ORIGINAL ARTICLE

The development of conceptual models for the functioning of geothermal systems using hydrogeological, hydrogeochemical and isotopic data: case studies from Rize (NE Turkey)

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Abstract

The hydrogeological and hydrogeochemical properties and isotopic composition of hot and cold water springs in the Ilıcaköy and Ayder geothermal areas were investigated and a conceptual model was developed to explain their function. Characteristics of hot groundwater from the Ilıcaköy area were: temperature, 63 °C; EC, 6913 μS/cm; pH, 7.2, DO content, 0.75 mg/L; and water type, Na–Ca–HCO$_3$. Characteristics of hot groundwater from the Ayder area were: temperature, 55 °C; EC, 255 μS/cm; pH, 9.2, DO content, 1.9 mg/L; and water type, Na–Ca–CO$_3$–SO$_4$. Ilıcaköy has acidic pH values, while those of the Ayder area are alkaline. Carbon in hot water in both areas was derived from inorganic carbon in groundwater and from CO$_2$ in pore spaces in the unsaturated zone. SO$_2$ in hot water was derived from Cenozoic-aged gypsum. Low tritium and high Cl contents in hot waters indicate deep circulation, and Sr was passed from granitic rocks to waters by simple dissolution. High total alpha and total beta values were obtained in the hot waters from the Ilıcaköy geothermal area. Ilıcaköy and Ayder geothermal spring formation occurred by infiltration of precipitation through fractures in granitic bedrock from the Kaçkar granitoid, which forms a regionally significant geothermal reservoir. Water of meteoric origin is heated under by a locally steep geothermal gradient, and it rises through bedrock fractures and re-emerges at the ground surface. In the Ilıcaköy and Ayder geothermal fields, which are low temperature geothermal systems, the reservoir rock temperature was 80 °C and 149 °C, respectively.

Article highlights

- **Eastern Black Sea Region is a very important area in the point of geothermal resources.**
- **The hot water resources in the Rize province have significant potential for the region.**
- **The objectives of the study are to study the hydrogeological and hydrogeochemical properties and isotopic compositions of the hot and cold water springs.**

Introduction

Located in the tectonically active Alpine–Himalayan system, Turkey is a country that is rich in geothermal energy. The biggest indicator of this wealth is the large number of natural hot springs throughout the country. Geothermal energy exploration and development activities were initiated in the 1960s and gained momentum in the 1980s after sites suitable for energy production were found. Geothermal energy studies are mostly concentrated in the western part of the country.

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Geothermal areas in Central and Eastern Anatolia are known to be associated with historical volcanic activity, and low and medium enthalpy geothermal areas in North Anatolia are associated with the North Anatolian Fault Zone (NAFZ) (Simsek 1984; Şimşek and Güleç 1994; Tarcan et al. 2000, 2005; Gemici and Tarcan 2002; Karamanderesi and Helvacı 2003; Pasvanoğlu and Gültekin, 2012). In the Eastern Black Sea region where Neogene and younger intrusions are located, including the Sarmaşık, Ilıcaköy, Ayder, and Ilıca areas, there are hot and mineral water springs with temperatures of 30–63 °C. A large body of research has been undertaken in the Ilıcaköy region to determine the geothermal resource characteristics of the region. For example, Yenal found that on the two sides of the valley in Ayder, there are two separate springs with temperatures of 33 °C and 46 °C and flow rates of 0.43 and 0.3 l/s. The first spring was defined as having a chemical composition that was dominated by sodium and sulfate ions, and it was physically hyperthermal, hypotonic, and oligometallic, discharging radioactive mineral water. The second spring also had a sodium sulfate chemical composition, and it was physically thermal, hypotonic, and had oligometallic mineral water.

Çetiner et al. (1987) indicated that a drilling program that had been undertaken in 1986 encountered artesian hot water at a temperature of 55.5 °C and a flow rate of 14–28 l/s.

Gürsel (1991) stated that artesian hot water at a temperature of 57 °C was obtained from drilling in the area and that calcium bicarbonate waters were discharged from the springs at a temperature of 33–47 °C. The geothermal gradient in the region was calculated to be 1 °C/13 m by examining the temperatures that were measured by drilling, and it was stated that the waters were heated by the local steep geothermal gradient.

In the Rize-İkizdere Spa well completion reports for hot water boreholes Ilıcaköy-1 and Ilıcaköy-2, Uzel indicated that waters at a temperature of 60 °C and 70 °C, depth of 40 m and 266 m, and flow rate of 2.5 l/s and 6.1 l/s, respectively, were obtained from the wells. A study titled "Hydrogeology of Hot Water Springs in Ilıcaköy, Fırat Ersoy 2001" determined that hot groundwater in the area was saturated with sodium bicarbonate, calcite, and dolomite. Ersoy calculated that the reservoir rock temperature was 198 °C using chemical geothermometers and they found that the hot waters in this region have a low enthalpy in terms of available geothermal energy (Uzel et al. 1998).

Akkus stated in the MTA (General Directorate of Mineral Research and Exploration) Turkey Geothermal Inventory that the Ayder geothermal area has two springs that have temperatures of 47 °C and 33 °C with flow rates of 0.5 l/s and 2 l/s, respectively (Akkuş et al 2005; MTA 2002). Akkus also indicated that two wells were drilled in this area between 1986 and 1999 to depths of 211 m and 263 m. The temperature measured in the discharge from both wells was 55.5 °C and the wells had flow rates of 14 l/s and 28 l/s, respectively. Artesian groundwater obtained from the wells is used in the spa facility and to heat the facility.

The same study also reported that there were three hot water springs at temperatures between 27 and 30 °C and with flow rates between 0.01 l/s and 0.4 l/s in the İkizdere–Ilıcaköy area. Additionally, boreholes drilled to depths of 40 m and 266 m occurred in the same area. These boreholes produced groundwater with water temperatures of 60 °C and 70 °C, and flow rates of 2.5 l/s and 6.1 l/s. These springs and boreholes were located in an area with late Cretaceous period-aged granitic rock outcroppings.

According to $\delta^{18}O$ and δD isotope studies that were conducted on samples of hot groundwater from the Ayder and Ilıcaköy areas, Gültekin et al. (2007) stated that geothermal water in these areas were of meteoric origin and had low tritium values.

The aim of this study was to determine the hydrogeochemical properties, origins, and recharge characteristics of hot and cold groundwater from the Ilıcaköy and Ayder geothermal fields. This work was undertaken to explain the mechanism of geothermal system formation in these areas and to develop a hydrogeological conceptual model of how these systems function. To achieve these objectives, surface water samples, and hot and cold groundwater samples were collected from springs and boreholes in the two study areas in four sampling campaigns to determine seasonal variations in the geothermal system characteristics.

The results of these investigations will help to determine the areas where higher temperatures can be obtained by assessing the geochemical spatial variations of fluids in these geothermal systems. The geological and hydrogeological characteristics of the study areas were determined and parameters such as temperature, pH, TDS (total dissolved solid), EC (electrical conductivity), and DO (dissolved oxygen) were measured in situ.

Characteristics of the study area

The Ilıcaköy (İkizdere–Rize) and Ayder (Çamlıhemşin–Rize) geothermal areas are located in the Eastern Black Sea region of Turkey. Because of topographic factors, the annual precipitation increases in an easterly direction in the Black Sea Region and reaches its highest level in the east part of Rize Province. Based on the averages from the last 65 years that were taken from the General Directorate of Meteorology, the maximum annual precipitation in Rize is 2239 mm (GDM 2016). The region has dense vegetation because of its climatic characteristics.

The study area is located on the northern slope of the Eastern Black Sea Coastal Mountain Range, which is mountainous and has a rugged topography. The width

of the coastline varies between 20 and 250 m except for the river valleys. The largest plains on this coastline are divided by many streams and are formed by base-level plains. Just behind the coastal plain, the elevation reaches 150–200 m. Both the main streams and the numerous side branches of these streams give the topography an uneven appearance.

The study area includes the geothermal areas of Ilıcaköy (İkizdere–Rize) and Ayder (Çamlıhemşin–Rize) in the Eastern Black Sea Region (Fig. 1).

Methodology

The field investigations in this study were carried out in two different areas in Rize province, namely: in the İkizdere District, Ilıcaköy; and in the Çamlıhemşin District, Ayder Plateau and its surroundings. The field studies were completed between April 2016 and October 2017 and consisted of geological investigations, in situ measurements and water quality sampling.

During the field work, the locations of hot and cold groundwater and surface water sampling points in each geothermal area were determined. During these investigations,

Fig. 1 Geological map of the study areas (simplified from Güven 1993)
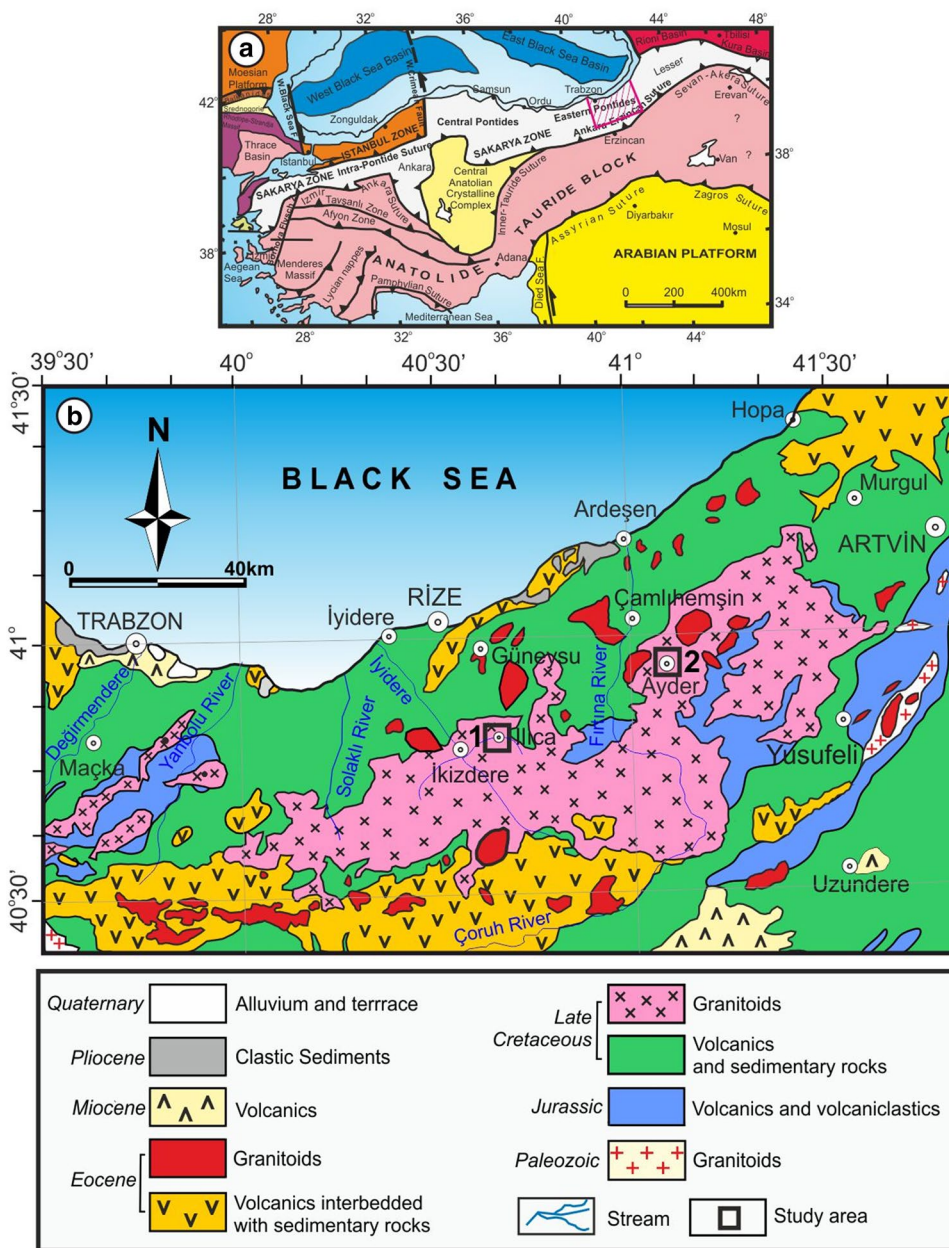
the geological and tectonic characteristics of the region were determined by utilizing field observations and information from previous studies. During this phase of the study, the distances between the hot and cold water springs and their morphological and tectonic relations were taken into consideration.

Sampling and in situ measurements in the geothermal area of Ilıcaköy (İkizdere–Rize) were carried out at four points: a hot water borehole used in the spa facility (ILKAP); a cold water spring located at higher elevations (ISK); and from recharges at a higher elevation above the hot water drilling carried out at Ilıca River the spa facility (IDERY); and from Ilıca River at lower elevations than the spa facilities (IDERA).

Hot water sampling and in situ measurements in the geothermal area of Ayder (Çamlıhemşin–Rize) were carried out at three points: a hot water borehole used in the spa facility (AYKAP); at the old hammam springs on the opposite slope of the valley (AYESH); and from the thermal spring in Kavron Creek, about 15 km north of the hot spring, (AYKOPK). Cold water measurements and sampling were carried out at three points: a cold water spring located at an elevation above the spa facility (HOSSU); from springs located above the hot water boreholes of Kavron Creek (AYDEREY); and from springs below the spa facility (AYDEREA).

During in situ measurements, T (temperature), EC (electrical conductivity), pH, salinity, TDS (total dissolved solids) and DO (dissolved oxygen) measurements were obtained with a YSI-556 model multi-parameter meter at the sampling location. Probes used during measurements were washed with deionized water before and after each measurement and used after daily calibration with buffer solution each day during the field investigation. H_2S, CO_2, CO, O_2 and CH_4 gas measurements at hot springs were carried out with an Ibrid MX6 model portable gas meter. Probes used during measurements were washed with deionized water before and after each measurement and used after daily calibration with buffer solution during each field study.

Water samples for the determination of major anions and cations, heavy metals and isotopes were collected in clean polyethylene bottles. Samples for the analysis of major anions and cations were collected in two 500 mL capacity bottles, samples for the analysis 100 of trace elements and tritium isotope measurements were collected in 100 mL capacity bottles, samples for total alpha and total beta analyses were collected in 1000 mL bottles, samples for for ^{18}O, ^{2}H and ^{13}C isotope analysis were collected in 50 mL bottles, and samples for ^{34}S isotope analyses were collected in 750 mL capacity bottles.

Bottles were washed well in the laboratory with diluted hydrochloric acid and then with deionized water. Before sampling in the field, each bottle was initially filled twice and emptied. Samples were filtered through 0.45 µm filter pad. Samples taken for cation and trace element analyses were acidified to pH < 1.5 (using a few drops of supra-pure quality HNO_3). Samples were kept at 4 ºC until analysis. Hydrochemical analyses were performed according to APHA (American Public Health Association), AWWA (American Water and Water Association) and WPCF (Water Pollution Control Federation) (APHA 1975) standards.

Major anions (F^-, Cl^- and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) in the water samples were determined with ion chromatography techniques while trace elements analyses were performed with inductively coupled mass spectrometry (ICP-MS) at the Water Chemistry Laboratory of Hacettepe University Hydrogeology Engineering Department (Ankara, Turkey). Alkalinity was determined with the standard titration method in the laboratory. Ion balance errors of the analyses were all below 5%.

The hydrogeochemical properties and saturation indexes (SI) of the water samples were determined using the hydrogeochemical software package AquaChem 2014.2 (Calmbach 1997) and the PHREEQC geochemical model and database (phreeqc.dat) (Parkhurst and Appelo 1999), respectively.

^{18}O, ^{2}H and ^{13}C isotope analyses were performed at ISO Analytical Laboratory (UK) with the Isotope Ratio Mass Spectrometer (IRMS) technique, and ^{18}O and ^{34}S analyses of the sulfate content of hot groundwater samples were performed with the isotope ratio mass spectrometry technique at Isotope Tracer Technologies Inc Laboratory (Canada), as were the $^{87}Sr/^{86}Sr$ isotope analyses. Tritium analyses were performed by the liquid scintillation counting technique at the Department of Mass Analysis Laboratory of Hacettepe University in the Hydrogeology Engineering Department (Ankara, Turkey).

Results

Geological setting of the geothermal areas

The Eastern Black Sea Region of Turkey forms part of the Eastern Pontid tectonic unit (Ketin, 1966). The geothermal areas studied (İkizdere–Rize and Ayder–Rize) are located in the North Zone of the Eastern Pontid. The metamorphic basement rocks in this area are of Paleozoic age and consist of schists, gneisses, marbles and amphibolites. A unit consisting of granite and granodiorite-monzonite which intrudes these metamorphic rocks was named the Gümüşhane Granite by Yılmaz (1972) and Kandemir (2004).

Liassic-aged volcano-sedimentary rocks that unconformably overlie the metamorphic basement are composed of conglomerates, gravelly sandstones, sandstones, siltstones together with basalt and pyroclastites. These rocks are in turn overlain by the Berdiga Formation (Pelin 1977; Uğuz

et al. 2011) which is composed of dolomitic, cherty, oolithic and sandy limestones and clayey limestones seen in blocks in some sections.

Two phases of volcanism took place in the Northern Zone during the Late Cretaceous. This period is represented by a basic volcanic–sedimentary sequence, dacites, rhyodacites and dacitic pyroclastic and andesites, basalt and basaltic pyroclastic rocks (Uğuz et al. 2011).

Rocks of Cenozoic age in the Eastern Pontides consist of clastic deposits (sandstone, sandy limestone and marl alternation) which are overlain by volcanic and volcano-sedimentary rocks.

An intrusive complex that consists of rocks of granitic to gabbroic composition cuts the Late Cretaceous-aged units and is intruded into the Eocene by subsequent regeneration in the area. This complex was named the Kaçkar Granitoid by Güven (1993), Aydin (2003), Arslan and Aslan (2006) and Kaygusuz and Aydinçakir (2009) (Fig. 1).

Hydrogeology and hydrogeochemical characteristics of thermal and cold waters

A large variety of rock types in the area have sufficient permeability to be locally important aquifers. For example, early-to-middle Jurassic-aged conglomerate, sandstone, and siltstone clastic rocks that comprise the oldest units in the İkizdere area are permeable. Similarly, late Cretaceous-aged volcano-sedimentary rocks and the Eocene-aged Kabaköy Formation are permeable in areas where pyroclastic rocks are represented by agglomerate and tuff form outcrops. Crystalline rocks that comprise the Kaçkar granitoid, which has extensive outcrops in the study area, are highly fractured, which creates permeable zones for groundwater flow. Consequently, there are many springs that discharge water from fracture zones of granitic rocks on the valley slopes in the Ilıcaköy geothermal area.

The in situ measurements of water from the ISK cold water spring indicate that the discharge has a temperature of 11 °C, an electrical conductivity of 22 µS/cm, a pH of 7.34, and a dissolved oxygen content of 11 mg/l. Hot groundwater with a temperature of 70 °C was obtained from a 266-m deep borehole drilled by the MTA, and this is used for heating spa baths, whereas another borehole that produces water with a lower temperature is not used at the facility. Field measurements indicate that a hot water borehole that is currently used at the site (ILKAP) has a temperature of about 63 °C, an electrical conductivity of 6913 µS/cm, a pH of 7.2, and a dissolved oxygen content of 0.75 mg/l. Gas measurements of water from the borehole indicated that the H2S content was 1.4–3.4 ppm, the CO2 content was 0.1–1.78 ppm, and the O_2 content was 14–20.4%V (Table 1).

There are many water springs that discharge from fractures in the crystalline rocks of the Kaçkar granitoid

throughout the year. One of these springs is HOSSU springs, which is located above the spa area and it is used as a drinking water fountain. Field measurements indicated that the discharge from this spring had a temperature of 10.8 °C, an EC value of 35 µS/cm, a pH of 7.15, and a DO content of 10.3 mg/l.

On two different sides of Kavron Creek in the study area, there are two springs that have temperatures of 33 °C and 47 °C and flow rates of 0.5 l/s and 2 l/s, respectively. However, artesian water with a temperature of 55.5 °C and with a flow rate of 14 l/s was obtained from a 211-m deep borehole (AK-2) that is located in the same area. Similarly, water at 55.5 °C and a flow rate of 28 l/s was obtained from a 263-m deep borehole in this area. Additionally, discharge from a spring that is located in the debris on the edge of the Kavron Creek on the Çamlıhemşin–Ayder Road was found to have a temperature of 30 °C.

During the fieldwork, it was determined that water at 55 °C was obtained from boreholes and this water is used to heat the spa facility. Field measurements indicated that discharge from the borehole that is currently used (AYKAP) has a temperature of approximately 55 °C, an EC of 255 µS/cm, a pH of 9.2, and a DO of 1.9 mg/l. The temperatures measured from the discharge at the spring in the old hammam (AYESH) and the creek (AYKOPK) were 20 °C and 31.7 °C, the EC was 33–296 µS/cm, the pH was 8.16 and 9.33, and the DO was 8 and 0.35 mg/L, respectively. Gas measurements of the borehole water indicated that the CO_2 concentration was 4 ppm and that the O_2 concentration was 21%V (Table 2).

In the Ilıcaköy geothermal area, an average temperature of 61.63 °C and pH of 7.17 were measured in situ at the geothermal borehole. The chemical analysis of water from this borehole indicated that the water had an average EC of 6764 µS/cm and that the chemical composition of the water was dominated by sodium and bicarbonate ions. The thermal water from this area also contained 110 mg/L of dissolved silica, 6 mg/L of lithium, and 60 mg/l of boron. The source of the high boron concentration in the hot water spring is likely to be the volcanic action that creates the young volcanic rocks in the basin and that provides the boron-containing minerals in the volcanic rocks. The source of the high lithium concentration in the hot water source is thought to be the basalts of magmatic rocks in the basin.

The highest nitrite ion concentration that was measured in a hot water borehole (ILKAP) was 0.54 mg/L in July 2017, and the mean nitrite concentration in this borehole was 0.14 mg/l. Nitrite concentrations in cold springs and in river water were determined to vary between 0.01 and 0.02 mg/l in May 2016. The purpose of the Criteria for Inland Surface Water Classification (WPCR 2004) is to determine the legal and technical principles that are required to prevent water pollution in accordance with sustainable

Table 1 Physical and chemical properties of waters in Ilıcaköy geothermal field

Sample name	T(°C)	pH	EC (uS/cm)	TDS (mg/l)	DO (mg/l)	Ca^{+2}	Mg^{+2}	Na^+	K^+	HCO_3^-
ILKAP										
May 16	60.00	7.03	6633	2587	0.88	331.31	79.02	965.65	140.66	2810.78
Oct. 16	63.00	7.20	6913	2620	0.75	348.80	83.92	966.60	135.00	2928.00
March 17	62.00	7.20	6755	2605	0.10	410.61	72.59	928.62	139.21	2806.00
July 17	61.50	7.24	6755	2589	0.51	401.88	81.42	981.56	135.69	2932.78
Mean	61.63	7.17	6764	2600	0.56	373.15	79.24	960.61	137.64	2869.39
ISK										
May 16	11.80	7.34	22.00	19.00	11.00	7.25	0.71	3.09	0.41	23.92
Oct. 16	11.00	8.25	27.00	24.00	10.70	6.48	0.62	3.15	0.48	18.30
March 17	5.10	6.96	22.00	20.00	11.82	4.59	0.67	1.75	0.34	12.20
July 17	14.90	8.50	34.00	22.00	10.38	6.58	0.60	3.74	0.38	29.90
Mean	10.70	7.76	26.25	21.25	11.00	6.22	0.65	2.93	0.40	21.08
IDERY										
May 16	9.10	6.40	17.00	16.00	13.00	6.82	0.73	1.33	0.38	23.92
Oct. 16	8.95	6.90	30.00	28.00	12.00	8.91	1.02	1.89	0.43	24.40
March 17	5.20	6.20	41.00	27.00	12.40	7.50	0.98	2.50	0.39	24.40
July 17	13.70	6.80	38.00	25.00	10.71	8.96	0.90	1.76	0.36	31.00
Mean	9.24	6.58	31.50	24.00	12.03	8.05	0.91	1.87	0.39	25.93
IDERA										
May 16	9.20	7.40	19.00	17.00	13.00	7.08	0.80	1.72	0.53	23.92
Oct. 16	10.11	7.13	46.00	33.00	11.80	9.16	1.09	2.71	0.54	30.50
March 17	6.40	7.20	50.00	33.00	12.00	9.92	1.05	3.58	0.63	36.60
July 17	14.10	5.70	46.00	30.00	11.07	9.21	0.95	2.49	0.46	37.59
Mean	9.95	6.86	40.25	28.25	11.97	8.84	0.97	2.62	0.54	32.15

Sample name	SO_4^{-2}	Cl^-	CBE	NO_2^-	NO_3^-	F^-	Li	Br	SiO_2	B	Water Type
ILKAP											
May 16	296.22	464.12	3.03	0.00	0.00	1.02	5.77	0.00	117.55	71.66	$Na-Ca-HCO_3$
Oct. 16	311.80	441.20	2.61	0.00	0.00	1.54	5.76	0.00	122.83	71.06	$Na-Ca-HCO_3$
March 17	353.97	460.72	3.46	0.00	2.22	0.76	5.41	0.00	111.20	51.00	$Na-Ca-HCO_3$
July 17	284.44	456.00	4.80	0.54	1.09	0.94	5.35	0.52	87.63	48.11	$Na-Ca-HCO_3$
Mean	311.61	455.51		0.14	0.83	1.06	5.57	0.13	109.80	60.46	
ISK											
May 16	1.50	0.31	2.98	0.02	5.91	0.09	0.00	0.00	14.52	0.25	$Ca-Na-HCO_3$
Oct. 16	3.69	0.87	− 1.43	0.00	7.98	0.16	0.00	0.00	17.08	< 1	$Ca-Na-HCO_3-SO_4$
March 17	2.09	0.33	− 1.51	0.00	6.46	0.01	0.00	0.00	8.73	< 1	$Ca-Na-HCO_3$
July 17	1.51	0.38	− 1.89	0.00	2.11	0.10	0.00	0.00	16.42	< 1	$Ca-Na-HCO_3$
Mean	2.20	0.47		0.00	5.61	0.09	0.00	0.00	14.19		
IDERY											
May 16	2.38	0.14	− 0.47	0.01	0.35	0.02	0.00	0.00	5.30	0.25	$Ca-HCO_3$
Oct. 16	7.73	0.53	2.07	0.00	1.03	0.07	0.00	0.00	10.42	0.25	$Ca-HCO_3-SO_4$
March 17	4.32	0.31	4.31	0.00	1.36	0.02	0.00	0.00	11.78	0.25	$Ca-HCO_3$
July 17	3.86	0.16	0.87	0.00	0.17	0.02	0.00	0.00	7.42	0.25	$Ca-HCO_3$
Mean	4.57	0.29		0.00	0.73	0.03	0.00	0.00	8.73	0.25	
IDERA											
May 16	2.49	0.38	− 0.62	0.02	0.45	0.02	0.00	0.00	6.41	0.25	$Ca-HCO_3$
Oct. 16	8.12	1.05	− 3.04	0.00	1.13	0.08	0.00	0.00	10.87	0.50	$Ca-HCO_3-SO_4$
March 17	4.73	0.68	0.54	0.00	1.35	0.03	0.00	0.00	11.54	0.25	$Ca-HCO_3$
July 17	4.05	0.38	− 4.19	0.01	0.24	0.02	0.00	0.00	7.71	0.25	$Ca-HCO_3$
Mean	4.85	0.62		0.01	0.79	0.04	0.00	0.00	9.13	0.31	

CBE: Charge Balance Error

development objectives and to protect and ensure the best use of the country's underground and surface water resource potential. According to the Criteria for Inland Surface Water Classification, cold water springs were in Class II and III for nitrite. The mean nitrate concentrations were determined to be 0.8 mg/L in the hot spring, 6 mg/L in the cold spring, and 0.7 and 0.8 mg/l in river waters. According to the Criteria for Inland Surface Water Classification, all springs were in Class I for nitrate (Table 1).

The discharge from the cold water spring in the Ilıcaköy geothermal area had a pH of 7.76, an EC of 26 µS/cm, and a DO of 11 mg/l. In the waters that were dominated by calcium and bicarbonate ions, the silica concentration was determined to be 14 mg/L, and the nitrate ion concentration was 6 mg/l. The chemical composition of the surface water from the Cimildere River that drains the basin was found to be dominated by calcium and bicarbonate ions. This water had a pH of approximately 6.7, an EC of 31–40 µS/cm, and a DO of approximately 12 mg/l. No changes in the chemical composition of the river water were observed in surface water samples that were collected below the spa facility.

In the Ayder geothermal area, samples from one geothermal borehole, two hot water springs, one cold water spring, and two surface water sources at the upper and lower elevations of the spa facility were analyzed, and in situ measurements were performed at the same points. In situ measurements showed that the average geothermal borehole temperature was 54.71 °C, the pH was 9.34, the EC was 242.50 µS/cm, and the DO was 1.78 mg/l.

The chemical composition of hot water from the boreholes was dominated by sodium, carbonate, and sulfate ions, and the silica concentration was determined to be 46 mg/l. The concentrations of lithium, boron, and bromide in these water samples were determined to be about 0.01 mg/l and the fluoride concentration was determined to be about 0.4 mg/l.

The concentrations of nitrite and nitrate ions measured in these samples were low (approximately 0.01 mg/l and 0.2 mg/l, respectively) (Table 2). The mean nitrite ion concentration in the hot water borehole that is currently used (AYKAP) was 0.01 mg/l, whereas the measured nitrite ion concentrations in the AYESH borehole was 0.01 mg/L and the maximum concentration measured in the cold spring (HOSSU) was 0.02 mg/l. According to the WPCR, the geothermal spring is in Class II and the cold spring is in Class III for nitrite.

The mean nitrate ion concentration in the hot spring (AYKAP) was 0.2 mg/l and that in the cold spring (HOSSU) was 7.5 mg/l. According to the Criteria for Inland Surface Water Classification (WPCR 20049, the AYKAP and HOSSU springs are in Class I, and the AYESH spring is in Class II for nitrate (Table 2).

The geothermal area currently contains two hot water springs that discharge naturally. Among these springs, the spring formerly used in a hammam has a water temperature of 20 °C, a pH of 3.38, and an EC of 56 µS/cm. In the spring water containing high concentrations of sodium and bicarbonate ions, the silica concentration was determined to be 27 mg/l, and the nitrate concentration was 7.5 mg/l. The spring discharging from the side of the Kavron Creek had a temperature of 30 °C, a pH of 9.59, and an average EC of 276 µS/cm. The chemical composition of water discharged from this spring was dominated by sodium and sulfate ions and the dissolved silica concentration was 42 mg/l.

Samples from the Hossu spring, which is typical of the cold water springs in the area, had pH values of 7.02, EC values of 47.5 µS/cm, and DO values of 11.54 mg/l, on average. The chemical composition of water from this spring was dominated by calcium and bicarbonate ions. The concentration of silica in water from this spring was 21.2 mg/l, and the lithium, boron, bromide, and fluoride concentrations were as low as 0.02 mg/l (Table 2). The water from Kavron Creek had a pH of approximately 8.8, an EC that ranged from 24 to 32 µS/cm, and a DO value of approximately 12 mg/l. The chemical composition of water in the creek was dominated by calcium and bicarbonate ions. The silica concentration in the creek water was 19.34 mg/l, and the NO_3 value was 0.11 mg/l, which was also quite low.

A piper diagram (Piper 1944) was used to classify geothermal waters, cold spring waters, and surface waters and to define their hydrogeochemical functions, while a Schoeller diagram (Schoeller 1962) was used to compare the chemical content of the waters.

The piper diagram indicated that thermal water samples from the Ilıcaköy (İkizdere–Rize) area contained a greater proportion of alkaline elements (Na + K) than alkaline earth elements (Ca + Mg). Similarly, the piper diagram indicated that the anionic composition of water from this area had a greater proportion of weak acids (CO_3 + HCO_3) than strong acid (Cl + SO_4) roots in the hot waters (Fig. 2). However, there was a greater proportion of alkaline earth elements (Ca + Mg) than alkaline elements (Na + K) in the cold water samples, although these waters had a similar anionic composition as the hot water samples.

Both the hot water and cold water spring waters in the Ayder area contained a higher proportion of sodium and potassium ions than calcium and magnesium ions. However, the anionic composition of these waters had a similar proportion of carbonate and sulfate ions when the water had a low salinity (Fig. 2).

Schoeller diagrams were prepared for all the water sampling sites in the study area. These indicated that hot waters and cold waters in the Ilıcaköy area had a similar chemical composition except for variations in their chloride content. However, the hot water samples generally had higher concentrations of the major ions than the cold

Table 2 Physical and chemical properties of waters in Ayder geothermal field

Sample name	T(°C)	pH	EC (uS/cm)	TDS (mg/l)	DO (mg/l)	Ca^{+2}	Mg^{+2}	Na^+	K^+	HCO_3^-	CO_3^{-2}
AYKAP											
May 16	54.95	9.15	233.00	97.00	1.62	8.74	0.06	39.93	0.74	0.00	35.28
Oct. 16	55.00	9.28	252.00	104.00	0.35	12.40	0.20	30.50	0.74	0.00	24.00
March 17	55.00	9.34	241.00	100.00	1.54	13.49	0.14	39.18	0.85	6.10	36.00
July 17	53.90	9.60	244.00	102.00	3.60	12.56	0.41	37.00	0.68	0.00	36.00
Mean	54.71	9.34	242.50	100.75	1.78	11.80	0.20	36.65	0.75	1.53	32.82
AYKOPK											
Oct. 16	31.70	9.32	296.00	171.00	0.35	16.77	0.26	63.66	1.06	0.00	24.00
March 17	32.00	9.59	267.00	173.00	0.23	17.42	0.27	68.10	0.88	6.10	24.00
July 17	31.80	9.86	264.00	171.00	0.50	16.17	0.21	71.20	0.98	0.00	24.00
Mean	31.83	9.59	275.67	171.67	0.36	16.79	0.25	67.65	0.97	2.03	24.00
AYESH											
Oct. 16	20.00	8.16	33.00	24.00	8.00	8.26	1.24	12.80	0.36	30.50	0.00
July 17	20.00	8.60	80.00	52.00	8.78	9.57	1.23	15.95	0.34	23.92	17.65
Mean	20.00	8.38	56.50	38.00	8.39	8.92	1.24	14.38	0.35	27.21	8.83
HOSSU											
May 16	10.80	7.56	35.00	31.00	12.00	9.25	1.73	3.84	0.89	0.69	0.00
Oct. 16	12.90	7.15	41.00	36.00	10.35	8.30	1.09	3.53	0.85	36.60	0.00
March 17	7.70	6.58	57.00	37.00	13.20	9.97	1.66	3.64	0.89	42.70	0.00
July 17	12.00	6.80	57.00	37.00	10.62	10.57	1.78	3.95	0.85	47.72	0.00
Mean	10.85	7.02	47.50	35.25	11.54	9.52	1.57	3.74	0.87	31.93	0.00
AYDEREY											
May 16	10.30	7.30	19.00	17.00	13.00	7.50	1.04	2.07	0.61	0.49	0.00
Oct. 16	7.00	6.69	26.00	22.00	10.49	3.91	0.87	1.98	0.71	18.30	0.00
March 17	5.00	5.92	26.00	22.00	13.50	5.59	0.96	2.03	0.53	24.40	0.00
July 17	12.60	6.38	26.40	171.00	10.27	7.72	1.04	2.38	0.61	35.64	0.00
Mean	8.73	6.57	24.35	58.00	11.82	6.18	0.98	2.12	0.62	19.71	0.00
AYDEREA											
Oct. 16	7.70	6.84	22.00	21.00	12.50	5.19	0.50	1.21	0.31	18.30	0.00
March 17	4.50	5.87	37.00	23.00	13.00	7.18	0.71	1.98	0.45	24.40	0.00
July 17	14.24	6.60	36.00	23.00	10.58	8.67	0.52	1.20	0.26	31.00	0.00
Mean	8.81	6.44	31.67	22.33	12.03	7.01	0.58	1.46	0.34	24.57	0.00

Sample Name	SO_4^{-2}	Cl^-	CBE	NO_2^-	NO_3^-	F^-	Li	Br	SiO_2	B	Water type
AYKAP											
May 16	38.19	2.69	2.97	0.01	0.26	0.45	0.03	0.00	43.30	0.25	Na–Ca–CO₃–SO₄
Oct. 16	47.54	2.78	2.42	0.00	0.26	0.41	0.02	0.00	46.45	< 1	Na–Ca–SO₄–CO₃
March 17	44.02	3.02	2.32	0.00	0.00	0.45	0.02	0.00	44.08	< 1	Na–Ca–CO₃–SO₄
July 17	35.93	2.89	2.99	0.01	0.30	0.42	0.02	0.00	51.49	< 1	Na–Ca–CO₃–SO₄
Mean	41.42	2.85		0.01	0.20	0.43	0.02	0.00	46.33	< 1	
AYKOPK											
Oct. 16	118.00	9.77	0.93	0.00	0.12	0.95	0.01	0.02	43.60	2.25	Na–Ca–SO₄–CO₃
March 17	134.00	9.89	0.93	0.00	0.00	0.78	0.00	0.00	38.50	< 1	Na–Ca–SO₄–CO₃
July 17	114.57	9.71	1.81	0.00	0.06	0.90	0.01	0.00	44.27	< 1	Na–Ca–SO₄–CO₃
Mean	122.19	9.79		0.00	0.06	0.88	0.01	0.01	42.12	< 1	
AYESH											
Oct. 16	12.50	1.36	4.29	0.00	11.47	0.17	0.01	0.00	27.78	< 1	Na–Ca–HCO₃–SO₄
July 17	7.60	0.82	2.27	0.01	3.61	0.11	0.01	0.00	26.24	< 1	Na–Ca–CO₃ –HCO₃–SO₄
Mean	10.05	1.09		0.01	7.54	0.14	0.01	0.00	27.01	< 1	

Table 2 (continued)

| Sample Name	SO$_4^{-2}$	Cl$^-$	CBE	NO$_2^-$	NO$_3^-$	F$^-$	Li	Br	SiO$_2$	B	Water type
HOSSU											
May 16	1.52	0.48	3.91	0.02	0.07	0.02	0.00	0.00	16.50	0.25	Ca–Na–Mg–SO$_4$–HCO$_3$
Oct. 16	1.81	0.49	1.52	0.00	0.35	0.02	0.00	0.00	31.62	< 1	Ca–Na–HCO$_3$
March 17	2.01	0.57	3.01	0.00	0.01	0.02	0.00	0.00	28.48	0.00	Ca–HCO$_3$
July 17	1.51	0.51	1.77	0.01	0.35	0.02	0.00	0.00	8.18	0.00	Ca–Na–HCO$_3$
Mean	1.71	0.51		0.01	0.20	0.02	0.00	0.00	21.20	< 1	
AYDEREY											
May 16	1.62	0.11	3.34	0.01	0.06	0.01	0.00	0.00	27.80	0.25	Ca–Na–Mg–SO$_4$–HCO$_3$
Oct. 16	2.00	0.10	3.22	0.00	0.18	0.01	0.00	0.00	16.09	< 1	Ca–Na–HCO$_3$–B
March 17	1.70	0.09	1.64	0.00	0.01	0.01	0.00	0.00	15.00	< 1	Ca–HCO$_3$
July 17	1.52	0.16	– 2.87	0.00	0.20	0.02	0.00	0.00	18.45		Ca–HCO$_3$
Mean	1.71	0.11		0.00	0.11	0.01	0.00	0.00	19.34		
AYDEREA											
Oct. 16	1.96	0.13	1.42	0.00	0.35	0.02	0.00	0.00	9.17	< 1	Ca–HCO$_3$–B
March 17	2.12	0.43	4	0.00	0.01	0.01	0.00	0.00	10.40	< 1	Ca–HCO$_3$
July 17	2.47	0.16	– 3.12	0.00	0.23	0.02	0.00	0.00	6.44	< 1	Ca–HCO$_3$
Mean	2.18	0.24		0.00	0.20	0.02	0.00	0.00	8.67	< 1	
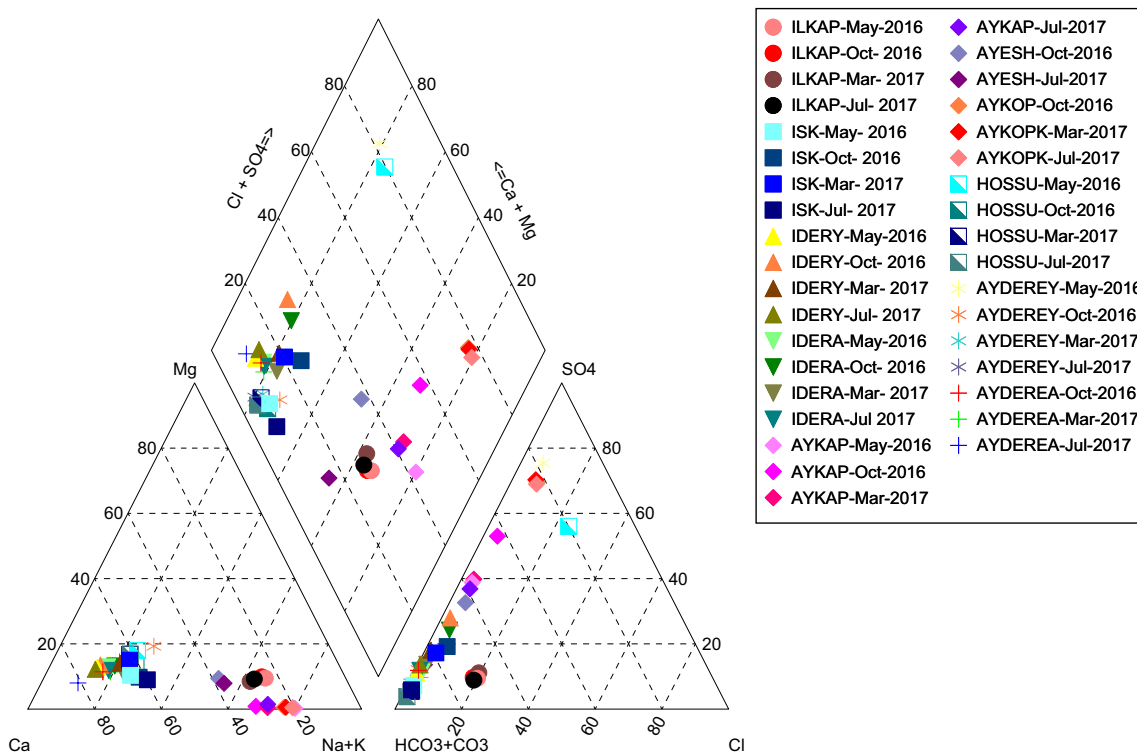
Fig. 2 Piper diagram of the water samples in Ilıcaköy (İkizdere) and Ayder (Çamlıhemşin) geothermal area

water samples (Fig. 3). In the Ayder area, the lines connecting hot water and cold water ions were almost parallel to each other. Concentrations of sodium, potassium, chloride, and sulfate ions were found to be particularly high in hot water samples compared to those from cold water springs (Fig. 3). The concentrations of major ions in the water samples from the Ilıcaköy hot water springs were particularly high.
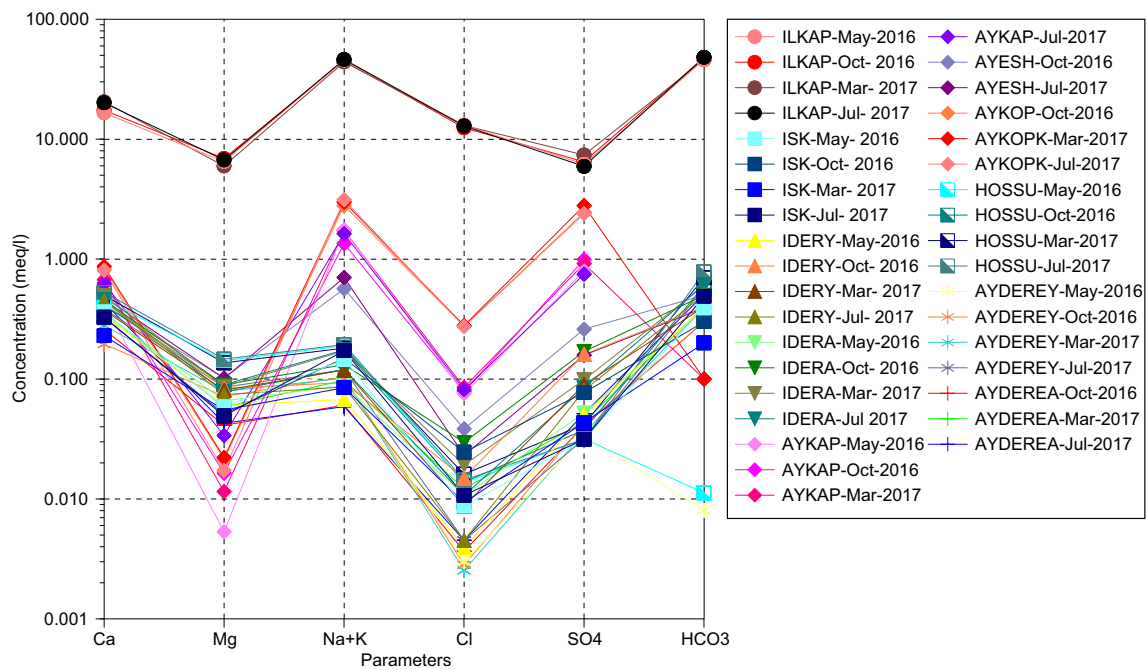
Fig. 3 Schoeller diagram of the water samples in Ilıcaköy (İkizdere) and Ayder (Çamlıhemşin) geothermal area

Reservoir rock temperature determination: geothermometer applications

The method applied to determine the aquifer temperatures of hot waters and to determine the equilibrium of the rocks with which they are in contact is the Na–K–Mg combined geothermometer developed by Giggenbach (1988). This geothermometer provides the test of the validity of cation geothermometers as well as providing a rapid interpretation of reservoir rock temperatures of thermal waters (Fig. 4).

As can be in the Giggenbach (1988) diagram, which is shown in Fig. 4, hot waters in the Ilıcaköy and Ayder geothermal areas plot in the field of "immature waters" on the diagram.

Silica geothermometers were used to determine the reservoir rock temperature in the geothermal areas studied (Tables 3, 4). This assessment indicated that the reservoir temperature of the Ilıcaköy geothermal waters was in the range of 119–149 °C and that the reservoir temperature of the Ayder geothermal waters was in the range of 41–80 °C.

Determination of mineral saturation indices

The degree to which water is saturated with respect to various mineral phases helps to determine the stages of hydrochemical evolution and shows which chemical reactions are likely to influence the water's chemical composition (Drever 1997; Langmuir 1997). Primary and secondary minerals were determined microscopically in the rock outcroppings in the study areas and the degree of saturation of all the water samples was examined according to these minerals using the PHREEQC (USGS, USA) software package.

According to the calculated saturation index (SI) values, the hot and cold waters in the studied areas are undersaturated with respect to sulfate minerals such as anhydrite and gypsum. Water samples in these areas are also undersaturated with respect to fluorite, halite, and vaterite.

The Ilıcaköy geothermal borehole water (ILKAP) was found to be saturated with aragonite, barite, calcite, and dolomite. The cold spring (ISK) and surface water samples (IDERY) were found to be undersaturated with respect to all of the selected minerals.

The Ayder hot geothermal borehole water (AYKAP) was calculated to be saturated with respect to aragonite, calcite, and dolomite, while the cold spring (HOSSU) and surface water samples (ADERY) were calculated to be undersaturated with respect to these mineral phases (Table 5). The Ikizdere hot spring water samples were found to be saturated with respect to a number of silicate minerals including K-feldspar, K-mica, kaolinite, and illite. However, the Ayder hot spring samples were undersaturated with respect to these mineral phases. Both the Ilıcaköy and Ayder hot spring samples were oversaturated with respect to goethite, hematite, and talc.

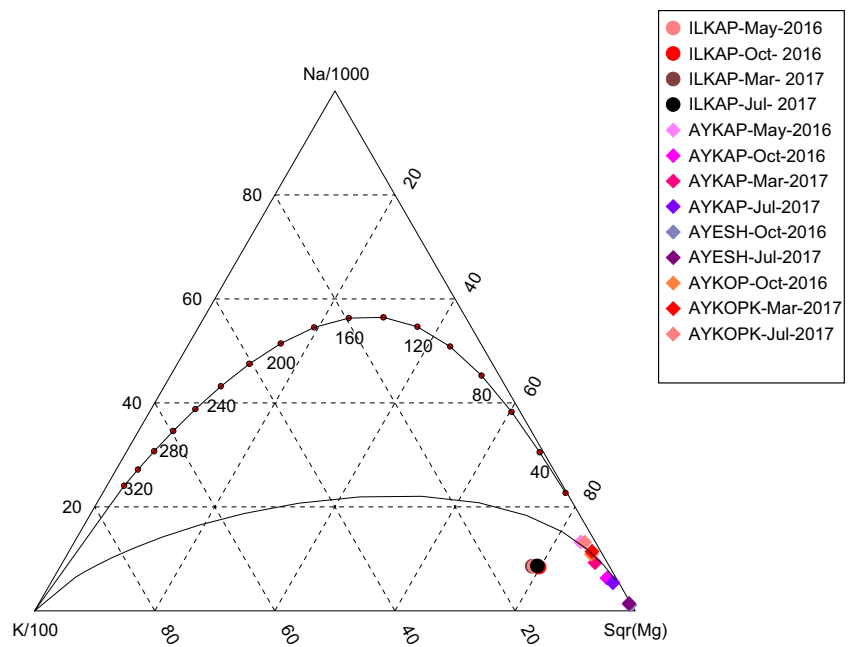**Fig. 4** Giggenbach's (1988) Na–K–Mg diagram for the studied geothermal waters

Table 3 Silica geothermometer calculations of Ilıcaköy (İkizdere) geothermal resources (ILKAP:SiO_2 = 122.83 mg/l)

Geothermometer	Equation	Source	Recommended temperature (^{0}C) ILKAP
1. SiO_2 (amorphous silica)	$t = 731/(4.52 - \log SiO_2) - 273.15$	Fournier (1977)	28
2. SiO_2 (α cristobalite)	$t = 1000/(4.78 - \log SiO_2) - 273.15$	Fournier (1977)	99
3. SiO_2 (β cristobalite)	$t = 781/(4.51 - \log SiO_2) - 273.15$	Fournier (1977)	50
4. SiO_2 (Chalcedony)	$t = 1032/(4.69 - \log SiO_2) - 273.15$	Fournier (1977)	124
5. SiO_2 (quartz-no steam loss)	$t = 1309/(5.19 - \log SiO_2) - 273.15$	Fournier (1977)	149
6. SiO_2 (quartz-maximum steam loss at 100 °C)	$t = 1522/(5.75 - \log SiO_2) - 273.15$	Fournier (1977)	143
7. SiO_2 (chalcedony conductive cooling)	$t = 1112/(4.91 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	121
8. SiO_2 (quartz steam loss)	$t = 1264/(5.31 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	119
9. SiO_2 (quartz steam loss)	$t = 1021/(4.69 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	119
10. SiO_2 (quartz steam loss)	$t = 1164/(4.9 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	141
11. SiO_2 (quartz steam loss)	$t = 1498/(5.7 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	142

Environmental isotope assessment

In hydrological and hydrogeological studies, it is possible to reveal the hydrogeological characteristics of geothermal systems by using natural isotopes, as geochemical tracers as ratios of isotopes of hydrogen, oxygen, and carbon in water are sensitive to temperature changes, physico-chemical processes, and water–rock interactions. Consequently, tritium (^{3}H) and carbon-14 (^{14}C) are usually used as radioisotope tracers, while oxygen–18 (^{18}O) and deuterium (^{2}H) isotopes are used as stable isotope tracers for the geochemical assessment of water samples. Tritium and carbon-14 are used to determine the age of groundwater, while oxygen-18 and deuterium are used to determine the sources of groundwater recharge, the origin of geothermal fluids and the temperature of the fluid in the aquifer, and as evaporation indicator in surface water bodies.

In this study, oxygen-18 and deuterium (Craig 1961) were used to calculate the possible discharge elevations of waters, while tritium was used to determine the relative age of groundwater samples and residence times in aquifers. Carbon-13 (Clark and Fritz 1997) was used to determine the origin of carbon in water, while oxygen-18 and sulfur-34 (Clark and Fritz 1997; Krouse and Mayer 2000; Izbicki et al. 2005; Krouse 1980) and strontium isotopes (Eyüboğlu et al. 2017; Kaygusuz and Aydınçakir 2009) were also used to determine the origin of sulfate in water. The isotope results

Table 4 Silica geothermometer calculations of Ayder (Çamlıhemşin) geothermal resources (AYKAP:SiO_2 = 46.45 mg/l, AYKOPK:SiO_2 = 43.6 mg/l, AYESH: SiO_2 = 27.78)

Geothermometer	Equation	Source	Recommended temperature (^{0}C)		
			AYKAP	AY KOPK	AYESH
1. SiO_2 (amorphous silica)	$t = 731/(4.52 - \log SiO_2) - 273.15$	Fournier (1977)	− 16	− 19	− 35
2. SiO_2 (α cristobalite)	$t = 1000/(4.78 - \log SiO_2) - 273.15$	Fournier (1977)	48	45	27
3. SiO_2 (β cristobalite)	$t = 781/(4.51 - \log SiO_2) - 273.15$	Fournier (1977)	2.0	− 1.0	− 18
4. SiO_2 (chalcedony)	$t = 1032/(4.69 - \log SiO_2) - 273.15$	Fournier (1977)	68	65	45
5. SiO_2 (quartz)	$t = 1309/(5.19 - \log SiO_2) - 273.15$	Fournier (1977)	98	96	76
6. SiO_2 (quartz steam loss)	$t = 1522/(5.75 - \log SiO_2) - 273.15$	Fournier (1977)	100	97	80
7. SiO_2 (chalcedony conductive cooling)	$t = 1112/(4.91 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	70	67	48
8. SiO_2 (quartz steam loss)	$t = 1264/(5.31 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	74	71	54
9. SiO_2 (quartz steam loss)	$t = 1021/(4.69 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	65	62	41
10. SiO_2 (quartz steam loss)	$t = 1164/(4.9 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	87	84	64
11. SiO_2 (quartz steam loss)	$t = 1498/(5.7 - \log SiO_2) - 273.15$	Arnorsson et al. (1983)	98	96	79

of water samples taken from each geothermal area are given in Table 6.

Oxygen 18 (^{18})–deuterium (^{2}H) relationships

The relationship between oxygen-18 and deuterium contents in rainfall across the world is as follows (Craig 1961):

$$\delta^2 H = 8 \times \delta^{18} O + 10.$$

This relationship defines the Global Meteoric Water Line (GMWL).

The Global Meteoric Water Line (GMWL) (Craig 1961), the Eastern Black Sea Meteoric Water Line (EBSML): $\delta^2 H = 8 \delta^{18} O + 16$) (Ekmekçi and Gültekin 2015), and the $\delta^{18}O$–$\delta^2 H$ relations of the waters in the study area are given in Fig. 5. The $\delta^{18}O$ and $\delta^2 H$ values of water samples from the study area have been assessed by comparison with the GMWL.

While the cold water samples in the Ilıcaköy area plot close to EBSML, the hot water samples have negative deuterium values (Fig. 5). This indicates that the supply of hot waters is from higher elevations than that of cold waters. The waters of the Ayder field generally plot close to the BSMWL (Fig. 5). The fact that δD and $\delta^{18}O$ values of surface water and cold water spring samples are more positive than hot water spring samples indicates that they are fed by rainfall with heavy isotopes: that is, by rainfall reaching to lower elevations.

The $\delta^{13}C_{VPDB}$ values determined in the waters of the geothermal areas studied have negative values in hot water samples from both the Ilıcaköy (− 7.81‰) and the Ayder (− 19.6‰) areas (Table 6). These values indicate that carbon in hot water originates from inorganic carbon in groundwater and from CO_2 in pore spaces in the unsaturated zone (Clark and Fritz 1997).

The results of the assessment of the ^{34}S isotope content of dissolved SO_4^{-2} ion in the waters in the studied geothermal areas are presented in Table 5. Potential sources of sulfate in groundwater in the area include the dissolution of sulfate minerals such as gypsum, the oxidation of sulfide minerals, and biological activity. The $^{34}S_{CDT}$ value in hot water in Ilıcaköy area is approximately 16‰, while in the Ayder area it is around 10‰. $^{34}S_{CDT}$ values in cold waters range from 10 to 3‰. According to Krouse (1980), sulfur (SO_2) in hot waters derives from Cenozoic-aged gypsum and sulfur in cold waters derives from igneous rocks.

Evaluation of the tritium content of water samples

^{3}H-Eİ, ^{3}H–Cl$^-$, and ^{3}H temperature relationships of the studied geothermal areas are shown in Fig. 6a, b. These relationships are inversely proportional in all areas as expected. When each area was evaluated alone, hot waters were shown to circulate deeper than cold waters.

Because the cold water springs in the Ilıcaköy and Ayder areas have almost the same tritium and EC values as the surface waters, this indicates that the springs are completely fed by the current precipitation (Table 6) and (Fig. 6a, b).

Evaluation of the Sr isotope data

Sr has a similar ionic radius and chemical properties to calcium and therefore the Sr concentration is generally high in Ca-containing minerals (calcite, fluorite, gypsum, anhydrite and plagioclase). The $^{87}Sr/^{86}Sr$ values in the water samples from the Ilıcaköy and Ayder hot water springs were measured as 0.70716 and 0.70740,

Table 5 SI values of Ilıcaköy and Ayder geothermal springs

Mineral	Formüla	İkizdere geothermal springs			Ayder geothermal springs				
		ILKAP	ISK	IDERY	AYKAP	AYKOPK	AYESH	HOSSU	AYDERY
Albite	$NaAlSi_3O_8$	0.49	− 2.71	− 4.40	− 3.42	− 1.79	− 1.99	− 1.79	− 2.89
Anhydrite	$CaSO_4$	− 1.06	− 4.33	− 4.15	− 2.88	− 2.30	− 3.39	− 4.22	− 4.27
Aragonite	$CaCO_3$	1.43	− 1.36	− 3.09	0.81	0.78	− 1.01	− 3.32	− 3.82
Barite	$BaSO_4$	0.43	− 1.34	− 1.59	–	− 1.30	− 1.01	–	–
Ca-Montmoril-lonite	$Ca0.165Al_233Si_367O_{10}(OH)_2$	3.40	3.54	3.79	− 5.05	− 2.22	1.20	3.79	3.56
Calcite	$CaCO_3$	1.55	− 1.93	− 2.93	0.94	0.92	− 0.86	− 3.17	− 3.66
Celestite	$SrSO_4$	− 1.1	− 4.9	− 4.82	− 2.99	− 3.16	− 3.45	− 4.76	− 4.70
Dolomite	$Ca–Mg(CO_3)_2$	2.99	− 4.71	− 6.73	0.28	0.45	− 2.26	− 6.93	− 8.05
Fluorite	CaF_2	− 1.22	− 3.70	− 5.04	− 2.94	− 1.77	− 3.24	− 4.89	− 5.56
Gibbsite	$CaSO_4{:}2H_2O$	− 1.08	− 4.08	− 3.90	− 2.85	− 2.11	− 3.16	− 3.97	− 4.01
Goethite	$FeOOH$	7.91	6.60	3.77	5.71	6.51	7.32	7.18	6.40
Halite	$NaCl$	− 5.13	− 10.51	− 11.21	− 8.59	− 7.79	− 9.28	− 10.22	− 11.12
Hematite	Fe_2O_3	17.98	15.15	9.47	13.56	15.06	16.61	16.30	14.74
Illite	$K0.6Mg0.25Al_23Si_35O_{10}(OH)_2$	3.35	1.86	1.40	− 5.11	− 2.14	0.31	2.51	1.97
K-Feldspar	$KAlSi_3O_8$	1.61	− 1.08	− 2.40	− 3.14	− 1.30	− 1.14	0.09	− 0.89
K-Mica	$KAl_3Si_3O_{10}(OH)_2$	9.67	8.49	8.94	− 0.93	2.36	5.66	8.58	8.60
Kaolinite	$Al_2Si_2O_5(OH)_4$	4.17	5.57	6.26	− 2.80	− 0.60	2.79	4.98	5.27
Quartz	SiO_2	0.49	0.24	− 0.16	− 0.08	0.26	0.38	0.63	0.28
Rhodochrosite	$MnCO_3$	− 0.06	–	− 4.56	–	–	–	–	–
Siderite	$FeCO_3$	− 0.52	− 2.32	− 3.16	− 8.12	− 6.90	− 3.54	− 3.85	− 4.40
Talc	$Mg_3Si_4O_{10}(OH)_2$	3.14	− 8.49	− 16.17	4.43	5.16	− 0.83	− 4.63	− 8.33
Witherite	$BaCO_3$	− 1.99	− 4.60	− 6.08	–	− 3.56	− 4.61	− 4.06	–

respectively (Table 6). The reservoir rock in the Ilıcaköy and Ayder geothermal areas is formed by the Kaçkar Granitoid. The $^{87}Sr/^{86}Sr$ values in the granitoid rocks outcropping in the region were determined to be in the range of 0.704319 and 0.706675 by Eyüboğlu et al. (2017), and between 0.705350 and 0.706660 by Kaygusuz and Aydınçakir (2009). Accordingly, the $^{87}Sr/^{86}Sr$ values in the samples from Ilıcaköy and Ayder hot water springs and the $^{87}Sr/^{86}Sr$ values in the granitoids overlap with each other. The proximity of these values suggests that Sr passes from granitic rocks to waters by simple dissolution without significant fractionation of the strontium isotopes.

Total alpha and total beta contents of water samples

The radioactivity of geothermal waters can affect their use in spas. Three of the sampling sites investigated in this study are used as sources of geothermal water for spa facilities. Therefore, total alpha and total beta levels were measured to determine the suitability of these water sources for this use (Table 7).

This assessment indicated that the highest total alpha and total beta levels were measured in the geothermal water obtained from the 266-m deep borehole in the Ilıcaköy geothermal area. The radioactivity of groundwater is known to be related to the geological environments from which they originate and waters from magmatic and volcanic rocks, which are generally richer in U, Th, and K, are more radioactive than the water from sedimentary rocks. The whole basin is composed of granitic rocks in the Ilıcaköy geothermal area, which causes a high level of radioactivity in groundwater in the area.

Conceptual model of the Ilıcaköy (İkizdere–Rize) geothermal system

The geological and hydrogeological studies in the Ilıcaköy geothermal area revealed that the Kaçkar granitoid underlies a very large area of the Cimildere Basin and acts as the reservoir rock for geothermal systems in the region. According to Evcimen (2011), the general rock assemblage of granitoid rocks that outcrop in the vicinity of the study area consists of granite, granodiorite, tonalite, quartz monzonite, diorite, and

Table 6 Isotopic results of the water samples in Ilicaköy (İkizdere) and Ayder (Çamlıhemşin) geothermal area

	Sample Name	Date	Type	δD V-SMOW	δ^{18}O V-SMOW	T (TU)	δ^{13}C ($_{V\text{-}PDB}$)	δ^{34}S (SO$_4$) VCDT	δ^{18}O (SO$_4$) V-SMOW	^{87}Sr/^{86}Sr
Ilıcaköy (İkizdere) geothermal area	ILKAP	May 16	Hot water	− 97.32	− 12.98	0.48	− 7.81	16.4	4.9	0.70716
		October 16		− 98.7	− 12.79	0.31				
		March 17		− 95.65	− 12.93	0.11	− 8.97	16.7	4.7	
		July 17		− 95.53	− 12.86	0.06				
	ISK	May 16	Cold Water	− 75.82	− 10.84	6.56	bdl	8.0	1.2	
		October 16		− 73.58	− 11.14	7.80				
		March 17		− 78.94	− 12.11	6.48	bdl	4.1	0.7	
		July 17		− 78.44	− 11.53	4.08				
	IDERY	May 16	Surface Water	− 88.01	− 12.99	6.06	− 22.13	4.2	1.1	
		October 16		− 81.66	− 12.17	6.58				
		March 17		− 90.80	− 13.28	6.30	− 6.80	3.7	1.4	
		July 17		− 92.12	− 13.21	5.73				
	IDERA	May 16	Surface Water			7.23				
		October 16		− 83.08	− 12.03	6.31				
		March 17		− 89.23	− 13.33	4.67				
		July 17		− 89.36	− 13.19					
	GUNKAR	March 17	Snow (600 m)	− 90.14	− 13.32	4.29				
	IKIZDKAR	March 17	Snow (950 m)	− 127.71	− 18.12	4.62				
Ayder (Çamlıhemşin) geothermal area	AYKAP	May 16	Hot Water	− 96.79	− 14.15	1.01	− 19.6	10.3	5.8	0.7070
		October 16		− 96.12	− 14.1	0.51				
		March 17		− 97.07	− 13.98	0.09	− 17.40	9.2	15.4	
		July 17		− 97.76	− 14.07	0.37				
	AYKOPK	October 16	Hot Water	− 96.20	− 14.15	0.76				
		March 17		− 96.98	− 14.39	0.43	− 14.32	6.4	6.0	
		July 17		− 98.84	− 14.14	0				
	AYESH	October 16	Hot Water	− 79.13	− 12.01	4.82				
		July 17		− 81.14	− 11.95	3.92				
	HOSSU	Mayıs 16	Cold Water	− 83.34	− 12.14	0.30	− 20.82	7.7	11.8	
		Ekim 16		− 81.84	− 12.01	4.00				
		Mart 17		− 82.59	− 11.60	5.14	− 10.64	5.2	− 0.4	
		Tem 17		− 81.46	− 11.93	4.44				
	AYDEREY	Mayıs 16	Surface Water	− 83.35	− 11.87	0.34	− 18.29	3.6	1.1	
		Ekim 16		− 82.04	− 12.00	5.31				
		Mart 17		− 93.16	− 13.58	5.25	− 9.12	4.9	− 1.2	
		Tem 17		− 83.86	− 12.04	5.05				
	AYDEREA	Ekim 16	Surface Water	− 79.10	− 11.77	6.60				
		Mart 17		− 95.07	− 13.70	5.45				
		Tem 17		− 90.10	− 13.20					
	AYDERKAR	Mart 2017	Snow sample	− 140.37	− 19.83	6.07				

gabbroic diorite host rocks, and monzonite, monzodiorite, and monzo gabbro compound enclaves.

A fracture system has developed in three directions in the unweathered granitoid, which has produced a secondary porosity in these rocks that is known to have a primary porosity of 1.35% (Tüdeş et al. 1991). In addition, the granitic rocks are highly weathered near hot spring outlets and this weathering has further increased the permeability of
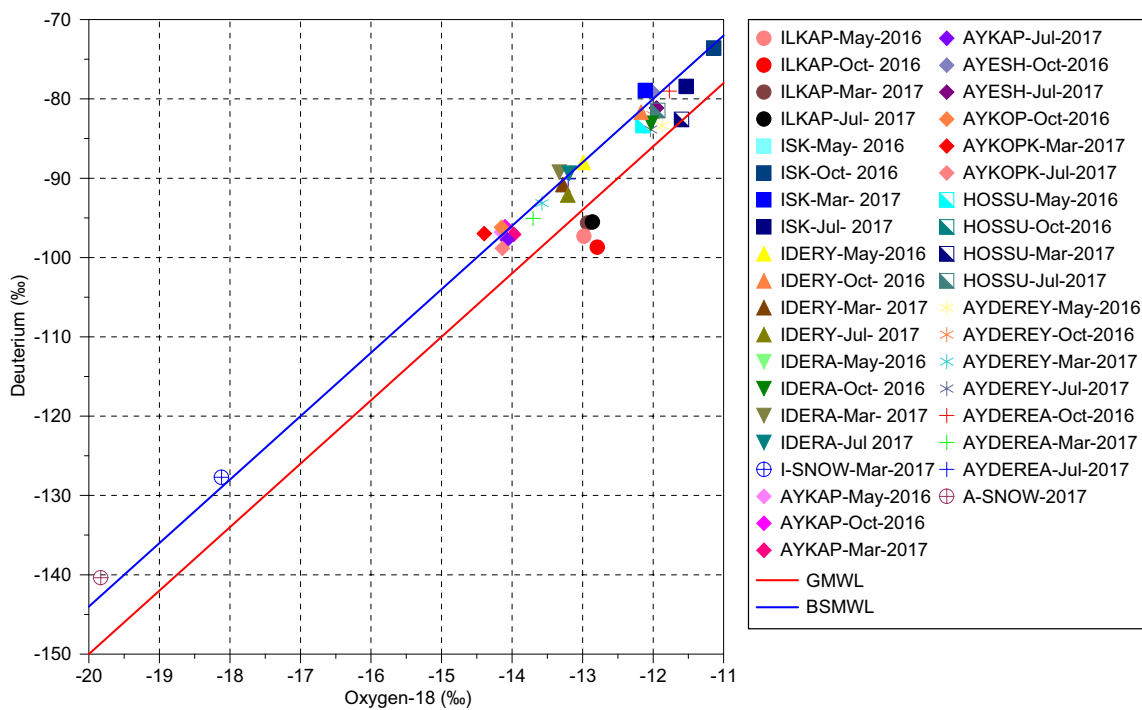
Fig. 5 $\delta 18O$–$\delta 2H$ relation for the Ilıcaköy (İkizdere) and Ayder (Çamlıhemşin) geothermal areas. *GMWL* Global Meteoric Water Line, *BSMWL* Black Sea Meteoric Water Line

the rock near the fractures. These factors enable the storage and circulation of water in the fracture system within the crystalline bedrock in the region.

The fluid in the geothermal reservoir formed by the Kaçkar granitoid is derived from the infiltration of water from precipitation into fractures in the granitic bedrock. The isotopic composition of geothermal water samples suggests that they are of meteoric origin and follow a deeper subsurface circulation path compared to cold spring water samples. A well-developed fracture system in bedrock allows water derived from precipitation to penetrate deep beneath the land surface.

The meteoric waters that infiltrate into the bedrock fracture system are heated by the effects of the local geothermal gradient. Water heated at depth then rises toward the surface where it eventually discharges to the surface in fracture zones of the granitoid bedrock (Fig. 7). The geothermal system in the region is not capped by a sealing rock unit. However, in the valleys with steep slopes, physically and chemically weathered products are stored as slope debris on the slopes. These new formations partially cover the granitic rocks and can help to retain heat in the geothermal system. The temperature of the reservoir in the Ilıcaköy area was estimated to be 125–150 °C with silica geothermometers. With these values, the area is classified as a low-to-moderate enthalpy geothermal system (Haenel et al. 1988; Hochstein 1990).

Conceptual model of the Ayder (Çamlıhemşin–Rize) geothermal system

The reservoir rock in the area is formed by crystalline rocks of the Kaçkar granitoid. In the unweathered parts of the bedrock, which mostly consist of granodiorites in this area, a three-way permeable fracture system occurs in crystalline bedrock. The distances between the fractures vary from several centimeters to several meters. The degree to which the granitic bedrock is weathered varies greatly in the area. In the slightly weathered areas, the original rock fabric is recognizable, but in areas where intensive weathering has taken place, minerals such as alkaline feldspar and plagioclase have been completely argillized. These fractured and weathered parts of the granitoid impart secondary porosity to the bedrock.

The fluid of the geothermal system is provided by the infiltration of meteoric waters into the fracture system in bedrock because of high annual precipitation in the area (1320 mm/a), and the water is heated by the local steep geothermal gradient. The heated water is stored in fractured bedrock to form a geothermal reservoir. Temperature measurements made in a borehole suggest that the geothermal reservoir is approximately 200 m deep in this area. Water in the reservoir rises to the surface along fractures in the granitic bedrock and is discharged to the surface (Fig. 8).

Fig. 6 3H-EC, 3H-Cl- ve 3H-Temperature relations for the **a** Ilıcaköy (İkizdere) and **b** Ayder (Çamlıhemşin) geothermal areas
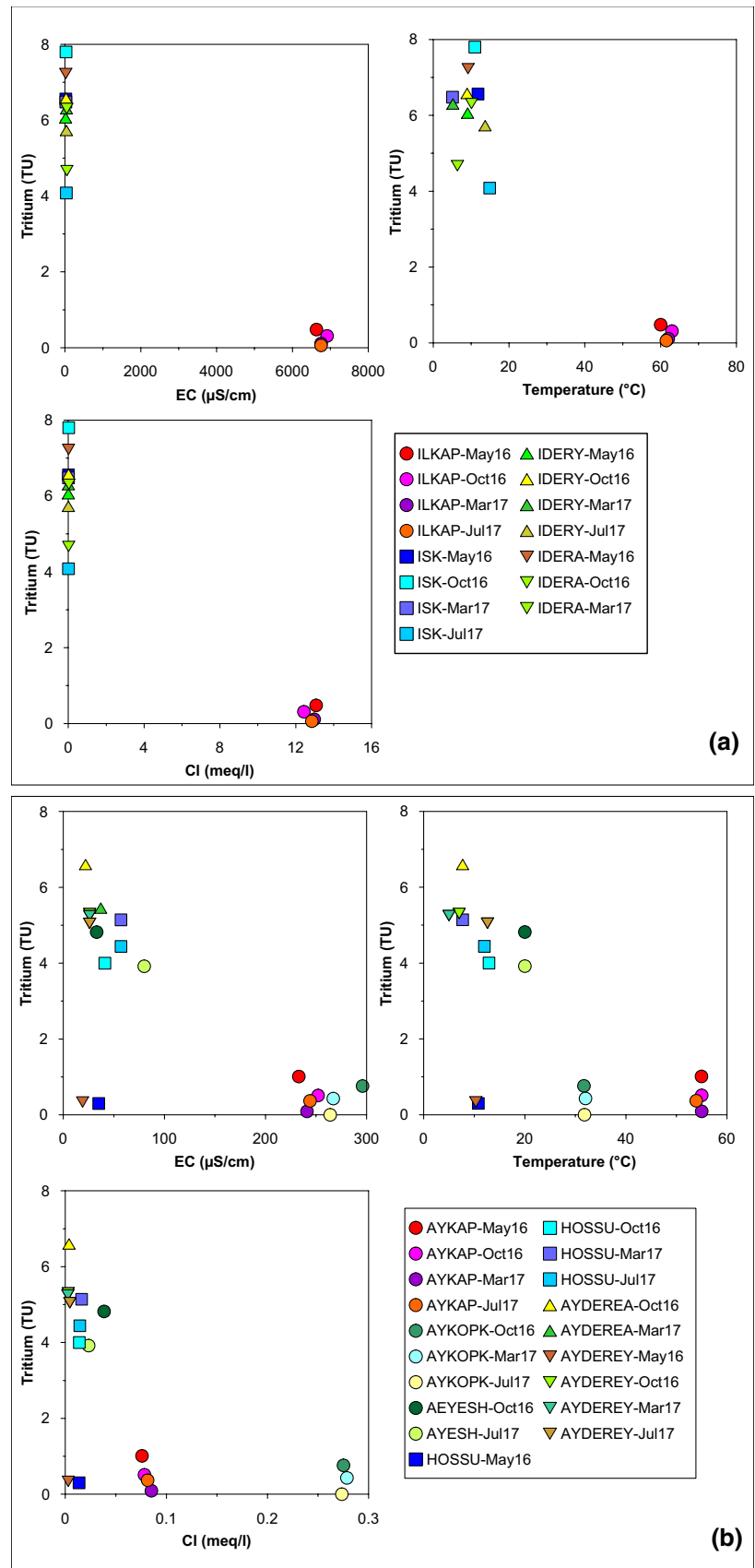
Table 7 Alpha and beta values of water samples in Ilıcaköy and Ayder Geothermal Areas

	Sample name	Date	Type	Alpha (Bq/L)	Beta (Bq/L)
Ilıcaköy (İkizdere) geothermal area	ILKAP	May 2016	Hot water	14.892	8.33
	ISK	May 2016	Hot water	0.017	0.03
	IDERY	May 2016	Cold water	0.035	0.04
	IDERA	May 2016	Surface water	0.03	0.03
Ayder (Çamlıhemşin) geothermal area	AYKAP	May 2016	Hot water	0.037	0.06
	HOSSU	May 2016	Cold water	0.011	0.03
	AYDEREY	May 2016	Surface water	0.013	0.03
	AYDEREA	October 2016	Surface water	0.024	0.03
	AYKOPK	October 2016	Hot water	0.023	0.02
	AYESH	October 2016	Hot water	0.041	0.03
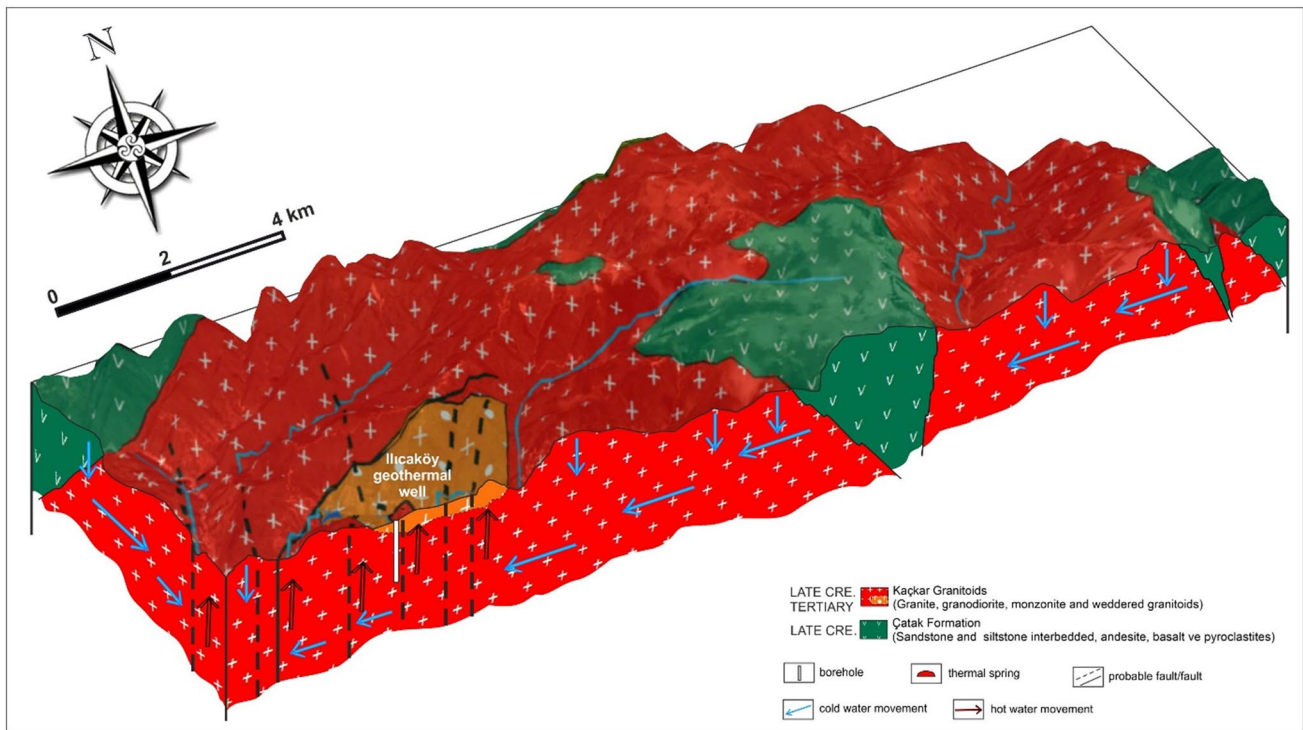
Fig. 7 Conceptual hydrothermal model for the Ilıcaköy (İkizdere) geothermal area

Conclusion and recommendations

This study aimed to determine the hydrogeological, hydrogeochemical, and isotopic characteristics of the Ilıcaköy (İkizdere–Rize) and Ayder (Çamlıhemşin–Rize) geothermal areas that are located in the north-eastern part of Turkey and to investigate the geothermal energy in these regions.

The hot water in the Ilıcaköy area is discharged from a geothermal borehole at a depth of 266 m. The temperature of the fluid discharged from the borehole is 63 °C, its EC value is 6913 µS/cm, and its pH is 7.2. The old spring outlets are completely dry. The temperature of the fluid obtained from an artesian well flows from a depth of 211 m in the Ayder

geothermal field and its temperature is 55 °C, EC is 255 µS/cm, and pH is 9.2.

The geothermal fluids have a chemical composition that is dominated by Na–Ca–HCO3 in the Ilıcaköy area, and by Na–Ca–CO_3–SO_4 in the Ayder area. It was determined that the hot waters were saturated with respect to aragonite, calcite, dolomite, quartz, K-mica, kaolinite, talc, and hematite, while they were undersaturated with respect to minerals including gypsum, anhydrite, halite, fluorite, rhodochrosite, and siderite. The reservoir rock temperatures of the immature Ilıcaköy and Ayder geothermal waters were calculated using silica geothermometers. The reservoir rock
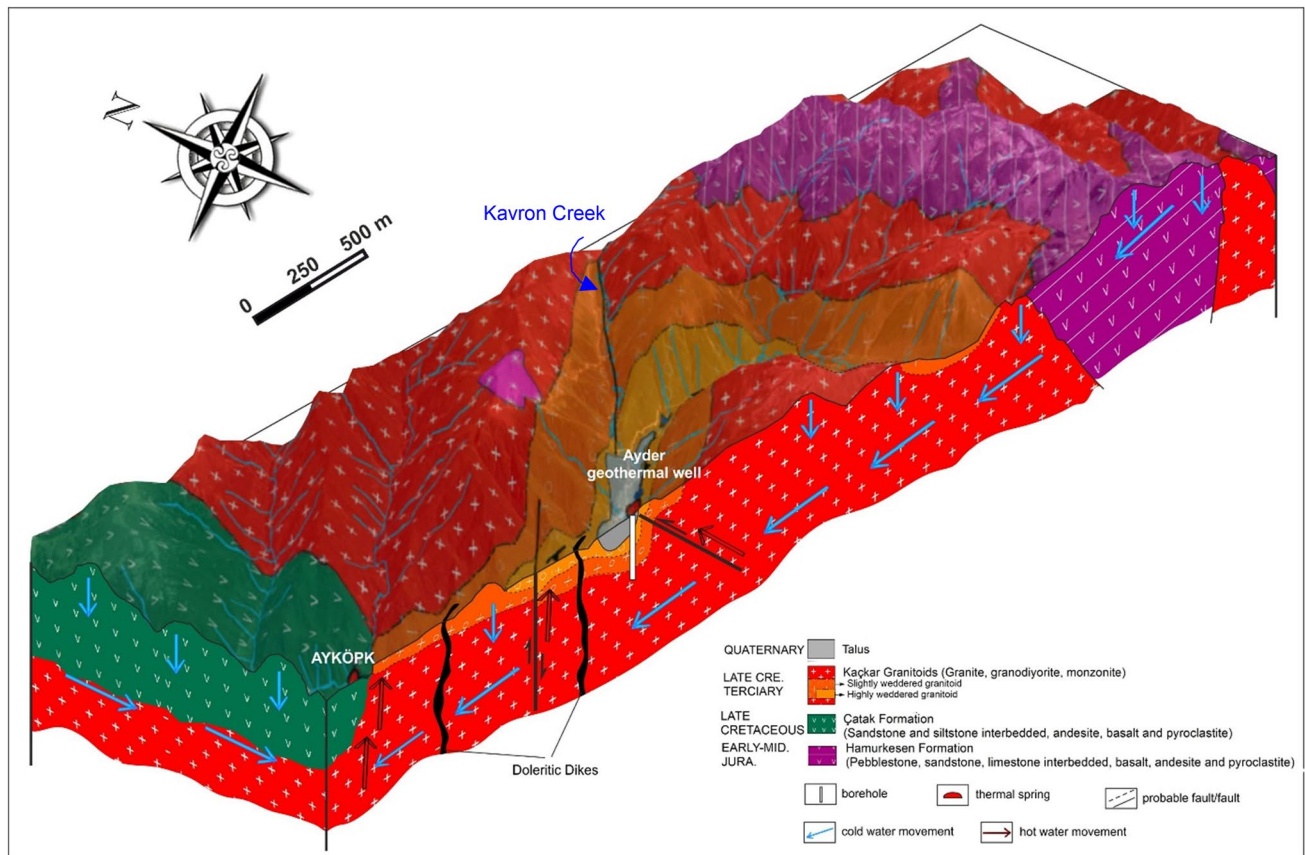
Fig. 8 Conceptual hydrothermal model for the Ayder (Çamlıhemşin) geothermal area

temperature was found to be 41–80 °C for the Ayder area and 119–149 °C for the Ilıcaköy area.

The δ^{18}O and δ^2H content of the water samples suggested that all the waters in the studied area were of meteoric origin.

While hot water samples did not show any seasonal changes in chemical composition, the cold water samples were affected by seasonal changes in composition. The geothermal waters in the study areas consisted of deeply circulating meteoric waters that interacted with hot bedrock. The observation that the cold water springs in the Ilıcaköy and Ayder areas have similar tritium contents and EC values compared to surface water samples suggests that the springs are fed completely by the current rainfall, and the hot waters circulate more deeply below the land surface than the cold water flow systems.

The δ^{13}CVPDB values suggest that carbon in the geothermal waters in the study areas were derived from inorganic carbon in groundwater and from CO_2 in pore spaces in the unsaturated zone. The δ^{34}SCDT values suggest that the source of sulfur in geothermal waters is of volcanic origin. The observation that the ^{87}Sr/^{86}Sr values in water samples from Ilıcaköy and Ayder hot water springs and values of the same ratio in granitic bedrock samples are similar to each other suggests that Sr passes from granitic rocks to water by simple dissolution without extensive fractionation.

In the Ilıcaköy (İkizdere–Rize) and Ayder (Çamlıhemşin–Rize) areas, the geothermal reservoirs consist of fractured and weathered granitic rocks from the Kaçkar granitoid. Quaternary-aged volcanic activity in the region is the reason for the high geothermal gradient.

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