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Hydrogeochemical similarities and differences between high temperature geothermal systems with similar geologic settings in the Büyük Menderes and Gediz Grabens of Turkey

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ABSTRACT

The Büyük Menderes Graben (BMG) and the Gediz Graben (GG) are two major graben systems and they have important medium-high temperature geothermal systems, with suitable reservoir temperatures (e.g. 170–276 °C) for electricity production such as Kızıldere (Denizli city), Germencik, Salavatlı, Pamukören (Aydın city) in the BMG and Alaşehir (Manisa city) in the GG.

These high temperature geothermal systems are located in a highly fractured zone because of the Aegean Extensional Zone effect. Although the main reservoir rocks retain similar compositions for each graben system, the geothermal fluids chemistry characterization can vary along the BMG and GG as a result of differing variables such as a paleo sea effect, the concentration of non-condensable gases (NCG), as well as mineral effects. The water chemistry results and $\delta^{18}O$-δD isotope values show remarkable differences within the Germencik and Kızıldere systems along the BMG, while the main reservoir rocks are of a similar composition. Chemical, isotope compositions and pH values of thermal waters in Alaşehir differ from those in the BMG geothermal systems.

Results for $\delta^{13}C$ isotopes indicate that the origin of the large amounts of CO_2 is the marble in metamorphic rocks in the reservoirs in both graben systems. $\delta^{34}S$, $\delta^{34}S$- SO_4 and $\delta^{18}O$-SO_4 values indicate that the origin of SO_4 indicates gypsum and also bacteria effect in the eastern part of the BMG, while different mechanisms such as; oxidation of sulfur, pH, temperature and possible buffer mineral effects on H_2S dissolution to the west of the BMG and GG display a greater impact.

1. Introduction

Turkey has a remarkable geothermal capacity evidenced in over 234 identified geothermal sites (MTA, 2018). Variable tectonic zones and the young volcanism have led to the manifestation of geothermal systems comprising differing characteristics across Anatolia. The country has been strongly affected by the Alpine-Himalayan orogenic belt that is emerging at the convergence of the Eurasia and African Plates and concludes with the crustal thickening resulting from tectonic compression in Eastern Anatolia.

The geodynamics of Western Anatolia differ from other parts of Anatolia, illustrated by the extensional tectonics, crustal thinning and the formation of large graben systems have been formed in that part (Doglioni et al., 2002; Şengör and Yılmaz, 1981). These graben structures provide optimum conditions for shallow and expansive heat sources across Western Anatolia (İlkışık, 1995). The Cenozoic volcanism can be seen from the North to the South (Doglioni et al., 2002; Ercan, 1979; Innocenti et al., 2005) and the youngest Quaternary basalts have been observed in Kula (Manisa city) in Western Anatolia (Tokçaer et al., 2005). Resulting from this tectonic regime, medium - high temperature geothermal systems have developed in the Western Anatolia Extension (Mutlu and Gülçe, 1998). Curie point temperature-depth studies indicate that the depth of the heat source is approximately seven kilometers in Western Anatolia; it reaches 30 km in Eastern Anatolia and 25 km in Central Anatolia (Aydın et al., 2005). These results look comparable to reservoir temperatures found in Western Anatolia graben systems (Koçak, 2012).

The main extensional zones are the Büyük Menderes Graben (BMG), the Gediz Graben (GG) (Fig. 1) and The Simav Graben, all demonstrating optimal geothermal potential in Western Anatolia.

The BMG, trending East-West for nearly 200 km, including the Menderes Graben, is one of the largest grabens in Turkey. There are

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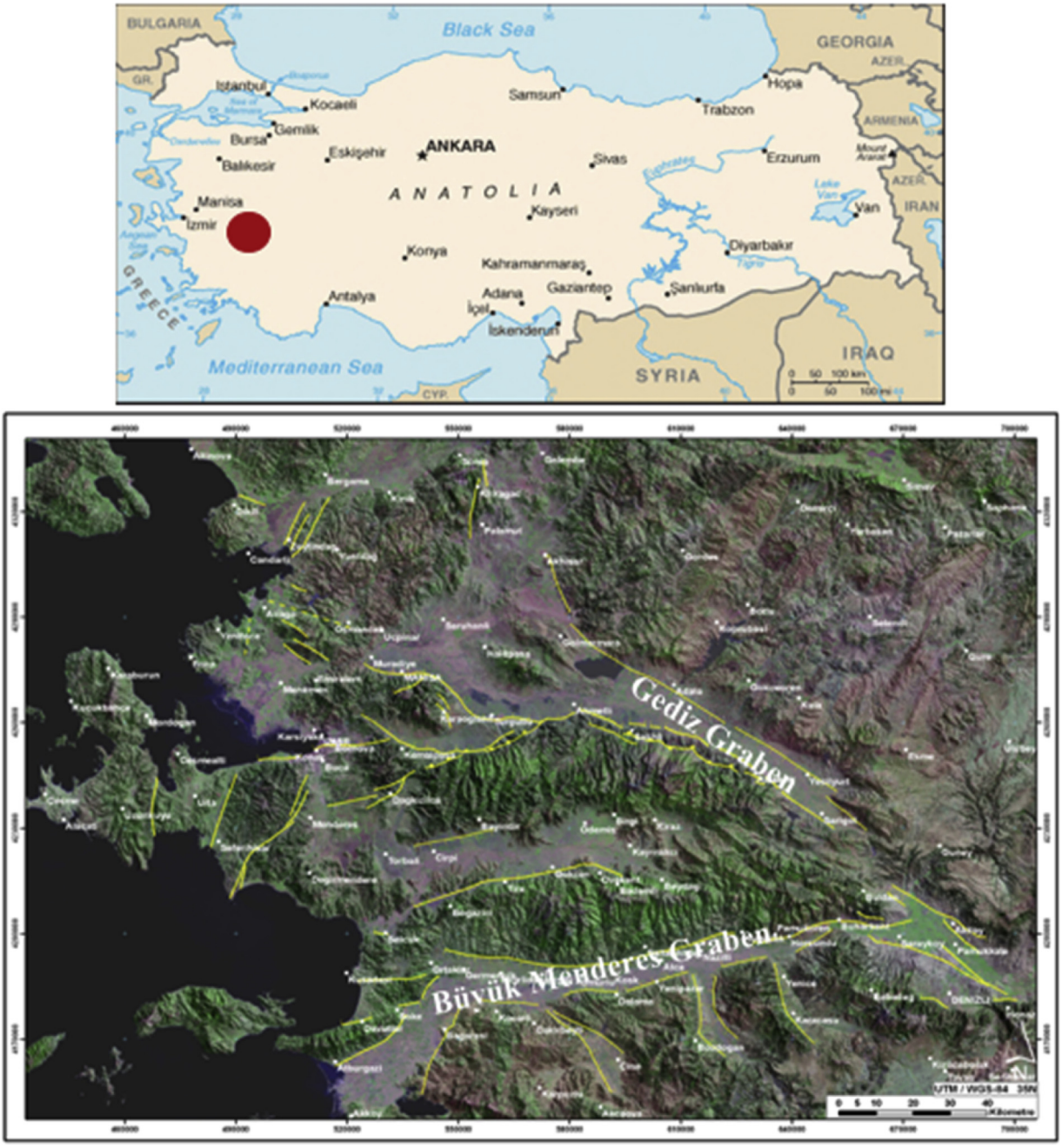

Fig. 1. The BMG and GG Systems in Western Anatolia.

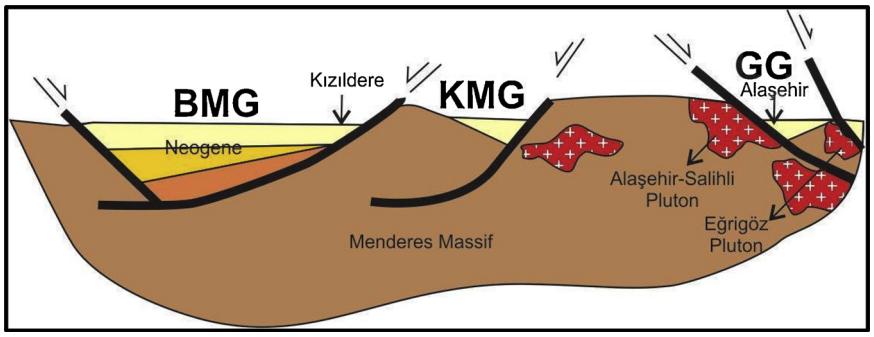

Fig. 2. Basic Conceptual Design of the Main Graben Systems in Western Anatolia (Dilek and Öner, 2009).

many geothermal manifestations from the west to the east (Şimşek, 2005). Along the BMG from west to east; the Germencik, Salavatlı, Pamukören, Kızıldere fields exhibit high temperature geothermal systems and reservoir temperatures reaching 245 °C in Kızıldere and Germencik (Haklıdır Tut and Güney, 2013; Şimşek, 2003; Fig. 2). There are a few identified low temperature geothermal systems, such as the Pamukkale, Gölemezli, Karahayıt fields (Şimşek et al., 2000; Tut, 2003) at the intersection of the BMG and the GG.

Although the BMG has been well explored by geoscientists since 1965, the geothermal capacity of the graben has only been understood since the mid-2000s, with a continued identification of new geothermal systems. For GG, the serious geothermal exploration-based studies for power production purposes began in Alaşehir in 2009. Since then, privatization of the geothermal fields was started by the Turkish government and following additional geological, geophysical and geochemical surveys, new geothermal drilling operations have commenced along the BMG (DiPippo, 2012; Haizlip Robinson and Haklıdır Tut, 2011, 2012; Haklıdır Tut et al., 2011; Kındap et al., 2010). Currently, a significant number of companies have conducted studies to establish different types of geothermal power plants along the two grabens. The high geothermal potential of the GG was realized in 2009, resulting in a few companies currently conducting power plant feasibility studies. The temperatures of water-dominated reservoirs along the graben may vary between 190–213 °C for high temperature systems such as Alaşehir Piyadeler and Kavaklı regions (Aydın et al., 2018; Haizlip et al., 2016; Bundschuh et al., 2013; Haklıdır Tut et al., 2012). Besides them, there are medium-low temperature geothermal systems such as; the Salihli, Sart, Urganlı, Kurşunlu systems whose water temperatures vary between 35° to 85 °C (Bundschuh et al., 2013; özen et al., 2012; Tarcan et al., 2005; Vengosh et al., 2002) along the graben. Along the SG, reservoir temperatures can reach 162 °C (Gemici and Tarcan, 2002) and geothermal district heating applications have been established near the graben (Köse, 2007; Palabıyık and Serpen, 2008).

In this study, the reservoir characteristics of the high temperature geothermal fields along the BMG and GG (Fig. 1) are evaluated from a hydro-geochemical perspective.

2. Geothermal energy developments in the study area

Between 1984–2018 39 geothermal power plants were installed along the BMG and GG. Most of them are located at between Denizli and Aydın (Kızıldere, Pamukören, Salavatlı, Germencik geothermal systems in this study) provinces from the east to the west edge of the BMG. The Alaşehir geothermal system is a part of the GG which is one of the high temperature systems and ones of the investigated one in this study.

The first geothermal exploration studies were initiated in the Kızıldere (Denizli) geothermal field, which is located east of the BMG in 1965 by the General Directorate of Mineral Research and Exploration (MTA) (Dam and Erentöz, 1970). With the first drillhole in 1968, called KD-1A, with a 198 °C bottom hole temperature in Kızıldere (Denizli), which takes place in the east edge of the BMG. The geochemistry studies were performed in the field (Dominco and Şamilgil, 1970). In Kızıldere, a 17.2 MWe_{gross} capacity single flash geothermal power plant (GPP) was established in 1984 and 25 wells were drilled until 2008 by the MTA (Şimşek et al., 2009). After the privatization of the geothermal field, more than 50 new geothermal wells drilled up to 3500 m. depth after the geological and geophysical surveys were conducted to build the Kızıldere-II GPP 80 MWe_{gross} capacity triple flash + binary system in 2013 and the Kızıldere-III GPP 165 MWe_{gross} capacity triple flash and binary systems in 2018 for the total power production to reach a 260 MWe_{gross} capacity in the Kızıldere geothermal field.

The Germencik (Aydın) geothermal field is located at the west edge of the BMG and geothermal studies started there in the 1980s (Şimşek, 1985), with the first geothermal well, ÖB-1, drilled at 1982, with a recorded temperature of 203 °C at depth in the field. After the privatization of the field in 2004, new wells were drilled by the company, and a 47.4 MWe_{gross} double-flash GPP was established and the capacity increased to 279_{gross} MWe with a new two double flash plant and five binary power plants in 2018.

The first drilling operation was started in the Salavatlı (Aydın) region by MTA in 1987. The reservoir temperature was measured as 167 °C in the AS-1 well (Karamanderesi and Helvacı, 2003). In 2006, with a new well, the company built a first binary type Dora-I GPP with 8.5 MWe_{gross} in the field (DiPippo, 2012). In Salavatlı region 4 binary type power plants were installed between 2010–2018 period. The geothermal power capacity increased to near 56 MWe.

The Pamukören (Aydın) geothermal field was discovered by the MTA in 2008. The reservoir temperatures were recorded as 188 °C, at 1150 m. and the geothermal power capacity reached around 114 MWe in 2018.

The Alaşehir geothermal field (Kavaklıdere-Manisa) in the GG was discovered in 2009 and subsequently geothermal exploration studies and drilling operations were performed in the region (Haklıdır Tut et al., 2013). The first geothermal power plant in the GG was installed as a 45 MWe_{gross} double flash + binary type and a few binary type GPPs were also put into use and the power capacity reached 198 MWe at the end of 2018. Exploration and capacity expanding studies have been continued for both graben systems (EMRA, 2019).

Today Turkey's installed geothermal power production capacity is around 1.8 Gwe for 2019 and it has been declared by the government that the geo-power target will be 4 GWe for 2030.

3. Methodology

Within the scope of this study, five high temperature geothermal fields, which are quite important for geothermal power production, along the BMG and GG have been selected. Based on the geological and geochemical information for deep geothermal wells in selected fields, reservoir characteristics were evaluated with a hydro-geochemical perspective. These selected wells are representative of each high temperature geothermal fields such as Kızıldere (wells number KD14, KD22, R1, R3A, KD18A, KD42), Germencik wells (OB8, OB9, OB14, OB17), Salavatlı wells (AS1, AS2), Pamukören wells (AP1, AP2, AP3), Alaşehir wells (Alkan1, Alkan2) in both graben systems and this will provide an opportunity to compare and understand the BMG and GG geothermal systems in Western Anatolia's similarities and differences. These wells depths vary from 603 to 3155 m in the BMG and 960–1500 m in the GG.

Except for the Kızıldere and Alaşehir geothermal fields, water and gas analysis results used in the present study were obtained from different researchers. The chemical analysis of Kızıldere and Alaşehir water samples was carried out by the MTA laboratory in Ankara, Turkey. The following parameters; K^+, Na^+, Ca^{2+}, Mg^{2+}, Li, boron, SiO_2 and As were analyzed by the Inductively Coupled Plasma (ICP) method. A volumetric method was used for HCO_3^- analysis. Anions such as Cl^-, SO_4^{2-}were analyzed using ion chromatography, while a titration method was used for NH_4^+.

In the Kızıldere and Alaşehir geothermal fields, water and gas samples were collected from the wells selected. There are two main reservoirs in Kızıldere field and the wells selected were in shallow and deep reservoirs. The procedure is similar to sampling the water and gas phases is similar, thus, the following statements are applicable for all high temperature geothermal fields. Sampling and field measurements performed by the authors. During the sampling period, brine, gas samples were collected by a test and sampling equipment such as; a sampling separator, a cooling condenser, a pH meter, a conductivity meter and polyethylene bottles for water sampling, Giggenbach glass bottles for steam (gas) sampling. During the gas sampling, steam condensate samples were also taken from each gas sampling period to understand sampling quality.

The sampling was carried out at certain production rates during the

sampling and it is controlled by the well-head and separator pressures during the sampling period. Brine samples were collected for chemical and δ^{18}O-δD isotope, $\delta^{13}C-CO_2$ and $\delta^{34}S$ and $\delta^{34}S$-SO_4 / δ^{18}O-SO_4 analysis with sampling separator and condenser systems. Silica samples were diluted 1/10 by distilled water and cation samples were filtered and preserved with nitric acid. Anion and cation samples were collected into 1000 ml containers and silica samples were collected into 250 ml polyethylene bottles.

δ^{18}O-D isotope samples were collected into 12 ml glass bottles, and $\delta\ ^{32}/^{34}S$ and $\delta^{34}S$-SO_4 / δ^{18}O-SO_4 isotope samples were collected into glass bottles during the sampling period (Haklıdır and Haizlip, 2012). δ^{18}O-D isotopes were analyzed by Thermo-finnigan MAT 253 model isotope ratio mass spectrometer at the National Metrology Institute isotope laboratory in the Scientific and Technological Research Council of Turkey (Kocaeli-Turkey).

Gas samples were collected from the steam discharge line of the sampling separator. The samples were collected by Giggenbach gas bottles, which were prepared with 40–80 ml 6 M NaOH solution, vacuum packed and analyzed by the National Research Council (CNR-Italy) gas laboratory in Italy. In the laboratory, gas chromatography (with thermal conductivity detector-TCD) has been used for H_2, N_2, O_2, Ar, He analysis. An acidimetric titration was used for CO_2 gas analysis. Ion chromatography was used after oxidation to SO_4 using H_2O_2 for H_2S gas analysis. $\delta^{13}C$-CO_2 analysis performed by CNR-Italy and $\delta^{34}S$ and $\delta^{34}S$-SO_4 / δ^{18}O-SO_4 analysis was carried out by the Stable Isotope Laboratories in Arizona University (USA).

4. Geological settings of the geothermal systems along BMG and Gediz Graben systems

4.1. Structural controls of geothermal systems along graben systems in Western Anatolia

Tectonic structures give evidence to the existence of extensive geothermal systems and Neogene volcanism in Western Anatolia and the Aegean Sea, which is due to the westward plate motion and the expansion of the Anatolian Plate (Fig. 2).

Geothermal systems due to tectonic activity have both good reservoir potential and fluid carrier properties. Low and medium temperature geothermal springs discharge along these graben systems such as; Ilıcabaşı (101 °C), Yılmazköy, (142 °C), Söke (26 °C) Aydın province; Pamukkale (36 °C), Karahayıt (59 °C), Gölemezli (101 °C) and Yenice (70 °C); Denizli province besides high temperature geothermal systems in Germencik, Salavatlı, Pamukören (Aydın) and Kızıldere (Denizli) (Şimşek, 2003). All these systems are directly affected by the Aegean extension zone. The greater the expansion rates of the BMG graben by the northern faults, which are affecting the graben asymmetrically, are generally decreasing rapidly towards deeper sloped listric normal faults. Directions of the traverses are E-W and ES E-W NW. In Kızıldere, faults of differing types and directions are observed (McKenzie, 1972; Şimşek, 1985; Seyitoğlu and Scott, 1992; Şimşek et al., 2009).

The BMG is predominantly influenced by the E-W and ES E-W NW directional listric faults by reason of the N-S directed drift. The northern faults, which are affecting the asymmetrical graben basin forms, generally tend to descend deeper as normal dip-slip faults. In addition, normal faults and grabens running N-S were observed in the region. N-S tectonic movement is a dominant factor in the region, although the presence of a lower level of E-W directional stress is expected (Emre and Sözbilir, 1997; Bozkurt and Oberhänslı, 2001; Yılmaz, 2017; Çırmık and Pamukçu, 2017) (Fig. 1).

The Gediz Graben has an approximate E-W and WNW-ESE trend with 140–150 km length and 10–40 km width (Yılmaz et al., 2000; Seyitoğlu et al., 2000; Bozkurt and Sözbilir, 2004). The graben structure was described by Sözbilir (2001) as four different types which are the Gediz detachment, extensional folds in the Gediz detachment, E-W to NW-SE trending high-angle normal faults and a regional unconformity between the supra detachment sequence deformed by W-NW to N-NE high-angle normal faults. Çiftçi and Bozkurt (2009) suggested that the GG is a continental expansion basin filled with Miocene-Present aged sediments and graben development occurred in two phases. In the first phase, a half graben controlled by a southern edge fault, Gediz, Alaşehir and Çaltılı Formations collapsed in this graben and in the second phase after Miocene they were relatively balanced with sedimentation and deepening together with faulting in the northern wing (Fig. 2). These intensive tectonic movements and the Salihli Granitoid provide geothermal reservoir possibilities at depth (Aydın et al., 2018) and they also suggest the heat source for the Alaşehir geothermal systems.

4.2. Reservoir geology characterization overview for the BMG and GG geothermal systems

The graben consists of Paleozoic aged Menderes Meramorphics and Pliocene aged sedimentary rocks, covered with a Quaternary aged alluvium (Şimşek et al., 2009). The geological units demonstrate continuity along the graben (Fig. 2) and it is also possible to observe coal levels in Miocene aged sedimentary rocks along the Büyük Menderes Graben (Kayseri özer and Emre, 2012). The oldest unit of the field is metamorphic rocks, which are from the basal geology forms called the Menderes Massif (Okay, 1989). The metamorphics formed by gneisses, and represented by a variety of schists, quartzite, and marble. The İğdecik Formation is recognized as a separate member of the Menderes Metamorphics due to the presence of thick marble layers and can be observed only in the Kızıldere geothermal system. The Kızılburun Formation has a dominant red color due to oxidation (iron oxide), followed by coarse basal conglomerates intercalated with sandstone, claystone and conglomerate, unconformably on the Menderes Metamorphics. The Sazak formation contains marl, claystone and limestone, and shows a gradual transition toward the bottom with the Kızılburun Formation, and at the top with the Kolankaya Formation, which consists of sandstone and marl intercalation. The Tosunlar Formation has been developed by a large strike-slip fault. Consisting of speckled red, yellowish colored conglomerate, sandstone, claystone and limestone units, this formation covers the whole geological sequence with an angular unconformity (Fig. 3; Şimşek et al., 2009). In the Quaternary period, alluvium, old alluvial terraces, talus and travertine structures have formed and been deposited over the graben.

Along the graben from the west to east part; in the Germencik, Salavatlı and Pamukören geothermal systems, the main and deep reservoir is seen to be abundantly fractured at fault levels of the Menderes Metamorphics as Paleozoic aged highly fractured rocks including quartz schist and marbles (Filiz et al., 2000; Fig. 4). The Salavatlı geothermal system is located in the middle of the BMG and the Pamukören geothermal system takes place lies between Salavatlı and Kızıldere system. The both two systems are formed in younger graben deposits beside the metamorphic rocks (Vengosh et al., 2002). During the evolution of Pamukören system, such as in the fields of Salavatlı and Germencik, a compressive tectonic is prevalent in the Pre-Miocene phase (Şimşek, 2003). The gneisses are evaluated as a good cap rock in these geothermal systems.

The Germencik geothermal system has multi-reservoirs which are not directly connected to each other, and they may be separated by different reservoir temperatures. There are two main reservoirs in Miocene sediments; fractured and consisting of sandstone. The conglomerate is defined as the first reservoir, with a deep reservoir as the second one, represented by Menderes Metamorphics. Reservoir temperatures are recorded as 203–217 °C for the first reservoir and higher than 230 °C for the second reservoir (MTA, 2005; Karakuş and Şimşek, 2013). The highest temperature is recorded as 276 °C in well OB-88 in Germencik along the BMG (Şimşek, 2015). There are more than 100 wells in the Germencik geothermal system alone. The average reservoir temperature is recorded below 200 °C in the Salavatlı and Pamukören (175–185 °C) geothermal systems (Karamanderesi and Helvacı, 2003;

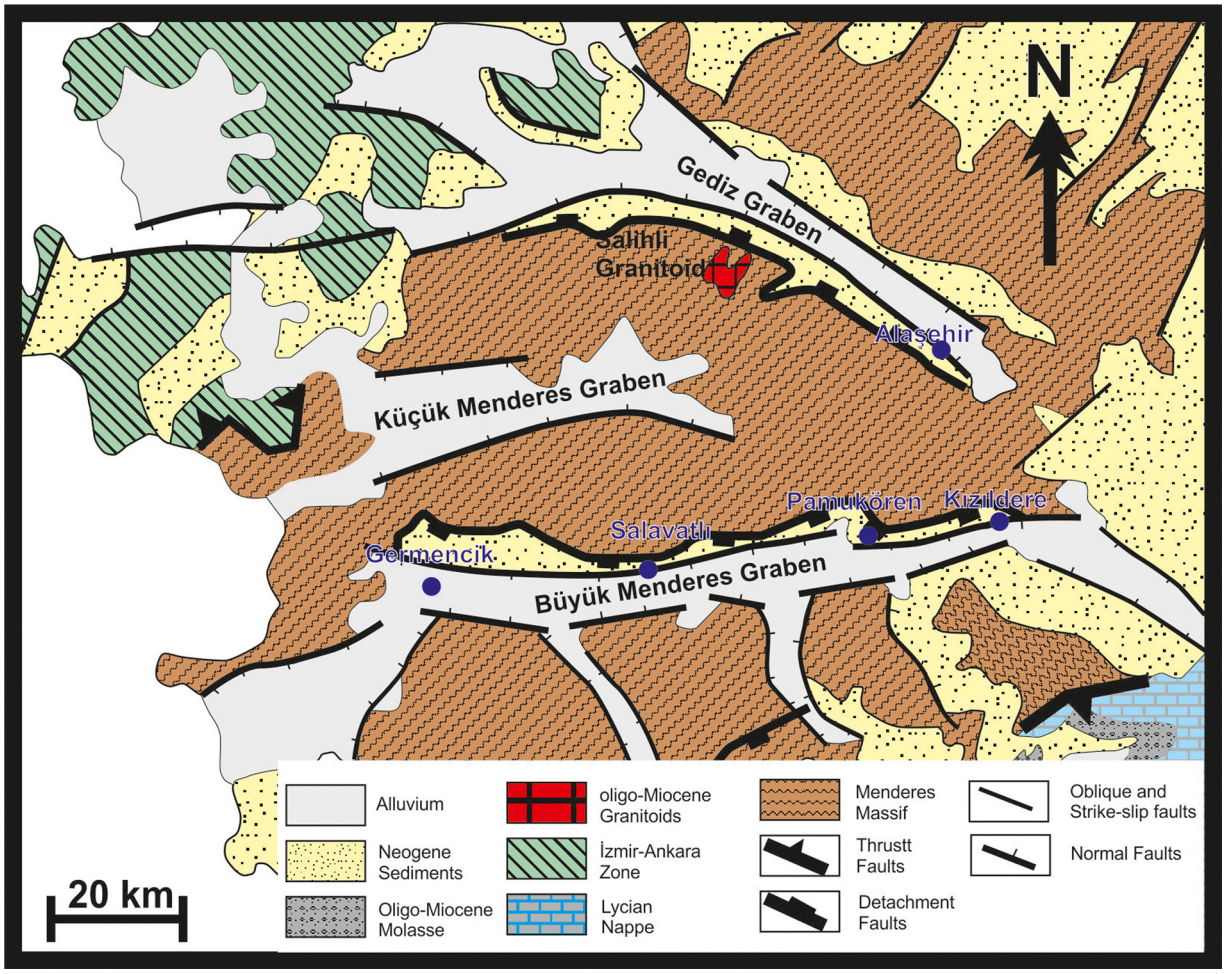

Fig. 3. The geological setting of the BMG and theGG. The study which represent high temperature geothermal systems are represented in red line (Karaoğlu and Helvacı, 2012).

Serpen and Aksoy, 2010).

The Kızıldere geothermal field is an important field in the BMG for its key location at the intersection of the Büyük Menderes and Gediz grabens. The Sazak Formation, the İğdecik Formation, and the lower layers of the Menderes Metamorphics constitute the reservoir rocks and they are identified as multi-reservoir systems with different temperatures (Şimşek, 2003). There is no direct connection between the reservoirs and they can be distinguished from each other by reservoir temperatures. The Sazak Formation, as the first reservoir rock, is intercalated with limestone and marl, which have become permeable due to tectonic moves (Şimşek, 1984; Karamanderesi and Özgüler, 1988) and uses for the limited reinjection. The İğdecik Formation is referred to as the second reservoir which made up of metamorphics, consisting of marble, mica schist, and quartzite intercalation. This formation is a more permeable structure than the first reservoir zone with a temperature of 155–170 °C (MTA, 2005). The third reservoir is characterized by the Menderes Metamorphics with deeper zones having as high a temperature as 245 °C (Şimşek, 2015). The zone consists of mica schist, quartzite, calc schist, more sericite schist, and more chlorite schist than the 2nd reservoir which has a temperature of around 200 °C (Şimşek et al., 2009). In the Kızıldere geothermal field, more than 100 geothermal wells were drilled during the capacity expanding studies. In the Kızıldere system, there are some organic material-based coal and oil deposits at 800–1300 m depth and these materials have been detected during drilling operations as oil drops on the sediments with quite good examples at Sazak formation in KD 46 well.

Some hydrothermal alteration minerals such as; chlorite, sericite, carbonate have been observed in all the geothermal systems selected along the graben. However, light colored chlorite, cubic pyrite, pyrrhotite and partial paragonite, sericite alteration minerals are observed in the deep reservoir of the Kızıldere geothermal system, which the temperature can reach to 245 °C (Uzun and Haklıdır Tut, 2012) while, chlorite, biotite, calcite, pyrite are dominant in Germencik and quartz, albite, calcite, illit, siderite, pyrite are abundantly included at reservoir level in the Salavatlı system (Karamanderesi and Helvacı, 2003).

The basement of the GG consists of Menderes Metamorphics just as the BMG. The Menderes Metamorphics include gneiss, hornblende, mica gneiss, marble, quartzite, chlorite, garnet and various schists. The Alaşehir Formation and Upper Miocene aged Gediz Formation on the Early Middle Miocene age are unconformably located in the western part of the graben. The Alaşehir Formation consists of lacustrine sediments, limestone and shale (Yazman et al., 1998; Seyitoğlu et al., 2002; Çiftçi and Bozkurt, 2009; Maddy et al., 2017). The Gediz Formation consists of conglomerate and sandstone and mudstone intercalation. The Pliocene Kaletepe Formation overlies these units and consists of conglomerate-sandstone intercalations. Quaternary alluvium settles on all units in the geological cross section. In the graben, oil reservoirs have been found in the Alaşehir region (İztan and Yazman, 1990).

The Alaşehir geothermal field is located in the E-W and WNW-ESE tending Gediz Graben in the southern section of the Manisa Province (Fig. 3) (Çiftçi and Bozkurt, 2009). The Paleozoic-Mesozoic Menderes Metamorphics which are composed of granitic augen-gneiss, various gneisses, meta-volcanic and meta-sedimentary units, are defined as basement rock unit, marbles and fractured quartzite zones in meta-

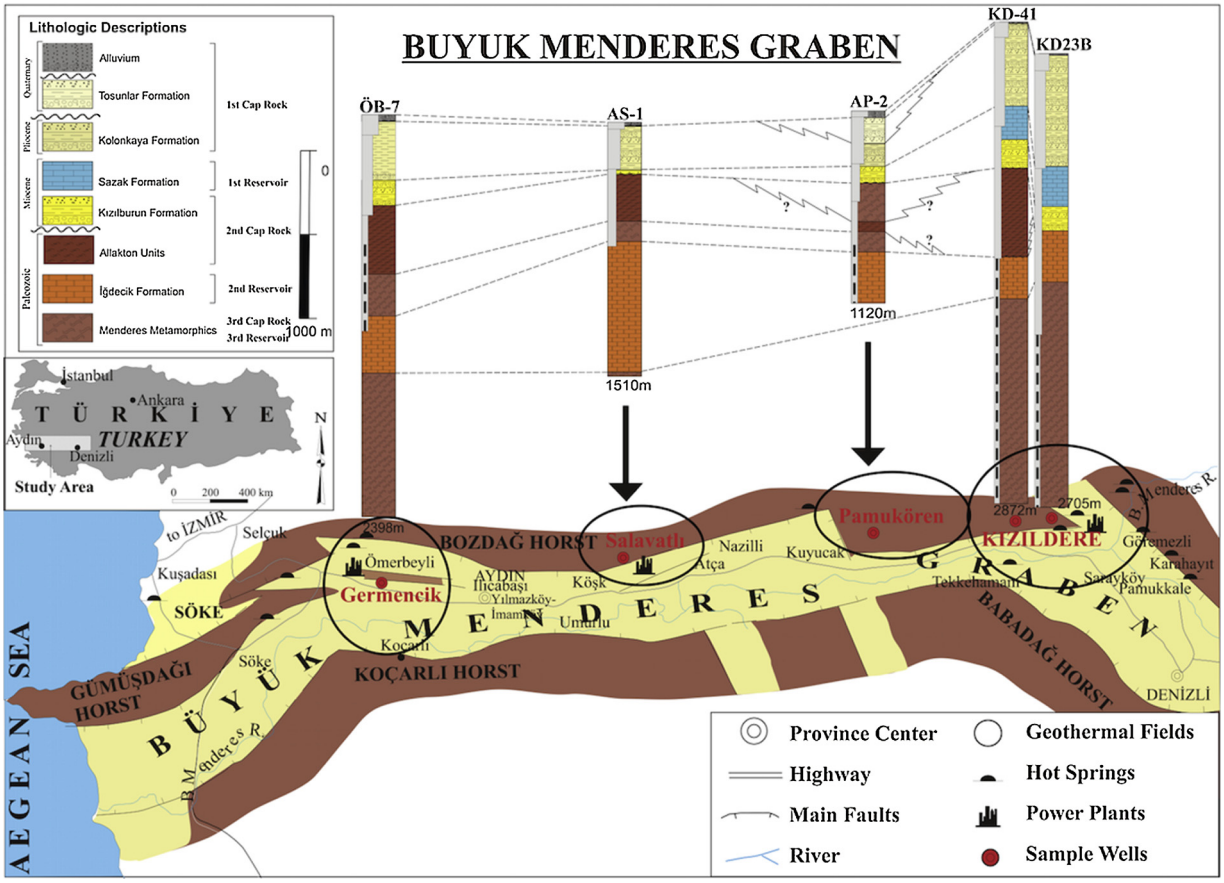

Fig. 4. Representative well logs in the BMG (modified after Şimşek, 2003; Haklıdır et al, 2012).

sedimentary units are evaluated as the main reservoir section like in the BMG geothermal systems in the Gediz Graben (Rabet et al., 2017). The geothermal gradient which rises with the tectonic effects of the graben, suggests the heat source of the system. The caprock of the Alaşehir geothermal reservoirs are observed as schist-shale levels of the metamorphics and mudstone level in Tertiary units. Reservoir temperatures reach 210–286 °C in water-dominated reservoirs (Baba, 2015). Due to tectonism, the marble unit in the reservoir has been deformed and calcite and sericite, carbonate and pyrite are observed in the cracks of quartzite-schist (İlhan and Kabak, 2018). The Alaşehir geothermal field is 10 km from the oil reservoir, which has been discovered in the Baklacı village (İztan and Yazman, 1990) and some hydrocarbon effect has been detected especially in gas phases of geothermal fluids.

5. Results of the hydrogeochemical survey

The geochemical evaluation of the thermal waters was started by Dominco and Şamilgil, 1970 and the studies were continued in the Kızıldere, Germencik, Salavatlı geothermal fields along the graben (Şimşek et al., 1980; Şimşek, 1982, 1985; Mutlu and Güleç, 1998; Özgür et al., 1998; Möller et al., 2004; Şimşek, 2003, 2005; and Karamanderesi and Helvacı, 2003). In these studies, water types, water chemistry, water-rock interaction, and the origin of the waters, scaling problems, and calculation of reservoir temperatures by geothermometers were carried out. Particularly after 2005, the steam + gas phase of the geothermal fluids also underwent research together with the water phase (Mutlu et al., 2008; Haklıdır Tut et al., 2011; Haizlip Robinson et al., 2013; Karakuş and Şimşek, 2013;).

In this study, some above-mentioned studies are used for the Germencik, Salavatlı and Pamukören fields, while the authors have collected new data from the Kızıldere and Alaşehir geothermal fields.

5.1. Water chemistry

The Germencik field is near the western end of the BMG (Fig. 3). It is a well known high-temperature geothermal system in Turkey.

Based on chemical analyses, thermal waters are characterized as Na-HCO_3 type for both the BMG and the GG geothermal systems in the study area. Electrical conductivity (EC) values range from 3400 to 6890 µS/cm for the BMG and 2500 µS/cm for the GG geothermal fluids. The highest electrical conductivity (EC) values were observed in the west and in the east of the BMG geothermal systems in the Germencik and Kızıldere deep reservoirs (5590 µS/cm). The EC values for geothermal fluids in intermediate reservoirs of these systems and slightly lower values than in the deep reservoirs in the study area have been observed in other geothermal systems (Table 1).

Cl^- concentrations in the fluids has been recorded up to 1622 mg/l in the Germencik system and the highest values are recorded for the BMG and the GG geothermal systems. In the water phase, Cl^- concentrations range from 230–284 mg/l in Salavatlı and Pamukören systems while it is around 117 mg/l in Kızıldere. The Cl^- concentrations in fluids from the Alaşehir geothermal field in the GG are slightly higher than in Kızıldere fluids which are between 80 to 170 mg/l. The lowest SO_4^{2-} concentration is recorded around 19.5 mg/l in water from Germencik among other geothermal systems along the BMG. SO_4^{2-} concentrations range from 183 to 200 in water from Salavatlı and Pamukören however, it has been observed to reach up 761 mg/l in the Kızıldere geothermal system and it is the highest value for both grabens. SO_4^{2-} concentrations range from 7 to 20 mg/l in the water phase in the Germencik system. Total boron levels range from 42 to 71 mg/l in the west part of the BMG and it tends to decrease 18 mg/l towards east of the graben at Kızıldere geothermal system (Table 1). Filiz et al. (2000) proposed that boron in thermal waters is linked to originate from

Table 1
Measured physical parameters and results of chemical analysis of thermal waters in the study area (BHT: bottom-hole temperature, SP: separator pressure).

Field	Well ID	Sampling date	Depth (m)	BHT (°C)	SP (bar)	Flowrate (tph)	pH	EC (µS/cm)	Na^+ (ppm)	K^+ (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Cl^- (ppm)	HCO_3^- (ppm)	SO_4^{2-} (ppm)	Bt (ppm)	Li (ppm)	SiO_2 (ppm)	Sampling point	References
Kızıldere	KD14	2012	603	208	4.1	150	8.3	4840	1258	152	5.74	< 1	106	2319	761	20	3.6	330	after seperator	*In this study*
	KD22	2013	885	201	3.8	108	8.3	4610	939	142	7.14	< 1	112	1752	709	18	2.5	300	after seperator	*In this study*
	R1	2013	2261	232	4	200	8.1	5510	1093	211	4.45	< 1	126	2356	694	26	3.6	516	after seperator	*In this study*
	R3A	2013	2443	237	8.3	295	8.2	5590	1093	214	3.96	< 1	129	2066	649	30	3.96	554	after seperator	*In this study*
	KD18A	2013	2195	215	7.5	250	7.2	5170	1332	157	7.33	< 1	115	2530	672	26	4.5	336	after seperator	*In this study*
	KD42	2014	3155	240	3	219	8.2	4670	1464	191	2.14	< 1	102	2917	648	30	4.9	460	after seperator	*In this study*
Germencik	OB8	2005	2000	214	*	148	7.8	5670	1449	135	0.86	< 1	1280	1810	53	62	7.9	452	after seperator	MTA, 2005; Gürmat, 2009
	OB9	2005	1466	212	*	424	7.7	6440	1527	102	13.8	4.4	1500	1363	30	55	7.7	515	after seperator	MTA, 2005; Gürmat, 2009
	OB14	2007	1205	228	*	809	7.8	6660	1364	149	17.9	< 1	1700	1428	26.6	55	7.8	409	after seperator	Karakuş and Şimşek, 2013
	OB17	2008	1706	228	*	321	7.6	6661	1565	174	12.3	< 1	1565	1461	20	59	10.6	535	after seperator	Karakuş and Şimşek, 2013
Salavatlı	AS-1	1987	1500	169.7	*	288	8.7	3400	1500	85	6	0	105	3208	196	66	4.7	227	WB	Karamanderesi and Helvacı, 2003
	AS-2	1988	960	175.6	*	334	7.7	4600	1100	90	14	1.1	100	2831	170	42	4.5	231	WB	Karamanderesi and Helvacı, 2003
Pamukören	AP1	2009	606	51.1	*	3	7.8	5730	1612	151	10.9	11.2	73	4060	155	1.2	0.6	124	WB	MTA, 2009
	AP2	2009	1150	188	*	561	8.8	5100	1272	196	3.27	1	276	2519	180	30	6.5	336	WB	MTA, 2009
	AP3	2009	1134	183	*	776	8.6	4970	1660	170	9.5	2.45	293	3378	222	4.8	7.3	182	WB	MTA, 2009
Alaşehir	Alkan-1	2010	1178	190	5	250	7.1	1029	534	90	2.09	< 1	166	1389	10.2	83	6.3	366	after seperator	*In this study*
	Alkan-2	2011	1701	200	3.7	285	7.1	993	560	79	2.27	< 1	182	1443	14.6	101	6.2	501	after seperator	*In this study*

mantle or marine sediments during metamorphism and illites and tourmalines in bedrock might be the boron carrier for thermal waters in Germencik. Boron concentration shows highest values in presented geothermal fields, and ranges from 80 to 150 mg/l in Alaşehir in the GG. The silica concentrations in waters is related to the reservoir temperatures and fluctuates between 300 mg/l and 554 mg/l at Kızıldere, 412–535 mg/l in the Germencik geothermal waters. Silica values are lower than expected possibly due to rapid precipitation of silica varying from 135 to 178 mg/l (Karamanderesi and Helvacı, 2003) Salavatlı and it is slightly higher at Pamukören waters at middle of the BMG. The silica values for the waters range between 200 and 500 mg/l in Alaşehir and are similar to Kızıldere intermediate values.

5.2. Stable isotopes

Stable isotopes provide important information on the origins of thermal waters and underground processes in geothermal reservoirs. The stable isotope results show that thermal waters have a meteoric origin in the study area and suggest substantial $\delta^{18}O$ isotope enrichment in thermal waters in Germencik (Table 2). The $\delta^{18}O$ isotope values vary between −1.46‰ and −2.26‰, and a δ D isotope value variation between −39‰ −41‰ in the thermal waters. In Salavatlı, the isotope values vary between -1.81‰ and −2.78 ‰ for $\delta^{18}O$ and −47 ‰ and −48 ‰ for δ D and they represent the middle of the BMG among the geothermal systems in the study area. The $\delta^{18}O$ isotope values vary between −4.74 ‰, −5.64 ‰ for the intermediate reservoir while it varies between −3.76 ‰ and −4.09 ‰ in the deep reservoir in the water phase of the Kızıldere geothermal system and look slightly higher than in the other geothermal systems at the BMG (Haklıdır Tut et al., 2011) and GG (Table 2). The $\delta^{18}O$ isotope values show variation between −1.94‰, and −2.33‰ and δ D values change from −48.51 to −50.41 for Alaşehir geothermal waters, the GG. The ^{13} δC-CO_2 value for Germencik water was determined as 0.33‰, for the deep reservoir thermal waters in the system (Karakuş and Şimşek, 2013). It is observed as −0.2 ‰ for Salavatlı (Karakuş and Şimşek, 2013) and −0.62 ‰ *for* intermediate, −0.03 ‰ for deep reservoir in the Kızıldere geothermal system (Table 2). The $^{13}\delta$C-CO_2 value is recorded as −3.13 ‰ in Alaşehir water in the GG.

In this study δ^{34} S analysis was performed on Kızıldere and Alaşehir geothermal samples. In Kızıldere, the δ^{34} S values look similar around 20 ‰ for intermediate and deep reservoir samples while δ ^{18}O ‰ (SO_4) values look slightly different for each reservoir and the deep reservoir value is 1.3 ‰ in this region (Table 3). In the Alaşehir geothermal system in the GG, δ^{34} S values vary between −1.7 and 4.8‰ and δ ^{18}O‰ (SO_4) isotope analysis show around 12‰ in the reservoir (Table 3).

5.3. Non-condensable gas compositions and the gas content in the reservoirs

In the steam phase, the analyses of gas composition indicate that the primary gas is CO_2 with 95–99 % for the BMG and the GG geothermal reservoirs (Yıldırım and Yıldırım, 2015; Haizlip Robinson et al., 2013) (Table 4).

The H_2S level, one of the important non-condensable gases (NCG) for a power plant design, is 0.21% in the Germencik reservoir while, H_2S in the steam is around 0.021% in the steam phase in Kızıldere (Haizlip Robinson et al., 2013) in the BMG. The H_2S value is observed around 0.05% in Alaşehir in the GG and the value is higher than the Kızıldere reservoir.

The non-condensable gas content changes from 1.5 to 2 wt% in the deep reservoir of the Germencik geothermal system (Osborn et al., 2007). It is around 1 wt% at Salavatlı (Serpen and Aksoy, 2010) and 1.3–1.7% at the Pamukören reservoir conditions (Yıldırım and Yıldırım, 2015; Table 4)). The NCG content of the reservoirs have been calculated as 1.5–2 %wt for the intermediate reservoir and as 3.0–3.2 %wt for the deeper reservoir. The NCG contents of the reservoirs have been

Table 2
$\delta^{18}O$ - δ D and $\delta^{13}C$- CO_2 isotopes for thermal waters in the study area.

Field	Well ID	Sampling date	$\delta^{18}O$ ‰	δ D ‰	References	$\delta^{13}C$-CO_2 ‰	References
Kızıldere	KD14	2013	−4.72	−52.09	*In this study*	−0.62	Mutlu et al., 2008
	KD22	2013	−5.64	−55.01	*In this study*		
	R1	2013	−4.09	−53.22	*In this study*		
	R3A	2013	−3.76	−54.37	*In this study*	−0.03	*In this study*
	KD18A	2013	−5.49	−58.44	*In this study*		
	KD42	2014	−4.1	−54.39	*In this study*		
Germencik	OB8	1998	−2.27	−41.9	Şimşek, 2003	−0.33	Karakuş and Şimşek, 2013
	OB9	1998	−1.74	−37.9	Şimşek, 2003		
	OB14	2007	−1.24	−38.9	Karakuş and Şimşek, 2013		
	OB17	2008	−1.46	−39	Karakuş and Şimşek, 2013		
Salavatlı	AS-1	2011	−2.78	−48.78	Tarcan et al., 2013	−0.2	Karakuş and Şimşek, 2013
	AS-3	2011	−2.17	−48.43	Tarcan et al., 2013		
Alaşehir	AL-1	2010	−2.33	−48.51	*In this study*	−3.13	*In this study*
	Al-2	2011	−1.94	−50.41	*In this study*		

Table 3
δ^{34} S- δ^{18} O (SO_4) isotopes of thermal waters in the study area.

Geothermal Systems	Graben System	δ^{34} S ‰	δ^{18}O in (SO_4) ‰	References
Kızıldere Intermediate	BMG	20	2.7	*In this study*
Kızıldere Deep	BMG	21	1.3	*In this study*
Alaşehir (AL-1)	GG	4.8	–	*In this study*
Alaşehir (AL-2)	GG	−1.6	–	*In this study*
Alaşehir (AL-3)	GG	−2.7	12.3	*In this study*
Alaşehir (AL-4)	GG	1.7	11.9	*In this study*

calculated as 1.5–2 % wt at Alaşehir geothermal reservoirs (Table 4).

6. Discussion

6.1. Regional distribution of main hydrogeochemical parameters at high temperature geothermal systems

Although the foundation of the BMG consists of the Menderes Metamorphics the depths of the wells have reached the intermediate reservoir only, which is known as the İğdecik formation, or the top of the Menderes metamorphics in the center of the graben. This affects reservoir temperatures and the composition of the water and gas phases, besides other impacts from marine sediments and oxidation-reduction effects along the graben.

Reservoir temperature distribution varies along the graben systems. The highest temperatures are recorded at the western end (Germencik; 276 °C) and at the eastern end (Kızıldere; 245 °C), while in the middle of the graben (Salavatlı and Pamukören), lower temperatures exist or between 169 °C–188 °C in production zones at depths in the BMG. Reservoir temperatures around 190 °C–200 °C are recorded in discovered geothermal systems in the GG, which are lower than in the BMG.

Na^+ and K^+ concentrations are controlled by temperature in geothermal waters (Nicholson, 1993). For this reason, the Na/K ratio is generally a useful guide to high temperature zones in geothermal systems. The water types of the thermal waters are given in Figs. 5 and 6.

In the study area, the distribution of reservoir temperatures is compatible with the Na/K ratio in thermal waters. The value tends to increase to middle of the BMG and it is higher than in the GG. A Na-K-Mg triangular diagram is used to evaluate equilibrium between the hot waters and rocks at depth to understand water-rock interaction at depth and to estimate reservoir temperature. Almost all the thermal waters plot as partially equilibrated waters in a Na-K-Mg diagram (Fig. 7). The figure shows that water-rock interaction in the west part of the BMG is slightly greater than in other thermal waters in the study area. It suggests a deeper or longer circulation for the BMG waters.

The results of the water chemistry studies demonstrate that the main differences are observed in the Cl^-, SO_4^{2-}, B and Li ion concentrations in the thermal waters of the study area. Boron, Li^+, Cl^- and SO_4^{2-} values increase from the east to the west along the BMG. The SO_4^{2-} concentration is generally controlled by dissolution of gypsum and/or oxidation of pyrite, which suggests a thermal water reservoir (Gemici and Tarcan, 2002). The Cl^-, SO_4^{2-} and boron concentration of thermal waters are similar to that in the west part of the BMG in the GG. Li^+ is generally present with Cl^- and B ions and these distinguish waters from common sources (Fig. 8). It also indicates a decrease in concentration with increasing flow to the surface and with increased lateral flow in geothermal reservoirs (Nicholson, 1993). High Cl^- concentrations indicate a deep feeding system of thermal waters, and that cold-water intrusion must be minimal in this case. However, if Cl-concentrations exceed 1000 mg/l in thermal waters, it suggests marine sediments in the reservoirs. (Nicholson, 1993).

In the study area, the highest Cl^- concentrations were observed in the Germencik field (1280–1740 mg/l), which is located 30 km from the Aegean Sea. The Cl^- concentrations range from 73 to 293 mg/l, suggesting a marine sediment (paleo sea) effect in the Germencik reservoir, as confirmed by Karakuş and Şimşek (2013), and Güner and Yıldırım (2005). The GG waters contain higher Cl^- concentrations than those of the eastern part of the BMG. For Cl/B ratios; seawater has a high Cl/B, while magmatic volatiles have a low Cl/B ratio (Aggarwal et al., 2000). The Cl/B ratio has been given as 1.941 for the Aegean Sea

Table 4
Gas composition of thermal waters in the study area ([a]Yıldırım and Yıldırım, 2015; [b,c] Aksoy et al., 2019; Tarcan et al., 2013; [d] Haizlip Robinson et al., 2013).

Geothermal Systems	Graben System	NCG (wt)%	CO_2%	H_2S %	Ar %	N_2 %	CH_4 %	H_2 %
Kızıldere Intermediate (KD22)	BMG	1.5	99.1	0.042	0.0036	0.568	0.24	0.0024
Kızıldere Deep (KD23B well)	BMG	2.5-3	98.8	0.08	0.0023	0.69	0.45	0.0043
Salavatlı[b,c]	BMG	1	98	0.112	0.184	0.91	0.25	0.036
Germencik[d]	BMG	1.3-1.7	98.5	0.21	0.001	0.44	0.7	0.035
Alaşehir	GG	1.5-2	98.5	0.2	0.004	0.4	0.8	0.007

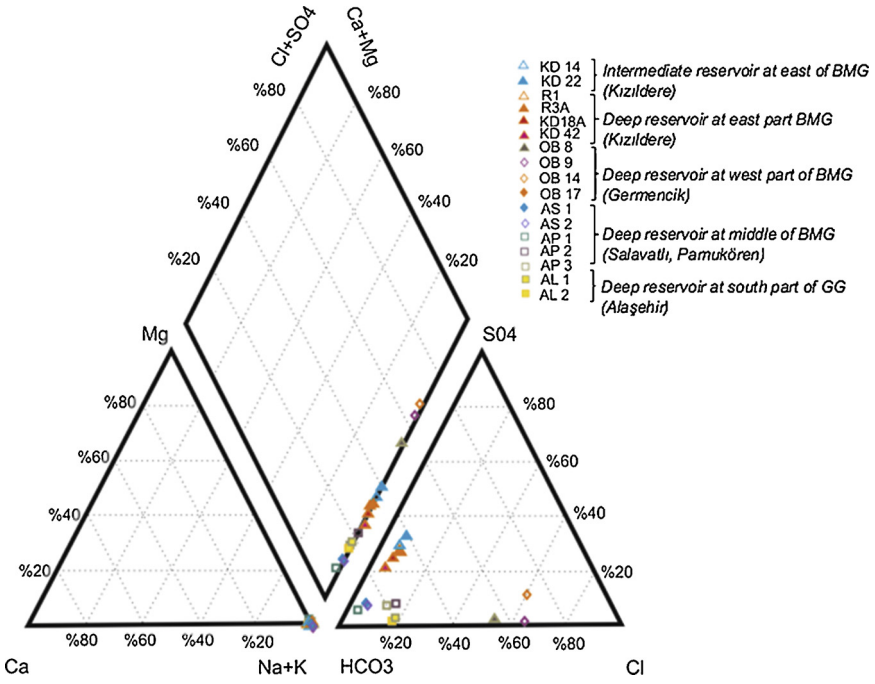

Fig. 5. Piper Diagram of the thermal waters in the study area.

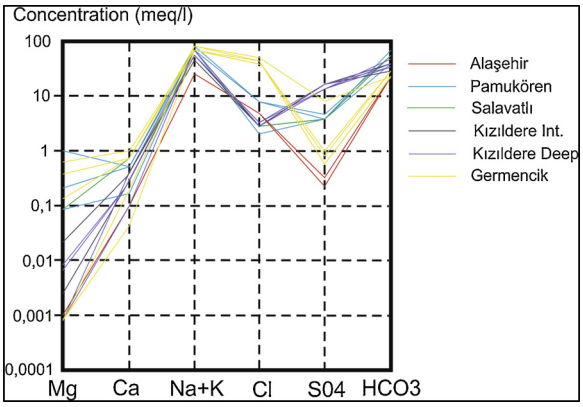

Fig. 6. Schoeller diagram of thermal waters in the study area.

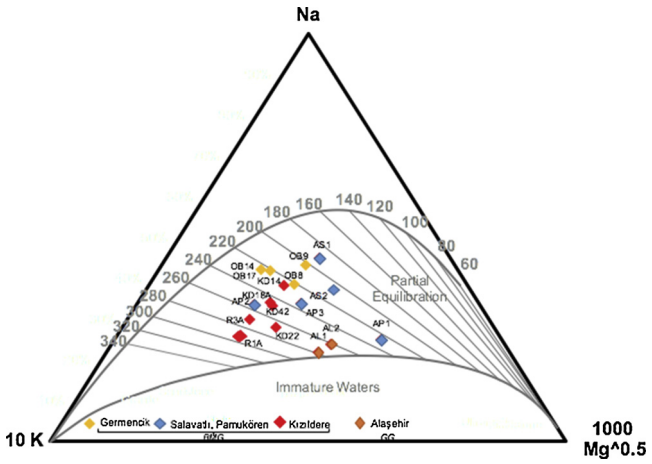

Fig. 7. Thermal waters on Na-K-Mg Triangular diagram for the study area (Giggenbach, 1988).

by Gemici and Tarcan (2002). The geothermal systems in the study area can be arranged with respect to Cl/B ratios from high to low as:

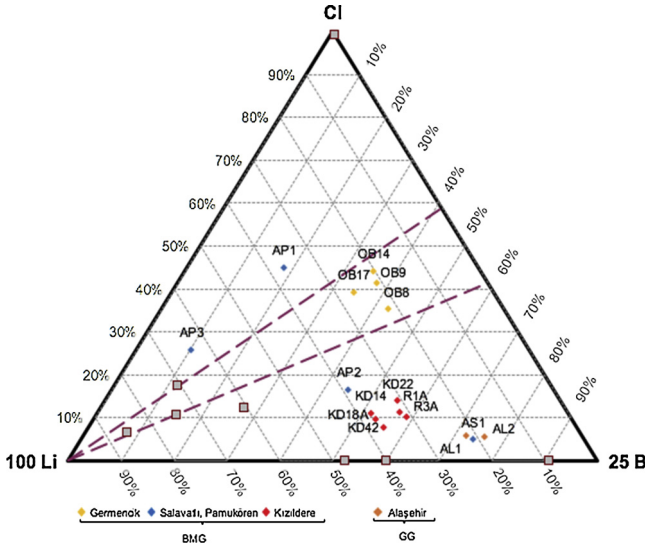

Fig. 8. A Li-Cl-B triangular diagram for thermal water in the study area.

Germencik (Cl/B: 30), Pamukören (Cl/B: 6.5) Kızıldere (Cl/B: 4.2), Salavatlı (Cl/B: 2.4) and Alaşehir (Cl/B: 2). Cl/B ratios of Pamukören samples look suspicious with quite different results and one of them is selected as representative in the evaluation. The origins of boron in thermal waters have been discussed by different researchers (Gemici and Tarcan, 2002; özgür et al, 2004; Vengosh et al., 2002; Tokçaer, 2007). Leaching B^{3+} from the boron-bearing mineral phases in the metamorphics and as magmatic volatiles, B $(OH)_3$ gas intrusions are a known origin of boron in geothermal systems (Karakuş and Şimşek, 2013). Although the Cl/B ratio suggests a common reservoir source for waters, sometimes the ratio may differ due to the effects of a change in lithology at deeper zones in a geothermal field (Nicholson, 1993). The sericite, illite, tourmaline minerals of the Menderes Massif are considered to be one reason for the high boron concentrations in thermal waters due to water-rock interaction. Linear correlation between HCO_3 and boron concentrations in thermal waters show that boron minerals have co-existed with carbonates in the reservoirs in Western Anatolia.

Gülensoy and Kocakerim (1978) mentioned that the solubility of boron minerals in carbonate (such as colemanite) increase with high CO_2 gas concentrations in thermal waters. Aqueous species of boron can be sensitive to the pH of fluids. At low pH $B(OH)_3$ and at high pH (> 8) conditions $B(OH)_4$ can be the dominant species (Gemici and Tarcan, 2002). Along the BMG, deep geothermal fluids are acid character with a pH around 5.5–5.9 in Kızıldere and 4.9–5.5 in the Germencik systems. This suggests that the Germencik deep reservoir fluids are slightly more acid than those in the Kızıldere reservoir and it is noted that their boron concentration is higher too. These results show similarity with those of Gemici and Tarcan (2002). The pH of thermal water is an important criterion for the solubility of boron in the reservoirs and it may also explain the boron concentration in the Alaşehir field waters.

Beside the all identified geothermal reservoir conditions, local rock leaching may affect water compositions in a geothermal system. The concentration of Cl^- and boron show differences in geothermal systems. The boron concentration in sedimentary rocks may higher than volcanic rocks (Ellis and Mahon, 1977). The boron concentration is prominently higher in the GG than the BMG waters. Li^+ is an alkali metal and is affected by secondary processes. Thus, it is used as a tracer for the initial deep rock dissolution process and to evaluate the possible origin of two important conservative constituents of thermal water. The boron concentration of thermal waters shows the degree of maturity of a geothermal system (Rahmani, 2017). Li^+ concentrations increase from the eastern part to the western part along the BMG. The Cl^- concentration shows the same trend at the GG and it is higher than Kızıldere waters in the BMG. Li^+ concentrations and the reservoir temperatures generally show a linear relation, however sometimes Li^+ may be absorbed by clay minerals at depth.

Remarkable variations can be observed in SO_4^{2-} concentrations along the BMG. The highest SO_4^{2-} concentrations were recorded in Kızıldere (649–761 mg/l) at the eastern end of the BMG, and the lowest SO_4^{2-} concentrations were recorded in Germencik (19.5–53 mg/l) in the west of the BMG. This is quite interesting because gypsum can be seen throughout the graben but the content of the SO_4^{2-} is quite different in the fluids of the geothermal fields at each end of the graben. A low SO_4^{2-} concentration in Alaşehir waters suggest a similar trend as in Germencik waters.

Dissolved silica is an important constituent for predicting geothermal reservoir temperatures at depth. Silica is an important parameter for geochemists, thus it is extremely important to prevent precipitation during the sampling preparation or collection of the sample and get representative results for the reservoirs. Silica concentrations are generally compatible with reservoir temperatures for both graben systems (Table 1).

6.2. Variations in stable isotope composition along the BMG and GG Systems

Water-rock interaction studies show that increasing reservoir temperatures provide positive $\delta^{18}O$ shifts from the global meteoric water line (GMWL; Craig, 1961), while there is no effect on δ D because of a small interaction with hydrogen in the reservoir rocks.

The maximum $\delta^{18}O$ shift (−2.27‰; −1.24‰) from the GMWL is shown in the Germencik geothermal field while $\delta^{18}D$ values vary between −37.9 and −41.9‰ (Fig. 9) in the west of the BMG. The $\delta^{18}O$ is more positive in the deep reservoir (−3.76; −4.09) than in the intermediate reservoir (−4.72 and −5.64‰) of Kızıldere geothermal system (Table 2). In Salavatlı, the $\delta^{18}O$ value is around −2.17‰. It is thought that the main reason of $\delta^{18}O$ shift in the geothermal system is the marbles of Menderes Metamorphics. In the Alaşehir fluid, $\delta^{18}O$ values for thermal waters are around −1,94‰ and δD values vary between −48.51 and −50.41‰ in the GG. The $\delta^{18}O$ values suggest that all the thermal waters in the study area are from deep feeds and have taken part in an intense water-rock interaction, but isotope values are lower for Kızıldere fluids than those from other fields in the BMG

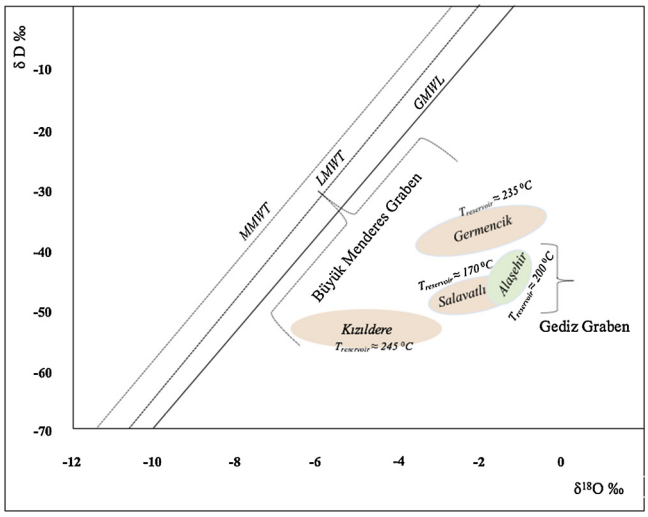

Fig. 9. $\delta^{18}O$ versus δD diagram for the study area thermal waters *(GMWL: Global Meteoric Water Line $\delta D = 8*\delta^{18}O+10$; (Craig, 1961); MMWT:Mediterranean Meteoric Water Line $\delta D = 8*\delta^{18}O+22$; LMWL:$\delta D = 8*\delta^{18}O+16$* (Karakuş and Şimşek, 2013)).

and Alaşehir, since reservoir permeability is lower in Kızıldere. It is noted that the CO_2 concentration in reservoir fluids may also affect the $\delta^{18}O$ shift in the GMWL fluids due to an increasing mineral dissolution in the reservoir (Fig. 9, Haklıdır Tut, 2013). The differences in stable isotope values could be likely related to differences in meteoric water recharge variations along the BMG.

$^{13}\delta C$ values can be used to understand the origin of CO_2 in a geothermal system. Thermal waters in volcanic areas or along tectonic zones have elevated P_{CO2} values that show a subsurface contribution. This mantle-derived CO_2 has been detected in geothermal waters and has been found to have a $^{13}\delta C$ value around −6‰ (Clark and Fritz, 1997). Another CO_2 source is thermal metamorphism of limestone in the reservoir. When rising magma comes into contact with carbonate decarbonation of $CaCO_3$ takes place, with loss of CO_2.

When $CO_{2(g)}$ diffuses into water, it forms four main components of dissolved inorganic carbon (DIC); dissolved or CO_{aq}, H_2CO_3, HCO_3^- and CO_3^{2-} and their relative concentration in water is a function of pH. Different isotope fractionation factors exist between these aqueous species and gas (Clark and Fritz, 1997). Ellis and Mahon (1977) state that bicarbonate ions decompose on reaction with weak acids in geothermal waters.

If a geothermal reservoir contains $CaCO_3$; thermal water is assumed to be in equilibrium with calcite and the solubility will be defined by Eq. (1); in the presence of acid dissolution of $CaCO_3$ forms CO_2 based on the following reaction (Ellis and Mahon; 1977; Eqs. (1) and (2));

$$CaCO_3(s) + 2H(aq) + \leftrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(aq) \quad (1)$$

where the equilibrium constant; $K_{CaCO3} = (a_{Ca^{2+}} * a_{CO2})/(a_{H^+})^2$ (2)

The second equation shows the dissociation of dissolved CO_2. Arnorsson (1989) describes the relationship of the equilibrium constants of these reactions as follows;

$$K_{calcite} * K_{H2CO3} * K_{HCO3} - = K_{calcite} \quad (3)$$

where K_{H2CO3} is the equilibrium constant for the first dissociation constant of dissolved CO_2. The dissociation of H_2CO_3 produces HCO_3^- as follows (Eq. (4));

$$H_2CO_3 = HCO_3^- + H^+ \quad (4)$$

The second dissociation constant of carbonic acid, K_{HCO3}, produces CO_3^{2-} as follows; $CO_3^{2-} + H^+ = HCO_3^-$ (5)

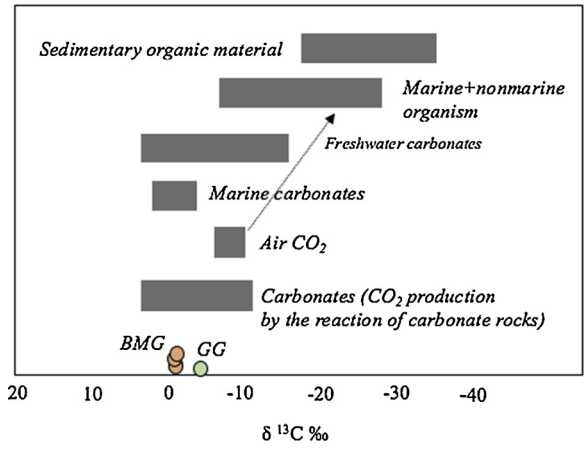

Fig. 10. $\delta^{13}C$ values for the thermal waters (modified after Hoefs, 1997).

The carbonate concentrations in most of geothermal reservoirs are observed in equilibrium with calcite;

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \quad (6)$$

Eq. (6) shows that at constant temperature in equilibrium with $CaCO_3$ while, CO_2 is controlled by a_{Ca2+} and a_{HCO3-}. However, a_{HCO3-} is controlled by the dissociation of dissolved CO_2 (Eq. (4)) and the pH value (Haizlip Robinson et al., 2016). In geothermal fluids, other acids may also affect the pH such as silicic acid, sulfuric acid, boric acid.

The $^{13}\delta$ C values for the thermal waters are quite similar in the BMG and the values are slightly lower in the GG (Table 2). The origin of the high CO_2 concentrations are mainly due to the decomposition of carbonate in the marble in the different geothermal reservoirs (Clark and Fritz, 1997) along the BMG and the GG (Fig. 10). In the study area; the main source of CO_2 is found marble in Paleozoic aged Menderes Metamorphics and there is no evidence of a magmatic influx in the BMG geothermal systems. Limited data exists on $^{13}\delta$ C in the GG region and it is not easy to explain differences in $^{13}\delta$ C in BMG (−0.03; −0.062‰) and GG (−3.13‰). The measured pH of the waters (pH is around 7) is lower in GG than BMG's waters (pH is around 8) and high sulfate (~500 mg/l) and weathering of silicate minerals in carbonate systems (Clark and Fritz, 1997) may be the reason of the slight differences in $^{13}\delta$ C values between the two graben systems (Fig. 10).

The concentration of SO_4^{2-} is generally lower than 50 mg/l in deep geothermal reservoirs but the concentration increases by the oxidation of condensed H_2S (Nicholson, 1993). The concentration of sulfate can also be highly variable that it may be derived from dissolution of sulfate minerals (e.g., gypsum and anhydrite), oxidation of sulfides (such as pyrite) and biological activity (Nicholson, 1993; Liua et al., 2017) in thermal waters.

Sulfur species are detected as dissolved sulfate (SO_4^{2-}), the dissolved sulfide (HS-) or H_2S gas in the water. The form of H_2S depends on the pH of the water and if the pH of the water is lower than 6, H_2S is mainly in the form of H_2S_{gas}. When the pH increases to 6–8, a part of the H_2S converts into HS- and a mixture of H_2S and HS- exists at these pH levels. Above a pH of 13, S^{2-} is the major ion in water (Mcvay, 2007).

SO_4^{2-} concentrations tend to decrease from east to west in thermal waters along the BMG (Fig. 11). The concentration of the ion reaches a maximum value of 760 mg/l in Kızıldere water and it decreases to 20 ppm in Germencik water. Oxidation of the fluid lowers the H_2S gas concentration as the gas is oxidised to the SO_4^2 ion and the CO_2/ H_2S ratio increases in geothermal systems (Nicholson, 1993). The H_2S gas percentages in NCG show an opposite trend to dissolved SO_4^{2-} along the graben (Fig. 11). H_2S% in the gas phase in Kızıldere and Germencik fluids show remarkable differences along the BMG. Geothermal fluid offers diversity in pH and temperature both of which increase the solubility. In Germencik, the pH of geothermal fluids is found to be lower than in Kızıldere fluids because of a marble dominated reservoir (Osborn et al., 2007). In addition to the pH value, the concentration of H_2S increases with temperatures (Blamey, 2006) and the highest reservoir temperature is recorded as 276 °C in Germencik along the BMG. The low pH and high reservoir temperatures conclude higher H_2S concentrations in Germencik and Alaşehir than the other geothermal fields.

It is supported by Giroud and Arnórsson (2005) that they referred to lower pH and high temperature effects, refer to specific mineral buffers with regard to CO_2 and H_2S concentrations in high temperature systems. Blamey (2006) also supports this idea and the purpose of a correlation between the H_2S concentration and temperature which is controlled by pyrite-pyrrhotite-magnetitE–Water equilibrium in geothermal systems. Norman et al. (1998) describes the CO_2-CH_4-H_2S-H_2O-magnetite-pyrite-pyrrhotite equilibrium conditions in geothermal systems with Eq.7. This may explain the lower H_2S concentration and trace CH_4 composition in Kızıldere but not in Germencik geothermal fluids, because of iron mineralization and the presence of magnetite in the Kolonkaya and Tosunlar formations (özgür, 2002).

$$2Fe_3O_4 + 12H_2S + CO_2 = 6FeS_2 + 10H_2O + CH_4 \quad (7)$$

In addition to the reservoir conditions in the study area, the tracer tests show that that there may be better connections between fractures in the Alaşehir and Germencik geothermal systems than in the Kızıldere geothermal system (Aydın et al., 2018; Hamendi, 2009; Yeltekin and Akın, 2006). The transmissibility of the Kızıldere reservoirs may give enough time for sulfide oxidation. One other possibility regarding high H_2S in Germencik is a possible paleo-sea water effect (Filiz et al., 2000). The field is only 30 km far away from the Aegean Sea and Güner and Yıldırım (2005) report a 7–8 % sea contribution; possibly from marine sediments, because of Mediterranean transgression in the Pleistocene in the Germencik geothermal reservoir. The may also explain the high compressed organic material concentration in sediments and the sulfur concentration in the reservoir fluids.

^{34}S isotopes have been used to interpret the origin of sulfur however, sulfur is highly fractionated due to biological effects and the $\delta^{18}O$ ratio of sulfate is an important tracer in understanding of the origin of sulfur (Clark and Fritz, 1997). These variations occur depending on differences in temperature and oxidation-reduction reactions which are acting on sulfur concentrations (Seal, 2006)

$\delta^{34}S$ values of Kızıldere thermal waters are around 20‰ while, the values for Alaşehir waters vary between −2,37 and 4‰. To better understand the origin of the sulfur for both grabens, SO_4^{2-} concentration versus $\delta^{34}S$ graph is given Fig. 12. Based on the graph; the source of sulfate is from evaporitic gypsum in Kızıldere thermal waters and a mantle sulfur contribution is important for Alaşehir thermal waters.

Clark and Fritz (1997) mentioned that terrestrial sulfate could be distinguished from marine sources by their isotopic composition. The $\delta^{34}S$ content of sulphate from oxidation of that form of sulfide is generally depleted from original sulfide. For $\delta^{18}O$ ratio of sulphate is more complex due to atmospheric O_2 and oxygen in water present during oxidation can have an influence. To minimize the fractionation, a $\delta^{34}S$-SO_4 versus $\delta^{18}O$ - SO_4 diagram can possibly explain the origin of the sulphur in a region. Rajchel et al. (2002) noted that $\delta^{34}S$ of total dissolved sulfur cannot be changed by probable bacterial reduction or by oxidation reactions in a closed system. Organic sulfur may suppose the presence of hydrocarbons in the reservoir and özdemir (2019) stated that the dykes and sills in BMG could be effective to formation of hydrocarbons. With this reason, it is proposed that the magmatic source contribute to the total sulfur amount beside the hydrocarbons in the west part of the BMG and Alaşehir in GG (Fig. 12).

In Fig. 13 Alaşehir and Kızıldere high temperature waters are shown in different parts of the graph. Alaşehir fluids contain a low SO_4^{2-}

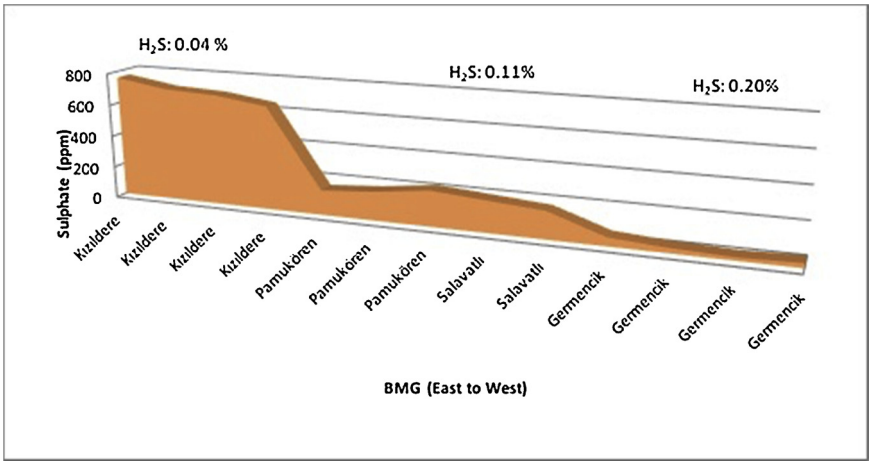

Fig. 11. Dissolve SO_4^{2-} and $H_2S_{(g)}$ distribution along the BMG.

concentration in the water phase and a high H_2S concentration in gas phase like the Germencik waters in the BMG (Table 2 and Table 3) However, Alaşehir is distinctly far from a sea intrusion effect and has lower Cl- concentration in thermal waters than Germencik. Based on Fig. 13, it is possible that sulfide minerals in the Alaşehir field can be oxidized at a near surface depth while, bacterial reduction is also possible in the Kızıldere field.

The chemical equation for the reaction between SO_4^{2-} and H_2S is shown for the geothermal waters in Eq. (8).

$$SO_4^{2-} + 2C_{organic} + 2H_2O + \text{microbial activity} = H_2S + 2\,HCO_3^- \quad (8)$$

6.3. Gas composition in the BMG and GG geothermal systems

The NCG composition in the steam phase is of importance for both emission calculation and power plant design in geothermal fields. Along the BMG graben, the gas ratios in the steam and gas phase are calculated as 1–2 %wt in the intermediate reservoir fluids (Haklıdır Tut et al., 2011; Serpen and Aksoy, 2010) and 3–3.2 %wt (Haizlip Robinson et al., 2013; Haklıdır Tut et al., 2011) in the deep reservoir fluids. The dominant gas is CO_2 with 95–99% in NCG both graben systems. CO_2 is the least soluble gas and it enters steam phase faster than H_2S and others (Nicholson, 1993). Ellis (1962) and Nicholson (1993) state that gas solubility in the liquid phase increases with temperature and H_2S may be 2–3 times more soluble over 200–260 °C and the solubility of these gases decrease with increasing salinity of the waters. The pH of water is one of the factor to solubility of H_2S between liquid and gas phases in a geothermal system (CEC, 1980). In the BMG geothermal systems, other, less prominent gases can be classified as minor amounts of N_2 and CH_4 and trace amounts of NH_3, H_2S and H_2. Detailed NCG data are available for the Kızıldere and the Germencik fields, allowing for the comparison of the non-condensable gas component concentrations, except for CO_2 in the western and eastern parts of the BMG.

One of the corrosive gases is H_2S, whose concentrations are very different in the Kızıldere and the Germencik fluids. The H_2S gas results indicate that H_2S concentrations in the Kızıldere geothermal fluids are one-tenth of the H_2S concentrations found in the Germencik geothermal fluids. The water chemistry supports these values, because the SO_4^{2-} concentrations are over ten times higher in the Kızıldere geothermal fluids than the Germencik fluids. This may be the result of oxidation of H_2S because of the higher reservoir pH in the Kızıldere waters than in the Germencik waters. The presence of high H_2S and high Cl- may generate a more acid milieu in the Germencik reservoir. NCG composition of Alaşehir reservoir fluids shows similarity to that of Germencik fluids. The H_2S concentration is also high in Alaşehir fluids. The origin of the H_2S may be due to hydrocarbon reserves almost 3 km away from the field. In 2008, a potential oil zone was discovered in Sarıkız-2 well at 1.8 km depth by a private company (Gürgey et al., 2014). Hydrocarbon traces in well logs have been detected during a few geothermal drilling operations (for example Piyadeler village; Zorlu Energy licence area) in the Alaşehir region.

CH_4 is a hydrocarbon gas and the concentration of CH_4 is slightly higher in Germencik reservoir fluids than Kızıldere reservoir fluids

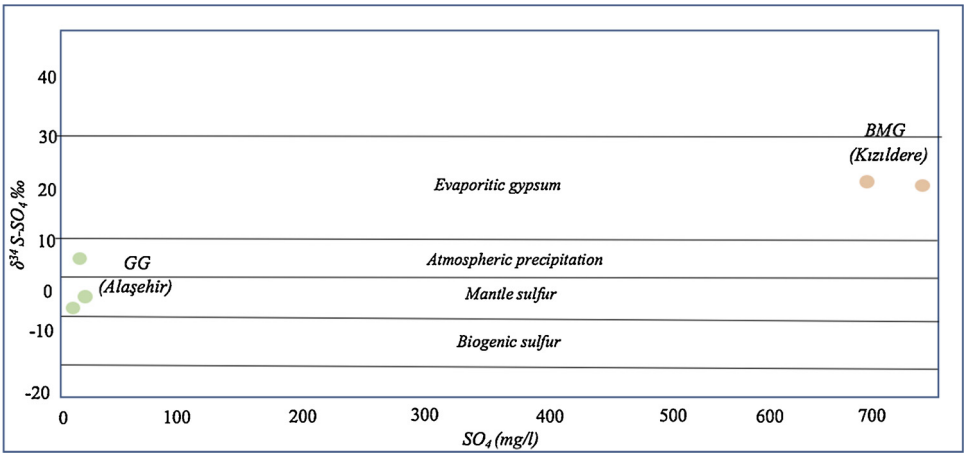

Fig. 12. $\delta^{34}S$ values for the BMG and GG Geothermal Systems (modified after Hoefs, 1997).

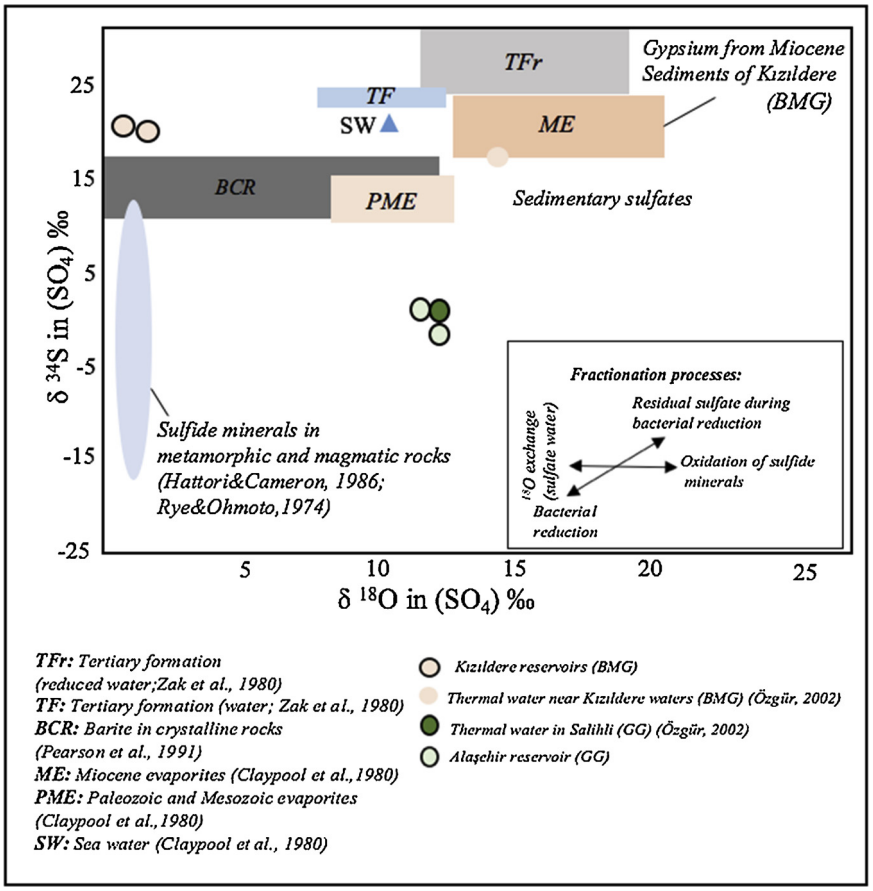

Fig. 13. $\delta^{34}S$ versus $\delta^{18}O$ - SO_4 for the BMG and GG Geothermal Systems (modified after Özgür, 2002).

along the BMG graben. The Germencik and Kızıldere fluids have quite similar He gas concentrations. Karakuş and Şimşek (2013) and Wiersberg et al. (2011) suggest a low mantle-He contribution for both fields based on their detailed ^3He isotope studies.

7. Conclusions

The large graben systems possess remarkable geothermal systems in Western Anatolia. Although the main reservoir geology indicates similarities between the BMG and the GG, the geofluids show different chemical and isotopic compositions. In the water phase, Cl^-, SO_4^{2-}, Li and boron ion concentrations show remarkable variations along the BMG from the western to the eastern line. The Germencik fluids have higher Cl^-, Li and B ion concentrations, and the lowest SO_4^{2-} concentration in the BMG. The Cl^- and boron concentrations tend to decrease from the Germencik to the Kızıldere geothermal reservoirs along the graben. The Kızıldere SO_4^{2-} values are the highest in the graben. In the Germencik field, where there is the highest water-rock interaction along the graben, stable isotope values indicate a marine sediment effect; although, similar reservoir temperatures exist within the Kızıldere geothermal field. The Alaşehir geothermal fluids contain the highest boron concentration as in the GG among all geothermal systems in the study area. The system is shallower than the BMG geothermal systems, the lower Na/K values indicate a shorter water-rock interaction duration. Meanwhile, the $\delta^{18}O$ values for the thermal waters demonstrate a positive shift from the GMWL. High Cl^-, boron concentrations may lead to lower pH values due to CO_2 effects in the Alaşehir geothermal fluids. Along the BMG, a striking change on SO_4 has been detected in the water phase. From the west to the east of the BMG, SO_4 ion concentration increase in water phase while, H_2S is decreasing in the gas phase. This may be the result of the lower pH, the higher temperature of the reservoir than in the other geothermal fields and a high concentration of organic material due to paleo-marine sediments in the Germencik geothermal field.

The origin of the sulfur appears different between the edges of BMG geothermal systems. The non-condensable gas compositions in the west edge of the BMG and the GG show similarity. The isotope results indicate that the origin of sulphur looks gypsum in the east edge of the BMG while mantle sulfur contribution is possible for Alaşehir geothermal system in the GG. Although both these graben systems have different type hydrocarbon evidences, oil wells exist close to Alaşehir geothermal system in the Gediz Graben.

It is proposed that high reservoir temperatures and magmatic origin gases cause more acidic reservoir conditions in the west part of the BMG and the GG geothermal systems. These acidic reservoir conditions directly affect fluid chemistry by leaching of rocks in these systems. It is suggested that together with the stable isotope values, the Germencik and the Alaşehir production wells are closer to the heat source than the Kızıldere and the other geothermal fields in the study area. It is thought that measured reservoir temperatures at 276 ^0C in the Germencik geothermal system and at 250 ^0C in the Alaşehir and at 287 ^0C 15 km far from the Alaşehir have been supported this suggestion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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