# Constraints on the Origin of the Balıkesir Thermal Waters (Turkey) from Stable Isotope ($\delta^{18}$O, $\delta$D, $\delta^{13}$C, $\delta^{34}$S) and Major-Trace Element Compositions

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**Abstract:** The Balıkesir thermal waters in northwestern Turkey have discharge temperatures in the range of 31.8–98.5 °C, near neutral pH values of 6.40 to 8.40 and TDS contents between 327 and 2578 mg/l. Samples display variable chemical compositions changing from high-temperature $Na_2SO_4$-$NaHCO_3$ waters to warmer $CaHCO_3$ waters. Trace element concentrations of the waters show significant variation. Comparison between the concentrations of alkaline earth metals in waters and carbonate deposits reveals mobile behavior for Mg and Ba. The ratio of strontium to calcium concentrations in solid and liquid phases was found to be almost the same. Li/Cs and B/Cl ratios of waters and carbonates are similar suggesting the operation of a simple rock leaching process. Mineral equilibrium calculations imply that the $CO_2$ concentration has a great effect on the chemistry of the thermal waters and that most fluid compositions are controlled by rock dissolution rather than equilibration. The chemical geothermometers applied to the Balıkesir thermal waters yield a maximum reservoir temperature of 200 °C. The $\delta^{18}$O-$\delta$D compositions clearly indicate a meteoric origin for the waters. $\delta^{34}$S contents of sulfate in thermal waters range from -5.5 to +25.2‰. Sulfur isotope compositions of some waters correspond to those of non-marine evaporates while sulfur in others is derived from sulfate reduction. The $\delta^{13}$C ratio for dissolved inorganic carbonate in the waters lies between -17.7 and +0.7‰. There are also multiple sources of carbon. In high-temperature waters carbon is thought to originate from the dissolution of marine carbonates, an interpretation supported by carbon isotope compositions of marine carbonate rocks in the region. Carbon in low-temperature waters is derived from an organic source.

**Key Words:** water-rock interaction, stable isotope compositions, major-trace element geochemistry, Balıkesir thermal waters, Turkey

## Duraylı İzotop ($\delta^{18}$O, $\delta$D, $\delta^{13}$C, $\delta^{34}$S) ve Ana-İz Element Bileşimleri ile Balıkesir (Türkiye) Sıcak Sularının Kökeninin İrdelenmesi

**Özet:** Kuzeybatı Anadolu'da yer alan Balıkesir bölgesi termal suları 31.8–98.5 °C arasında değişen sıcaklık, 6.40 ile 8.40 arasında seyreden nötre yakın pH ve 327–2578 mg/l aralığındaki Toplam Çözünmüş Madde (TDS) değerleri sergilemektedir. Bölgede, sıcaklıkları yüksek olan sular $Na_2SO_4$-$NaHCO_3$, ılık sular ise $CaHCO_3$ tipte bir bileşime sahiptir. Balıkesir bölgesi sıcak sularındaki iz element bileşimleri önemli değişimler göstermektedir. Sulardaki ve karbonat çökellerindeki alkali toprak metal bileşimlerinin karşılaştırılması sonucunda, magnezyum ve baryumun hareketli davranış sergiledikleri tespit edilmiştir. Katı ve akışkan fazlardaki stronsiyum bileşimi genellikle sabit bir değer göstermektedir. Sulardaki ve karbonat çökellerindeki Li/Cs ve B/Cl oranlarının benzer değerler göstermeleri, bu iyonların basit kayaç çözünme işlevi neticesinde suya katıldıklarına işaret etmektedir. Mineral-denge hesaplamaları, $CO_2$'in termal suların kimyasal bileşimi üzerinde önemli bir etkisi olduğunu göstermiş ve akışkan bileşimlerinin denge durumu ile değil kayaç çözünme işlevi tarafından denetlendiğini ortaya koymuştur. Balıkesir bölgesi termal sularına uygulanan jeotermometre hesaplamaları 200 °C'lik maksimum rezervuar sıcaklığı öngörmüştür. $\delta^{18}$O-$\delta$D bileşimleri suların kökeninin meteorik olduğunu göstermiştir. Termal sulardaki sülfat için analiz edilen $\delta^{34}$S bileşimleri -5.5 ile +25.2‰ arasında değişmektedir. Bazı suların kükürt izotop bileşimleri karasal evaporitlere karşılık gelirken, bir kısım sulardaki kükürt ise sülfat indirgenme işlevi neticesinde oluşmuştur. Termal sulardaki çözünmüş inorganik karbon üzerinde analiz edilen $\delta^{13}$C bileşimleri -17.7 ile +0.7‰ arasında değişmektedir. Kükürt gibi, karbonun da farklı kökenler sergilediği tespit edilmiştir. Sıcaklıkları yüksek olan sulardaki karbonun denizel karbonatların çözünmesinden kaynaklandığı düşünülmektedir. Bölgedeki denizel karbonat kayalarının karbon izotop bileşimleri bunu destekler niteliktedir. Buna karşın, düşük sıcaklıktaki sulardaki karbon ise organik bir köken sunmaktadır.

**Anahtar Sözcükler:** su-kayaç etkileşimi, duraylı izotop bileşimleri, ana-iz element jeokimyası, Balıkesir sıcak suları, Türkiye

## Introduction

Neotectonic activity and Neogene volcanism have given rise to the development of numerous geothermal manifestations all over the Anatolian peninsula (e.g., Mutlu & Güleç 1998). The Balıkesir region in northwestern Anatolia hosts several geothermal fields with outlet temperatures up to 98 ºC and is one of the largest geothermal provinces in Turkey. Thermal waters in this region are used for central heating as well as for curative purposes. There are eight geothermal fields in the Balıkesir region comprising the Gönen, Manyas, Pamukçu, Bigadiç, Sındırgı, Edremit, Balya and Susurluk geothermal fields (Figure 1). Information regarding sample locations, coordinates, elevation and type of water samples as well as depth and discharge rate of the wells sampled and the reservoir rocks of each geothermal area are listed in Table 1.

Geothermal studies in the Balıkesir region were started in 1965 by the General Directorate of Mineral Research and Exploration of Turkey (MTA). In the Gönen area, a total of 17 wells (four are re-injection wells) were drilled to depths ranging from 230 to 800 m. The temperature of waters produced from these wells is ~60–80 ºC (Management of Gönen Geothermal District Heating System, personal communication 2005). District heating started in the Gönen town in 1984 has since been expanded to include the Edremit and Bigadiç areas. A number of hot springs have been reported in most of the areas in previous years; but all are now extinct due to intensive drilling (Ölmez et al. 2001a).

The aim of this study is to discuss the geochemical evolution of the Balıkesir thermal waters on the basis of various water-rock interaction models taking into account the major and trace element contents of the thermal waters as well as potential host rocks and travertine deposits. In addition, the source of water and its dissolved constituents are discussed.

## Materials and Methods

A total of 31 thermal and cold water samples were collected from the geothermal wells and springs in the Balıkesir region in August 2005. Locations of the water samples are shown in Figure 1. Due to the establishment of a district heating system in Gönen (for the heating of about 3400 houses), 17 wells have been drilled since 1976, but only 3 of them (G-7, G-8 and G-16 wells) were sampled during this study. In addition to thermal waters, one cold water sample (GCW) was also collected from a fountain in the Gönen town. One hot (EKS-1) and two cold (EKS-2 and EKS-3) water samples were collected from the Ekşidere area, 20 km south of Gönen (Figure 1). Waters from two production wells and one cold spring were sampled from the Manyas (MK-1, MK-2 and MCW), Pamukçu (PMK-1, PMK-2 and PCW) and Bigadiç (BHS-1, BHS-2 and BCW) fields. Although there are numerous springs of relatively high-temperature in the Sındırgı geothermal area, only four (SHS-1, SHS-2, SHS-3 and SHS-4) and one cold spring (SCW) were sampled. There are two geothermal fields in the Edremit area in the western part of the region. Two well waters (EDR-1 and EDR-2) were sampled in Edremit and waters from one thermal well (GDR-1) and cold spring (GDR-2) were collected in the Güre area on the Aegean coast. In the Balya field, two hot springs (BLY-1 and BLY-2) and one cold spring (BLY-3) were sampled. Waters of two springs (SLK-1 from the Ömerli village and SLK-2 from the Yıldız village) and one cold spring (SLK-3 from the Yıldız village) were collected from the Susurluk area (Figure 1). In addition to water samples, carbonate rocks and travertines in the vicinity of water collection sites were collected.

All water samples were collected into high-density polyethylene containers and 0.2 ml concentrated $HNO_3$ added to 100-ml samples for cation and trace element analyses. The other batch (500 ml) taken for anion analyses was untreated. 100-ml and 500-ml samples were collected for $\delta^{18}O$-$\delta D$ and $\delta^{13}C$-$\delta^{34}S$ analyses, respectively. The temperature of the waters, the pH, electrical conductivity and oxidation-reduction potential at discharge temperatures were measured at the sampling locations.

Titration methods were used for alkalinity ($HCO_3$) and Cl analyses. $SO_4$ and $SiO_2$ concentrations were determined by spectrophotometry. Silica and anion analyses were carried out at the Laboratory of State Water Works (DSİ) in Eskişehir, Turkey. The total elemental analysis in waters and the geochemical analyses of rock samples were performed at Acme Laboratories, Canada. Charge-balance of the thermal waters is generally less than 6–7%.

The $\delta^{18}O$-$\delta D$ analysis of waters (maximum standard deviations are 1.81‰ for $\delta D$ and 0.57‰ for $\delta^{18}O$) and $\delta^{18}O$-$\delta^{13}C$-$\delta^{34}S$ analysis of the carbonate samples

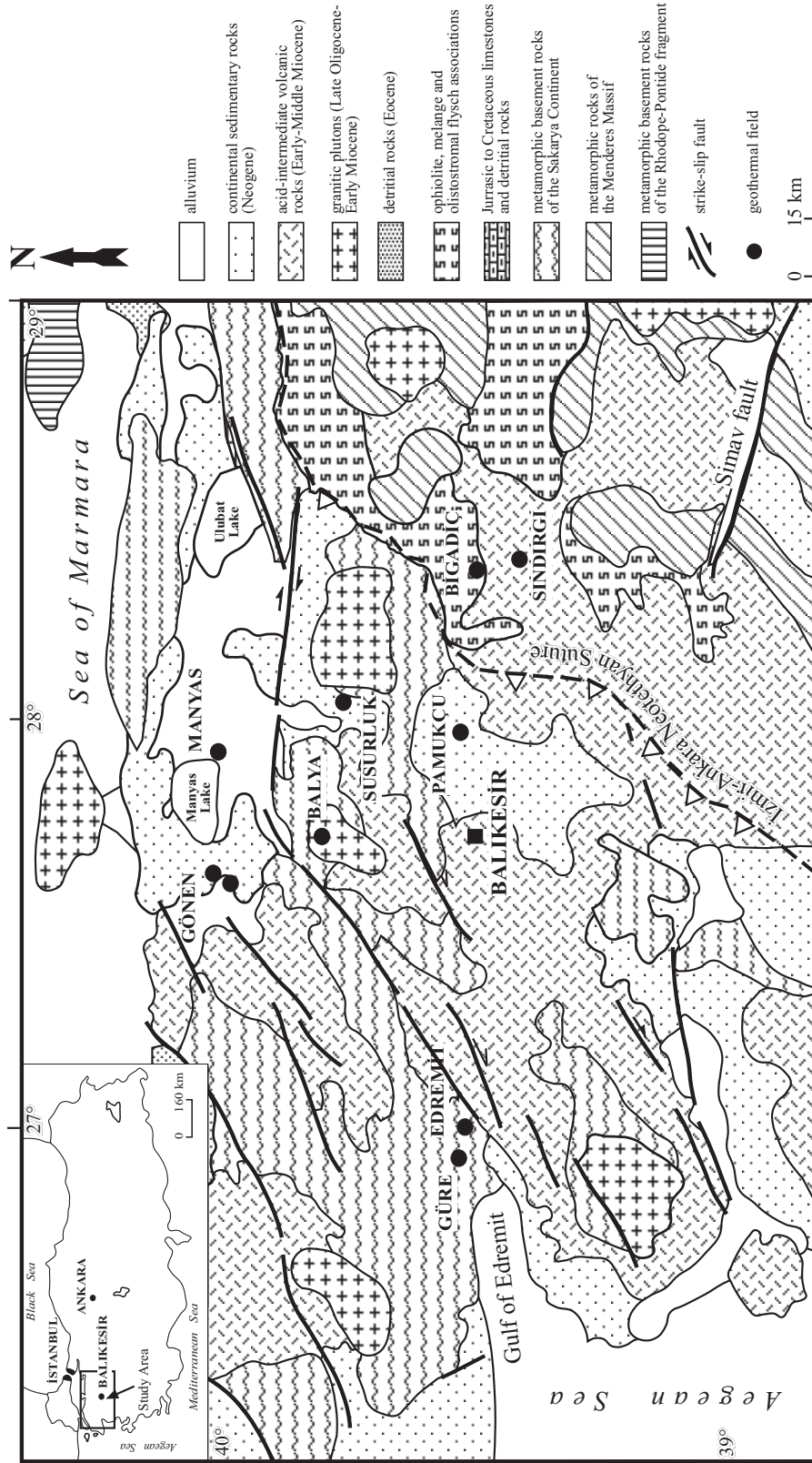Figure 1. Geological map of the Balıkesir region (from Genç 1998 and MTA 2004).

Legend:

- alluvium
- continental sedimentary rocks (Neogene)
- acid-intermediate volcanic rocks (Early-Middle Miocene)
- granitic plutons (Late Oligocene-Early Miocene)
- detritial rocks (Eocene)
- ophiolite, melange and olistostromal flysch associations
- Jurrasic to Cretaceous limestones and detritial rocks
- metamorphic basement rocks of the Sakarya Continent
- metamorphic rocks of the Menderes Massif
- metamorphic basement rocks of the Rhodope-Pontide fragment
- strike-slip fault
- geothermal field

0    15 km

Table 1.    Locational, logistical and host-rock data for geothermal wells and springs in the Balıkesir region.

| Geothermal Field | Sample No | Sample Type | Coordinate | Elevation (m) | Well Depth (m)* | Discharge (l/sec)* | Reservoir Rock |
|---|---|---|---|---|---|---|---|
| Gönen | G-7 | thermal water well | N40°06.931' E27°38.976' | 29 | 380 | 30.0 | gneiss, crystallized limestone, marble |
| | G-8 | thermal water well | N40°06.965' E27°39.011' | 29 | 280 | 27.0 | |
| | G-16 | thermal water well | N40°06.932' E27°39.150' | 29 | 230 | 33.0 | |
| | GCW | cold spring | N40°06.568' E27°38.208' | 35 | | | |
| | EKS-1 | hot spring (Ekşidere village) | N40°01.759' E27°33.748' | 300 | | | crystallized limestone |
| | EKS-2 | cold mineral spring (Ekşidere village) | N40°01.669' E27°33.712' | 310 | | | |
| | EKS-3 | cold spring (Ekşidere village) | N40°01.759' E27°33.748' | 300 | | | |
| Manyas (Kızık) | MK-1 | thermal water well | N40°03.923' E27°54.633' | 38 | 390 | 15.0 | gneiss, calc-schist, crystallized limestone |
| | MK-2 | thermal water well | N40°03.838' E27°54.648' | 60 | 73 | 24.0 | |
| | MCW | cold spring | N40°03.579' E27°53.867' | 60 | | | |
| Pamukçu | PMK-1 | thermal water well | N39°30.538' E27°54.932' | 136 | 193 | 7.0 | marble, quartzite, crystallized limestone |
| | PMK-2 | thermal water well | N39°30.538' E27°54.932' | 136 | 50 | 18.0 | |
| | PCW | cold spring | N39°31.269' E27°54.348' | 120 | | | |
| Bigadiç (Hisarköy) | BHS-1 | thermal water well | N39°25.721' E28°17.109' | 340 | 429 | 60.0 | ophiolitic rocks, crystallized limestone |
| | BHS-2 | thermal water well | N39°25.619' E28°16.941' | 335 | 307 | 60.0 | |
| | BCW | cold spring | N39°25.813' E28°17.252' | 350 | | | |
| Sındırgı (Hisarlan) | SHS-1 | hot spring | N39°16.307' E28°19.076' | 330 | | | crystallized limestone |
| | SHS-2 | hot spring | N39°16.269' E28°19.094' | 340 | | | |
| | SHS-3 | hot spring | N39°16.155' E28°19.089' | 350 | | | |
| | SHS-4 | hot spring | N39°16.152' E28°18.980' | 330 | | | |
| | SCW | cold spring | N39°15.853' E28°18.723' | 275 | | | |
| Edremit | EDR-1 | thermal water well | N39°34.265' E27°02.585' | 20 | 495 | 18.0 | marble, crystallized limestone |
| | EDR-2 | thermal water well | N39°33.625' E27°01.965' | 16 | 196 | 75.0 | |
| | GDR-1 | thermal water well (Güre) | N39°35.307' E26°53.053' | 3 | 86 | 21.0 | |
| | GDR-2 | cold spring (Güre) | N39°36.043' E26°53.469' | 20 | | | |
| Balya | BLY-1 | hot spring | N39°52.511' E27°46.315' | 130 | | 1.5 | marble, granodiorite |
| | BLY-2 | hot spring | N39°52.518' E27°46.249' | 120 | | 1.8 | |
| | BLY-3 | cold spring | N39°52.549' E27°46.233' | 120 | | | |
| Susurluk | SLK-1 | hot spring (Ömer village) | N39°50.266' E28°04.357' | 118 | | | marble, granodiorite |
| | SLK-2 | hot spring (Yıldız village) | N39°50.017' E28°11.650' | 130 | | | |
| | SLK-3 | cold spring (Yıldız village) | N39°48.785' E28°10.811' | 50 | | | |

*Öktü & Dilemre (1997); Ölmez *et al.* (2001a, b); Kara *et al.* (2002).

(standard deviation averages are 0.76‰ for $\delta^{13}C$, 0.90‰ for $\delta^{18}O$ and 0.21‰ for $\delta^{34}S$) were conducted at the Marmara Research Center Laboratory of TÜBİTAK (The Scientific and Technological Research Council of Turkey) in Kocaeli, Turkey. The $\delta^{13}C$-$\delta^{34}S$ analysis of waters was carried out at Iso-Trace Laboratories, New Zealand. Precision of analysis for $^{13}C$ (as VPDB) is 0.17‰ and for $^{34}S$ (as CDT) is 0.40‰.

### Geology of the Balıkesir Region

Final closure of the Neotethyan Ocean defined the beginning of the Neotectonic period in Turkey (e.g., Şengör & Yılmaz 1981; Bozkurt 2001). The convergence between the African and Eurasian plates in the Late Cretaceous and the Arabian and Anatolian plates in the Miocene resulted in the emplacement of huge ophiolite nappes along the Izmir-Ankara-Erzincan Suture in northern Turkey. The compressional tectonic regime was succeeded by a transpressional-extensional regime in the Miocene accompanied by the development of major strike-slip faults including the North Anatolian Fault System, along which Anatolian blocks have moved westwards; widespread magmatic activity in W–NW Turkey is also characteristic (Genç & Yılmaz 1997; Yılmaz *et al.* 2001).

The basement in the Balıkesir region is represented by metamorphic rocks of the Menderes Massif and consists of gneiss, schist, marble and ophiolites of Palaeozoic to Early Mesozoic age and a mélange association of Late Cretaceous age (Genç 1998). Late Eocene–Middle Miocene pyroclastic rocks and lavas of andesite, dacite and rhyolite composition are typical products of the compressional regime (Figure 1). In the region, there are also several granitic plutons (Delaloye & Bingöl 2000; Yücel-Öztürk *et al.* 2005) with ages ranging from Oligocene to Middle Miocene; they were formed during the collisional regime. All of these magmatic rocks are covered with the Upper Miocene–Pliocene continental sediments deposited in post-tectonic lacustrine and fluvial environments (Akyüz 1997; Erkül *et al.* 2005; Aldanmaz 2006).

The Balıkesir region is located in a seismically active part of Anatolia. There are several NE–SW-trending normal and strike-slip faults, some of which have generated large earthquakes in the near past (e.g., M= 7.2 Gönen earthquake in 1952 and M= 7.0 Manyas

earthquake in 1960). These faults are thought to be branches of the North Anatolian Fault System. All the geothermal fields in the region are closely related to volcanism and recent tectonism which have acted to provide the heating source and suitable conduits for the water circulation respectively.

### Water Chemistry

The results of chemical analysis of waters from the Balıkesir region are presented in Table 2. The pH values for thermal waters are between 6.40 (SLK-2) and 8.40 (GDR-1) but those for cold springs range from 3.91 (EKS-3) to 8.05 (SLK-3). Cold waters from the Gönen area (GCW, EKS-2 and EKS-3) are noticeable for their relatively low pH values. The TDS (total dissolved solids) content of thermal waters ranges from 327 (EKS-1) to 2578 (BHS-2) mg/l. The cold waters attain a maximum TDS value of 706 (BCW) mg/l. Temperatures of the thermal waters are between 31.8 (SLK-1) and 98.5 ºC (SHS-1). Cold water temperatures range from 16.8 to 28.8 ºC. The measured oxidation-reduction potential (Eh) values range from -84 (GDR-1) to +52 (SLK-2) mV for thermal waters and -54 to +188 mV for cold waters and show an inverse relationship with the pH of the waters. Electrical conductivities range from 685 (SLK-1) to 3330 (BHS-2) µS/cm for thermal waters and from 65 to 707 µS/cm for cold waters (Table 2).

Results of chemical analysis, illustrated using the Langelier & Ludwig (1942) diagram, indicate that waters from the Gönen, Pamukçu, Edremit and Balya areas are Na-$SO_4$ type waters (Figure 2). The Bigadiç and Sındırgı areas are characterized by Na-$HCO_3$ type waters. The Ekşidere thermal water is of Ca-$HCO_3$ type and the Manyas and Susurluk fields are represented by Na-Ca-$HCO_3$ type waters. Low chloride concentrations in hot waters may indicate that water circulation in most of the geothermal areas is shallow. Surprisingly, cold waters from Ekşidere (EKS-2 and EKS-3) in the Gönen area are also $SO_4$-enriched, which is also shown by their low pH and alkalinity values. Sulfate in these waters is most probably derived from oxidation of metallic sulfides.

Trace element concentrations of the Balıkesir waters are presented in Table 3. Among the siderophile elements, concentrations of Fe and Mo in the waters are 9–1016 µg/l and 0.1–388 µg/l, respectively. High iron concentrations are observed in the Gönen area while high

Table 2. Major ion compositions of the Balıkesir thermal waters (mg/l)*.

| Sample No. | T (°C) | pH | ORP (mV) | E. C. (µS/cm) | Na | K | Ca | Mg | $HCO_3$ | $SO_4$ | Cl | $SiO_2$ | TDS | Water Type |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G-7 | 60.4 | 7.15 | + 1 | 2410 | 479.0 | 28.8 | 67.1 | 3.2 | 383.1 | 467.5 | 249.9 | 58.0 | 1736.6 | $Na-SO_4$ |
| G-8 | 57.8 | 7.42 | - 20 | 2390 | 494.7 | 28.5 | 69.7 | 3.3 | 386.7 | 469.4 | 248.9 | 57.2 | 1758.4 | $Na-SO_4$ |
| G-16 | 77.5 | 6.97 | + 10 | 2930 | 488.1 | 29.3 | 48.7 | 2.5 | 346.5 | 452.5 | 256.3 | 74.7 | 1698.6 | $Na-SO_4$ |
| GCW | 24.1 | 4.93 | + 130 | 65 | 5.5 | 0.6 | 2.8 | 1.3 | 6.1 | 13.3 | 7.2 | 16.9 | 53.7 | $Na-SO_4$ |
| EKS-1 | 42.7 | 7.26 | - 8 | 329 | 12.2 | 2.0 | 51.4 | 13.0 | 192.2 | 16.6 | 8.5 | 31.3 | 327.2 | $Ca-HCO_3$ |
| EKS-2 | 18.8 | 4.16 | + 172 | 171 | 9.2 | 1.4 | 6.3 | 2.1 | 0.0 | 43.4 | 14.6 | 36.5 | 113.5 | $Na-SO_4$ |
| EKS-3 | 21.5 | 3.91 | + 188 | 113 | 6.7 | 2.1 | 3.3 | 1.0 | 0.0 | 26.7 | 9.5 | 24.2 | 73.5 | $Na-SO_4$ |
| MK-1 | 49.8 | 6.57 | + 35 | 1570 | 259.9 | 29.6 | 140.5 | 10.5 | 497.2 | 83.9 | 278.3 | 38.7 | 1338.6 | $Na-HCO_3$ |
| MK-2 | 34.4 | 6.87 | + 17 | 877 | 88.7 | 10.8 | 140.4 | 10.6 | 439.2 | 44.0 | 84.9 | 33.4 | 852.0 | $Ca-HCO_3$ |
| MCW | 17.8 | 7.26 | - 7 | 637 | 10.7 | 0.7 | 159.6 | 8.8 | 430.7 | 22.8 | 14.5 | 15.2 | 663.0 | $Ca-HCO_3$ |
| PMK-1 | 64.9 | 7.56 | - 32 | 1972 | 376.1 | 20.1 | 47.3 | 4.1 | 216.6 | 357.3 | 219.1 | 109.0 | 1349.6 | $Na-SO_4$ |
| PMK-2 | 55.5 | 7.34 | - 14 | 1433 | 318.3 | 13.9 | 32.9 | 3.0 | 278.2 | 291.3 | 131.5 | 91.2 | 1160.3 | $Na-SO_4$ |
| PCW | 16.8 | 7.02 | + 6 | 609 | 12.8 | 1.5 | 133.0 | 18.9 | 350.1 | 39.1 | 16.1 | 27.2 | 598.7 | $Ca-HCO_3$ |
| BHS-1 | 94.6 | 7.29 | - 11 | 2820 | 706.4 | 74.0 | 8.4 | 11.7 | 1051.6 | 381.5 | 206.7 | 119.0 | 2559.3 | $Na-HCO_3$ |
| BHS-2 | 82.9 | 6.95 | + 12 | 3330 | 678.4 | 70.5 | 30.4 | 11.8 | 1110.2 | 349.7 | 206.7 | 120.0 | 2577.7 | $Na-HCO_3$ |
| BCW | 27.8 | 6.97 | + 10 | 707 | 31.7 | 2.8 | 84.7 | 51.7 | 450.8 | 13.7 | 31.5 | 39.1 | 706.0 | $Ca-HCO_3$ |
| SHS-1 | 98.5 | 7.01 | + 10 | 1454 | 321.6 | 20.8 | 22.0 | 2.9 | 577.1 | 96.8 | 81.5 | 114.0 | 1236.7 | $Na-HCO_3$ |
| SHS-2 | 97.3 | 7.38 | - 18 | 1422 | 322.0 | 20.6 | 66.3 | 3.1 | 565.5 | 93.5 | 81.5 | 113.0 | 1265.5 | $Na-HCO_3$ |
| SHS-3 | 95.1 | 6.97 | + 11 | 1451 | 318.2 | 20.6 | 22.4 | 3.3 | 580.7 | 92.6 | 82.6 | 114.0 | 1234.4 | $Na-HCO_3$ |
| SHS-4 | 87.0 | 6.72 | + 30 | 1631 | 314.2 | 20.6 | 22.8 | 4.1 | 567.3 | 92.7 | 82.2 | 111.0 | 1214.9 | $Na-HCO_3$ |
| SCW | 27.4 | 7.42 | - 16 | 472 | 32.1 | 1.7 | 77.0 | 12.7 | 298.9 | 10.9 | 19.5 | 25.3 | 478.1 | $Ca-HCO_3$ |
| EDR-1 | 57.6 | 7.83 | - 47 | 1354 | 272.7 | 5.2 | 50.2 | 0.8 | 48.8 | 506.9 | 59.6 | 42.9 | 987.1 | $Na-SO_4$ |
| EDR-2 | 44.7 | 7.56 | - 27 | 968 | 198.8 | 4.0 | 70.3 | 3.0 | 108.0 | 391.3 | 51.6 | 30.6 | 857.6 | $Na-SO_4$ |
| GDR-1 | 56.6 | 8.40 | - 84 | 1260 | 306.0 | 6.0 | 22.4 | 0.1 | 50.0 | 493.3 | 60.6 | 55.9 | 994.3 | $Na-SO_4$ |
| GDR-2 | 17.5 | 7.76 | - 42 | 208 | 5.2 | 0.9 | 40.0 | 6.2 | 138.5 | 6.08 | 5.0 | 11.1 | 213.0 | $Ca-HCO_3$ |
| BLY-1 | 59.0 | 8.21 | - 71 | 1240 | 263.7 | 4.3 | 16.6 | 0.1 | 79.3 | 350.6 | 79.1 | 61.2 | 854.9 | $Na-SO_4$ |
| BLY-2 | 58.1 | 8.10 | - 68 | 1234 | 269.5 | 4.2 | 15.8 | 0.1 | 75.0 | 357.2 | 79.4 | 61.0 | 862.2 | $Na-SO_4$ |
| BLY-3 | 28.8 | 6.17 | + 60 | 252 | 24.0 | 1.6 | 26.5 | 8.6 | 111.0 | 16.0 | 9.6 | 53.1 | 250.4 | $Ca-Na-HCO_3$ |
| SLK-1 | 31.8 | 7.05 | + 6 | 685 | 62.8 | 7.5 | 83.1 | 29.5 | 339.8 | 120.2 | 10.5 | 25.3 | 678.7 | $Ca-Na-HCO_3$ |
| SLK-2 | 72.8 | 6.40 | + 52 | 1605 | 380.4 | 13.1 | 22.4 | 0.6 | 595.4 | 190.3 | 57.1 | 106.0 | 1365.3 | $Na-HCO_3$ |
| SLK-3 | 25.7 | 8.05 | - 54 | 207 | 19.9 | 2.1 | 21.6 | 7.3 | 106.1 | 19.7 | 11.1 | 43.3 | 231.1 | $Ca-Na-HCO_3$ |

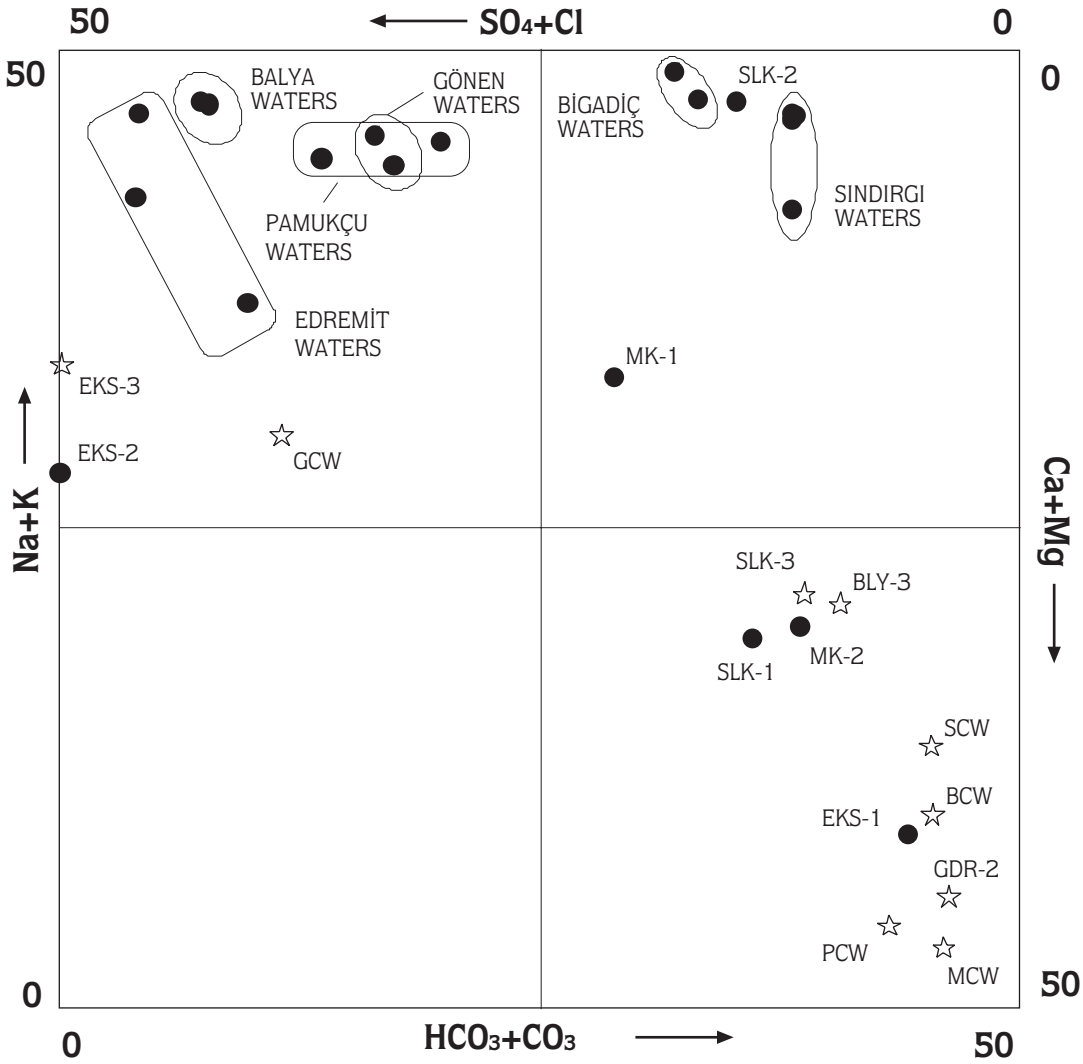*Detection limit of elemental analysis is 0.05–0.5 ppm.

**Figure 2.** Langelier-Ludwig diagram for the Balıkesir waters.

Mo contents are found in the Pamukçu and Balya waters. Chalcophile elements are generally dominant in sulfate waters. Concentration ranges for As, Cu, Pb, Sb and Zn in these waters are 0.4–1266 µg/l, 0.3–120 µg/l, 0.1–59 µg/l, 0.1–134 µg/l and 0.4–1056 µg/l, respectively (Table 3).

Lithophile element concentrations of the waters also vary significantly. With the exception of Ekşidere samples, the maximum aluminum content in waters is 143 µg/l. High Al, Fe, and in part Zn, concentrations of the Ekşidere samples are probably due to acidic alteration (i.e., low pH). The $SO_4$-rich waters of the Balya, Edremit,

Gönen and Pamukçu areas have comparatively high B contents up to 11.5 mg/l (Table 3). The boron in the Balıkesir thermal waters is suggested to have a volcanic origin (Palmer & Helvacı 1997). Among the other lithophile elements, concentrations of Ba and Br reach 310 and 791 µg/l. Li, Rb and Cs concentrations are closely related to TDS values of the waters and their maximum abundances are 1632, 309 and 285 µg/l, respectively (Table 3). Strontium concentrations of the waters vary over a wide range from 22 to 3017 µg/l. Concentrations of yttrium and uranium are very low (the maxima are 0.7 and 13.3 µg/l). The maximum Mn and W abundances are 164 and 516 µg/l, respectively (Table 3).

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Table 3.   Trace element compositions of the Balıkesir thermal waters (μg/l).

| Sample No. | Al | As | B | Ba | Br | Cs | Cu | Fe | Li | Mn | Mo | Pb | Rb | Sb | Sr | U | W | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G-7 | 16 | 283.2 | 5573 | 35.9 | 766 | 214.1 | 3.6 | 640 | 1586.6 | 117.9 | 46.1 | 0.5 | 230.4 | 25.8 | 1327.8 | 0.12 | 216.9 | 0.06 | 3.6 |
| G-8 | 81 | 253.3 | 5476 | 36.9 | 766 | 217.5 | 20.0 | 321 | 1602.8 | 103.7 | 49.8 | 4.3 | 232.9 | 30.5 | 1412.8 | 0.13 | 207.8 | 0.07 | 71.5 |
| G-16 | 61 | 61.4 | 6354 | 47.5 | 791 | 280.6 | 4.0 | 1016 | 1632.4 | 118.9 | 8.6 | 5.6 | 282.0 | 15.8 | 1203.8 | 0.02 | 341.8 | 0.17 | 11.2 |
| GCW | 1011 | 0.4 | 40 | 113.1 | 29 | 0.01 | 3.1 | 33 | 1.4 | 11.7 | 0.2 | 17.5 | 2.3 | 0.2 | 28.9 | 0.18 | 2.23 | 0.70 | 29.5 |
| EKS-1 | 5 | 56.8 | 39 | 309.5 | 28 | 3.2 | 0.3 | 30 | 25.3 | 0.4 | 1.3 | <0.1 | 8.6 | 7.9 | 464.9 | 0.03 | 5.83 | <0.01 | 0.4 |
| EKS-2 | 2542 | 3.4 | 28 | 40.0 | 42 | 4.3 | 3.8 | 766 | 32.9 | 39.5 | 0.2 | 59.4 | 9.1 | 0.7 | 43.9 | 0.87 | 0.28 | 0.36 | 22.8 |
| EKS-3 | 2108 | 0.4 | 24 | 43.2 | 33 | 1.2 | 120.3 | 229 | 4.4 | 46.9 | <0.1 | 7.3 | 7.6 | 0.1 | 21.8 | 0.79 | 0.13 | 0.84 | 308.6 |
| MK-1 | 6 | 279.9 | 6601 | 147.5 | 437 | 94.5 | 2.6 | 509 | 729.6 | 163.5 | 2.1 | 0.3 | 193.6 | 29.1 | 644.0 | 1.15 | 6.88 | 0.12 | 6.6 |
| MK-2 | 2 | 162.5 | 2157 | 145.1 | 172 | 51.4 | 0.4 | 9 | 290.3 | 0.2 | 2.5 | <0.1 | 93.4 | 12.2 | 418.1 | 1.60 | 0.73 | 0.01 | 0.4 |
| MCW | 32 | 3.3 | 19 | 104.3 | 68 | 0.02 | 3.5 | 39 | 2.3 | 8.0 | 0.1 | 1.2 | 1.7 | 0.2 | 171.9 | 1.42 | 0.16 | 0.13 | 5.9 |
| PMK-1 | 2 | 895.3 | 11475 | 28.3 | 598 | 229.2 | 1.4 | 9 | 987.5 | 39.7 | 245.9 | <0.1 | 185.0 | 58.7 | 917.8 | 1.92 | 186.4 | <0.01 | 1.1 |
| PMK-2 | 21 | 900.8 | 7084 | 18.4 | 350 | 166.9 | 5.5 | 10 | 790.0 | 35.0 | 387.8 | 1.2 | 135.4 | 134.1 | 599.4 | 3.22 | 130.3 | 0.06 | 31.3 |
| PCW | 56 | 27.7 | 70 | 194.7 | 70 | 0.2 | 2.6 | 42 | 13.3 | 4.5 | 2.7 | 2.6 | 1.1 | 0.4 | 404.8 | 2.00 | 1.1 | 0.13 | 290.7 |
| BHS-1 | 143 | 1232.8 | 9162 | 54.7 | 491 | 271.1 | 2.5 | 98 | 1510.9 | 9.6 | 5.5 | 1.7 | 309.4 | 43.3 | 334.0 | 0.05 | 119.6 | 0.14 | 5.7 |
| BHS-2 | 35 | 1265.5 | 8896 | 78.8 | 494 | 285.2 | 1.8 | 307 | 1501.8 | 21.5 | 5.5 | 1.9 | 304.6 | 66.1 | 931.2 | <0.02 | 124.8 | 0.04 | 6.8 |
| BCW | 9 | 11.6 | 100 | 119.7 | 114 | 14.5 | 1.0 | 9 | 52.2 | 0.6 | 0.5 | 0.7 | 12.3 | 1.3 | 646.2 | 5.91 | 1.5 | 0.07 | 2.4 |
| SHS-1 | 37 | 107.1 | 5002 | 126.3 | 140 | 184.7 | 2.2 | 35 | 1113.8 | 36.7 | <0.1 | 6.1 | 138.5 | 6.4 | 533.6 | <0.02 | 197.9 | 0.03 | 5.7 |
| SHS-2 | 33 | 99.5 | 4766 | 200.9 | 149 | 187.7 | 1.1 | 97 | 1054.6 | 116.0 | 0.1 | 1.9 | 141.1 | 7.9 | 1420.4 | <0.02 | 199.7 | 0.07 | 2.4 |
| SHS-3 | 22 | 115.2 | 4739 | 129.6 | 150 | 195.7 | 1.2 | 11 | 1121.5 | 44.5 | <0.1 | 2.9 | 139.6 | 8.2 | 559.6 | <0.02 | 198.3 | 0.02 | 1.8 |
| SHS-4 | 21 | 108.7 | 4522 | 133.6 | 148 | 183.3 | 1.2 | 30 | 1054.1 | 57.5 | 0.1 | 1.0 | 137.7 | 7.7 | 581.2 | 0.04 | 198.4 | 0.02 | 2.1 |
| SCW | 6 | 1.9 | 55 | 68.1 | 80 | 0.01 | 0.7 | 9 | 13.8 | 0.8 | 0.4 | 3.1 | 2.6 | 0.6 | 680.3 | 13.27 | 1.8 | 0.24 | 1056.2 |
| EDR-1 | 66 | 4.3 | 1190 | 28.3 | 141 | 39.2 | 15.1 | 192 | 305.3 | 34.5 | 17.5 | 1.2 | 39.5 | 0.8 | 1264.2 | 0.13 | 125.8 | 0.03 | 22.0 |
| EDR-2 | 7 | 2.1 | 820 | 13.5 | 155 | 11.8 | 2.7 | 9 | 59.6 | 5.2 | 16.9 | 0.3 | 8.4 | 0.2 | 409.1 | 0.69 | 34.0 | <0.01 | 14.3 |
| GDR-1 | 8 | 5.1 | 2401 | 4.6 | 147 | 3.4 | 1.7 | 9 | 273.5 | 0.8 | 17.4 | <0.1 | 31.9 | 1.3 | 352.9 | <.02 | 102.9 | <0.01 | 1.5 |
| GDR-2 | 18 | 0.5 | 49 | 4.1 | 21 | 0.01 | 2.5 | 16 | 0.7 | 0.7 | 0.6 | 1.3 | 0.9 | <0.05 | 50.2 | 0.33 | 0.5 | 0.02 | 5.0 |
| BLY-1 | 35 | 85.9 | 1944 | 14.2 | 242 | 63.0 | 1.9 | 12 | 466.9 | 21.5 | 102.8 | 1.2 | 42.1 | 1.6 | 466.6 | 0.18 | 516.1 | 0.02 | 5.3 |
| BLY-2 | 36 | 81.5 | 2025 | 13.3 | 233 | 61.6 | 16.0 | 9 | 461.0 | 9.2 | 101.1 | 0.9 | 40.7 | 1.3 | 453.6 | 0.03 | 509.7 | <0.01 | 5.8 |
| BLY-3 | 22 | 1.7 | 72 | 233.4 | 47 | 0.1 | 7.8 | 13 | 16.4 | 3.9 | 1.9 | 2.2 | 0.7 | 0.1 | 196.1 | 1.81 | 2.8 | 0.02 | 437.3 |
| SLK-1 | 14 | 38.2 | 227 | 46.9 | 35 | 10.9 | 5.2 | 31 | 66.4 | 13.0 | 1.5 | 1.2 | 24.9 | 1.1 | 3016.9 | 0.71 | 2.6 | 0.02 | 8.7 |
| SLK-2 | 44 | 40.7 | 894 | 47.4 | 176 | 129.5 | 1.8 | 112 | 700.8 | 123.9 | 8.0 | 0.7 | 91.3 | 2.1 | 1144.5 | <0.02 | 92.5 | 0.03 | 7.3 |
| SLK-3 | 22 | 0.6 | 45 | 71.7 | 40 | 2.9 | 3.5 | 22 | 33.6 | 3.2 | 0.5 | 1.6 | 9.3 | 0.1 | 333.8 | 5.07 | 1.1 | 0.05 | 21.2 |

There are moderately high correlations between the concentrations of lithophile elements and chloride in thermal waters. Correlation coefficients computed for Cl-Br, Cl-Rb, Cl-B, Cl-Li and Cl-Cs pairs are 0.870, 0.746, 0.620, 0.586 and 0.498, respectively. Rb, Li and Cs are also strongly correlated between themselves. Correlation coefficients calculated for these elements are 0.858 for Rb-Li, 0.850 for Rb-Cs and 0.918 for Li-Cs. Strong correlations obtained between K and Rb-Li-Cs (K-Rb: 0.787, K-Cs: 0.600 and K-Li: 0.564) may indicate that these elements substitute for potassium in clay minerals.

Major and trace element contents and their elemental ratios in travertines and Mesozoic limestones sampled in the vicinity of water collection sites, are shown for comparison in Table 4. Concentrations of alkaline earth metals in thermal waters, limestones and travertine deposits may be evaluated by considering element mobility during dissolution and precipitation. The Ca/Mg ratios of the thermal waters in this study vary significantly between 3 and 224 with an average of 38. Springs around the travertine sites at Bigadiç and Sındırgı have an average Ca/Mg ratio of 7. The ranges of Ca/Mg ratios for limestones and travertine deposits are 172–1111 and 27–133, respectively. It therefore seems that Mg tends to be more soluble and it is not precipitated in the travertines at the same rate as calcium. The Ca/Sr ratios of recent travertine deposits and thermal springs in the Bigadiç (~29) and the Sındırgı (~41) fields are similar implying that strontium is precipitated in the travertines at the same rate as calcium. The Sr/Ba ratios of the travertines (~9 to 24) are higher than those of thermal springs (~4 to 12) in the same fields indicating that barium behaves in a mobile manner.

Rare alkalis such as Li, Rb and Cs are least affected by secondary processes in the reservoir and, therefore, they are very useful for determining the source rock components. In the Li-Rb-Cs diagram of Giggenbach (1991), Balıkesir thermal waters define a rock dissolution trend (Figure 3). Li/Cs ratios of waters (excluding cold waters and sample GDR-1) range from 4.31 to 7.91 indicating that they are derived from acidic rocks. The Li/Cs ratio of limestone, the potential host rock, is 5.8, which is in good agreement with the ratios of the waters. Li/Cs ratios of the travertines (4.2 to 8.6) are also consistent with those of the waters. Cl, Li and B contents of the thermal waters are plotted on another Giggenbach (1991) diagram (Figure 4) where they display two dissolution paths with average B/Cl ratios of 0.02 and 0.05. The B/Cl ratio of limestone, the potential host rock, is about 0.07 and that of the travertines is between 0.08 and 0.12 or slightly higher than the waters (Table 4).
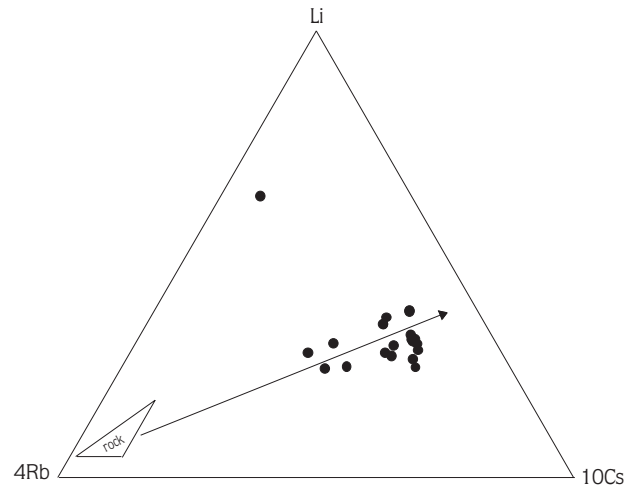


Figure 3. Li-Rb-Cs diagram for the Balıkesir thermal waters.

Table 4. Major oxide (%) and trace element (ppm) compositions of various carbonate rocks in the Balıkesir region.

| Sample | Li | Rb | Cs | B | Cl | Sr | Ba | MgO | CaO | B/Cl | Li/Cs | Ca/Mg | Ca/Sr | Sr/Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MK (limestone) | 7.6 | 3.1 | 1.3 | 20 | 282 | 2626 | 141 | 0.37 | 54.3 | 0.07 | 5.8 | 174 | 148 | 18.6 |
| PMK (limestone) | 1.2 | 1.0 | <0.1 | <2 | 33 | 342 | 27 | 0.06 | 56.2 | - | - | 1111 | 1173 | 12.6 |
| GR (limestone) | 0.9 | 1.5 | <0.1 | <2 | 11 | 327 | 68 | 0.38 | 55.1 | - | - | 172 | 1204 | 4.8 |
| SHS-1 (travertine)* | 2.5 | 2.5 | 0.6 | 9 | 76 | 2271 | 3945 | 2.29 | 52.5 | 0.12 | 4.2 | 27 | 165 | 0.6 |
| SHS-2 (travertine)** | 3.4 | 0.6 | 0.4 | 10 | 132 | 9366 | 1049 | 0.48 | 53.9 | 0.08 | 8.5 | 133 | 41 | 8.9 |
| BHS (travertine)** | 27.5 | 3.6 | 3.2 | 114 | 1192 | 12304 | 504 | 1.61 | 50.2 | 0.10 | 8.6 | 37 | 29 | 24.4 |

(* old example; ** Recent examples)

21
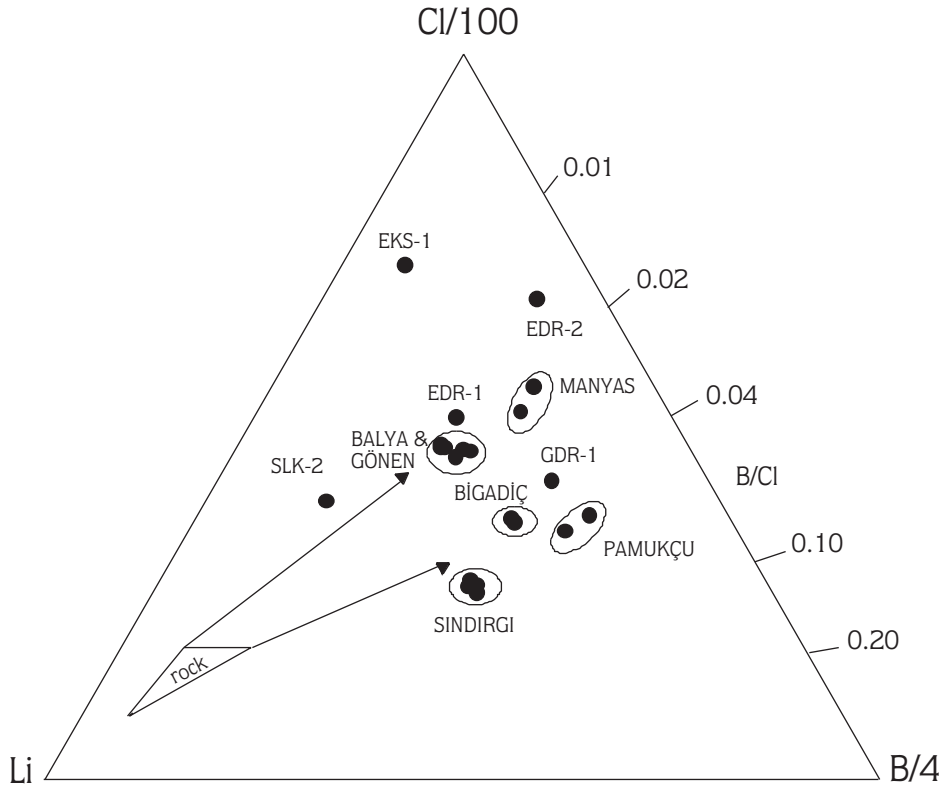
**Figure 4.** Cl-Li-B diagram for the Balıkesir thermal waters.

Waters of higher B/Cl ratios were sampled from the Bigadiç and Sındırgı areas where water temperatures are between 82.9 and 98.5 °C. High boron contents in these waters are also accompanied by relatively high concentrations of some other volatiles, such as As and Sb (Table 3).

## Water-Rock Interaction

### Fluid-Mineral Equilibria

Water-rock equilibrium conditions of the Balıkesir geothermal waters are discussed with reference to their Ca, K and Mg contents. Calcite is a ubiquitous mineral in geothermal systems, and thermal waters are likely to be saturated with calcite on many occasions (Arnórsson *et al.* 1983). The most important reaction leading to the formation of calcite in geothermal systems is the conversion of Ca-Al silicates to calcite by $CO_2$, probably of deep origin (Giggenbach 1988). $CO_2$ partial pressures of the Balıkesir geothermal waters can be evaluated in the K-Mg-Ca geoindicator diagram which assumes

equilibrium with calcite (Figure 5). The equations for constructing this diagram are given by Giggenbach (1988) as:

$$L_{kc} = \log (C^2_K / C_{Ca})$$
$$L_{kc} = \log P_{CO_2} + 3.0$$
$$L_{km} = \log (C^2_K / C_{Mg})$$

The Gönen, Pamukçu and Susurluk waters plot close to the full equilibrium line at reservoir temperatures of 90–113 °C in this diagram. Waters below the equilibrium line correspond to immature fluids with higher $CO_2$ fugacities and are, therefore, reactive with respect to hydrogen metasomatism. In this respect, compositions of the Bigadiç and Sındırgı waters are controlled by rock dissolution rather than equilibration. High TDS (Table 2) and trace element contents (Table 3; e.g., As, B, Li) and also high $CO_2$ partial pressure values of BHS-1 and BHS-2 waters may indicate the presence of an intense alteration system dominated by the acidic fluids.
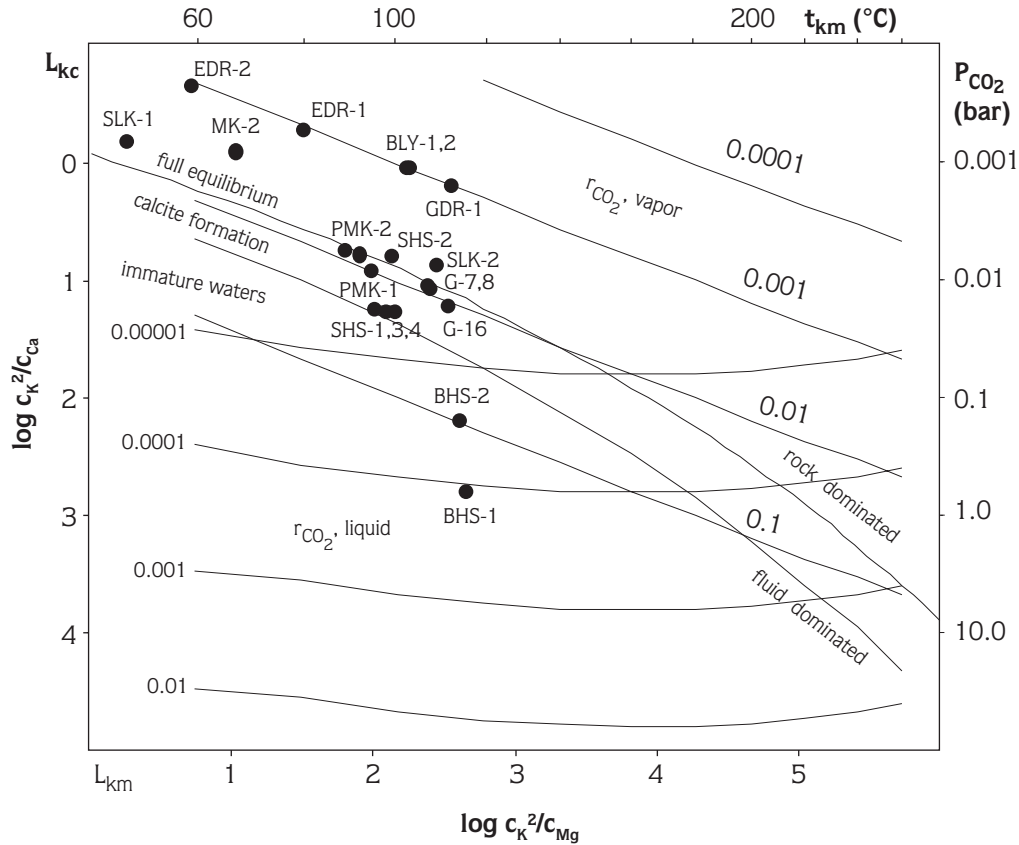
**Figure 5.** K-Mg-Ca geoindicator diagram for the Balıkesir thermal waters.

Waters that plot above the full equilibrium line (samples from the Balya and Edremit areas) are characterized by low proportions of deep $CO_2$-rich vapors (Figure 5). As these waters are likely to originate from a rock-dominated, $CO_2$-deficient environment, their TDS values (Table 2) and reservoir temperatures are comparatively low (e.g., 60 °C for sample EDR-2).

*Mineral Equilibrium Calculations*

Equilibrium states for the 13 most common hydrothermal minerals which are likely to be precipitated from the thermal waters of Balıkesir region were investigated using the saturation diagram (Figure 6). The WATSPEC program (Wigley 1977) was used to compute the saturation index (SI) of various carbonate, sulfate, silica and silicate minerals at the outlet temperatures of the waters. The results show that most of the waters are slightly oversaturated with respect to calcite and slightly undersaturated with respect to aragonite and dolomite.

Although most samples are sulfate-enriched, none of them is oversaturated or in equilibrium with gypsum and anhydrite. This may imply that the $SO_4$ concentration of the waters is controlled by a steady state dissolution process (Grasby *et al.* 2000).

Microcline, albite, and partly adularia show oversaturation trends, but the degree of saturation is always higher for the first. Quartz and chalcedony are slightly oversaturated in all waters. Saturation indices computed for goethite and kaolinite are the highest among the minerals of interest. Illite is highly undersaturated except in the Susurluk waters (Figure 6).

**Geothermometer Applications**

*Na-K-Mg Diagram*

The applicability of cation geothermometers was evaluated on the Na-K-Mg diagram (Figure 7) proposed by Giggenbach (1988). Figure 7 shows that none of the
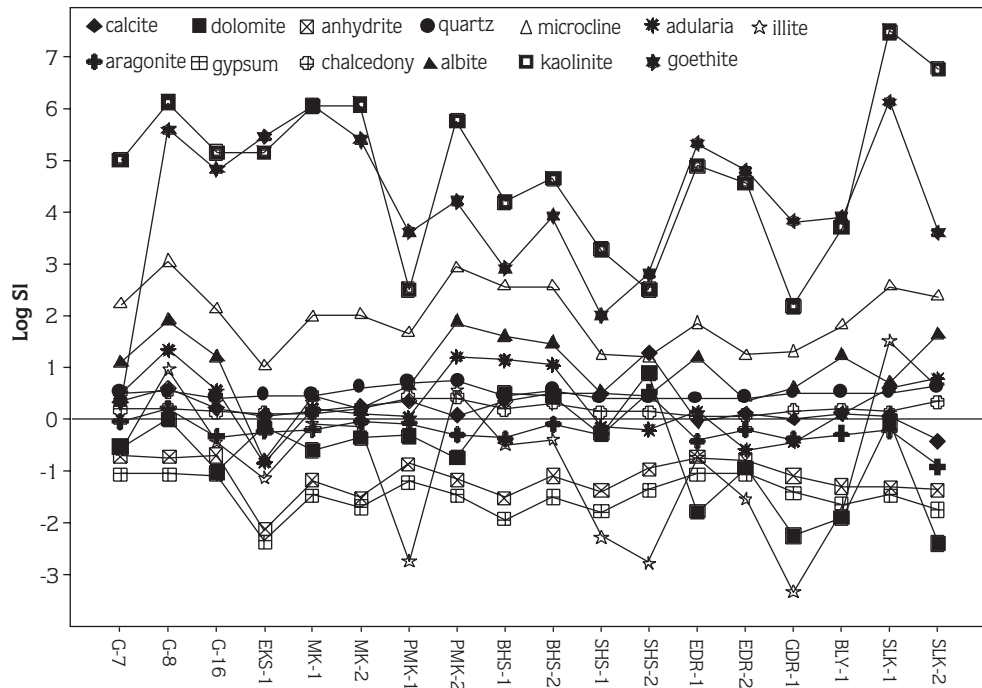
**Figure 6.** Mineral equilibrium diagram for the Balıkesir thermal waters.
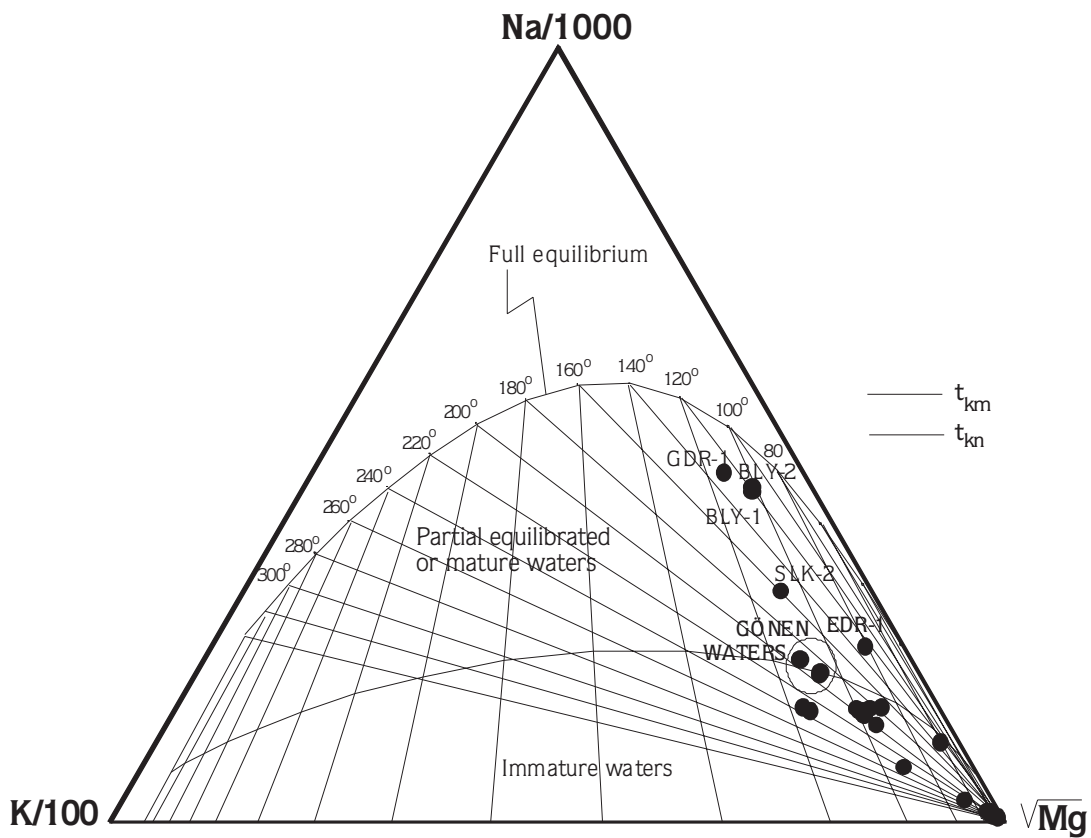


**Figure 7.** Na-K-Mg diagram for the Balıkesir thermal waters.

Balıkesir waters attains a water-rock equilibrium and most of the samples plot in the 'immature waters' (shallow or mixed waters) field. Only GDR-1, BLY-1, BLY-2, SLK-2, EDR-1 and partly Gönen samples are plotted in 'partly equilibrated waters" field. For the samples plotting far into the immature waters field, the application of both K-Na and K-Mg, and indeed any type of cation geothermometers, is doubtful and the interpretation of the temperature predictions of such waters should be made cautiously (Giggenbach 1988). However, for samples plotting in the partial equilibrium field, temperature estimates can be performed with some degree of confidence.

*Chemical Geothermometers*

In order to determine reservoir temperatures of the Balıkesir geothermal waters, chemical geothermometers were applied, and the results are shown in Table 5. Of the silica geothermometers, the quartz and chalcedony geothermometers yield reservoir temperatures of 81–143 °C and 41–122 °C, respectively. As suggested by Kharaka & Mariner (1988) and Giggenbach (1991), the silica solubility at temperatures below 180 °C is governed by amorphous silica and/or chalcedony and, the quartz geothermometer might be unreliable for the carbonate hosted springs. The amorphous silica geothermometer gives temperatures below those measured at the surface indicating that the solubility of silica in carbonate terrains is controlled by a more stable phase such as chalcedony. In this respect, temperature estimates by the chalcedony geothermometer are believed to be more realistic for most of the Balıkesir thermal waters.

Results obtained for various cation geothermometers yield a wide range of temperatures. The absence of consistency between the silica and cation geothermometers suggests that secondary processes such as mixing, precipitation and/or dissolution take place in the upflow zones. Several Na-K geothermometers have been proposed by different workers. Although they yield

Table 5. Chemical geothermometers for the Balıkesir thermal waters (°C).

| Sample No. | T °C (meas.) | Quartz[1] | Chal.[2] | Amorp. Silica[3] | Na-K[4] | Na-K[5] | K-Mg[5] | Na-K-Ca[6] | Na-K-Ca-Mg[7] | Probable Temperature Range (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| G-7 | 60.4 | 109 | 79 | -8 | 143 | 195 | 109 | 130 | – | 110–150 |
| G-8 | 57.8 | 108 | 79 | -9 | 139 | 192 | 108 | 129 | – | 110–150 |
| G-16 | 77.5 | 120 | 93 | 3 | 143 | 195 | 113 | 141 | 137 | 110–150 |
| EKS-1 | 42.7 | 82 | 50 | -31 | 259 | 275 | 32 | 16 | – | ~50 |
| MK-1 | 49.8 | 91 | 60 | -24 | 210 | 243 | 93 | 104 | – | 60–90 |
| MK-2 | 34.4 | 85 | 53 | -29 | 218 | 249 | 68 | 59 | – | 60–90 |
| PMK-1 | 64.9 | 138 | 116 | 21 | 133 | 187 | 96 | 121 | 116 | 110–140 |
| PMK-2 | 55.5 | 130 | 105 | 12 | 116 | 174 | 90 | 114 | 114 | 100–120 |
| BHS-1 | 94.6 | 143 | 122 | 26 | 200 | 236 | 118 | 220 | 82 | ~200 |
| BHS-2 | 82.9 | 143 | 122 | 26 | 199 | 235 | 116 | 205 | 98 | ~200 |
| SHS-1 | 98.5 | 140 | 119 | 24 | 150 | 200 | 101 | 143 | 115 | 110–150 |
| SHS-2 | 97.3 | 140 | 118 | 23 | 149 | 199 | 100 | 112 | – | 110–150 |
| SHS-3 | 95.1 | 140 | 119 | 24 | 150 | 200 | 99 | 142 | 100 | 110–150 |
| SHS-4 | 87.0 | 139 | 117 | 22 | 151 | 201 | 96 | 141 | 103 | 110–150 |
| EDR-1 | 57.6 | 96 | 64 | -19 | 60 | 127 | 82 | 68 | – | 50–70 |
| EDR-2 | 44.7 | 81 | 49 | -32 | 63 | 130 | 60 | 51 | – | 50–70 |
| GDR-1 | 56.6 | 107 | 78 | -10 | 62 | 129 | 114 | 92 | 79 | 60–90 |
| BLY-1 | 59.0 | 111 | 82 | -6 | 51 | 120 | 104 | 86 | 82 | 50–90 |
| BLY-2 | 58.1 | 111 | 82 | -6 | 49 | 118 | 104 | 86 | 84 | 50–90 |
| SLK-1 | 31.8 | 73 | 41 | -38 | 216 | 247 | 49 | 55 | – | <50 |
| SLK-2 | 72.8 | 137 | 114 | 20 | 98 | 159 | 111 | 125 | – | 90–120 |

[1] Arnórsson (1985); [2] Fournier & Potter (1982); [3] Fournier (1977); [4] Tonani (1980); [5] Giggenbach (1988); [6] Fournier & Truesdell (1973); [7] Fournier & Potter (1979); –: Mg-correction not needed.

similar values at around 300 °C, the values vary widely at low temperatures. Temperatures computed from the Na-K geothermometer of Giggenbach (1988) are between 120 and 275 °C and the one suggested by Tonani (1980) yields reservoir temperatures ranging from 51 to 259 °C. The difference in the results from these geothermometers is attributed to the fact that they are based on experiments with different mineral assemblages. The Na-K geothermometer of Giggenbach (1988) tends to give the highest values and is avoided in this study since the nature of geothermal systems and mineral assemblages in the Balıkesir region are not believed to be similar to those that Giggenbach worked with. However, the one proposed by Tonani (1980) gives lower temperature estimates and tends to have a wider applicability than that of Giggenbach (1988). As shown from Table 5, reservoir temperatures of samples EKS-1, MK-1, MK-2, BHS-1, BHS-2 and SLK-1 calculated from the Na-K geothermometer of Tonani (1980) are as high as 259 °C since these waters seem to be mixed with significant cold groundwater components; this is also shown by their high Mg concentrations (Table 2). Therefore, the Na-K geothermometer is not applicable to these waters. Temperatures calculated for waters with low Mg concentrations (e.g., Pamukçu and Sındırgı samples) are consistent with those computed from the quartz geothermometer.

In order to eliminate the possible effect of calcium on the Na-K geothermometer, the Na-K-Ca geothermometer was used. The reservoir temperatures computed from this geothermometer range from 51 to 220 °C which is generally higher than those of silica geothermometers. However, in some cases, temperature estimates from the Na-K-Ca geothermometer correlate well with the results of quartz and Na-K geothermometers (e.g., around 130–140 °C for the Gönen waters, 120–130 °C for the Pamukçu waters, 200 °C for the Bigadiç waters and 140–150 °C for the Sındırgı waters) (Table 5).

For most of the waters, the predictions of the K-Mg geothermometer are consistent with either chalcedony or quartz geothermometers. For example, temperatures computed from the chalcedony – K-Mg geothermometers are 122–118 °C for the Bigadiç, 105–96 °C for the Pamukçu and 114–111 °C for the Susurluk areas (sample SLK-2). Consistent estimates from the quartz – K-Mg geothermometers are 91–93 °C for the Manyas, 109–109 °C for the Gönen, 81–82 °C and 107–114 °C

for the Edremit and 111–104 °C for the Balya fields. Due to their high Ca concentrations, K-Mg temperatures of samples EKS-1, SLK-1, MK-2 and EDR-2 are lower than those of silica geothermometers. For low-temperature fields, the Na-K-Ca-Mg geothermometer yields more reliable results around 80 °C (e.g., Balya and Güre samples).

The probable temperature ranges for each geothermal field in the Balıkesir region are presented in Table 5. In this respect, Bigadiç waters with a temperature of about 200 °C have the maximum reservoir temperature in the region.

## Stable Isotopes

### $\delta^{18}O$-$\delta D$ Compositions

Results of the $\delta^{18}O$-$\delta D$ ratios of Balıkesir thermal waters are presented in Table 6. The $\delta^{18}O$ ratio of thermal waters ranges from -12.91 to -9.61 and that of cold waters is between -12.17 and -9.25‰. Deuterium values for thermal and cold waters are -77.39 to -52.10 and -61.79 to -46.75‰, respectively. In the $\delta^{18}O$-$\delta D$ diagram (Figure 8), except for the Bigadiç waters, most of the Balıkesir waters indicate a common meteoric origin on the Local Meteoric Water Line (LMWL) which has a regression equation of $\delta D = 7.28 \, \delta^{18}O + 16.9$. This equation is very similar to that for the Marmara Meteoric Water Line ($\delta D = 7.30 \, \delta^{18}O + 16.0$) (Yalçın 1997). The unusual position of the Bigadiç thermal waters with an $^{18}O$ shift about 2.5‰ units from the LMWL is explained by water-rock interaction which has resulted in an increase of $\delta^{18}O$ content of these waters. This is confirmed by the relatively high TDS contents and temperatures of these waters (Table 2). In each geothermal area, $\delta^{18}O$-$\delta D$ ratios of cold waters are slightly higher than those of thermal waters. Enrichments for $^{18}O$ and deuterium are about 0.22 to 1.32‰ and 2.55 to 20.15‰, respectively (Table 6). This may indicate that thermal waters are recharged from a different source probably from a higher elevation.

### $\delta^{34}S$ and $\delta^{13}C$ Compositions

In order to investigate the origin of sulfur and carbon in the waters, all Balıkesir thermal waters were analyzed for their $\delta^{34}S$ and $\delta^{13}C$ contents. Analyses were carried out on sulfate for $\delta^{34}S$ and dissolved inorganic carbon (DIC) for $\delta^{13}C$ (Table 6).

Table 6. Isotopic ratios (‰) for thermal waters and some carbonate rocks in the Balıkesir region.

| Sample No | $\delta^{18}O$ | $\delta D$ | $\delta^{13}C$ | $\delta^{34}S$ |
|---|---|---|---|---|
| G-7 | -12.12 | -76.83 | 0.0 | 11.5 |
| G-8 | -12.78 | -77.05 | 0.0 | 12.3 |
| G-16 | -12.50 | -77.39 | 0.7 | 12.5 |
| GCW | -12.17 | -61.79 | n.a. | n.a. |
| EKS-1 | -11.94 | -60.91 | -1.7 | n.a. |
| EKS-2 | -11.21 | -55.95 | -17.7 | -5.5 |
| EKS-3 | -11.44 | -58.36 | n.a. | n.a. |
| MK-1 | -9.91 | -61.36 | -3.6 | 16.1 |
| MK-2 | -10.77 | -58.05 | -8.4 | 7.7 |
| MCW | -10.45 | -55.90 | n.a. | n.a. |
| PMK-1 | -10.67 | -63.81 | -8.9 | 7.7 |
| PMK-2 | -9.92 | -58.47 | -11.2 | 12.1 |
| PCW | -9.25 | -49.69 | n.a. | n.a. |
| BHS-1 | -9.94 | -71.10 | -2.0 | 25.2 |
| BHS-2 | -9.86 | -71.80 | -1.2 | 24.2 |
| BCW | -9.68 | -51.30 | n.a. | n.a. |
| SHS-1 | -11.61 | -68.49 | -4.7 | 15.5 |
| SHS-2 | -11.78 | -69.02 | -4.8 | 16.8 |
| SHS-3 | -11.53 | -69.28 | -4.7 | 17.0 |
| SHS-4 | -11.73 | -68.85 | -3.4 | 16.2 |
| SCW | -10.04 | -53.75 | n.a. | n.a. |
| EDR-1 | -10.05 | -55.15 | -10.5 | 11.1 |
| EDR-2 | -10.03 | -53.38 | -14.7 | 10.2 |
| GDR-1 | -9.61 | -52.10 | -7.2 | 10.3 |
| GDR-2 | -9.69 | -46.75 | n.a. | n.a. |
| BLY-1 | -12.50 | -76.80 | -6.6 | 13.6 |
| BLY-2 | -12.91 | -75.89 | -6.7 | 13.4 |
| BLY-3 | -11.38 | -57.69 | n.a. | n.a. |
| SLK-1 | -11.05 | -63.16 | -1.4 | 18.6 |
| SLK-2 | -12.36 | -72.37 | -1.8 | 18.8 |
| SLK-3 | -10.53 | -57.24 | n.a. | n.a. |

CARBONATES

| Sample No | $\delta^{18}O$ | $\delta D$ | $\delta^{13}C$ | $\delta^{34}S$ |
|---|---|---|---|---|
| MK (Limestone) | 7.96 | | -3.40 | |
| PMK (Limestone) | 8.89 | | 0.17 | |
| GR (Limestone) | -5.90 | | 2.59 | |
| SHS-1 (Trav.-old) | -10.00 | | -2.97 | 14.2 |
| SHS-2 (Trav.-Recent) | -6.51 | | -2.21 | |
| BHS (Trav.-Recent) | -6.12 | | 0.07 | |

n.a.: not analyzed; Trav.: travertine

$\delta^{34}S$ values of thermal waters range from -5.5 to +25.2‰. In Figure 9, $\delta^{34}S$ values of waters are plotted versus $SO_4$ contents. Apart from the most negative $\delta^{34}S$ value (-5.5‰) for the sample EKS-2, the $\delta^{34}S$ ratios for the samples range between +7.7 and +25.2‰. The fact that the $\delta^{34}S$ values vary within a narrow range independent of their sulfate contents may indicate that the waters probably have a similar sulfur source.

In natural environments, $\delta^{34}S$ ratios have a wide range from -50 to +50‰ due to the various oxidation states of sulfur (-2 to +6) (Krouse & Mayer 2000; Izbicki *et al.* 2005). The source of sulfate in thermal waters is highly variable. It could be derived from dissolution of sulfate minerals (e.g., gypsum and anhydrate), oxidation of sulfides (e.g., pyrite) and biological activity. $SO_4$ in modern seawater has a uniform $\delta^{34}S$ value between +20 and +21‰ (Krouse 1976; Rees *et al.* 1978). The $\delta^{34}S$ ratio of $SO_4$ in marine sediments in the geological past varied from +10 to +35‰ depending on the time of deposition (Krouse 1980; Clark & Fritz 1997). Negative $\delta^{34}S$ values are related to diagenetic environments which are characterized by reduced sulfur compounds. The $\delta^{34}S$ ratio of sulfate from oxidation of juvenile sulfur is generally between -5 and +5‰ (Clark & Fritz 1997).

As Table 6 shows, $\delta^{34}S$ values for the Balıkesir waters are consistent with those of ancient marine sulfate deposits. However, since there is no sulfate deposit of marine origin in the Balıkesir region, marine deposits cannot be the source of sulfate in these waters. Indeed, nonmarine Neogene evaporate deposits (e.g., borate and gypsum) occur widely in northwestern Anatolia including most parts of the Balıkesir region (Helvacı *et al.* 1993; Palmer & Helvacı 1997). The $\delta^{34}S$ range of nonmarine evaporates is between -15 and +10‰ (Clark & Fritz 1997) which may correspond to sulfur isotope ratios of some thermal waters in the region (e.g., Gönen, Manyas, Pamukçu, Edremit waters).

In a recent study of sulfur isotope ratios of marine and nonmarine evaporites in Anatolia (including the Balıkesir region), Palmer *et al.* (2004) state that high $\delta^{34}S$ values for the sulfate minerals are due to isotope fractionation during microbially mediated reduction of $SO_4^{-2}$ to $S^{-2}$ bearing species and that marine and nonmarine evaporites contain similar $\delta^{34}S$ values. It is believed that sulfate in other geothermal waters in the region (e.g., Manyas, Bigadiç, Sındırgı, Balya and Susurluk areas) has undergone sulfate reduction which
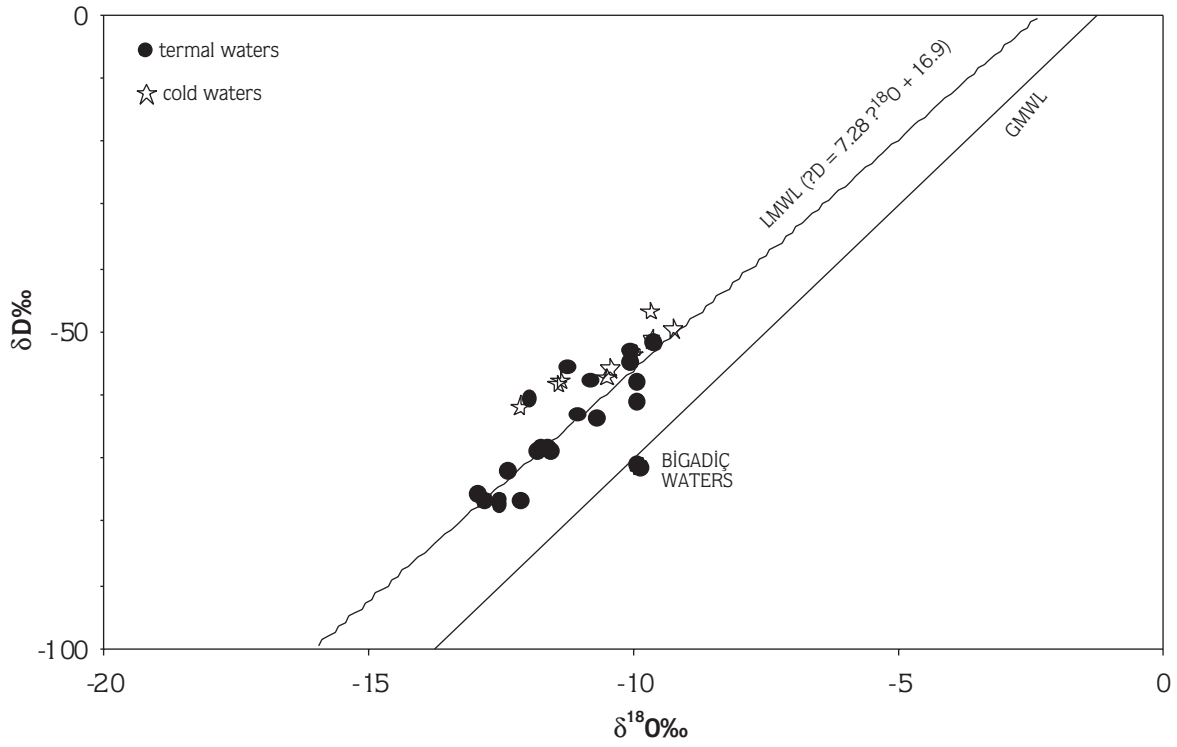
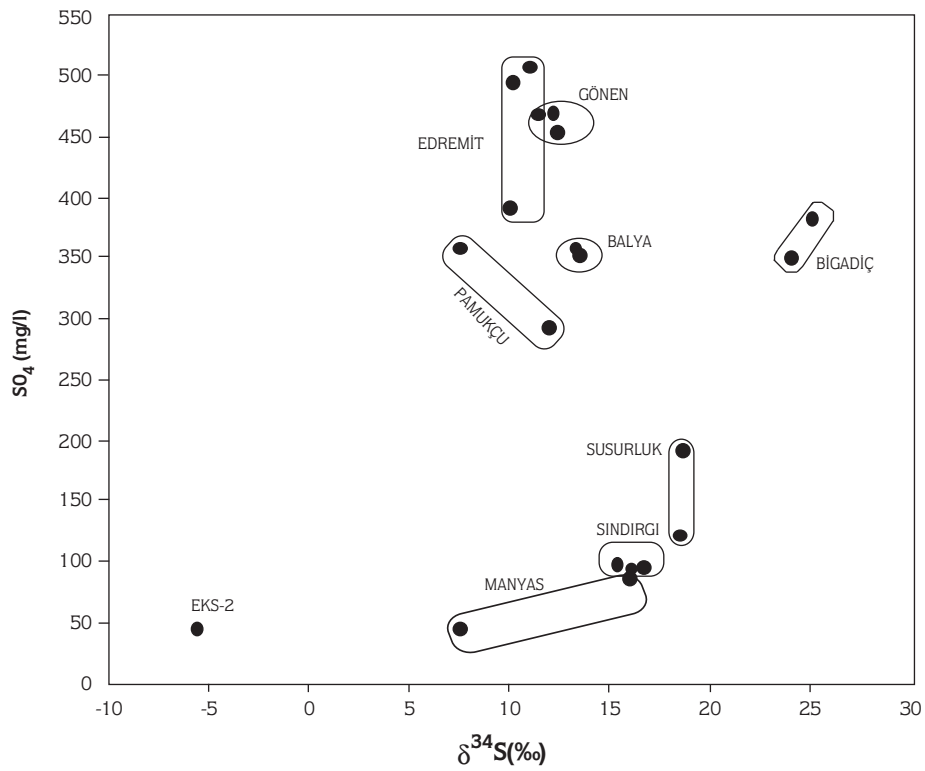Figure 8. $\delta^{18}O$-$\delta D$ diagram for the Balıkesir waters.



Figure 9. $SO_4$-$\delta^{34}S$ diagram for the Balıkesir thermal waters.

has resulted in a slight enrichment of the heavy sulfur isotope in the residual $SO_4$ pool.

The low $\delta^{34}S$ ratio (-5.5‰) and low pH (4.16) of sample EKS-2 may be indicative of sulfide oxidation. A travertine sample (SHS-1) in the vicinity of the thermal waters in the Sındırgı area has a $\delta^{34}S$ ratio of 14.2‰ which is very similar to the sulfur isotope ratios of spring waters (15.5 to 17.0‰) (Table 6). This suggests that the sulfur isotope ratios in the Sındırgı geothermal area have not significantly changed during the precipitation process.

The major sources of carbon contributing to DIC in the waters are $CO_2$ derived from the decay of organic matter in soils and from the dissolution of carbonate, while in general the contribution of atmospheric $CO_2$ is negligibly small. Soil limestone of marine origin and biogenic soil $CO_2$ produces a $\delta^{13}C$ for the dissolved carbonate of about -12‰. Additional biogenic $CO_2$ at pH values below 7.5 may reduce the $\delta^{13}C$ of DIC to more negative values (-14 ± 2‰). Another source is the acid (atmospheric $CO_2$) weathering of silicate rocks, with a $\delta^{13}C$ value nearly equal to that of the atmospheric $CO_2$ (-6 to -7‰).

The isotopic ratios in dissolved inorganic carbon (DIC) in the Balıkesir thermal waters range from -17.7 to +0.7‰ (Table 6). The $\delta^{13}C$ values of total dissolved inorganic carbon are plotted versus alkalinity (expressed as $HCO_3$) in Figure 10. As anticipated, there is an approximate trend of increasing alkalinity with increasing $\delta^{13}C$ values.

It is likely that the isotope ratios for inorganic carbon in the Gönen, Susurluk, Bigadiç, Sındırgı and one of the Manyas waters (-4.8 to +0.7 per mil) closely resemble those of marine limestones which are represented by $\delta^{13}C$ values of about -3 to +3‰ (Clark & Fritz 1997). Carbon isotopic ratios in travertines and Mesozoic marine limestones are also shown in Table 6. Carbon isotope ratios in limestones sampled from the Manyas, Pamukçu and Edremit areas range from -3.40 to +2.59‰ and from -2.97 to +0.07‰ in travertine samples from the Bigadiç and Sındırgı areas (Figure 11). The relatively high discharge and calculated reservoir temperatures, and perhaps higher $CO_2$ partial pressures of the Bigadiç, Sındırgı, Gönen and Susurluk thermal waters, might have promoted carbonate dissolution and thus provided these
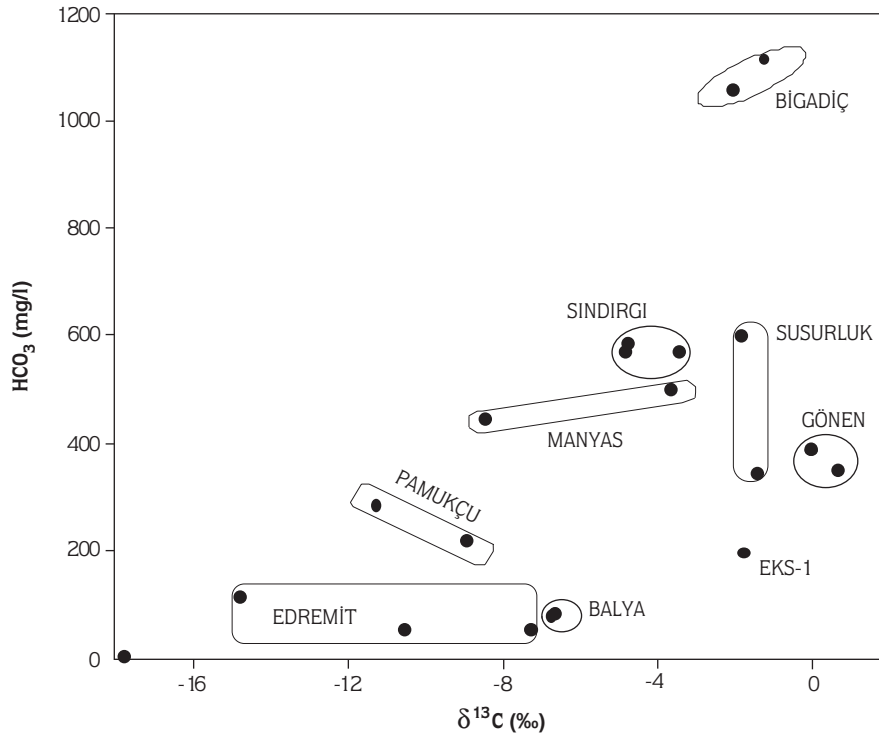


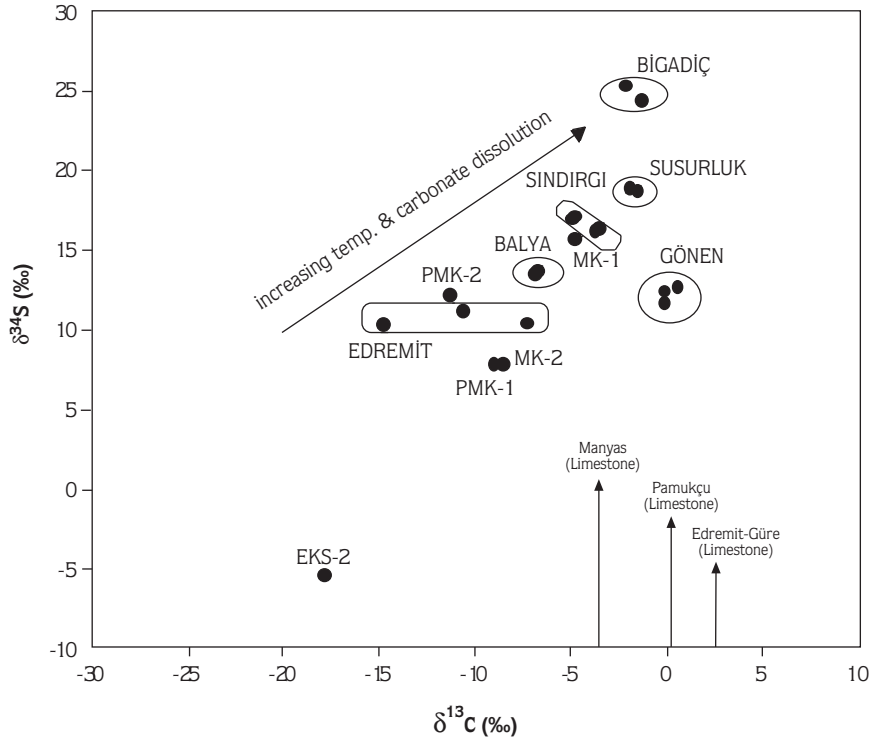Figure 10. $HCO_3$-$\delta^{13}C$ diagram for the Balıkesir thermal waters.

Figure 11.    $\delta^{13}C$ -$\delta^{34}S$ diagram for the Balıkesir thermal waters.

waters with carbon isotope ratios similar to those in marine limestones. Similar $\delta^{13}C$ values for limestones and thermal waters may also be due to very little fractionation during the carbonate dissolution. Carbon in low-alkalinity and low-temperature waters (e.g., Balya, Pamukçu, Edremit waters) could also be derived from dissolution of Mesozoic carbonate rocks that comprise the basement in most parts of the Balıkesir region. However, any organic source of carbon would mask the relationship between $\delta^{13}C$ and carbonate dissolution. Considering their lower alkalinity, temperature and TDS values, it is most likely that carbon in these waters has its origin in an organic pool.

Yalçın (1997) studied the stable isotope ratios and geochemistry of the Gönen and Ekşidere thermal waters. Tritium ($^3H$) values for thermal waters at Gönen and Ekşidere were reported as <0.7 and <1.1 TU, respectively. In addition, on the basis of $^{14}C$ isotopic measurements, the uncorrected age of the Gönen thermal water was found to be 23,000 years. All these data may indicate that the Gönen waters have a deep circulation and a sufficient residence time and temperature for the water-rock interaction.

## Conclusions

The Balıkesir thermal waters in northwestern Anatolia comprise one of the high-temperature geothermal provinces in Turkey. Neogene tectonism and volcanism are the dominant agents producing the numerous geothermal fields not only in Balıkesir but also throughout Turkey. Thermal fluids in the Balıkesir region are of two distinct water types. High-temperature waters are enriched in $Na_2SO_4$-$NaHCO_3$ while warmer waters are dominated by $CaHCO_3$. With the exception of Gönen area, cold waters of other areas are exclusively $CaHCO_3$-rich.

Among the trace elements, lithophile elements have the highest concentrations in thermal waters. The concentrations of B, Sr and Li are as high as 11.5, 3.0 and 1.6 mg/l, respectively. Rb, Li and Cs with calculated correlation coefficients of up to 0.918 are strongly correlated between themselves. Alkaline earth metal analysis of waters and travertine deposits at the water sampling sites indicate that Mg and Ba tend to be enriched in the liquid phase. On the contrary, strontium ratios both in water and travertine samples were observed unchanged. Li/Cs and B/Cl ratios in water and

carbonates are nearly identical and imply a simple rock leaching process.

On the basis of mineral equilibrium calculations performed at the discharge temperatures of the thermal waters, carbonate and silica minerals show equilibrium saturation. Although most of the samples are sulfate-enriched, all waters were undersaturated with respect to gypsum and anhydrite and this may indicate that the $SO_4$ concentration of the waters is controlled by a steady state dissolution process. Chemical geothermometers yield inconsistent estimates for the reservoir temperatures. However, temperatures computed from the K-Mg together with one of the silica geothermometers (quartz or chalcedony) give more realistic results. With a calculated maximum reservoir temperature of about 200 °C, waters of the Bigadiç area have the highest reservoir temperature in the Balıkesir region.

Using the ratios of various stable isotopes, the sources of the waters and some of their dissolved constituents have been investigated. The $\delta^{18}O$-$\delta D$ ratios of the waters indicate a meteoric origin as they plot on the Local Meteoric Water Line (LMWL) which is very similar to the Meteoric Water Line of the Marmara region. Sulfate in thermal waters has a $\delta^{34}S$ composition varying between -5.5 to +25.2‰. Sulfur in some of the waters (e.g., Gönen, Manyas, Pamukçu, Edremit waters) might be derived from dissolution of nonmarine evaporates. On the other hand, high $\delta^{34}S$ values for some samples (e.g., Manyas, Bigadiç, Sındırgı, Balya and Susurluk waters) are indicative of sulfate reduction. The isotopic ratios for dissolved inorganic carbon (DIC) in the thermal waters vary from -17.7 to +0.7‰. The $\delta^{13}C$ isotope ratios for inorganic carbon in the Gönen, Susurluk, Bigadiç, Sındırgı and one of the Manyas waters (-4.8 to +0.7 per mil) correspond to those in marine limestones that are characterized with values of about -3 to +3‰. This is also supported by the carbon isotopic ratios in marine carbonates (-3.40 to +2.59‰) in the Balıkesir region. Carbon in other waters (e.g., Balya, Pamukçu, Edremit areas) could also be derived from the dissolution of Mesozoic carbonate rocks. However, any organic source of carbon in these waters might be masking the relation between $\delta^{13}C$ and carbonate dissolution.

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