğlu, S., Chandrasekharam, D. 2011. Hydrogeochemical and isotopic study of mineral and thermalized waters from the NevŞehir (Kozakli) area, Central Turkey. Journal Volcanology and Geothermal Research. 202 (3-4), 241-250.

Pekkan, E., Bayarı, S., Şensoy, A, Şorman, A., Arıkan, A. 2008. Investigation of the precipitation-discharge dynamics of Kırkgoze basin (upper euprates, Erzurum-Turkey) by using sTab. isotopes, III. Isotope Tecniques in Hydrology Symposium, S.205-213. (In Turkish).

Petraccia, L., Liberati, G., Masciullo, S.G. 2005. Water, mineral waters and health. Clin. Nutrit. 25 (3) 377-385.

Piper, A.M. 1944. A graphic procedure in the geochemical interpretation of water analyses. American Geophysical Union, 25, 914-923

Schoeller, H. 1962. Les Eaux Souterraines. Masson and Cie, Paris, 642pp.

Sheppard, S.M.F. 1981. STab. isotope geochemistry of fluids. D. T. Rickard and F.E. Wickman (Eds.), Chemistry and geochemistry of solutions at high temperatures and pressures. Physics and Chemistry of the Earth. 13/14, 419-445.

Sorensen, J.A., Glass, G.E. 1987. Ion and Temperature Dependence of Electrical Conductance for Natural Waters. Analytical Chemistry, 59, 1594-1597.

Truesdell, A.H. 1984. Introduction to chemical calculations. Fluid Mineral Equilibria in Hydrothermal Systems, R. W. Henley et al. (eds.). Revised Economic Geology. 1, 1-8.

Yazgan, E., Gültekin, M.C., Poyraz, N., Sirel, E., Yıldırım, H. 1987. Malatya güneydoğusunun jeolojisi ve Doğu Toroslar'ın jeodinamik evrimi. Maden Tetkik ve Arama Genel Müdürlüğü Rapor No: 2268, Ankara. (In Turkish) (unpublished).