

Mustafa Afşin
İlkay Kuşcu
Hatim Elhatip
Kadir Dirik

Hydrogeochemical properties of CO₂-rich thermal–mineral waters in Kayseri (Central Anatolia), Turkey

Received: 15 August 2005
Accepted: 13 December 2005
Published online: 12 January 2006
© Springer-Verlag 2006

M. Afşin (✉)
Department of Geological Engineering,
Niğde University, 68100 Aksaray, Turkey
E-mail: mafsin@superonline.com
Tel.: +90-382-2150953
Fax: +90-382-2150592

İ. Kuşcu
Department of Geological Engineering,
Muğla University, 48000 Muğla, Turkey

H. Elhatip (✉)
Department of Environmental Engineering,
Niğde University, 68100 Aksaray, Turkey
E-mail: hnaim@superonline.com
Tel.: +90-382-2150953
Fax: +90-382-2150592

K. Dirik
Department of Geological Engineering,
Hacettepe University, 06532 Ankara,
Turkey

Abstract The present study highlights the hydrogeological and hydrogeochemical characteristics of the CO₂-rich thermal–mineral waters in Kayseri, Turkey. These waters of Dokuzpınar cold spring (DPS) (12–13°C), Yeşilhisar mineral spring (YMS) (13–16°C), Acısu mineral spring (ACMS) (20–22.5°C), Tekgöz thermal spring (TGS) (40–41°C), and Bayramhacı thermal-mineral spring (BTMS) (45–46.5°C) have different physical and chemical compositions. The waters are located within the Erciyes basin in the Central Anatolian Crystalline complex consisting of three main rock units. Metamorphic/crystalline rocks occur as the basement, sedimentary rocks of Upper Cretaceous-Quaternary age form the cover, and volcanosedimentary rocks Miocene-Quaternary in age represent the extrusive products of magmatism acting in that period. All these units are covered unconformably by terrace and alluvial deposits, and travertine occurrences have variable permeability. Dokuzpınar cold spring, YMS and ACMS localized mainly along the faults within the region have higher Na⁺ and Cl⁻ contents whereas TGS and BTMS have

higher amounts of Ca²⁺ and HCO₃⁻. The high concentrations of Ca²⁺ and HCO₃⁻ are mainly related to the high CO₂ contents resulting from interactions with carbonate rocks. Whereas the high Na⁺ content is derived from the alkaline rocks, such as syenite, tuff and basalts, the Cl⁻ is generally connected to the dissolution of the evaporitic sequences. These waters are of meteoric-type. BTMS deviates from meteoric water line. The content is related to the increases in the δ¹⁸O compositions due to mineral–water interaction (re-equilibrium) process. CO₂-dominated YMS and ACMS with low temperatures have higher mineralizations. Yeşilhisar mineral spring, ACMS, TGS and BTMS are oversaturated in terms of calcite, aragonite, dolomite, goethite and hematite, and undersaturated with respect to gypsum, halite and anhydrite. Yeşilhisar mineral spring, ACMS and BTMS are also characterized by recent travertine precipitation. Dokuzpınar cold spring is undersaturated in terms of the above minerals. The higher ratios of Ca/Mg and Cl/HCO₃, and lower ratios of SO₄/Cl in BTMS than TGS suggest that TGS has shallow

circulation compared to BTMS, and/or has much more heat-loss enroute the surface. The sequence of hydrogeochemical and isotopic compositions of the waters is in an

order of DPS > YMS > ACMS > TGS > BTMS and this suggests a transition period from a shallow circulation to a deep circulation path.

Keywords Erciyes volcanism · CO₂ gas · Thermal–mineral waters · Hydrogeochemistry · Shallow and deep circulation · Kayseri-Turkey

Introduction

Kayseri region and Sultansazlığı depression is not only one of the main wetlands but also a significant geothermal field possessing several thermal and mineralized waters. The objective of this study is to correlate and compare Acisu mineral spring (ACMS), Yeşilhisar mineral spring (YMS), Tekgöz thermal spring (TGS) and Bayramhacı thermal–mineral spring (BTMS) with Dokuzpınar cold spring (DPS). The springs are located at the western and eastern margins of the Sultansazlığı basin (Fig. 1). The thermal and mineral waters lie at the central (ACMS and YMS) and western margin (BTMS and TGS), whereas cold waters are at the eastern margin of the basin. The diversity in the geographical distribution of the waters is also worthy of interest in terms of the hydrogeological properties. The thermal–mineral waters are associated with the lacustrine sediments as the dominant constituent of the basin. Others are associated with meta-carbonates (ACMS, BTMS and TGS) which constitute the western outline of the basin. However, the cold waters are associated with basaltic flows forming the western margin (DPS), or are confined to the fault zones outlining the southwestern margin of the basin (YMS) (Fig. 1). A study of the hydrogeochemistry and isotope compositions of the waters and the properties and structure of the circulation of the ground water systems with compositional variation in the waters will help to define briefly the geothermal system.

The geological characteristics of the regions around the springs were studied. The water samples were collected into double capped 1,000 mL polyethylene bottles, acid (pure HNO₃) was added for cation analysis and the samples unacidified for anions. On the other hand, water samples for pollution analyses were collected by adding H₂SO₄. All analyses were carried out at the International Research and Application Center for Karst Water Resources (UKAM) water chemistry laboratories at the Hacettepe University (Ankara). The isotopic analyses of the samples taken from November 1999 to May 2000 were done at the isotope laboratories of the Technical Research-Quality Control (TAKK) Directorate of the State Hydraulic Works (DSI) (Ankara). The geochemical analyses of the rock samples collected at the vicinities of the spring sites were performed by atomic absorption spectrometric (AAS) methods at the chemical laboratories of Kale Seramik Ltd. (Çanakkale, Turkey).

The hydrochemical analyses were done according to APHA, AWWA and WPCF (1989) standards. Ca²⁺, Mg²⁺, Na⁺ and K⁺, pollution parameters and heavy metals were analyzed by AAS. SO₄²⁻ content was detected spectrophotometrically along with alkalinity standard titrimetry. Cl⁻ anion was analyzed by AgNO₃ titrimetric methods; while the B ion was analyzed by spectrophotometer. Some of the chemical and physical characteristics of the waters were measured in situ. Temperature measurements were done by thermometer, pH measurements by pH meter with 0.01 precision, free CO₂ content was measured by CA-23 HACH-CO₂ test kit, dissolved oxygen (DO) by oxygenmeter (model YSI-55), and oxygen 18 and deuterium by mass spectrometry. For natural tritium abundance, liquid scintillation technique was applied. Analytical error of δ¹⁸O and δ²H measurements were typically in the order of 0.1 and 0.01 based upon the Vienna Standard Mean Ocean Water (VSMOW) standard, respectively.

The saturation indices of some minerals presumed to exist in the depositional environments, which have a vital importance for the hydrochemical interpretations were calculated by using the PhreeqCi (a computer-coded chemical equilibrium software) (Parkhurst and Appelo 1999). The evaporation ratio, together with the relative fit to meteoric water line, were determined referring to the relationship between δ¹⁸O and δ²H isotopes.

Hydrogeological and hydrochemical properties of the waters

The springs investigated in this paper are mainly located to the southeasternmost edge of a triangularly-shaped unit termed as the Central Anatolian Crystalline Complex (CACC) (Göncüoğlu et al. 1991, 1993) (Fig. 1). In the regional context, this unit consists of three main rock formations. Of these, metamorphic/crystalline rocks occurring at the basement, the sedimentary units of Upper Cretaceous-Quaternary age form the cover, and finally volcanics and volcanosedimentary rocks Miocene-Quaternary in age represent the extrusive products of magmatism. All these units are covered unconformably by terrace and alluvial deposits, and travertine occurrences around the thermal and mineral waters. The rock units exposed at the spring sites have different hydrogeological properties. The massive and foliated levels of the metacarbonates forming the basement are

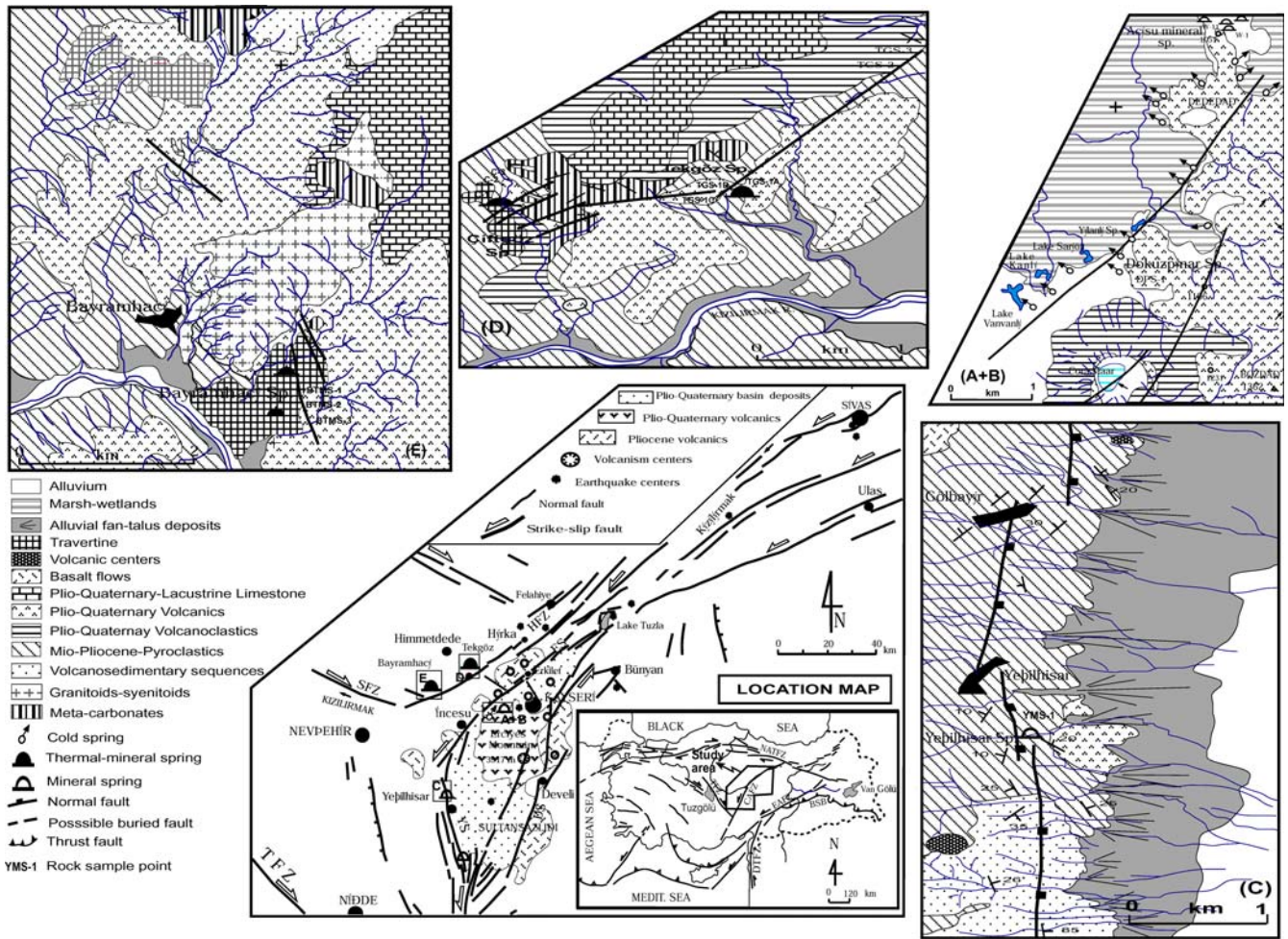


Fig. 1 Location and geological map of the study area (A, B Dokuzpınar cold and Acisu mineral waters; C Yeşilhisar mineral waters; D Tekgöz thermal waters; E Bayramhacı thermal-mineral waters. TFZ Tuzgözü fault zone, CAFZ Central Anatolian fault zone, DTFZ Deadsea transformation fault zone, SFZ Salanda fault

zone, HF Hırka fault zone, EAFZ: Eastern Anatolian fault zone, NATFZ North Anatolian transformation fault zone, ES Erkilet segment, DS Develi segment, YS Yeşilhisar segment, BSB Bitlis suture belt

impervious, whereas the fractured, joined and karstic parts are permeable. Although the granitic and syenitic rocks are impervious in general, the upper and marginal levels that were subjected to alteration and fracturing are permeable. The loosely cemented conglomeratic and sandy levels are permeable. Siltstones are semipermeable; however, all other lithologies of continental clastic rocks (Late Cretaceous-Paleocene age) are impermeable. The alluvial fan and shallow marine sedimentary rocks are permeable; the flysch Paleocene rocks are impervious. The blocky, loosely cemented and well-rounded conglomeratic and sandy levels are permeable; whereas marl, gypsum and coal bearing levels of fluvial sequences (Oligo-Miocene in age) are impervious. Of the Miocene-Pliocene aged volcanic-volcanosedimentary rocks, the agglomerates, basalts with columnar jointing, disintegrated andesites, and cross-bedded, loosely-cemented

conglomerates are permeable, but the tuffs are impervious. The loosely-cemented conglomerate and sandstones, lacustrine limestone and ignimbrite-bearing levels, alluvial fan and talus deposits are generally permeable. Tuff, claystone and marl-bearing levels of the sequences Plio-Quaternary in age, are impervious. The conglomeratic and sandy levels are permeable. The clay-bearing levels of talus, alluvial and terrace deposits along the course of the Kızılırmak river are impervious.

The majority of the springs in the study area are located along the major strike-slip faults and/or minor parallel faults (Fig. 1) which indicate that the exposure is controlled by structural features. Dokuzpınar, for example, discharges at several locations at the surface along the NE-SW trending Erkilet Segment; Yeşilhisar is localized along the NW-SE trending Yeşilhisar Segment; and ACMS emerges along the NE-SW trending

Erkilet Segment of the Ecemiş Fault zone. TGS is located on one of the NE–SW trending faults parallel or sub-parallel to the Hırka fault zone. The BTMS is confined mainly to faults trending in NNW–ENE.

The waters in the region have different physical properties regarding the temperature, pH, and electrical conductivity (EC). For example, the temperature (°C) values change between 12 and 13 in DPS, 13 and 22.5 in YMS and ACMS, and 40 and 46.5 in TGS and BTMS. The pH values (as pH unit) are in the region 7.3–8.1 in DPS, 6.3–6.8 in YMS and ACMS, and 6.5–7.3 in TGS and BTMS. The EC values (in $\mu\text{S}/\text{cm}$) are in the range 300–537 in DPS, 5,600–14,600 in YMS and ACMS, and 452–1,640 in TGS and BTMS. The DPS emerges at nine points in a comparatively wide area and has a total discharge of about 100 L/s. The discharge of the other waters ranges from 1.0 to 1.5 L/s (YMS=2.5, ACMS=10, TGS=1.5, BTMS: old bath=1, pool bath=15). The DPS is used as drinking and irrigation purposes and is comparable to TSE (1997) and WHO (1993) standards. However, the TGS and BTMS are used as spa. About 11 CO₂-supplying wells (about 200 m in depth) penetrate the area of the ACMS.

In addition to mixing with diverse water types and water–rock interactions along the flow path, the parameters such as chemical interaction, processes of dissolution, hydration, hydrolysis, oxidation–reduction, attack by acids, chemical precipitation, base exchange, sulfate reduction, concentration, and ultrafiltration or osmosis (Holysh and Toth 1996; Tóth 1999) play important roles in the variable hydrogeochemical and isotopic characteristics (pH, temperature, flow rate, etc.) of the waters.

Hydrogeochemical features of the waters are presented in Table 1. The parameters which are presumed to affect these characteristics were plotted on several diagrams showing the ion ratios and major ion exchanges. The water types have been defined according to IAH (1979) based on the cation and anion values exceeding the 20% meq/L. Five hydrochemical facies have been identified through the interaction between rock and water (Table 1). The hydrochemical facies of the waters were defined on the basis of DO and bei (base exchange index) values. The DPS has lower bei and EC, and higher DO values. The DO values of the waters flowing in unconfined aquifer conditions are high; whereas, the waters emerging from magmatic and metamorphic rocks have negative bei values caused by contribution from the alkaline ions due to alteration and decomposition of silicate minerals (Şahinci 1991). Dokuzpinar with notable Na–Mg–Ca–Cl–HCO₃ hydrochemical facies may occur during rapid flow-through times, which results in low ionic concentrations during high recharge in shallow zones unconfined volcanic aquifer conditions (Afşin 1997).

Waters flowing throughout the confined aquifer in closed system show lower DO, EC, Cl[−] values with the Na–Mg–Cl–HCO₃ water type in YMS, and Na–Cl–HCO₃ water type in ACMS. Water type of TGS is mainly of the Ca–Mg–HCO₃. The Ca–Na–HCO₃–Cl water type of BTMS showed that ACMS and BTMS are older waters, and have longer circulation paths than YMS and TGS, respectively (Table 1, Fig. 2) The predominant ions in the waters have diverse origin. The Ca²⁺ in the DPS is mainly related to the alteration of the anorthites; whereas, Ca²⁺ and HCO₃[−] contents in thermal and mineral waters are attributed to the CO₂ contents of the waters flowing throughout the carbonate rocks, which constitute the main aquifer in this part of the study area. The high Ca²⁺ and HCO₃[−] values and the same sequential order of CO₂ contents of the waters as ACMS > YMS > BTMS > TGS confirm this pattern. Furthermore, the higher CO₂ contents cause lower pH, while HCO₃[−] contents increase due to reduction of sulphates. The source of the CO₂ in the waters may well be coal-bearing organic clays within the lacustrine sediments exposed widely at the discharge area of ACMS, as well as the Erciyes volcanics. High temperature is the dominant factor in water–rock interaction in many geothermal systems because the solubility of most minerals (except for alkaline earth metals) increases with rising temperatures. This is not the case in CO₂-dominated systems. Since, the solubility of CO₂ in water increases with decreasing temperature, water–rock interaction is favored by low temperatures in a CO₂-dominated system (Greber 1994). Likewise, CO₂-dominated ACMS and YMS with low temperatures (13–22.5°C) have much higher mineralization. The Na⁺ ion occurs as the first predominant ion DPS, YMS and ACMS and as the second predominant ion in BTMS. The origin of the Na⁺ is attributed to albite-rich syenitic rocks with strong alkaline nature around the discharge area. This, in turn, is related to the solubility of albite that increases considerably with rising partial pressure of CO₂ (Stumm and Morgan 1981), and is also related to the ion exchange process between Ca²⁺ and Mg²⁺ and Na⁺ (Fig. 2) during the interactions of water with tuff, clay and sandstone-bearing sequences. The higher abundances of SiO₂, Al₂O₃, Fe₂O₃ and Na₂O in the argillitized (kaolinized) tuff and basaltic units. Higher abundances of CaO, SiO₂ and Al₂O₃ in the travertine and limestones around the TGS and BTMS show that the dissolution is predominant in the waters flowing through these rocks (Table 2).

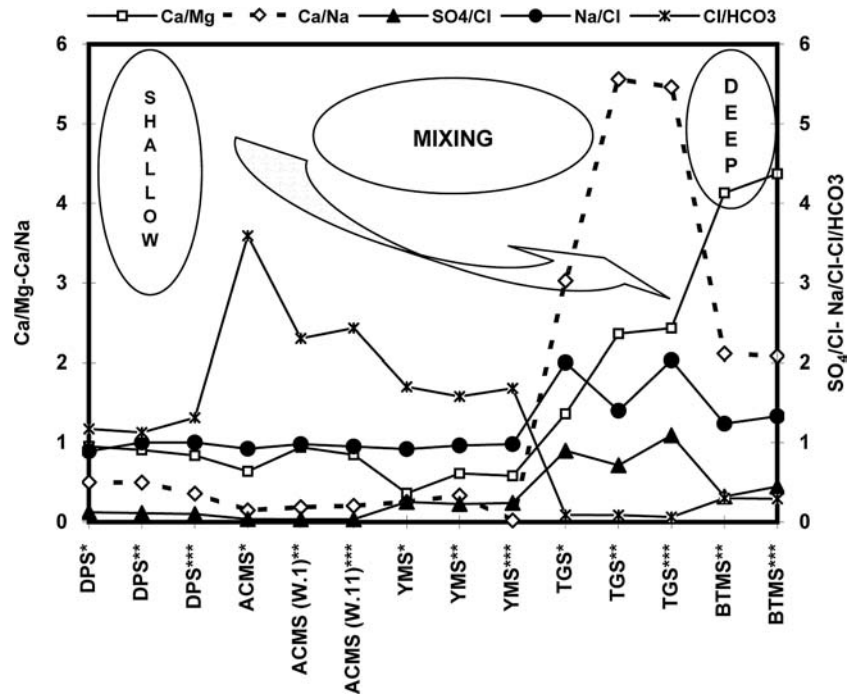
The analyses of the precipitates formed at the dumping site of the CO₂-separating plants around the ACMS show that Fe₂O₃ abundance is between 25–30% and CaO between 9–16%. Iron content ranges between 14.03 and 18.95 mg/L (Tables 1, 2) in ACMS. Iron is leached from the minerals, such as biotite, pyroxene, and pyrite during water–rock interactions. The abundance of

Table 1 Results of physical and chemical analysis of water

Sample	TGS ^a	TGS ^b	TGS ^c	BTMS ^b	BTMS ^c	DPS ^a	DPS ^b	DPS ^c	ACMS ^a	ACMS ^b	ACMS ^c	ACMS ^b	ACMS ^c	YMS ^a	YMS ^b	YMS ^c
T (°C)	40	40.5	41	46.5	45	12	13	13	22	20	20	20	22.5	13	14.5	16
pH	6.5	7.6	7.6	7.1	7.3	7.3	8	8.1	7.75	6.28	6.7	6.7	6.3	6.3	6.8	6.4
EC (µS/cm)	452	556	500	1,640	1,058	377	537	300	9,400	14,600	11,980	11,980	9,385	8,750	8,210	5,600
DO (mg/L)	ND	ND	3.43	ND	3.3	ND	ND	9.17	ND	2.8	1.9	1.9	ND	ND	ND	6.4
CO ₂ (mg/L)	ND	25	ND	150	ND	ND	ND	ND	ND	275	465	465	ND	ND	165	ND
Ca ²⁺	2.42	3.89	3.89	10.87	11.5	0.898	1.34	1.22	10.97	23.95	20.58	20.58	19.46	8.10	17.94	16.84
Mg ²⁺	1,768	1.64	1.6	2.63	2.63	0.945	1.48	1.46	17.27	25.49	22.82	22.82	23.02	22.41	29.4	28.99
Na ⁺	0.800	0.700	0.713	5.13	5.52	1.78	2.7	3.41	74.82	129.19	95.96	95.96	96.35	32.08	53.89	53.28
K ⁺	0.089	0.115	0.064	0.179	0.192	0.14	0.153	0.179	3.197	3.85	3.32	3.32	3.26	1,279	0.959	1.08
Cl ⁻	0.400	0.500	0.35	4.15	4.15	2.00	2.7	3.4	81	132	98	98	101.5	35	56	54.5
SO ₄ ²⁻	0.358	0.350	0.383	1.329	1.85	0.247	0.300	0.343	2.86	4.36	3.68	3.68	3.35	11.67	12.65	12.98
HCO ₃ ⁻	4.51	4.89	5.69	13.43	14.21	1.70	2	2.59	18.29	47.50	42.50	42.50	41.66	13.95	35.5	32.41
CO ₃ ²⁻	–	0.83	–	0.410	–	–	0.400	–	4.25	–	–	–	–	6.63	–	–
NO ₃ ⁻	ND	6.46	7.39	4.68	1.69	ND	10.02	6.75	ND	7.46	23.56	23.56	1.481	ND	16.01	13.94
NO ₂	ND	0.000	0.000	0.000	0.000	ND	0.000	0.000	ND	0.000	0.000	0.000	0.000	ND	0.000	0.000
PO ₄	ND	0.074	0.039	0.000	0.159	ND	0.124	0.151	ND	0.091	0.069	0.069	0.070	ND	0.245	0.181
NH ₃	ND	0.268	0.068	0.580	0.143	ND	0.400	0.068	ND	2.55	1.92	1.92	2.56	ND	0.400	0.111
Cu	ND	0.276	0.766	0.225	0.107	ND	0.353	0.532	ND	0.383	0.000	0.000	0.397	ND	0.098	0.723
Fe	ND	0.068	0.102	0.023	0.112	ND	0.056	0.103	ND	18.95	0.057	0.057	14.03	ND	0.023	0.114
Zn	0.020	0.000	0.041	0.012	0.019	0.040	0.014	0.014	0.030	0.030	0.000	0.000	0.042	ND	0.022	0.052
Pb	ND	0.000	0.105	0.143	0.160	ND	0.067	0.127	ND	0.231	0.138	0.138	0.323	ND	0.140	0.241
Mn	ND	ND	0.000	ND	0.134	ND	ND	0.000	ND	ND	ND	ND	1.566	ND	ND	0.014
Ni	ND	ND	0.000	ND	0.000	ND	ND	0.000	ND	ND	ND	ND	0.156	ND	ND	0.148
Cd	ND	ND	0.005	ND	0.015	ND	ND	0.000	ND	ND	ND	ND	0.036	ND	ND	0.023
Cr	ND	ND	0.027	ND	0.010	ND	ND	0.022	ND	ND	ND	ND	0.023	ND	ND	0.024
B	ND	ND	2,756	ND	3,976	ND	ND	1,615	ND	ND	ND	ND	13,500	ND	ND	6,765
Water Type	Ca-Mg-HCO ₃	Ca-Mg-HCO ₃	Ca-Mg-HCO ₃	Ca-Na-HCO ₃ -Cl	Ca-Na-HCO ₃ -Cl	Na-Mg-Ca-Cl-HCO ₃	Na-Mg-Ca-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Cl-HCO ₃	Na-Mg-Cl-HCO ₃	Na-Mg-Cl-HCO ₃	Na-Mg-Cl-HCO ₃

DPS Dokuzpinar cold spring, ACMS Acisu mineral spring and well (W.1: Well 1; W.11: Well 11), YMS Yeşilhisar mineral spring, TGS Tekgöz thermal spring, BTMS Bayramhacı thermal–mineral spring, √ major ions are meq/L, √√ minor ions are mg/L, ND Not determined
 Sampling dates: ^a01.03.1999; ^b13.11.1999; ^c13.05.2000

Fig. 2 Water types and ion changes of the waters (abbreviations are as in Table 1)



Mg^{2+} is the highest in YMS comparing to ACMS, BTMS, TGS and DPS, respectively (Fig. 2). The origin of Mg^{2+} is mainly due to the Mg^{2+} -rich olivine, pyroxene and amphiboles within the basalts, which are exposed widely around the discharge area of YMS. In addition to the widespread ophiolitic rocks, isotropic gabbros and spillitic basalts are exposed along deeply eroded valleys to the west of Yeşilhisar. The abundance of Mg^{2+} at samples collected from the carbonate-cemented conglomerate is higher than the basalts at YMS; and is very low at TGS with the tuffaceous wall rocks. The lower abundance of Mg^{2+} of the waters emerging from the Mg^{2+} -rich mineral bearing basalts than tuffaceous and conglomeratic-agglomeratic rocks rich in silica, may be due to the fact that YMS and ACMS are more acidic and have relatively lower temperatures compared to DPS. This may well result in dissolution of Mg^{2+} -bearing minerals at higher ratios, and subsequent leaching of magnesium.

The main contribution of SO_4^{2-} in the waters may be dissolution of gypsum, oxidation of pyrite and coal-bearing levels of volcanosedimentary sequences in the area. However, the exact origin of the SO_4^{2-} ion in the waters could be obtained by $\delta^{34}S$ compositions. Therefore, the samples should also be analyzed in terms of $\delta^{34}S$ isotope.

For the origin and reservoir characteristics of geothermal systems, Cl^- is usually considered to be one of the most useful tracers owing to its relatively 'conservative' nature (Güleç 1994). Moreover, it is accepted that Cl^- ion is considered to be conservative only if it is

added to solution by means of reactions due to water-rock interaction, and remains in the solution. Thus, the concentrations of the major ions of the studied waters are plotted against Cl^- (Fig. 3a). The Cl^- content in ACMS is higher than that of YMS, BTMS, DPS and TGS, respectively. Most of the major ions are positively correlated with Cl^- . $Ca^{2+}-Cl^-$ and $Mg^{2+}-Cl^-$ show strong positive correlation (0.84) (Table 3). This relation denotes that the waters having different mixing ratios contain significantly high levels of Ca^{2+} and Mg^{2+} .

The plot of the samples in the $HCO_3^-Cl^-$ (0.92) diagram generally resembles the $Ca^{2+}-Cl^-$ diagram in all waters. Ca/Mg ratios that are about 1.0 in DPS and ACMS, reach a minimum in YMS (0.3–0.5) and a maximum in TGS and BTMS (1.3–4.3) (Table 4, Fig. 3b). Ca/Na ratios are lower than 1.0 in DPS, ACMS and YMS due to the high Na^+ values, and are about 2.0 and 5.5 in BTMS and TGS, respectively. The decrease of Ca/Na ratios of the waters with high Ca/Mg values confirms the presence of the ion exchange process in these waters. While Cl/HCO_3 ratios increase from DPS to ACMS with a strong association with salt-bearing rocks, it decreases in TGS and BTMS with higher HCO_3 values. Therefore, DPS, ACMS, YMS and BTMS have high Cl^- values, and their Na/Cl and SO_4/Cl ratios are similar. The Na/Cl values are about 1.0 and SO_4/Cl values are low (0.033–0.44). However, Na/Cl and SO_4/Cl values in TGS having low Cl^- values, are relatively higher, 1.4–2.0 and 0.71–1.09, respectively. Cl^- ion is a significant indicator for mixing and dilution processes in most crystalline media (Frape and Fritz 1987).

Table 2 Results of chemical analysis of rock samples in the spring areas

Rock sample point	SiO ₂ (%)	Al ₂ O ₃ (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	Au (%)	MnO (%)	P ₂ O ₅ (%)	ZnO (%)	CuO (%)	ZrO ₂ (%)	Loss in fire (%)
Basalt (altered) (TGS-1A)	71.31	9.10	0.34	9.94	1.53	1.32	0.13	0.43	0.006	0.028	0.035	0.010	ND	0.014	5.69
Vesicular basalt (TGS-1B)	59.64	20.20	1.00	3.98	3.76	0.31	5.38	3.35	0.007	0.030	0.393	0.012	ND	0.052	1.72
Pervasively altered basalt (TGS-1C)	55.90	12.64	0.59	10.48	2.56	0.40	3.27	1.99	0.008	0.098	0.24	0.007	ND	0.032	11.67
Travertine-like limestone (Ç-1)	2.02	0.75	0.02	1.33	52.83	0.39	0.02	0.04	0.003	0.035	0.024	0.019	0.002	ND	42.37
Travertine-like limestone (Ç-2)	1.02	0.45	0.01	0.06	54.04	0.54	0.02	0.02	ND	ND	0.018	0.018	ND	ND	43.69
Basalt (Ç-3)	58.74	20.27	1.00	5.30	3.15	0.49	5.00	3.38	0.005	0.031	0.40	0.012	ND	0.055	2.01
Travertine (BTMS-1))	1.67	0.75	0.01	0.17	53.31	0.37	0.04	0.05	0.002	0.043	ND	ND	ND	ND	43.29
Travertine (BTMS-2)	7.38	2.62	0.10	0.78	47.88	0.75	0.25	0.27	0.003	0.103	0.089	0.001	0.002	0.004	39.57
Travertine (Pool) (BTMS-3)	0.84	0.26	0.01	0.17	53.64	0.61	0.07	0.02	0.002	0.105	0.019	n	0.07	ND	43.59
Conglomerate with carbonate cement (YMS)	32.95	8.13	0.59	6.23	23.64	3.80	1.42	0.63	0.005	0.082	0.115	0.008	ND	0.014	22.13
Precipitate from waste water (ACMS-W.1)	36.32	8.54	0.21	25.04	9.86	1.17	2.76	1.35	0.006	0.060	1.18	0.003	ND	0.007	12.51
Vesicular basalt (DPS-1)	59.53	18.68	0.77	5.14	5.17	2.69	4.30	1.94	0.005	0.084	0.23	0.008	ND	0.025	1.32
Precipitate from waste water (ACMS-W.11)	25.42	0.92	0.03	30.63	16.54	1.72	1.06	0.20	0.006	0.074	1.95	ND	ND	ND	19.97
Ignimbrite (Tuft) (TGS-2)	34.66	10.13	0.20	1.77	25.06	1.15	1.84	1.58	0.003	0.061	0.083	0.004	ND	0.015	23.24
Kaolenzed tuff (ignimbrite) (TGS-3)	65.86	16.88	0.18	1.51	1.86	2.19	2.15	0.63	0.009	0.055	0.039	0.004	ND	0.012	6.31

ND Not determined

A linear positive correlation is determined between Na⁺-Cl⁻ (0.99) and Cl⁻-EC (0.96) (Table 3). The YMS and ACMS ascending through the carbonate aquifer to the surface have interacted with the evaporites under a relatively high solubility (10–30 times higher than carbonates) (Bögli 1980; Kaçaroğlu et al. 2001), and enriched in terms of Na⁺ and Cl⁻ ions (Fig. 3a). Moreover, high salt concentration in these waters is likely to be the result of mixing between older waters that were preserved deep below the surface during the closure of the Tertiary Central Kızılırmak Basin and mineral waters (Afşin 2002). Lower EC and temperature values in TGS compared to BTMS and YMS relative to ACMS is likely to be the result of dilution due to mixing with cold groundwaters caused by hyperfiltration. Potassium occurs as a major element within K-feldspars, mica group and some clay group minerals. The K⁺ and Cl⁻ relationship show linear positive correlation of 0.96. Except for a few samples, K⁺ concentrations of the waters were derived from a single source. The increase in K⁺ concentrations in ACMS and YMS compared with other waters, suggests that an alteration effect may take place in ACMS and YMS sampling points, and K⁺ content in rocks is directly added to the waters. The Yeşilhisar samples are also enriched in Mg²⁺ due to the chloritic alterations, so the high K⁺ values in ACMS could also be related from the derivation of K⁺ by the same alteration and addition to the waters. The ions other than SO₄²⁻ have positive correlation coefficient. The poor correlation between SO₄²⁻ and Cl⁻ (0.45) shows that the SO₄²⁻ ion in these waters has a different origin.

According to saturation indice calculations based on minerals presumed to precipitate with respect to the exposed rocks, DPS is undersaturated with respect to calcite, dolomite, aragonite, gypsum, anhydrite and halite minerals, and is capable of dissolving these minerals (Table 4). Yeşilhisar mineral spring, ACMS, TGS and BTMS are generally oversaturated by calcite, aragonite, goethite and hematite, and may precipitate these minerals; but are undersaturated by gypsum, anhydrite and halite, and may dissolve these minerals. High saturation indices, particularly for calcite, may be related to the residence time during low recharge (Scanlon 1989) which gives rise to high ionic concentration along the groundwater flow path (Afşin 1997). For this reason, travertine-depositing thermal-mineral waters which have high ionic concentrations may also have long circulation time. As mentioned before, apart from the ancient travertine occurrences, recent travertine deposition occurs in ACMS, YMS and BTMS rich in CO₂. This is caused by CO₂ loss, evaporation and probably algal activity (Emeis et al. 1987; Bayarı and Kurttaş 1997) along groundwater flowpaths (Afşin et al. 2002). Besides, the increase of travertine deposition in the mineral waters rich in Ca²⁺ and HCO₃⁻, is related to the consequences of Na⁺ and Cl⁻ as exotic ions (Figs. 2, 3a).

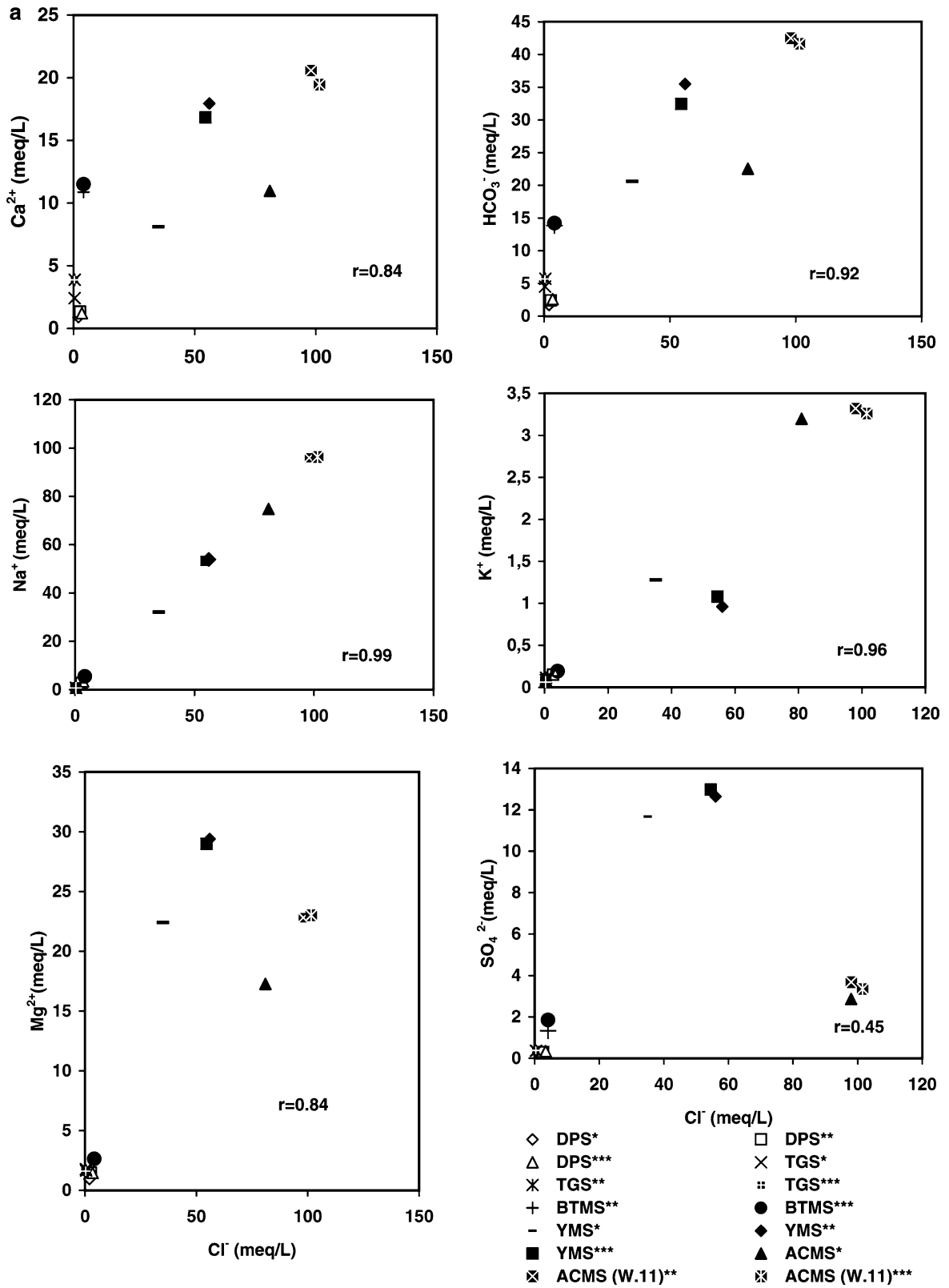


Fig. 3 a. Relations between various ions and chloride ion for the waters (abbreviations are as in Table 1). Fig. 3b. Ionic changes of the waters (abbreviations are as in Table 1)

Fig. 3 (Contd.)

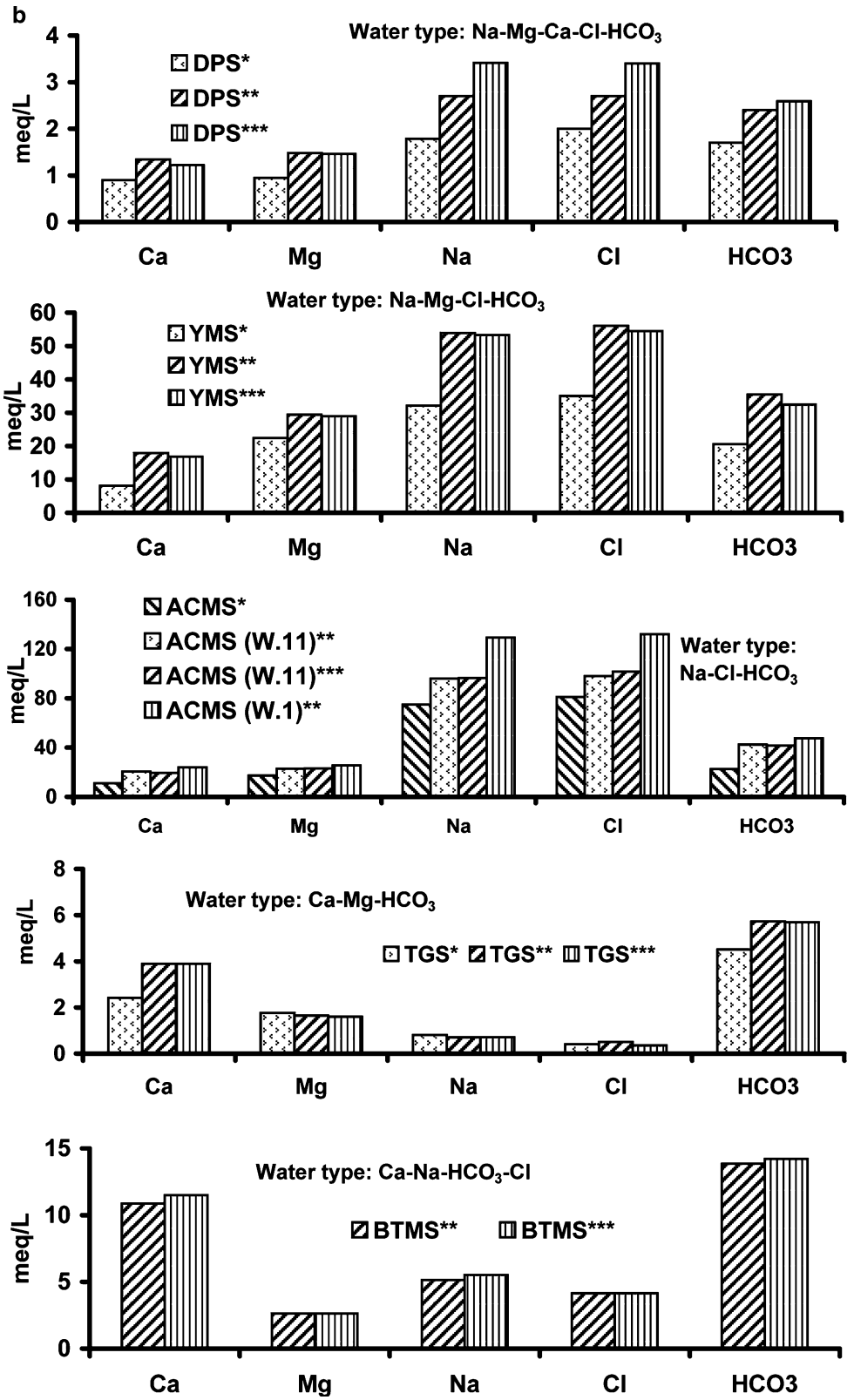


Table 3 Correlation coefficients between major ions in the waters

EC	T (°C)	pH	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	Na/Cl
	-0.30	-0.37	0.83	0.85	0.96	0.93	0.96	0.52	0.92	-0.50
		-0.19	-0.09	-0.41	-0.29	-0.23	-0.30	-0.39	-0.22	0.84
			-0.63	-0.41	-0.46	-0.31	-0.44	-0.21	-0.58	-0.11
				0.83	0.85	0.72	0.84	0.58	0.97	-0.37
					0.84	0.69	0.84	0.86	0.91	-0.51
						0.96	0.99	0.45	0.93	-0.49
							0.96	0.26	0.81	-0.46
								0.45	0.92	-0.50
									0.63	-0.42
										-0.437

Bold values show the positive good correlations

Table 4 Ionic ratios (values are meq/L) and saturation indices (SI) in the waters

	Ca/Mg	Ca/Na	Na/Cl	SO ₄ /Cl	Cl/HCO ₃	bei	SI _{Ca}	SI _{Do}	SI _{Ar}	SI _{Gy}	SI _{Ha}	SI _{An}	SI _{Go}	SI _{He}
DPS ^a	0.95	0.50	0.89	0.123	1.17	0.038	-0.95	-1.94	-1.10	-2.97	-7.06	-3.22	-	-
DPS ^b	0.905	0.496	1.00	0.111	1.125	-0.056	-0.96	-1.82	-0.81	-2.80	-6.77	-3.06	12.88	5.46
DPS ^c	0.835	0.357	1.00	0.100	1.31	0.056	-0.19	-0.42	-0.04	-2.78	-6.57	-3.03	8.06	18.07
ACMS ^a	0.636	0.146	0.92	0.035	3.59	0.0368	2.13	4.23	1.98	1.61	-4.02	-1.84	-	-
ACMS ^b (W.1)	0.939	0.185	0.033	0.978	2.77	0.008	0.27	0.66	0.13	1.30	-3.61	-1.54	13.14	5.58
ACMS ^b (W.11)	0.902	0.214	0.037	0.979	2.3	0.013	0.80	1.73	0.65	1.37	-3.85	-1.60	4.88	11.75
ACMS (W.11) ^c	0.845	0.202	0.949	0.033	2.43	0.0186	0.40	1.00	0.26	1.45	-3.84	-1.67	6.24	14.48
YMS ^a	0.361	0.252	0.916	0.252	1.699	0.046	1.50	3.41	1.34	1.04	-4.71	-1.29	-	-
YMS ^b	0.61	0.332	0.962	0.225	1.577	0.021	0.63	1.48	0.48	0.82	-4.32	-1.07	4.26	10.48
YMS ^c	0.58	0.018	0.978	0.238	1.681	0.0026	0.28	0.81	0.13	0.83	-4.33	-1.08	4.12	10.20
TGS ^a	1.36	3.02	2.00	0.895	0.089	1.22	-0.56	-0.98	-0.69	-2.52	-8.19	-2.66	-	-
TGS ^b	2.36	5.56	1.4	0.712	0.087	0.63	0.76	1.41	0.62	2.36	-8.16	-2.50	7.20	16.47
TGS ^c	2.43	5.46	2.03	1.09	0.061	1.22	0.82	1.53	0.68	2.34	-8.31	-2.47	7.36	16.80
BTMS ^b	4.13	2.11	1.236	0.32	0.299	0.28	1.37	1.74	1.24	1.54	-6.43	-1.64	3.83	9.76
BTMS ^c	4.37	2.08	0.445	1.33	0.292	0.376	1.28	2.21	1.15	1.45	-6.41	-1.56	7.28	16.65

Bold values show the oversaturated indices

Ca Calcite, Do dolomite, Ar aragonite, Gy gypsum, Ha halite, An anhydrite, Go goethite, He hematite; bei = [Cl-(Na + K)/Cl]; sampling dates and the other abbreviations are as in Table 1

Evaluation of isotopic data

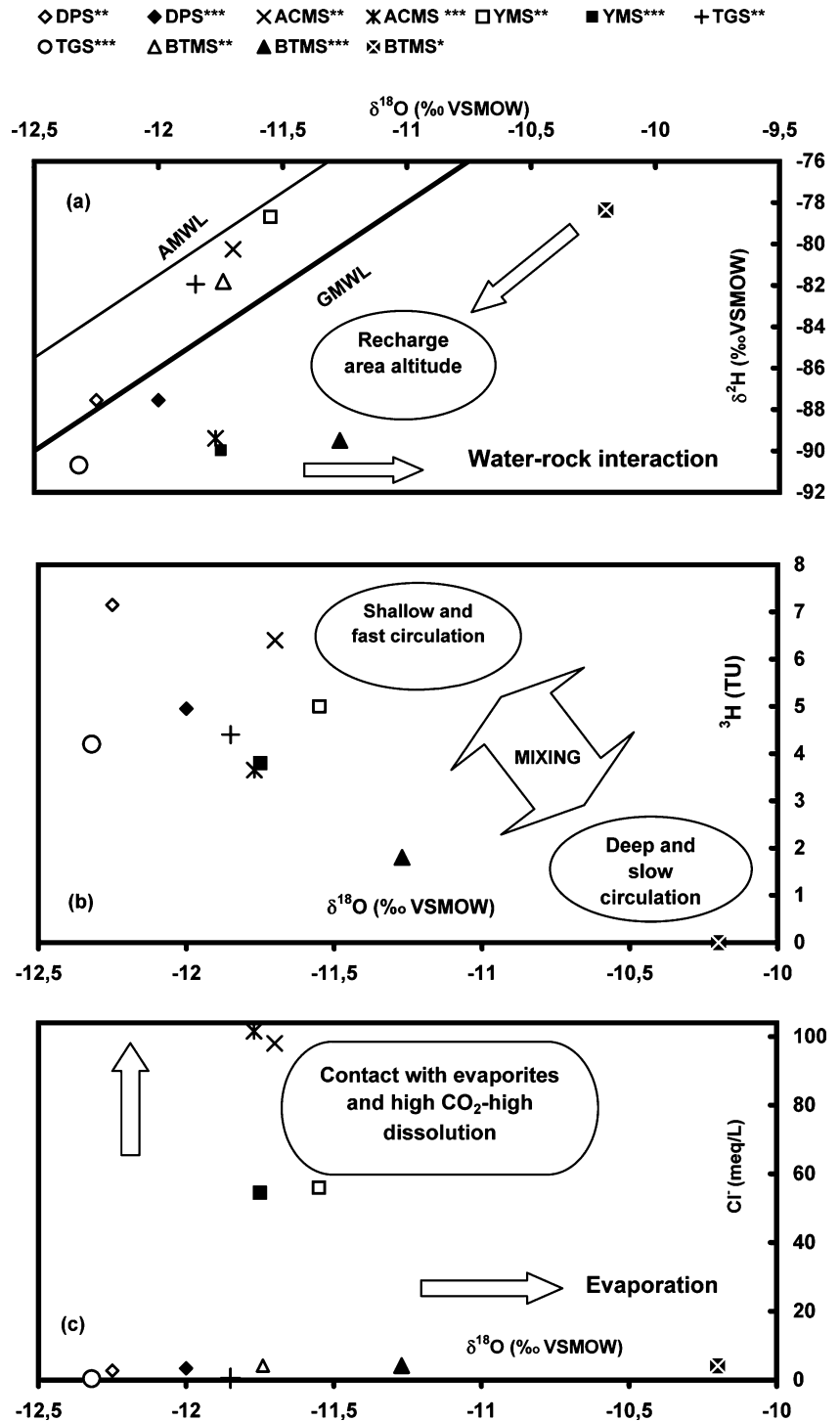
The isotopic data of the waters were evaluated compared with the global meteoric water line (GMWL) “($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$)” (Yurtsever and Gat 1981) and Ankara meteoric water line (AMWL) “($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 14.5$)” (Güven 1996) (Fig. 4a). The plots showed that all the waters are of meteoric origin, and are less affected by evaporation. The increase in $\delta^{18}\text{O}$ values of BTMS deviating from the meteoric water line is mainly due to the intense water-rock interaction at relatively high temperature.

On this diagram, the isotopic values of the waters in dry season (13.11.1999) are between AMWL and GMWL, and it is below GMWL in the rainy season (13.05.2000). The waters are affected by high precipitation rates in the rainy season. If the excess deuterium (d) on GMWL is accepted as base line, d values of all the waters in the dry season are higher than 10 (Table 5).

There are many causes of variations of the d values such as the source of evaporation and factors affecting precipitation elevation of the recharge area (Gat 1980). During the dry season, the waters are of atmospheric water vapour-type due to rapid evaporation. During the rainy season, the d values of all the waters are lower than 10. These waters are of groundwater-type due to evaporation.

Furthermore, BTMS with minimum d values verify that the waters are affected by evaporation as a result of water-rock interaction. The most negative values of $\delta^{18}\text{O}$ occur due to the dilution by heavy isotopes, as the recharge altitudes of the waters increase. Therefore, the TGS and DPS with maximum $\delta^{18}\text{O}$ values are recharged by precipitation at higher elevations. The BTMS, YMS and ACMS with minimum $\delta^{18}\text{O}$ values are recharged by precipitations at lower elevations. According to the $\delta^{18}\text{O}$ - ^3H diagram, which illustrates the relationships between the elevation of the recharge areas and

Fig. 4 Isotopic relations for the waters; a) $\delta^{18}\text{O}$ - $\delta^2\text{H}$, b) $\delta^{18}\text{O}$ - ^3H , and c) $\delta^{18}\text{O}$ - Cl^- (abbreviations are as in Table 1)



the residence time within the aquifer, the DPS has 4.95–7.15 TU (Tritium Unit); ACMS and YMS have 3.65–6.4 TU, TGS has 4.2–4.4 TU and BTMS has 0.00–1.80 TU. The waters of TGS (13.11.1999) and DPS (13.05.2000) are recharged from the highest elevations, whereas BTMS is recharged from lower elevations (Fig. 4b, Table 5). The tritium values are depleted due to

the radioactive decay of tritium isotope representing the increases of the residence time of meteoric originated waters. During the dry season, the ACMS and DPS have the same tritium values. The values are about 3–5 TU in DPS, ACMS, YMS and TGS in rainy season. The waters are of meteoric type and are recharged by precipitations at the same elevations. Therefore, DPS is

Table 5 Results of isotope analysis of the waters

Sample Symbol	Sampling date	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	^3H (TU) \pm analysis error	d (Excess deuterium)
DPS ^b	13.11.1999	-12.25	-84.54	7.15 \pm 1.20	13.46
DPS ^c	13.05.2000	-12.03	-87.55	4.95 \pm 1.00	8.69
ACMS ^b	13.11.1999	-11.7	-80.26	6.40 \pm 1.15	13.34
ACMS ^c	13.05.2000	-11.77	-89.39	3.65 \pm 0.85	4.77
YMS ^b	13.11.1999	-11.55	-78.69	5.00 \pm 1.15	13.71
YMS ^c	13.05.2000	-11.75	-89.96	3.80 \pm 1.00	4.04
TGS ^b	13.11.1999	-11.85	-81.94	4.40 \pm 1.15	12.86
TGS ^c	13.05.2000	-12.32	-90.69	4.20 \pm 1.00	7.87
BTMS ^b	13.11.1999	-11.74	-81.81	–	12.11
BTMS ^c	13.05.2000	-11.27	-89.50	1.80 \pm 0.95	0.66
BTMS ^a	28.06.1998 (Afşin 1999)	-10.2	-78.35	0.0 \pm 0.8	3.25

Abbreviations are as in Table 1

considered to be the youngest water with shallow and relatively rapid circulations; BTMS should be the oldest water with deep and relatively slow circulations. Others have shallow-intermediate circulations. The $\delta^{18}\text{O}$ – Cl^- diagram is evaluated to outline the effects of evaporation in waters (Fig. 4c). There is no contribution from Cl^- values to isotopic exchange reactions in ACMS and YMS with higher CO_2 contents. Hence, it is argued that the isotopic exchange is driven by precipitation (Mahlknecht et al. 2004), whereas the salinity is driven by dissolution of evaporates due to the interactions with evaporitic rocks.

Discussion and conclusion

The waters in the study area are hosted by several rock types. Metamorphic/crystalline rocks in the area occurring as the basement, sedimentary units of Upper Cretaceous-Quaternary age form the cover. Volcanosedimentary rocks Miocene-Quaternary in age represent the extrusive products of magmatism activity. Terrace and alluvial deposits, and travertine occurrences around the vicinities of the thermal–mineral waters cover all these units unconformably. The waters DPS (12–13°C), YMS (13–16°C), ACMS (20–22.5°C), TGS (40–41°C) and BTMS (45–46.5°C), have a close association with the structural elements in the region. These are also characterized by different hydrochemical facies, such as Na–Mg–Ca–Cl– HCO_3 (DPS), Na–Mg–Cl– HCO_3 (YMS), Na–Cl– HCO_3 (ACMS), Ca–Mg– HCO_3 (TGS) and Ca–Na– HCO_3 –Cl (BTMS). The basalts act as unconfined aquifers for DPS; metacarbonates are of primary confined aquifers for YMS, ACMS, TGS and BTMS; the other permeable units are from secondary aquifers. The cover rocks represent the impermeable units. Granites and syenites are presumed to be the heat source for the thermal waters. Different water types and/or hydrochemical facies resulted from factors such as alteration, dissolution, ion exchange,

mixing with cold waters, oxidation–reduction and precipitation.

The calculations and hydrochemical interpretations show that the high concentrations of Ca^{2+} and HCO_3^- as predominant ions in the waters are mainly attributed to carbonate rocks, and high CO_2 contents. High Na^+ concentration is mainly related to syenite, tuff, basalts, and clayey units. The Cl^- values are driven by the interactions with evaporites. All the waters are of meteoric origin. The deviation of BTMS from the GMWL is mainly due to the increase in $\delta^{18}\text{O}$ contents as a result of the mineral–water interaction. The higher ion concentrations in YMS (with high CO_2 values) and ACMS (with low temperatures) is caused by the prolonged gas–mineral–water interaction, which may result in significant oxygen changes and shifts in equilibrium positions. Yeşilhisar mineral spring, ACMS and BTMS are oversaturated by calcite, aragonite, goethite and hematite; and undersaturated by gypsum, halite and anhydrite. DPS is undersaturated with respect to minerals. In addition to the ancient travertine occurrences around the springs, recent travertine deposition takes place along the flow paths of the ACMS, YMS, TGS and BTMS rich in CO_2 , due to higher rates of CO_2 loss and possible algal activities. The rate of travertine precipitation is higher in the YMS and ACMS due to the excessive contributions of Na^+ and Cl^- as exotic ions. Tekgöz thermal spring is of a shallow to intermediately circulated thermal water with higher interactions and mixing with the cold waters compared to BTMS. The Ca/Mg and Cl/ HCO_3 ratios of BTMS are higher; SO_4/Cl ratio is lower than TGS. Tekgöz thermal spring is of a shallow to intermediately circulated thermal water with higher interactions and mixing with the cold waters compared to BTMS. Bayramhacı thermal–mineral spring is of deeply circulated thermal–mineral water with relatively lower heat-loss compared to TGS. The sequence of hydrogeochemical and isotopic compositions of the waters is in the order of DPS > YMS > ACMS > TGS > BTMS and this suggests a transition period from a shallow circulation to a deep circulation path.

Acknowledgements This study was granted by The Scientific and Technical Research Council of Turkey (TÜBİTAK; Grant No. YDABÇAG-199Y041). The authors wish to express their sincere

thanks to TÜBİTAK for financial support, and their gratitude to colleagues Murat Kavurmacı and Yakup Kurmaç for field and sampling work.

References

- Afşin M (2002) CO₂'ce zengin Çorak, Karakaya ve Gümüşkent (Nevşehir) mineralli sularının hidrojeokimyası (in Turkish). *HÜ Yerbilimleri Dergisi* 26:1–14
- Afşin M, Elhatip H, Kuşcu İ, Dirik K, Kavurmacı M, Kurmaç Y (2002) Kayseri-İncesu-Himmetdede ve dolayındaki sıcak ve mineralli su kaynaklarının hidrojeokimyasal ve izotopik açıdan değerlendirilmesi (in Turkish). TÜBİTAK YDABÇAG 199Y041 nolu proje, 62 p
- Afşin M (1999) Traverten çökelten kaynakların hidrojeokimyasal ve izotopik incelemesi (Nevşehir-Çorak, Karakaya ve Salanda içmeceleri) (in Turkish). Niğde Üniversitesi Araştırma Fonu, FEB-97/07 nolu proje, 41p
- Afşin M (1997) Hydrochemical evolution and water quality along the groundwater flow path in the Sandıklı plain, Afyon, Turkey. *Environ Geol* 31(3/4):221–230
- American Public Health Assn (APHA), American Water Work Assn (AWWA) and Water Pollution Control Federation (WPCF) (1989) Standard methods for the determination of water and wastewater, 15th edn. APHA Publ 1134 pp
- Bayarı CS, Kurttaş T (1997) Algae: an important agent in deposition of karstic travertines: observations on natural-bridge Yerköprü Travertines, Aladağlar, Eastern Taurids, Turkey. In: Günay G, Johnson AI (eds) *Karst waters & environmental impacts*. Balkema, Rotterdam, pp 269–280
- Bögli A (1980) *Karst hydrology and physical speleology* (Translated by June C. Schmidt). Springer Verlag, Berlin, 284 pp
- Emeis KC, Richnow H, Kempe S (1987) Travertine formation in Plitvice National Park: chemical versus biological control. *Sedimentology* 34:595–610
- Frape SK, Fritz P (1987) Geochemical trends for groundwaters from the Canadian shield. In: *Saline water and gases in crystalline rocks*. In: Fritz P, Frape SK (eds) *Geological Association of Canada*, vol 33. Special Paper, pp 19–38
- Gat J (1980) The isotopes of hydrogen and oxygen in precipitation. In: Fritz P, Fontes J Ch (eds) *Handbook of environmental isotope geochemistry*, vol 1A. Elsevier, New York, pp 21–47
- Göncüoğlu MC, Toprak V, Kuşcu İ, Erler A, Olgun E (1991) Orta Anadolu Masifi batı bölümünün jeolojisi, Bölüm 1: Güney Kesim (in Turkish). TPAO Rep No: 2909
- Göncüoğlu MC, Erler A, Toprak V, Olgun E, Yalınz K, Kuşcu İ, Köksal S, Dirik K (1993) Orta Anadolu Masifinin Orta Bölümünün Jeolojisi, Bölüm III: Orta Kızılırmak Tersiyer Baseninin Jeolojik Evrimi (in Turkish). TPAO Rap. No: 3313, 104 p
- Greber E (1994) Deep circulation of CO₂-rich palaeowaters in a seismically active zone (Kuzuluk/Adapazarı, Northwest-ern Turkey). *Geothermics* 23(2):151–174
- Güleç N (1994) Geochemistry of thermal waters and its relation to tectonism in the Kızılcahamam (Ankara) area, Turkey. *J Volcanol Geothermal Res* 59:295–312
- Güven F (1996) Sakaryabaşı kaynaklarının çevresel izotop hidrolojisi incelemesi (in Turkish). MSc Thesis, Hacettepe Üniversitesi Fen Bilimleri Enstitüsü, 118 p
- Holysh S, Tóth J (1996) Flow of formation waters: likely cause of poor definition of soil gas anomalies over oil fields in east-central Alberta. In: Schumacher D, Abrams MA (eds) *Hydrocarbon migration and its near-surface expression*. AAPG Memoir 66:255–277
- IAH (International Association of Hydrogeologists) (1979) *Map of mineral and thermal-mineral water of Europe*. Scale 1:500,000, International Association of Hydrogeologists
- Kaçaroğlu F, Değirmenci M, Cerit O (2001) Water quality problems of a gypsiferous watershed: Upper Kızılırmak Basin, Sivas, Turkey. *Water, Air Soil Pollut* 128:161–180
- Mahlknecht J, Schneider JF, Merkel BJ, Navarro de Len I, Bernasconi SM (2004) Groundwater recharge in a sedimentary basin in semi-arid Mexico. *Hydrogeol J* 12:511–530
- Parkhurst DL, Appelo CAJ (1999) *User's Guide to PHREEQC (Version-2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*
- Scanlon BR (1989) Physical control on hydrochemical variability in the Inner Bluegrass karst region of Central Kentucky. *Ground Water* 27(5):639–646
- Stumm W, Morgan JJ (1981) *Aquatic chemistry—an introduction emphasizing chemical equilibria in natural waters*, 2nd edn. Wiley, New York, 780 pp
- Şahinci A (1991) *Doğal suların jeokimyası* (in Turkish). Reform Matbaası, İzmir, 548 p
- Tóth J (1999) Groundwater as a geological agent: an overview of the causes, processes, and manifestations. *Hydrogeol J* 7:1–14
- TSE, İçme suyu standartları (1997) *Türk Standartları Enstitüsü* (in Turkish), Ankara, 97 p
- WHO (World Health Organization) (1993) *Drinking water standards*. In: *Engineering Geology and Environmental Approach*, 2nd edn
- Yurtsever Y, Gat JR (1981) Atmospheric waters in stable isotope hydrology: deuterium and oxygen-18 in the water cycle. In: Gat JR, Gonfiantini R (eds) *Tech Rep Series No: 210*, IAEA, Vienna, pp 103–142