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Geochemical and Isotopic Characteristics of the Balıkesir Thermal Waters, Turkey

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ABSTRACT

The Balıkesir geothermal waters in northwestern Turkey are represented by discharge temperatures in the range of 32-99ºC and TDS contents between 327 and 2578 mg/l. The waters in the region are of Na-SO_4, Na-HCO_3 and Ca-HCO_3 type character. It was determined that the solubility of silica in most of waters is controlled by the chalcedony phase. Equilibrium states of the Balıkesir thermal waters studied by means of the Na-K-Mg-Ca diagram, mineral saturation calculations and activity diagrams approximate a reservoir temperature of about 120ºC. Most waters are found to be equilibrated with calcite, chalcedony±quartz and muscovite at predicted temperature ranges similar to those calculated from the chemical geothermometers. $\delta^{18}O$-δD compositions clearly indicate a meteoric origin for these waters. $\delta^{34}S$ contents of sulfate in thermal waters ranging from -5.5 to +25.2‰ correspond to nonmarine evaporates while sulfur in some others is derived from the sulfate reduction process. $\delta^{13}C$ composition of dissolved inorganic carbonate in waters is between -17.7 and +0.7‰. Carbon in high-temperature waters is thought to have originated from dissolution of marine carbonates. On the contrary, carbon in low-temperature waters is derived from an organic source.

1. INTRODUCTION

Turkey, situated on a tectonically and magmatically active part of the eastern Mediterranean region, is represented by extensive geothermal activity which is noticeable with numerous geothermal areas throughout the country (Mutlu and Güleç, 1998). The Balıkesir region in northwestern Anatolia is one of the promising geothermal provinces in Turkey (Figure 1). Thermal waters in this region with discharge rates ranging from 1.5 to 75 l/sec and temperatures up to 98ºC are used for greenhouse, house heating and therapeutic purposes. In the region, application of central heating was initiated in the Gönen area in 1984 and has been expanded to include the Edremit and Bigadiç areas (Mutlu, 2007).

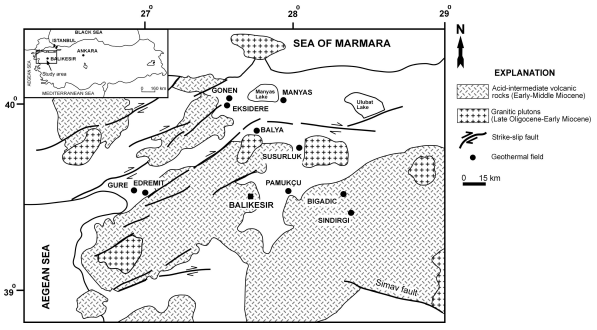

Figure 1: Geological map of the Balıkesir region showing studied geothermal areas (simplified from Mutlu, 2007).

In this study geochemical characteristics of the Balıkesir thermal waters are investigated on the basis of various water-rock interaction models and the equilibrium states of geothermal minerals and reservoir temperatures of thermal waters are examined. Moreover, the source of water and its dissolved constituents are discussed.

2. WATER CHEMISTRY

A total of 21 thermal 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. Waters of the Gönen, Manyas, Pamukçu, Bigadiç and Edremit areas are collected from wells while those of the Ekşidere, Sındırgı, Balya and Susurluk fields are sampled from hot springs.

Results of chemical analyses illustrated in the Langelier and Ludwig (1942) diagram indicate that waters from the Gönen, Pamukçu, Edremit and Balya areas are Na-SO_4 type waters (Figure 2).

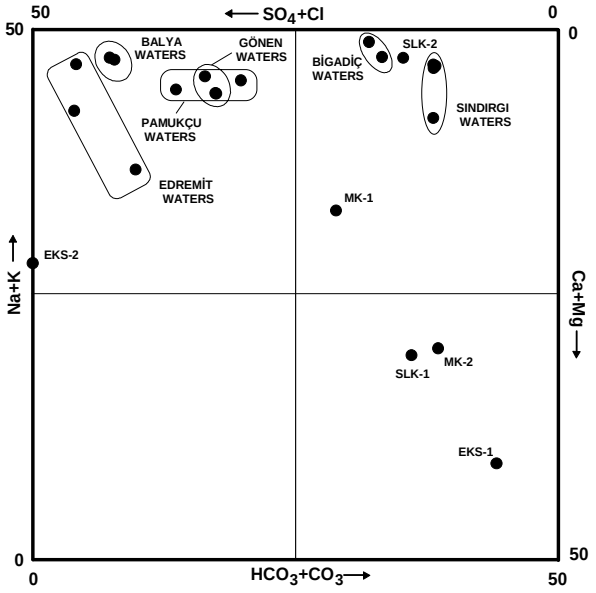

Figure 2: Langelier-Ludwig diagram for the Balıkesir thermal waters.

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 with Na-Ca-HCO_3 type waters. Low chloride concentrations in hot waters may indicate that water circulation in most of geothermal areas is shallow. Surprisingly, cold waters from Ekşidere (EKS-2 and EKS-3) in the Gönen area also yield SO_4-enriched trends. At first glance, the SO_4-rich nature of waters may be attributed to steam-heated process (e.g. oxidation of H_2S), however, since pH values of most of the samples are well above 7, this may not to be the case. Alternatively, dissolution of Neogene

evaporates (e.g., borate and gypsum) which widely occur in the northwest Turkey is probably the main source of sulfate in the waters (Palmer et al., 2004).

3. MINERAL EQUILIBRIUM CALCULATIONS

Equilibrium states of common hydrothermal minerals which are likely to be precipitated in the thermal waters of Balıkesir region were investigated on the saturation diagram (Figure 3). The WATSPEC program (Wigley, 1977) was used to compute the saturation index (SI) of various carbonate, sulfate, silica and silicate minerals at discharge temperatures of waters. Results yield that most 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 equilibrated with gypsum and anhydrite. This may imply that SO_4 concentration in waters is controlled by steady state dissolution process (Grasby et al., 2000).

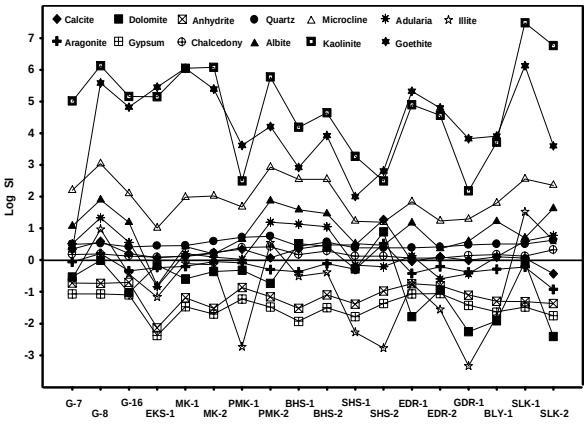

Figure 3: Mineral equilibrium diagram for the Balıkesir thermal waters.

Microcline, albite and partly adularia show over saturation trends, but the degree of saturation is always higher for the former. Quartz and chalcedony are also supersaturated in all waters. Saturation indices computed for goethite and kaolinite are the highest among the minerals of interest. Illite displays strong under saturation behavior except for the Susurluk waters (Figure 3**).**

4. GEOTHERMOMETRY APPLICATIONS

In this section, reservoir temperatures of Balıkesir thermal waters are estimated with various geochemical methods including chemical geothermometers and mineral saturation calculations and, the results obtained from these techniques are discussed.

4.1 Chemical Geothermometers

In order to estimate reservoir temperatures of the Balıkesir thermal waters, various chemical geothermometers were used. In Figure 4, silica contents of waters are plotted vs. their discharge temperatures. The trend between these two parameters shows a broad positive correlation (R^2=0.811). Also displayed in this figure is the range of quartz and chalcedony geothermometers. In general, reservoir temperatures computed from the quartz geothermometer (Arnórsson, 1985) are about 20-30ºC higher than those of chalcedony geothermometer (Fournier and Potter, 1982). Since chalcedony, rather than quartz, controls the silica solubility at temperatures less than 180ºC (Fournier, 1991), it seems that chalcedony geothermometer attaining a maximum temperature of around 120ºC better reflects the reservoir temperatures for the Balıkesir region.

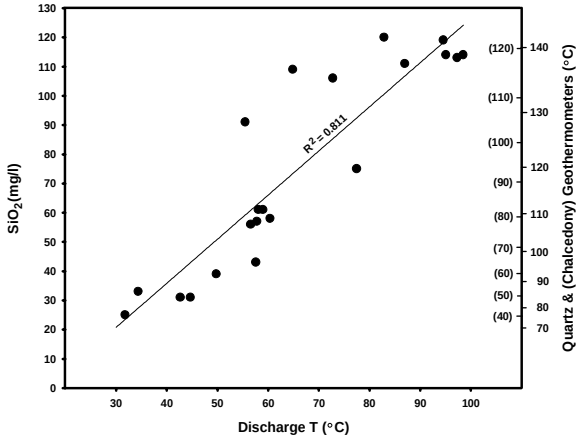

Figure 4: Silica-temperature relations for the Balıkesir thermal waters.

The reservoir temperatures computed from the cation geothermometers for each sample are generally greater than those of silica geothermometers. Na-K geothermometer of Tonani (1980) and K-Mg geothermometer of Giggenbach (1988) yield temperature ranges of about 50-260ºC and 30-120ºC, respectively. Because Na/K ratios of waters are more sensible to changes in temperature compared to K/Mg ratios (Giggenbach, 1988), the temperature range obtained from the Na-K geothermometer is significantly wider than that from the K-Mg geothermometer (Figure 5a and b).

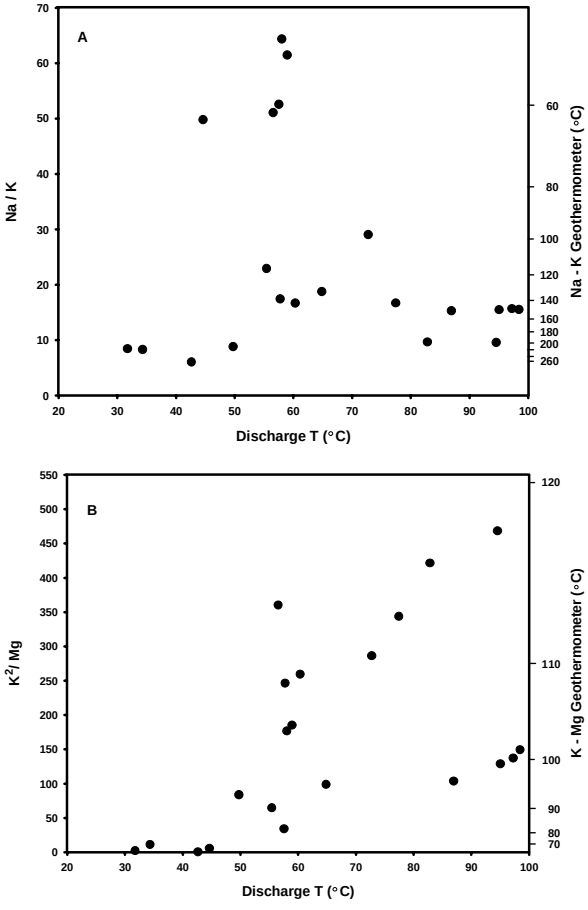

Figure 5: Cation temperatures for the Balıkesir thermal waters: A) Na-K and B) K-Mg geothermometers.

Given that correlation between K-Mg and chalcedony geothermometers (R^2=0.494) is much greater than that between Na-K and chalcedony geothermometers (R^2=0.005), K-Mg geothermometer gives more suitable reservoir temperatures (maximum 118ºC) for the region.

4.2 Na-K-Mg-Ca Diagram

In Figure 6, 10Mg/(10Mg+Ca) vs. 10K/(10K+Na) ratios (Giggenbach, 1988) of the Balıkesir thermal waters are plotted. The trend of samples does not suggest any equilibrium between the reservoir rock and thermal waters. The diagram in Figure 6 also implies that the solutes in the Balıkesir waters are not derived from the dissolution of average crustal rock or they have gained their TDS by simple rock leaching or mixing. Given that the range of 10K/(10K+Na) ratio (0.16 to 0.62) of samples is less than that of 10Mg/(10Mg+Ca) (0.21 to 0.93) suggests that K/Na ratios of the waters are not greatly affected by the precipitation-dissolution processes. The Mg/Ca ratios of the waters with a rather wide range imply mixing or precipitation-dissolution processes of Ca- and Mg-bearing minerals (e.g., carbonates). Although Balıkesir waters do not achieve a full equilibrium, if a trend through the samples is extended to the full equilibrium line (R^2=0.450), it intersects this line at a temperature of about 120ºC (Figure 5) agreeing with temperature estimates from the chemical geothermometers (chalcedony and K-Mg) (Figures 4 and 5b).

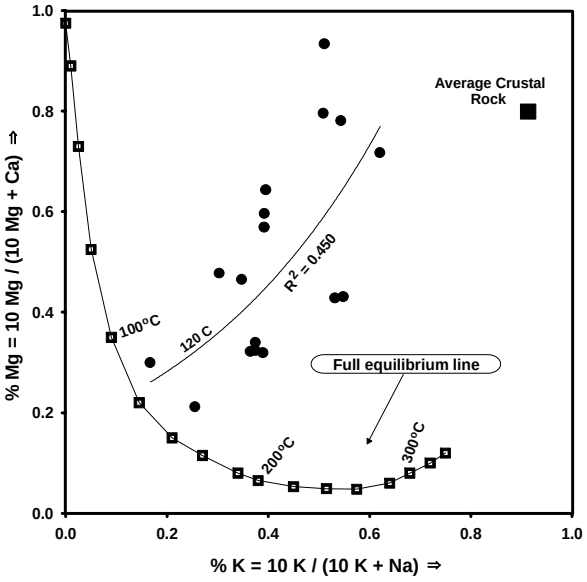

Figure 6: 10Mg/(10Mg+Ca) vs. 10K/(10K+Na) plot of Giggenbach (1988).

4.3 Mineral Saturation

In this approach, the saturation behavior of water compositions is examined at different temperatures with respect to various minerals which are likely to equilibrate with the water of interest. If a group of minerals is close to equilibrium at a particular temperature, it can be said that the water is equilibrated with these minerals and the temperature resembles the reservoir temperature. However, because this technique of temperature estimation is principally based on the state of saturation with respect to pure end-members in solid solution minerals, the results obtained cannot be considered as more than an approximation. Furthermore, mixed waters and non-equilibrated waters, such as shallow or immature waters, show no equilibrium saturation with hydrothermal minerals at a given temperature.

The WATSPEC program (Wigley, 1977) was used to calculate saturation indices (SI) of 15 most common geothermal minerals (adularia, albite, analcime, aragonite, calcite, chalcedony, dolomite, goethite, kaolinite, laumontite, microcline, K-mica, quartz, Ca-montmorillonite and Na-montmorillonite). It is important to note that not all the minerals but those shifting closer to the equilibrium line (log SI=0) are plotted in the diagrams in Figure 7. The measured temperatures and temperatures computed from the chalcedony and K-Mg geothermometers are also shown in the figures for comparison. Possible reservoir temperatures of the selected thermal waters of the Balıkesir region, estimated with the mineral equilibrium calculations, are presented in Figure 7a and b (SHS-1: ~120ºC and SLK-2: ~125ºC). These diagrams imply that the reservoir temperatures determined from the equilibrium calculations agree well with the temperature estimations of the chemical geothermometers (Figure 4 and 5b) and K-Na-Mg-Ca diagram (Figure 6).

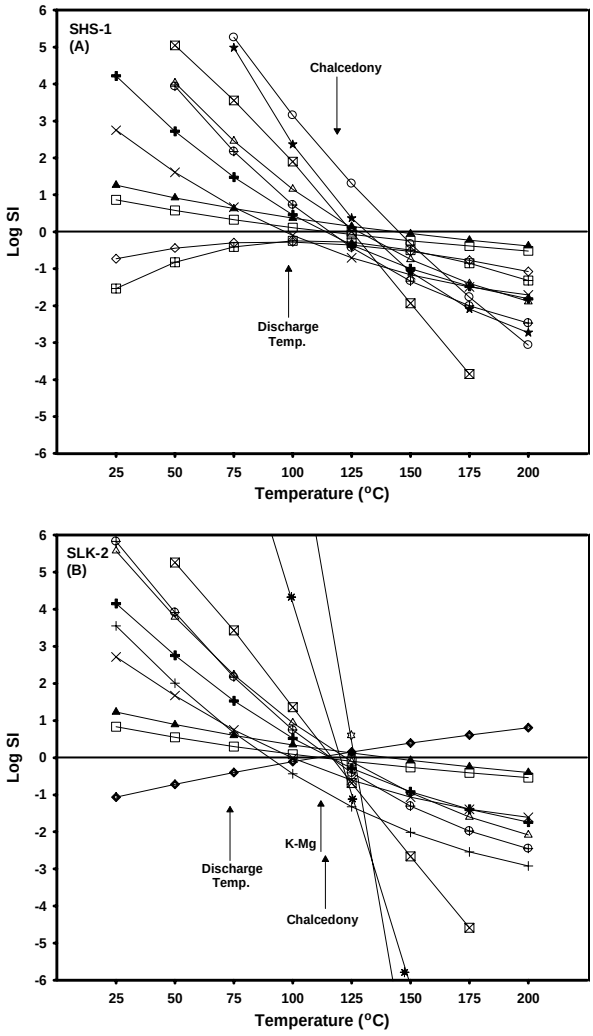

Figure 7: Mineral equilibrium diagrams for A) SHS-1 and B) SLK-2 samples.

5. STABLE ISOTOPES

5.1 δ^{18}O-δD Compositions

δ^{18}O content of thermal waters ranges from -12.91 to -9.61 ‰. Deuterium values for thermal and cold waters are -77.39 to -52.10 and -61.79 to -46.75‰, respectively. In the δ^{18}O-δD 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 of the Marmara Meteoric Water Line ($\delta D = 7.30\ \delta^{18}O + 16.0$) (Yalçın, 1997). Unusual position of the Bigadiç thermal waters with an ^{18}O shift about 2.5‰ units from the LMWL is explained with water-rock interaction process which resulted in an increase of $\delta^{18}O$ content of these waters. This is confirmed with relatively high TDS contents and temperatures of these waters. In fact, some other thermal waters (e.g. G-7, G-8, G-16, PMK-1, PMK-2, MK-1) displaying slight ^{18}O shifts might have also undergone oxygen exchange reactions (Figure 8). In each geothermal area, $\delta^{18}O$-δD compositions 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. This may indicate that thermal waters are recharged from a different source or a higher elevation.

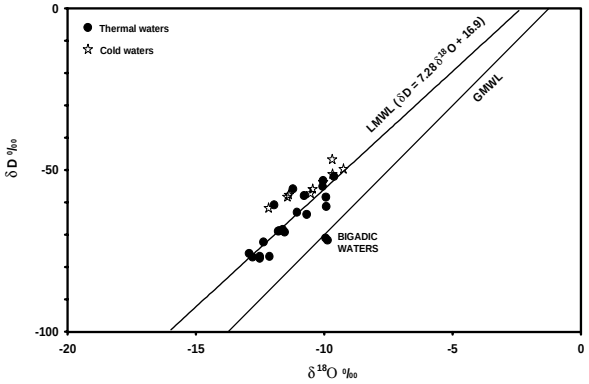

Figure 8: $\delta^{18}O$-δD diagram for the Balıkesir waters.

5.2 $\delta^{34}S$ and $\delta^{13}C$ Compositions

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

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

In a recent study on sulfur isotope contents of marine and nonmarine evaporites in Anatolia (including the Balıkesir region), Palmer et al. (2004) state that high $\delta^{34}S$ values of 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 process which resulted in a slight enrichment of heavy sulfur isotope in the residual SO_4 pool.

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

Isotopic composition of dissolved inorganic carbon (DIC) in the Balıkesir thermal waters ranges from -17.7 to +0.7‰. It is likely that isotope content of inorganic carbon in the Gönen, Susurluk, Bigadiç, Sındırgı and one of the Manyas waters (-4.8 to +0.7 per mil) closely resembles marine limestones which are represented with $\delta^{13}C$ values of about -3 to +3‰ (Clark and Fritz, 1997). Carbon isotopic compositions of travertines and Mesozoic marine limestones are also given in Table 6. Carbon isotope contents of limestones sampled from the Manyas, Pamukçu and Edremit areas range from -3.40 to +2.59‰ and from -2.97 to +0.07‰ for travertine samples from the Bigadiç and Sındırgı areas (Figure 9). The relatively high discharge and calculated reservoir temperatures of the Bigadiç, Sındırgı, Gönen and Susurluk thermal waters might have promoted carbonate dissolution process and thus provided these waters to have carbon isotope compositions similar to marine limestones. Similar $\delta^{13}C$ values of limestones and thermal waters are also 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 the Mesozoic carbonate rocks that comprise the basement at most part of the Balıkesir region. However, any organic source of carbon would be masking the relation between $\delta^{13}C$ and carbonate dissolution. Considering their lower alkalinity, temperature and TDS values, it is most likely that carbon in these waters is originated from an organic pool.

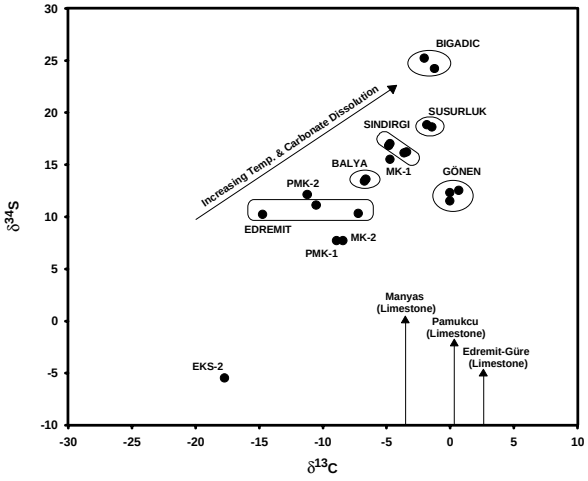

Figure 9: $\delta^{13}C$-$\delta^{34}S$ diagram for the Balıkesir waters.

6. CONCLUSIONS

Thermal waters of the Balıkesir region are generally enriched in $Na\text{-}SO_4$ and $Na\text{-}Ca\text{-}HCO_3$.

Among the chemical geothermometers applied to the region, chalcedony and K-Mg geothermometers yield reservoir temperatures agreeing well with each other and not exceeding 125ºC. Another geochemical technique, the Na-K-Mg-Ca diagram of Giggenbach (1988), gives a reservoir temperature of about 120ºC which is within the temperature range estimated from the chemical geothermometers.

Equilibrium temperature ranges obtained from the saturation index vs. temperature diagrams constructed for selected

waters of the Balıkesir geothermal region generally fit the reservoir temperatures computed from the chemical geothermometers (chalcedony, K-Mg and Na-K-Ca-Mg).

The $\delta^{18}O$-δD compositions of waters indicate a meteoric origin 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 changing 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 the nonmarine evaporates. On the other hand, high $\delta^{34}S$ values of some samples (e.g. Manyas, Bigadiç, Sındırgı, Balya and Susurluk waters) are indicative of sulfate reduction process.

Isotopic composition of dissolved inorganic carbon (DIC) in the thermal waters changes from -17.7 to +0.7‰. Isotope content of inorganic carbon in the Gönen, Susurluk, Bigadiç, Sındırgı and one of the Manyas waters (-4.8 to +0.7 per mil) corresponds to marine limestones that are characterized with $\delta^{13}C$ values of about -3 to +3‰. This is also supported with carbon isotopic composition of 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 dissolution of the Mesozoic carbonate rocks. However, any organic source of carbon in these waters might be hiding the relation between $\delta^{13}C$ and carbonate dissolution.

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