

Geochemical Properties and Determination of Turnover Time by Using ^{14}C Isotope, in Kizildere and Tekkehamam Geothermal Field of Turkey

Nazim YILDIRIM*, Ismail Noyan GUNER

General Directorate of Mineral Research and Exploration of Turkey

Energy Department, R&D Section 06520 Balgat, ANKARA-TURKEY

nazim@mta.gov.tr

Keywords: Kizildere, isotope, geochemistry, ^{14}C

ABSTRACT

There are many geothermal manifestations, in the temperature range from 35 to 242°C, on the eastern part of Buyuk Menderes Graben section. The investigated section of the Graben extends between Buhrakent-Yenice and Pamukkale in the Aegean Region. Thermal springs, cold springs and deep wells of the fields were investigated by means of field measurements, chemical analyses and isotope analyses. By the means of this investigation the origin, the turnover time, the chemical characteristics and the recharge elevation of the area were determined. On these purposes, complete hydrochemical, $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^3\text{H}$, ^{14}C , $\delta^{34}\text{S}$ - SO_4 and $\delta^{18}\text{O}$ - SO_4 isotope analyses were realized. On the basis of topographical structure, geological formation and chemical properties, four primary and six intermediate types of ground water are recognized in the studied area. The deuterium-altitude relation of the shallow ground waters shows that the Kizildere and Tekkehamam field's thermal waters are approximately fed from 1300 - 1900 m.a.s.l. The $\delta^{34}\text{S}$ - SO_4 and $\delta^{18}\text{O}$ - SO_4 isotope analysis, reveal that the origin of the SO_4 ion in Tekkehamam and its surrounding thermal springs, is from the dissolution of gypsum layers of the Pliocene aged Kolonkaya Formation. Due to the existence of high temperature in the reservoir, exchange between the $\delta^{18}\text{O}$ - SO_4 and $\delta^{18}\text{O}$ - H_2O isotopes takes place in the Kizildere's geothermal reservoir fluid. The rate of the exchange is calculated to range between 46 % and 84%. NETPATH was used in the interpretation. The ^{14}C isotope calculation results refer to 22000 - 31000 years of turnover time for the geothermal fluid of the area.

1. INTRODUCTION

Kizildere and Tekkehamam geothermal fields are located on the eastern part of Buyuk Menderes Graben (Fig. 1) which are 200 km away from Aegean coast. The width of graben varies from 3 and 35 km. The western part is wider than the eastern part. Step faulting systems have been defined on both the north and south flanks. Geothermal activity in the northern flank is more widely spread than in south flank due to greater inclination of the faults. Presently, General Directorate of Mineral Research and Exploration of Turkey (Maden Tetkik Arama Genel Mudurlugu-MTA) has drilled approximately 50 shallow and deep wells for their exploration and exploitation. There are 15 thermal springs at the Tekkehamam and its surroundings. In 1984 a power plant of capacity 20 MWe was installed in Kizildere geothermal field. Similarly, a dry- CO_2 production plant with a capacity of 20 tons/day was installed in 1989.

MTA initiated a project "Determination of Age and Origin of the High Enthalpy Geothermal Fluids of the Büyü

Menderes Graben Project" for the assessment of horizontal and vertical extension of the Kizildere geothermal field in order to plan a future geothermal development between 2000-2003. The present work is the part of this project. The aim of this study is to determine the recharge area and turnover times of the water resources found in the region, by the combination of related isotope techniques and hydrogeochemical data

2. GEOLOGICAL SETTINGS

Metamorphic Menderes massif, which overlies on the one third of Aegean Region, consists of two major units as the core and cap rock series. The core series are formed of Precambrian-Cambrian aged high-grade schist, gneisses, migmatites and metagabbros. The cap rock series contain mica schist, quartzite, phyllite, marble, chlorite and sericite. Metamorphism occurred in amphibole and green-schist facies.

Simsek (1985) identified and clarified Pliocene aged post metamorphic units as Kizilburun formation, Sazak formation, Kolonkaya formation and Tosunlar formation. Kizilburun formation consists of unconsolidated clay, sandstone and gravel. On the other hand, Sazak formation is formed of limestone, marl, clay, sand and gravel, and overlay conformity Tosunlar formation. Kolonkaya formation, which overlay Sazak formation with conformity, consists of marl, conglomerate, siltstone, and limestone with interbedded gypsum. Tosunlar formation, the latest post tectonic unit, overlays Kolonkaya formation with unconformity and formed conglomerate, sandstone, claystone and limestone.

3. ANALYTICAL PROCEDURES

Field work was carried out in May, 2000. The water samples for $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^3\text{H}$ were collected from hot springs, cold springs, drilled wells for drinking water, deep geothermal wells of Kizildere and the Buyuk Menderes River. Samples for radiocarbon analysis and dissolved SO_4 were collected only from thermal waters. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses were conducted in the stable isotope laboratory in Weizmann Institute, Israel. $\delta^3\text{H}$ samples were analyzed with Liquid Scintillation Counting facility while radiocarbon analyses with Accelerator Mass Spectrometry facility. Analytical errors are ± 0.1 for $\delta^{18}\text{O}$, ± 1 for $\delta^2\text{H}$, ± 0.3 for $\delta^3\text{H}$ and ± 0.1 for radiocarbon analyses. Dissolved SO_4 samples were analyzed at Environmental Isotope Lab. in Waterloo University, Canada. The analytical errors are ± 0.2 for $\delta^{34}\text{S}$ and ± 0.5 for $\delta^{18}\text{O}$. Isotope data are given in Table 1.

Hydrochemical samples were analyzed in the geochemistry laboratories of Geothermica Italiana (Enel, 1988) and MTA (Yildirim and Guner, 2002).

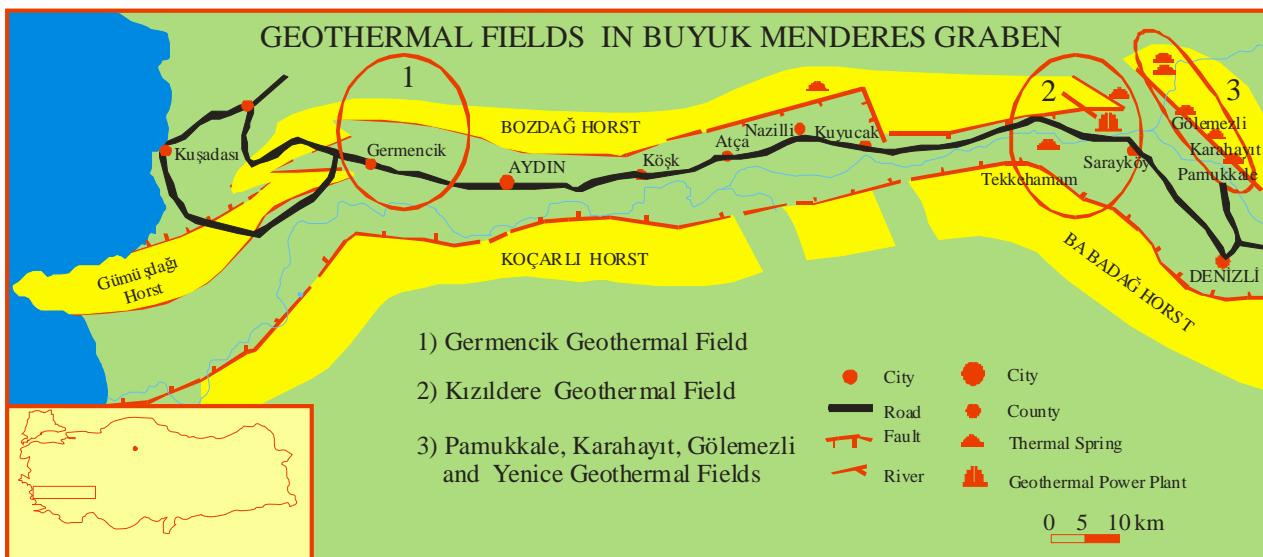


Figure 1: Location map of Kizildere Geothermal Field and its neighborhood geothermal fields (Simsek 2004).

Table 1: Isotope analyses thermal and cold waters in Kizildere geothermal field ($T=^{\circ}\text{C}$, $\text{EC}=\mu\text{S}/\text{cm}$, $\delta^{18}\text{O}$ and $\delta^2\text{H}=\text{‰ VSMOW}$, $\delta^3\text{H}=\text{TU}$, $\delta^{13}\text{C}=\text{‰ PDB}$, $^{14}\text{C}=\text{pmc}$, CS=cold water, TS=Thermal spring, TW=Thermal water well,).

| Name | Type | EC | T | ^{18}O | ^2H | ^3H | $^{13}\text{C}_{\text{TDIC}}$ | $^{14}\text{C}_{\text{TDIC}}$ |
|------------------------|------|------|------|-----------------|--------------|--------------|-------------------------------|-------------------------------|
| Babacik | TS | 3400 | 54 | -7.4 | -51.6 | 0.1 | nd | nd |
| Kiline C. | CS | 101 | 12.9 | -8.9 | -49.6 | 9.8 | nd | nd |
| Geleyli | CS | 150 | 14.6 | -8.5 | -50 | 6.4 | nd | nd |
| T.H. Hayuzlu | CS | 403 | 13.1 | -8.6 | -48.2 | 6.7 | nd | nd |
| Gökböl | CS | 150 | 14.6 | -9.5 | -53.7 | 4.4 | nd | nd |
| Gölyeri | CS | 101 | 13.6 | -8.2 | -52.7 | 10.6 | nd | nd |
| BM River | CS | 410 | 13 | -7.3 | -49 | 5.5 | nd | nd |
| Inalti | TS | 4170 | 96 | -6.7 | -57.5 | 0.1 | nd | nd |
| Karlik T. South | CS | 180 | 13.6 | -8.6 | -49.4 | 9.5 | nd | nd |
| Karlik T. North | CS | 118 | 9.9 | -9 | -54.9 | 9.5 | -19.8 | 116 ± 0.1 |
| KD 6 | TW | 4750 | 194 | -6.6 | -55.3 | 0.1 | 0.38 | 0.21 ± 0.1 |
| KD 14 | TW | 5350 | 210 | -5.1 | -53.3 | 0.1 | 0.32 | 0.35 ± 0.11 |
| KD 15 | TW | 5190 | 208 | -5.3 | -53.2 | 0.1 | 0.78 | 0.24 ± 0.1 |
| KD 21 | TW | 5090 | 205 | -5.8 | -54 | 0.3 | 0.5 | 0.48 ± 0.12 |
| R1 *** | TW | 5630 | 96 | -4.10 | -51.30 | 0.33 | 1.26 | 2.27 ± 0.1 |
| Sahin Tepesi | TS | 5320 | 38 | -4.5 | -28 | 2 | nd | nd |

4. RESULTS AND DISCUSSION

4.1 Hydrochemical composition

Several hydrochemical processes for controlling the major ion components of groundwater have been identified by using NETPATH software (Plummer et al. 1996). The processes are the dissolution of carbonate, gypsum and silicate minerals, CaCO_3 weathering under high temperature condition, which causes underground production of CO_2 , and Na^+ - Ca^{++} ions exchange reaction in wall rock, diopside and illite minerals precipitation. The concentrations of Na , Cl , HCO_3 ions and pH values of $\text{Ca}-\text{HCO}_3$ group

groundwater found in the studied area are slightly lower than in the $\text{Na}-\text{HCO}_3-\text{SO}_4$ type of groundwater in the same region

Hydrochemical analyses indicate that there are four primary and six intermediate types of ground water in the studied area (Fig. 2). The waters of Kizildere geothermal field, that interact for a long time with high grade metamorphic rocks, at high temperature (up to $220-242^{\circ}\text{C}$) belongs to $\text{Na}-\text{HCO}_3$ primary hydrogeochemical type. It represented with TW. The chemistry of this $\text{Na}-\text{HCO}_3$ group is mainly dominated

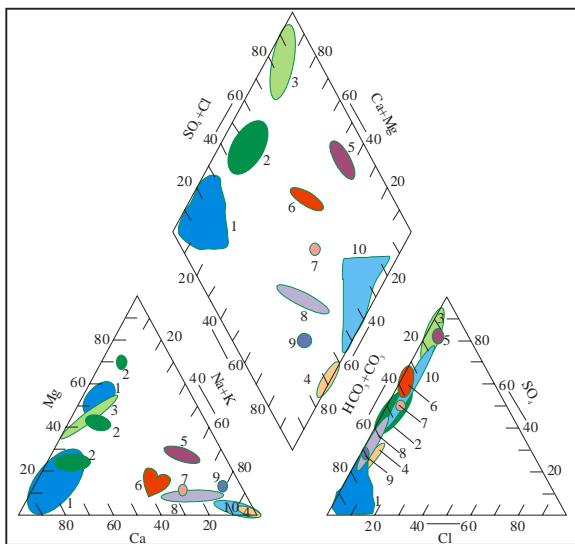


Figure 2: Piper diagram of cold and thermal water samples from study area. 1) Cold waters; 2) Pamukkale TS, Karahayit TS, Çukurbag TS, Bolmekaya TS, Menderes River; 3) Bolmekaya CS, Asagi Tirkaz CS; 4) Kizildere TW; 5) Gokdere CW; 6) Golemezli TS, Golemezli TW, Babacik TS, Demirtas TS; 7) TH-1 TW; 8) Kamara TS, Yenice TS, Ortakci TS, 9) Golemezli individually MTA-1 TW; 10) Tekkehamaam TS Group (CS=cold water, CW=Cold water well, TS=Thermal spring, TW=Thermal water well.).

by Na^+ and HCO_3^- ions. In other words the percentage of these two ions in the total cation and anion concentration individually is more than 50 %

The cold water (CS) in the vicinity of thermal water environment are of the alkaline earth bicarbonate ($\text{Ca}-\text{CO}_3$) type. This type of the water group is related to shallow groundwater circulation in the study area. Both $\text{Na}-\text{HCO}_3$ and $\text{Ca}-\text{CO}_3$ types water in the region circulate in the same stratum. The different interaction time and the temperature dominate the hydrogeochemical characteristics of these two types.

Third primary type (TS) is Ca and SO_4 ions dominated waters group. This CaSO_4 type of water, containing up to 110 meq/l TDS. It gains its characteristic by interacting mainly with anhydrite bearing Neogene sedimentary rocks found in southern part of the Buyuk Menderes Graben ($18-58^\circ\text{C}$).

The fourth primary hydrogeochemical type (NaSO_4) containing approximately 70 meq/l TDS, can be ascribed to $\text{Na}-\text{HCO}_3-\text{SO}_4$ waters characteristic of the margins of liquid-dominant geothermal system.

All the other waters of the region have hydrogeochemical futures intermediate among the above-described four primary types of $\text{Na}-\text{HCO}_3$, $\text{Ca}-\text{HCO}_3$, $\text{Ca}-\text{SO}_4$ and $\text{Na}-\text{SO}_4$. They have been formed by different proportion of mixtures among the primary types and having the following characteristics:

$\text{Na}-\text{HCO}_3-\text{SO}_4$ ($75 < \text{TDS} < 104$ meq/l)

$\text{Ca}-\text{SO}_4-\text{HCO}_3$ ($26 < \text{TDS} < 84$ meq/l)

$\text{Na}-\text{Mg}-\text{SO}_4$ ($\text{TDS} \leq 220$ meq/l)

$\text{Na}-\text{Ca}-\text{HCO}_3$ ($55 < \text{TDS} < 94$ meq/l)

$\text{Na}-\text{Ca}-\text{SO}_4-\text{HCO}_3$ ($34 < \text{TDS} < 115$ meq/l)

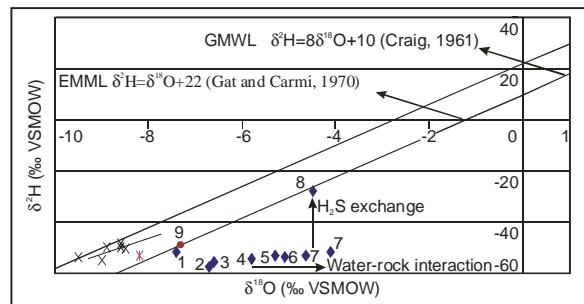


Figure 3: $\delta^{18}\text{O}$ - $\delta^2\text{H}$ diagram of water samples in Kizildere geothermal area. 1) Babacik, 2) Inalti, 3) KD-6, 4) KD-21, 5) KD-15, 6) KD-14, 7) R1*, 8) Sahintepesi, 9) B.M. River, X) Cold Waters (R1 data from Simsek, 2002)

4.2 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopes

Figure 3 shows $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ for groundwater samples. Recent groundwater samples in the recharge area are along the local meteoric line ($\delta^2\text{H} = \delta^{18}\text{O} \cdot 5.5361 + 7.001$). According to the slope of 5.5361, precipitation which recharges the high altitude springs, originate from the evaporation occurred over the Mediterranean Sea and the calculated relative humidity is 83% (Gonfiantini, 1986).

$\delta^{18}\text{O}-\delta^2\text{H}$ relation indicates that all the thermal waters in the Kizildere geothermal field are of meteoric origin. A gradual increase in $\delta^{18}\text{O}$ isotope values are due to the water-rock interaction at high temperatures. The enrichment of $\delta^2\text{H}$ content of Sahintepesi spring is caused by the H_2S exchange process. This process takes place quickly and occurs in conditions, which contain high ratio of dissolved gases (Clark and Fritz, 1999).

The isotopic data does not show any hydraulic effects of Buyuk Menderes River on the Kizildere geothermal waters. The mean $\delta^2\text{H}$ value of thermal waters in the Kizildere geothermal field is 2.4‰ lighter than the values of cold waters in the recharge area. This reveals that the geothermal waters resulted from paleorecharge conditions.

By using ^{14}C isotope, the ages of groundwater in Southern France, near Mediterranean coast, having $\delta^2\text{H}$ isotope values in the range -50 to -60‰ and deuterium excess +14 were calculated to be between 20,000 and 30,000 years, (Huneau et. al., 2000). The calculated recharge area elevation of Kizildere geothermal field lies between 1300–1900 m.a.s.l. Topographically, these elevations correspond to the schist and gneisses of Menderes Massive. The result is in agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes data indications (Vengosh et al., 2002).

4.3 $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved SO_4

16 samples for dissolved SO_4 were collected from thermal waters in Kizildere geothermal field and its surroundings in 2000. In Figure 4, it can be seen that the dissolved SO_4 contents of thermal waters in (2), (4), (7), (9) and (10) type are ranging between 7.1 and 39.4 meq/l. These values indicate that the origin of SO_4 ion of the thermal waters has derived from the gypsum layers in the Kolonkaya formation except the ones named the Sahintepesi (a swamp) and the Bolmekaya springs. The origin of SO_4 ion in those springs is atmospheric (Yildirim and Guner, 2002).

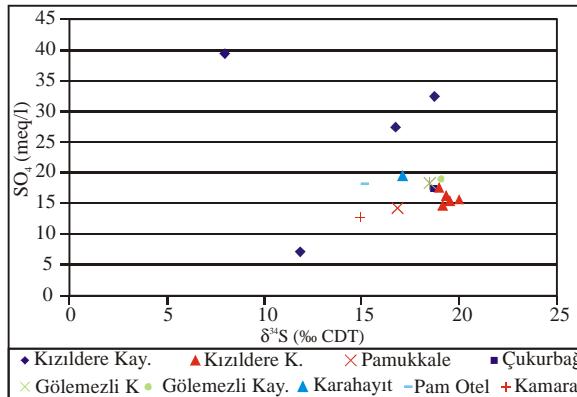


Figure 4: $\delta^{34}\text{S}$ - SO_4 diagram of water samples in Kizildere geothermal field and its environs (from Yildirim and Guner, 2002).

The SO_4 ions of all the thermal waters and wells were derived from gypsum layers in Pliocene aged Kolonkaya formation (Fig. 5). The SO_4 ion of Sahintepesi spring is likely to be formed by the oxidation of H_2S gas. Dissolved H_2S gas in the spring water has been produced by the reduction of SO_4 in the gypsum layers of Kolonkaya formation. When thermal water interacts with atmospheric oxygen, the H_2S gas converts to SO_4 . The geothermal production wells have the ^{18}O exchange reactions between H_2O and SO_4 . According to van Everdingen and Krouse (1985) model, the exchange rates were calculated to be 46–84% (Yildirim and Guner, 2002).

4.4 Tritium

The tritium values of the shallow groundwater samples collected from recharge area are found between 10.6 - 4.4 TU. These values indicates the recent recharge pattern. While the tritium value of Sahintepesi is 2 TU, the other thermal waters are found less than 0.33 TU. It has been indicating mixing processes with recent shallow ground waters for Sahintepesi spring.

4.5 Carbon isotopes and age determination

According to Clark and Fritz (1999), although rainwater contains ^{14}C from atmosphere, the soil zone that gives recharging groundwater its radiocarbon signal. Atmospheric ^{14}C is incorporated into vegetation by photosynthesis and later released in the soil by decay and root respiration. The result is huge reservoir of ^{14}C in the soil zone. In general, dilution and loss of ^{14}C by geochemical reaction within the soil zone and along flow path must be addressed. Typical reactions such as calcite dissolution, dolomite dissolution, exchange with aquifer matrix, oxidation of organics in aquifer matrix and diffusion of ^{14}C into aquifer matrix, cause dilution of ^{14}C content of groundwater and increase apparent age of the groundwater. Consequently, dilution correction should be considered for correct age determination.

In the study area, $\delta^{13}\text{C}-\text{CO}_2$ values that lie between -0.9‰ and -1.4‰ PDB indicate the occurrence of marine carbonates decomposition (Blavoux et al, 1982, Ercan et al, 1995). TDIC sample from recharge area of the Kizildere geothermal field has 116 pmc of ^{14}C and -19.8‰ PDB of $\delta^{13}\text{C}$. However, the fluids from the geothermal production wells have TDIC values of about 40.28 - 44.71 meq/l, ^{14}C and of 0.21 – 2.27 pmc (Fig 6). The value of 2.27 pmc encountered R1 production well's water (242 °C), indicates

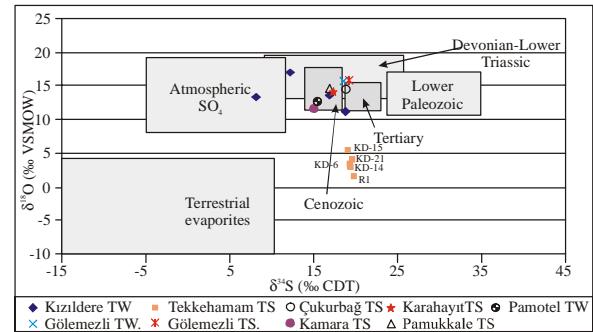


Figure 5: $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ distribution in dissolved SO_4 ion in Kizildere geothermal field and its environs, adopted from Clark and Fritz (1999) and Yildirim and Guner (2002).

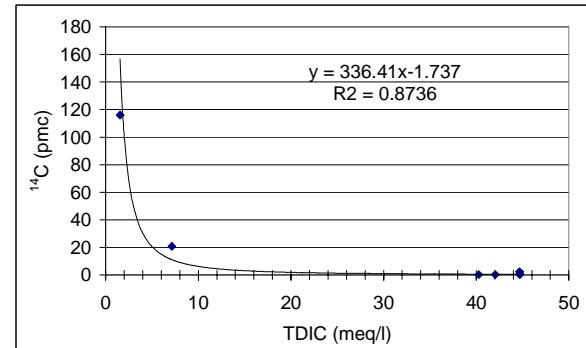


Figure 6: $\delta^{13}\text{C}$ -TDIC diagram of water samples in Kizildere geothermal field.

that there is mixture between Ca HCO_3 and $\text{NaHCO}_3-\text{SO}_4$ types of the groundwaters in the area. After these mixing processes, the new hydrogeochemical type is equilibrated due to high temperature conditions. This occurrence is observed in the production well abbreviated as KD in Table 1. $\delta^{13}\text{C}$ of TDIC in the geothermal waters are enriched with respect to $\delta^{13}\text{C}$ in CO_2 gas.

After infiltration, ^{14}C concentration of the water decreases because of dilution and radioactive decay. In Fig 6, to visualize the effect of the dilution, ^{14}C values plotted versus their TDIC concentrations. The infiltration originally begins with 1.55-meq/l TDIC concentration and 116 pmc. Afterwards, carbonate dissolution and geogenic CO_2 participation cause dilution in the ^{14}C concentration of the groundwater.

The ages of the Groundwater in the area were modeled by using NETPATH (Plummer et. al., 1996). The initial CaHCO_3 and CaSO_4 characteristics of recharge water in the investigated area, by passing time and with the different mixing proportion, change respectively to $\text{Ca-Na-HCO}_3-\text{SO}_4$, $\text{Na-Ca-HCO}_3-\text{SO}_4$ and finally to $\text{Na-HCO}_3-\text{SO}_4$ types. The last end member ($\text{Na-HCO}_3-\text{SO}_4$) geothermal waters have very low Ca (1 mg/l) and Mg (0.2 mg/l) ions concentration. To run the model, calcite, gypsum, SiO_2 , CO_2 (gas), chlorite, K-spar with Ca/Na, exchange, diopside and illite phases were selected. As a representative of the geothermal fluid, R1 production well fluid, due to its high ^{14}C content, was selected to run the model.

Table 2: Calculated mass transfers within water-rock interaction and ^{14}C ages by using NETPATH (Plummer et. al., 1996).

| | KD-6 | KD-14 | KD-15 | KD-21 | R1 | | |
|-------------------------|----------------|----------|----------------|----------|----------------|-------|----------------|
| Initial | Karlik | Karlik | Karlik | Karlik | Karlik | 0.24 | |
| Final | KD-6 | KD-14 | KD-15 | KD-21 | R1 | KD-15 | 0.76 |
| Calcite | 28.22466 | 27.50415 | 38.11365 | 29.15605 | 29.15605 | | |
| Gypsum | 6.54833 | 7.65179 | 11.00578 | 6.794 | 6.794 | | |
| SiO ₂ | 3.04463 | 5.21747 | 51.00629 | -7.60619 | -7.60619 | | |
| CO ₂ | 0.51129 | 1.07532 | -1.2053 | -1.00064 | -1.00064 | | |
| Chlorite | 1.02941 | 1.16432 | 5.75181 | -0.48755 | -0.48755 | | |
| K-spar | 6.39098 | 6.89749 | 6.36946 | 5.60785 | 5.60785 | | |
| Diopside | -4.21609 | -4.81062 | -26.81794 | 2.95289 | 2.95289 | | |
| Illite | -3.6625 | -4.00112 | -7.7631 | -2.00313 | -2.00313 | | |
| Exchange | 30.84665 | 30.63787 | 22.53996 | 39.19326 | 39.19326 | | |
| Isotopes | Meas. | Calc. | Meas. | Calc. | Meas. | Calc. | Meas. |
| $\delta^{13}\text{C}$ | 0.38 | 0.38 | 0.32 | 0.32 | 0.78 | 0.78 | 0.52 |
| | | | | | | | 0.50 |
| $\delta^{34}\text{S}$ | 21.95 | 19.16 | 21.95 | 19.35 | 21.97 | 18.2 | 21.95 |
| | | | | | | | 19.50 |
| $\delta^{14}\text{C}$ | 6.05 | 0.21 | 6.08 | 0.35 | 4.31 | 0.24 | 5.58 |
| | | | | | | | 0.38 |
| Model | A ₀ | Age | A ₀ | Age | A ₀ | Age | A ₀ |
| Fontes & Garnier (1979) | 104.6 | 27782 | 104.6 | 23882 | 104.6 | 23882 | 104.6 |
| | | | | | | | 22207 |
| | | | | | | | 145.85 |
| | | | | | | | 31033 |

The model can be used to calculate the output of ^{14}C , in 9 different methods. The observed $\delta^{13}\text{C}$ -TDIC and $\delta^{34}\text{S}$ -SO₄ values were found to be in accordance with calculated values by the model. All the applied ^{14}C age determination methods' results confirmed each other. For the ^{14}C age calculation of R1 sample, "Ingerson & Pearson" model does not give any results. Also "Original Data" model calculation was yielded negative value. That might be the effects of the mixing processes. Fontes & Garnier (1979) model result can be accepted as the representative for the turnover time of the thermal waters in the study area. With this model, it was found that carbonate dissolution during infiltration enriches $\delta^{13}\text{C}_{\text{TDIC}}$ concentration of the groundwater. After calcite saturation established in the fluids, Na cation exchange reduce the Ca ion concentration. For equilibration, calcite dissolution starts again and TDIC concentration begins to increase afterwards.

5. CONCLUSION

According to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plotting, the Kizildere thermal waters, which isotopically enriched due to high temperature water-rock interaction, are of meteoric origin. There is no evidence to prove that there is hydraulic contribution of Menderes River to the geothermal reservoir. In other words The Kizildere geothermal field has not been fed from Buyuk Menderes River. By using $\delta^2\text{H}$ - elevation relationship, the recharge area of the Kizildere thermal waters was found to be between 1300 and 1900 m a.s.l. These ranging elevations correspond to gneisses and schist of Menderes Metamorphic (Yildirim and Guner, 2002). Vengosh et al. (2002) determined the source rock of Kizildere geothermal as schist and gneisses by using $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes. The groundwater in the recharge area flows through fissures and cracks of these units then heated by magma indirectly and convectively before ascending along the faults, which form Menderes Graben. $\delta^{13}\text{C}_{\text{CO}_2}$ value indicates that the CO₂ gas in fluid, have formed by decomposition of marine carbonates (Blavoux et al., 1984).

SO₄ ion in Sahintepesi, Ortakci and Bolmekaya springs was found to be derived from atmosphere, but the origin of SO₄ ion in thermal waters of the Kizildere geothermal field is the gypsum layers in the Kolonkaya formation. The production wells of the Kizildere power plant show that there is $\delta^{18}\text{O}$ exchange between SO₄ and H₂O molecules due to high temperature conditions. This exchange rate is 46% - 84%. There is no magmatic origin of H₂S gas in the

geothermal fluids. Because the observed $\delta^{34}\text{S}$ content is not so depleted in the fluid.

Yildirim and Olmez (1999) determined the presence of mixing processes from the north to the south direction in the Kizildere geothermal field. The ^{14}C calculation result of the thermal water from R1 well in the studied area in Table 2 confirms this identification. Turnover time calculation for the deepest and hottest well named R1 well was resulted 873 years without mixing option in NETPATH (Plummer et. al., 1996). Calculated turnover times of the other geothermal wells water in the Kizildere geothermal field correspond to Pleistocene time recharge.

REFERENCES

Blavoux B., Dazy J., Reynaud, S.: Information About The Origin of Thermomineral Waters and Gas By Means of Environmental Isotopes In Eastern Azerbaijan, Iran And Southeast France, Journal of Hydrology, 56, (1982), 23-38.

Clark, I.D. And Fritz, P.: Environmental Isotopes in Hydrogeology, 2nd Edition, , Lewis Publishers, 328p, (1999).

Craig, H.: Isotopic Variations in Meteoric Waters, Science, 133, (1961), 1833-1834.

ENEL: Optimization And Development of The Kizildere Geothermal Field, Appendix 3, Integrative Prospectings Geochemical Report, Pisa, Italy, (1988).

Ercan, T., Matsuda, J., Nagano, K., Kita, I.: Noble Gas Isotopic Compositions In Gas And Water Samples From Anatolia, In: A. Erler, T. Ercan, E. Bingol And S. Ören (Eds) Geology Of The Black Sea Region, General Directorate Of Mineral Research And Exploration Of Turkey (MTA) And Chamber Of Geological Engineers, Turkey, pp. 197-206, (1995).

Fontes, J. -Ch., Garnier, J-M.: Determination of the Initial ^{14}C Activity of Total Dissolved Carbon: A Review of Existing Models and a New Approach. Water Resources Research, 15, Pp 399-413, (1979).

Gat, J. R., Carmi, I.: Evolution of the Isotopic Composition of Atmospheric Waters in the Mediterranean Sea Area, Journal of Geophysical Research, 75, (1970), 3039-3048.

Gonfiantini, R.: Environmental Isotopes in Lake Studies, In: P. Fritz and J.-Ch Fontes (Eds) *Handbook of Environmental Isotope Geochemistry*, Vol. 2, the Terrestrial Environment., B, Elsevier, Amsterdam, the Netherlands: 113-168, (1986).

Gulec, N.: Helium-3 Distribution in Western Turkey, MTA Bull., 108-35-42, (1988).

Huneau, F., Blavoux, B., Aeschbach-Hertig, W., Kipfer, R.: Paleogroundwaters Of The Valréas Miocene Aquifer (Southeastern France) As Archives of The Lgm/Holocene, Transition In The Western Mediterranean Region, In Proceeding, C&S Papers Series 13/P, IAEA International Conference Held In Vienna, 23-27 April, pp 84-90, (2001).

Plummer, L. N., Prestemon E.C., And Parkhurst D.L.: An Interactive Code (NETPATH) For Modeling Net Geochemical Reactions Along A Flow Path, Version 2.0, U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130p., (1996).

Simsek, S.: Geothermal Model of Denizli, Saraykoy-Buldan Area, Geothermics 14, (1985), 393-417.

Simsek, S.: Hydrogeological and isotopic survey of geothermal fields in the Buyuk Menderes Graben, Turkey, Geothermics, 32, (2003), 669-678

van Everdingen, R.O and Krouse, H.R.: Isotope Composition of Sulphates Generated By Bacterial and a Biological Oxidation, Nature, 315, (1985), 395-396.

Vengosh, A., Helvaci, C., Karamanderesi, I.H.: Geochemical Constraints For Origin of Thermal Waters, From Western Turkey, Applied Geochemistry 17, (2002), 163-183.

Yildirim, N., Guner, N.I.: Isotopic And Hydrogeological Properties Of Waters Encountered In The Geothermal Area of Menderes Graben, In: M. Sayin, C. Cifter, S. Ozcan Eyupoglu, A. Temel Dilaver, I. Yalcin (Eds), Symposium on Isotope Techniques in Hydrology, State Hydraulic Works, Adana,Turkey, pp.79-98, (2002).

Yildirim, N., Olmez, E.: Hydrogeochemical relationship between newly drilled wells (R1 and TH2) and former production wells in Kizildere geothermal field, 1 st Western Anatolian Raw Material Symposium, pp 336-345, (1999).