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Source of arsenic based on geological and hydrogeochemical properties of geothermal systems in Western Turkey

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ABSTRACT

Turkey is an area of complex geology with active tectonics and high geothermal potential. Especially, the western part of Turkey is a region of abundant geothermal activity. Faults accommodating the deep circulation of hydrothermal fluids of meteoric origin are the primary means by which of geothermal systems are controlled in this region. Many of the thermal activities are related to the improved dilation on the ~E–W-strikes of the graben faults. This situation serves as a suitable environment for the presence of high levels of arsenic in geothermal water resources. The highest concentrations of naturally occurring aqueous arsenic (As) are found in certain types of geothermal waters, generally those related to major graben faults. In this regard, high arsenic concentrations in geothermal resources have been detected in Western Turkey, including but not limited to Biga Peninsulla, Gediz Graben, Kucuk, and Buyuk Menderes Graben with values ranging from 1 to 1419 ppb in geothermal fluids. The thermal waters have surface temperatures of up to 100 °C and reservoir temperatures range from 150 to 248 °C in the Menderes Graben, from 120 to 287 °C in the Gediz Graben, and from 153 to 174 °C in Biga Peninsula. Hydrogeochemically, the Menderes graben and Gediz Graben thermal waters are of the Na-HCO_3, Ca-HCO_3, and Na-SO_4 types, whereas some geothermal fluids such as those of Tuzla and Kestanbol in the Biga Peninsula, Çeşme, and Urla are of the Na-Cl type.

1. Introduction

Occurrence of arsenic (As) in groundwater and its impacts on millions of individuals worldwide is a serious environmental health issue. The sources of As are both natural and anthropogenic and affect different regions of the world both on a local, as well as on a regional scale (Van Halem et al., 2009; Bundschuh et al., 2010; Gunduz et al., 2010a). In many countries such as India and Bangladesh As is naturally found in the subsurface strata within volcanic and sedimentary formations as well as in areas of geothermal systems related to tectonic activity. For well over 100 years, high As concentrations have been reported for many thermal waters and fumaroles (Nordstrom, 2010). Arsenic concentrations at the geothermal field, El Tatio (North Chile), Copper River (USA), Yellowstone National Park (USA), and Los Humeros (Mexico), have been reported to be as high as 48 ppm, 48.2 ppm, 15 ppm, and 74 ppm respectively (Ellis and Mahon, 1967; Motyka et al., 1989; Ball et al., 1998; Gonzalez-Partida et al., 2001; Romero et al., 2003). Generally, a high concentration of As is found where there is sulfide-mineral precipitation as a result of diagenetic-hydrothermal-tectonic cycles.

Turkey is located within the Mediterranean Earthquake Belt where complex rock deformation results from the continental collision between the African and Eurasian plates (Bozkurt, 2001a). The border of these plates constitutes seismic belts marked by young volcanics and active faults, with the latter allowing circulation of water, as well as heat flow and geothermal energy. The distribution of hot springs in Turkey roughly parallels the distribution of the fault systems, young volcanism, and hydrothermally altered areas (Simsek et al., 2002). There are a total of about 1000 thermal and mineral water spring groups in the country (MTA, 1980; Simsek et al., 2002) (Fig. 1). This natural setting serves as a suitable environment for the presence of high levels of arsenic in geothermal fluids. The most prospective regions are the Menderes Massif, a large basement complex within the Tethyan orogenic belt that has experienced tectonic denudation and extension, accompanied by widespread hydrothermal activity, since the Miocene age. Geothermal circulation in the Menderes Massif is not driven by igneous activity, but by high thermal gradients in the extended continental lithosphere. A heat flow map of the region shows the presence of high heat flow anomalies along the grabens (Simsek, 2010a, 2010b), most likely due to magmatic intrusions. Filiz (1982) suggested that the origin of CO_2 gas from the geothermal fluid along the edges of the Menderes and the Gediz Grabens is magmatic. Gulec determined that for the western part of Turkey such geothermal fluids are coming from the mantle (Gulec, 1988). Results show that meteoric waters which percolate deep into the crust gain heat from magmatic intrusions (Gokgoz et al., 2010). Although igneous activity was present during the Early Tertiary and Late Tertiary ages in

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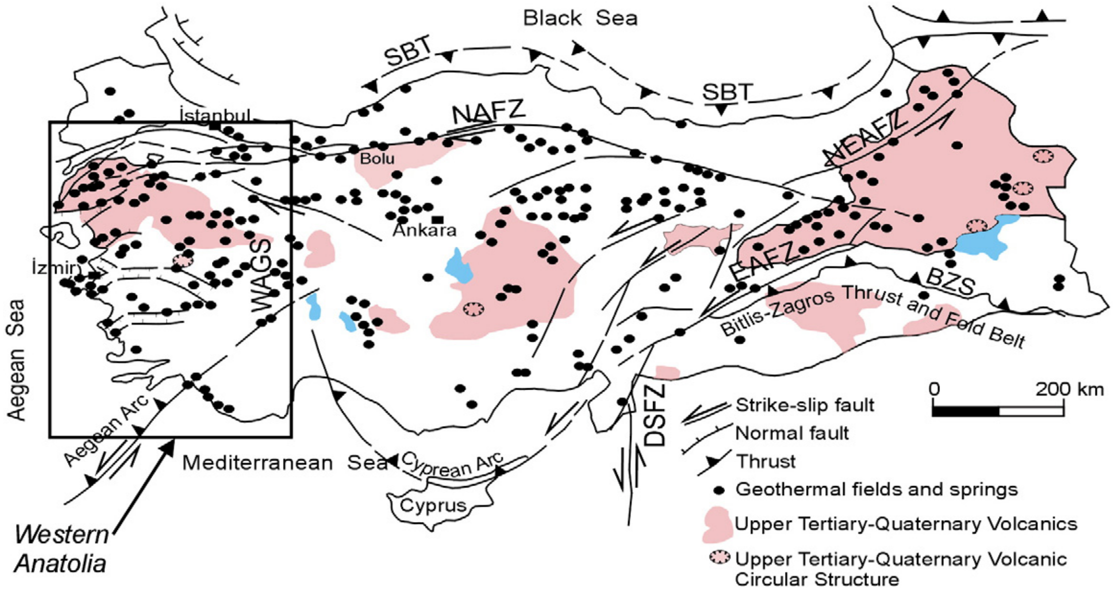

Fig. 1. Tectonic map of the eastern Mediterranean region showing structures developed during the Miocene to Holocene time and distribution of geothermal areas around Turkey (compiled from; Simsek et al., 2002 and Yigitbas et al., 2004). (SBT, Southern Black Sea Thrust; NAFZ, North Anatolian Fault Zone; NEAFZ, Northeast Anatolian Fault Zone; EAFZ, Eastern Anatolian Fault Zone; WAGS, Western Anatolian Graben System; DSF, Dead Sea Fault Zone; BZS, Bitlis-Zagros Suture) (Baba and Ármannsson, 2006).

this region, today only one small volcanic center–producing asthenospheric melts–remains in the area (Seyitoglu et al., 1997).

This study discusses the potential sources and levels of arsenic in geothermal resources of the region with particular emphasis on the sedimentological and tectonic properties of the Western Anatolian Plate.

2. Geological setting

Western Anatolia forms one of the most seismically active and rapidly extending regions in the world and has been currently experiencing an approximate N–S continental extension since at least Miocene times. The N–S extension in the region has resulted in many Neogene to Quaternary continental basins trending mainly in the E–W and NE–SW directions (Şengör et al., 1985; Yılmaz et al., 2000). The activity of the bounding high-angle normal faults is shown via numerous earthquakes (Arpat and Bingol, 1969; Şengör et al., 1985). North of the Gediz and Buyuk Menderes graben are NE-trending basins that are generally oriented at high-angles to the E–W-running basins. The best-known of these are the Gordes, Demirci, Selendi, and Usak-Gure basins (Seyitoglu et al., 1997; Bozkurt, 2003; Purvis and Robertson, 2004; Ersoy et al., 2008; Fig. 2).

Much progress have been made in the last ten years toward understanding the extensional event that affected the province (Fig. 2), especially the Gediz and the Büyük Menderes Graben and their subprovince should be classified as highly extended terranes (HET) as is the case for the Basin and Range Provinces. These terranes led to the structural juxtaposition of ductilely deformed mid-crustal rocks against brittle-deformed supracrustal rocks in an area known as the Menderes Metamorphic core complex (Bozkurt and Park, 1994), which was formed by the development of a bivergent fault system (e.g. Hetzel et al., 1995), and also containing a northerwardly dipping low-angle normal fault along the southern margin of the Gediz Graben (Hetzel et al., 1995; Emre, 1996; Emre and Sözbilir, 1997; Bozkurt, 2000; Sözbilir, 2001, 2002; Seyitoğlu et al., 2002; Yılmazer et al., 2010) and a southwardly dipping low-angle normal fault along the northern edge of the Büyük Menderes Graben (Emre and Sözbilir, 1997; Bozkurt, 2000, 2001b; Lips et al., 2001). Detachment fault systems in this province are associated with domal uplift of the Menderes metamorphic core complex, specifically of its lower plate, and the formation of asymmetric supradetachment basins in the upper plate. However, there are some studies revealing the presence of a number of NE–SW trending strike-slip faults controlling the NE-trending Miocene deposition on the western Anatolian crust onshore (Kaya, 1981; Genç et al., 2001; Kaya et al., 2004, 2007; Erkül et al., 2005; Uzel and Sözbilir, 2006, 2008; Sözbilir et al. 2008) and offshore (Ocakoğlu et al., 2004). This transversely oriented strike-slip-dominated zone that accommodates the lateral termination of E–W-trending graben-faults, linking spatially the discrete loci of the terranes, includes the İzmir–Balıkesir Transfer Zone. The İzmir–Balıkesir Transfer Zone has been described as a NE-trending strike-slip dominated zone, which because of its relative inactivity limits the extensional growth of the eastern coastlines of the Aegean Sea that lie between Balıkesir and İzmir (Okay and Siyako, 1991; Ring et al., 1999; Sözbilir et al., 2003; Özkaymak and Sözbilir 2008; Uzel and Sözbilir, 2008).

Seismic tomography shows that the African slab under western Turkey is decoupled from the African Plate. This detached slab is a single, coherent body, representing the lithosphere and has been retracting since 90 Ma. There was no subduction re-initiation after slab break-off. The Anatolide–Tauride Block collision with Europe therefore did not immediately lead to slab break-off but instead to the delamination of subducting lithospheric mantle from the accreting Anatolide–Tauride Block crust, while staying attached to the African Plate. This led to asthenospheric inflow below the Anatolide–Tauride crust, high-temperature metamorphism and felsic magmatism. Slab break-off in western Turkey probably occurred ~15 Ma ago, after which an overriding plate compression and rotation accommodated ongoing Africa–Europe convergence (Hinsbergen et al., 2010).

3. Tectonostratigraphic units in western Anatolia

The Late Palaeozoic–Early Mesozoic units in the western Anatolian region define four distinct tectonostratigraphic units, from north to south: (i) the Sakarya Zone (e.g. the Karakaya complex) (Şengör et al., 1984; Okay and Tüysüz, 1999; Okay and Altıner, 2004), (ii) Izmir–Ankara–Erzincan Suture Zone including the Karaburun Belt (Erdoğan, 1990; Okay et al., 2001; Çakmakoğlu and Bilgin, 2006) (Fig. 2), (iii) Menderes Massif-Cycladic Massif and (iv) Lycian nappes (Şengör and Yılmaz, 1981; Robertson and Pickett, 2000; Bozkurt and Oberhänslı, 2001). These units have distinct characteristics in terms of stratigraphy,

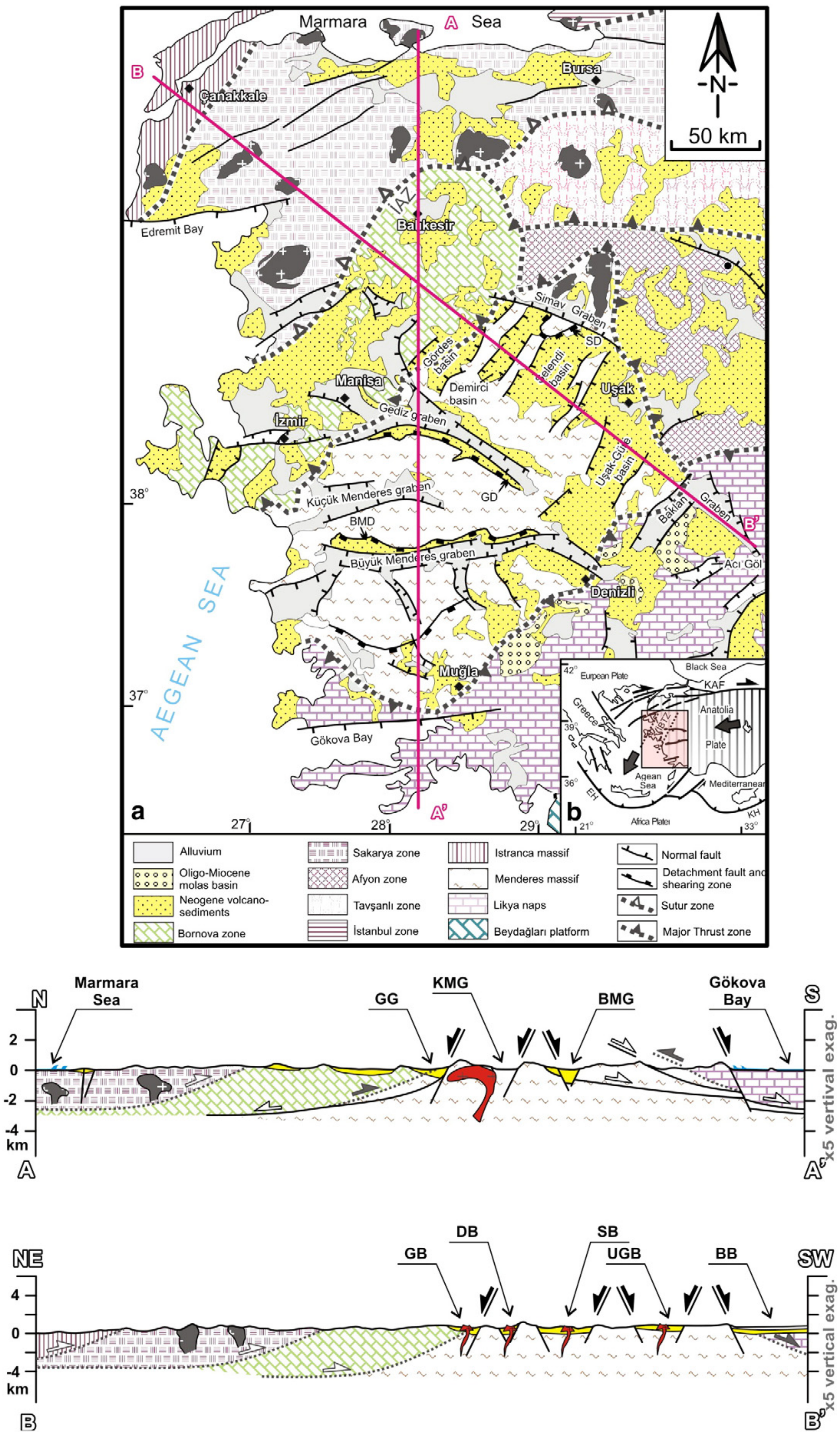

Fig. 2. Geological map and cross section of western Turkey (modified from MTA, 2002 and Sozbilir et al., 2011).

structure, and degree of metamorphism. The Sakarya Zone consists of a highly deformed and slightly metamorphized clastic and volcanic series existing since the Permian and Triassic ages. The Izmir–Ankara–Erzincan Suture Zone is characterized by Palaeocene and younger thrust zones that form the main boundary between the Karakaya complex in the north and the Anatolide-Tauride block in the south (Erdoğan, 1990; Okay et al., 1996; Okay and Tüysüz, 1999; Okay and Altıner, 2007). The Izmir–Ankara ocean was one of the northern Neo-Tethyan strands in Anatolia. Its closure during the Palaeogenic age caused the collision between the Sakarya continent (SC) and the Taurus–Menderes platform (TMP) along the Izmir–Ankara suture zone (Şengör and Yılmaz, 1981). This collision resulted in contractional deformation during the Palaeogenic age which was succeeded by an Oligo-Miocene extension in western Anatolia (e.g. Seyitoğlu and Scott, 1996; Işık et al., 2004; Purvis and Robertson, 2004; Kaya et al., 2007).

The Karaburun Belt lies to the far west of the Izmir–Ankara–Erzincan Suture Zone with a platform-type carbonate succession, and is included in the continuation of the Sakarya continent in the classification of the cratonic realms of western Turkey (Şengör and Yılmaz, 1981). The Karaburun Belt, also known as Karaburun Mélange, is made up of Silurian—Upper Carboniferous exotic blocks within a sheared matrix of siliciclastic turbidites (Robertson and Pickett, 2000). The underlying structure of the Cycladic Massif is composed of eclogites, blueschists, and high-pressure olistostromal units (Oberhänsli et al., 2001). The Cycladic units rest on the Menderes Massif, consisting of metasediments, metabasic rocks, and Early-Middle Triassic granitic rocks (Koralay et al., 2001), and orthogneisses. Both the Cycladic and Menderes massifs are structurally overlain by metasediments that have undergone high-pressure metamorphism, and ophiolites of the Lycian nappes (Oberhänsli et al., 2001; Güngör and Erdoğan, 2002). The stratigraphy of the Menderes Massif was based principally on the metamorphic sequences of the Cine submassif where a Pan-African core sequence is overlain by a Palaeozoic–Mesozoic metasedimentary cover sequence (Schuiling, 1962). However, recent studies show that this simple subdivision is incorrect (e.g. Ring et al., 1999; Gessner et al., 2001; Lips et al., 2001; Ozer and Sözbilir, 2003). According to these studies, the massif is made up of four tectonoctratigraphic units which are, from bottom to top, rudist-bearing metamorphic rocks of the Bayındır unit, a high-grade metamorphic unit intruded by Pan-African and Triassic granites, the metasedimentary Bozdag unit, the gneiss-dominated Cine unit with Pan-African granitic protoliths, and the Selimiye metasedimentary unit of the Permo–Triassic age (Gessner et al., 2001; Okay, 2001; Ozer and Sözbilir, 2003).

4. Volcanism/magmatism of Western Anatolia

Western Anatolia includes several different types of mineral deposits such as epithermal, porphyry, and skarn, related to the complicated tectonic and magmatic history of the region (Ozturk and Helvacı, 2008). In western Anatolia, these tectonostratigraphic units are cut by some granitoids which are sources of heat in the geothermal system of western Turkey (Fig. 2). Arsenic mobilization from rocks into the hydrosphere and pedosphere occurs in western Anatolia with mineralization and hence is a very common process in this region with volcanism and magmatisim mineralization. Mineralized rock and hydrothermal circulation, which are frequently contained in altered form are often produced by these conditions.

The genesis of Late Cenozoic volcanic and plutonic rocks throughout the Aegean Sea region was formerly ascribed to the southward migration of the Aegean subduction (e.g. Fytikas et al., 1984), but most are now considered as having resulted from regional extension and derived mainly from a hybrid magma formed by mixing of coeval mafic and felsic melts. The source of mafic magma is usually attributed to sub-continental lithospheric mantle (Seyitoğlu and Scott, 1992; Pe-Piper et al., 1995; Aldanmaz et al., 2000; Okay and Satır, 2000; Pe-Piper and Piper, 2001) or mafic lower crust (Aydogan et al., 2008; Ozgenç and Ilbeyli, 2008). Altunkaynak and Dilek (2006) and Dilek and Altunkaynak (2007) have studied in detail the chrono-spatial evolution of the Cenozoic postcollisional magmatism in western Anatolia and concluded that the magmatism has occurred in three distinct pulses becoming younger from north to south. The first magmatic episode occurred during the Eocene and Oligo-Miocene regional compression and is attributed to an enriched subcontinental lithospheric mantle and crustal material which was also affected by an influx of asthenospheric heat and melts provided by lithospheric slab breakoff (Dilek and Altunkaynak, 2007). The second magmatic episode is ascribed to subduction-modified lithospheric mantle, crustal material and asthenospheric mantle during the Middle Miocene extensional regime as a result of delamination of the lowermost part of the lithospheric mantle, and/or partial convective removal of the subcontinental lithospheric mantle (Dilek and Altunkaynak, 2007). The third magmatic episode was generated by decompressional melting of asthenospheric mantle which commenced around 12 Ma and continued through the Late Quaternary under the extensional tectonic regime (Dilek and Altunkaynak, 2007); the continental extension is the current tectonic regime of the western Anatolia (Bozkurt and Oberhänslı, 2001; Emre and Sözbilir, 2007).

5. Source for arsenic formation

The volcanic activity that has been dominant in the geological formation of Turkey and particularly in Western Anatolia is the primary mechanism for the presence of numerous trace elements in earth's crust, including but not limited to arsenic (Baba et al., 2009c; Gunduz et al., 2010b). Arsenic levels up to 4% have been observed in mineral deposits, particularly in the Kütahya-Emet region, which is known to contain the world's largest boron deposits (Helvacı, 1986; Helvacı and Orti, 1998; Helvacı and Alonso, 2000). In the Western Anatolia region, arsenic is typically observed in the alteration zones of volcanic formations, in addition to its presence in some sedimentary rocks. Based on the tectonic characteristics (see Fig. 1) and the geological structure, many parts of Turkey are likely to have arsenic-containing geological formations within which geothermal resources are also expected to contain high arsenic levels (Table 1). Most of these rocks are altered and fractured, due as a result of active tectonics. Also, in Western Turkey's geothermal regions, metamorphic and sedimentary rocks are noted as being intensely hydrothermally alterated, as represented by the phyllic, argillic, and silicic-hematitic alteration zones (Ozgur et al., 1997; Baba, 2010; Gunduz et al., 2010a). Especially in some parts of western Turkey, volcanic activity led to the delineation of wide-ranging areas of alteration within mineral assemblages, from advanced argillic type to silica type to prophylitic type at deep levels. The advanced argillic alteration zones are typified by enrichments of sulfur in volcanic rocks in some

Table 1
Arsenic concentrations in rocks of Western Anatolia, Turkey (Gunduz et al., 2010a, 2010b).

Site	Province	Type	As (ppm)	Reference
Bayındır-Sarıyurt	İzmir	Ore	200	Bulut and Filiz (2005)
Kızıldere	Denizli	Rock	268	Ozgur (2002)
Etili	Çanakkale	Rock	700	Unpublished data from Alper Baba
Çan	Çanakkale	Coal	6413	Baba et al. (2009a, 2009b)
Emet	Kütahya	Rock	3900	Dogan and Dogan (2007)
İğdeköy-Emet	Kütahya	Ore	40,000	Colak et al. (2003)
Simav Sb Mine	Kütahya	Ore	660	Gunduz et al. (2010a, 2010b)
Dulkadir	Kütahya	Rock	4197	Atabey (2009)
Emet	Kütahya	Rock	19,487	Atabey (2009)
Kırka Borate Mine	Kütahya	Ore	>2000	Helvacı and Alonso (2000)
Alaşehir Hg Mine	Manisa	Waste rock	1164	Gemici (2008)

parts of Western and Northwestern Turkey. Such areas are also enriched in arsenic. Oxidation of sulfide minerals, particularly of pyrite, leads to the production of ferric iron and sulfate. A similar situation can be seen for arsenopyrite (Atabey, 2009). The chemical equation of this process is given below.

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe + 2SO_4 + 2H$$

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe + 4AsO_4 + 4SO_4 + 12H$$

Dogan and Dogan (2007) mention that a natural source of arsenic (As) in some parts of western Turkey comes from evaporitic minerals, carbonate, volcanic rocks, and coal. They point out that the sources of arsenic are mainly evaporitic minerals, including colemanite (269–3900 ppm) and gypsum (11–99,999 ppm), but also alunite (7–10 ppm) and chert (54–219 ppm). Also they are present in secondary epithermal gypsum, which has a high concentration of As in the form of realgar and orpiment along the fracture zones of Mesozoic and Cenozoic carbonate aquifers. In addition to this they mention that limestone/dolomite (3–699 ppm) and travertine (5–4736 ppm) are relatively more enriched in As than they are in volcanics (2–14 ppm), probably because of secondary enrichment through hydrological systems.

The sulfur isotopic composition of orpiment/realgar samples of the Emet deposits in the Hisarcık open pit mine located in western Turkey shows very low $\delta^{34}S_{sulfide}$ values (-33.7 ± 2.3‰; $n = 4$). These values, which are lower than any published data for the presence of dissolved sulfide in geothermal fluids, have been attributed to a microbial-mediated sulfate reduction process (Palmer et al., 2009). García-Veigas et al. (2011) assume that periodic changes in redox conditions during early diagenesis led to dissolution of colloidal arsenopyrite, probably induced by micro-organisms, and to the precipitation of arsenic sulfides.

6. Hydrogeochemical properties of geothermal resources

Several studies were carried out about the hydrological, hydrogeochemical and geochemical features of geothermal fields in Western Turkey (Samilgil, 1966, 1985; Kasap, 1984; Simsek, 1984; Tarcan, 1995; Karamanderesi, 1997; Mützenberg 1997; Mutlu, 1998; Tarcan et al., 2000; Aksoy, 2001; Gemici and Tarcan, 2001; Tarcan and Gemici, 2001; Vengosh et al., 2002; Baba, 2003; Baba and Özcan, 2005; Baba et al., 2005; Baba and Ármannsson, 2006; Baba and Ertekin, 2007; Sanlıyüksel and Baba, 2007; Deniz et al., 2010). All these studies focus on each geothermal system. No studies focus on the potential sources and levels of arsenic in geothermal resources of the region especially with regard to particular emphasis on the sedimentological and tectonic properties of the Western Anatolian Plate. Also very few researchers measured arsenic in the geothermal fluids of Western Turkey. Most of the geothermal fluids originated from the Menderes Massif which discharges along the rims of east–west-trending faults that form the Büyük Menderes, Küçük Menderes, Gediz, and Simav grabens. Some thermal springs originate from the Kazdağı Massive in Northwestern Turkey; the circulation of the geothermal fluid is closely related to the major faults and fractured zones in these regions (Fig. 3). The Menderes Massif consists of gneisses, schists, karstic marbles, and granodiorite, including the aquifers of the geothermal systems. Also, Mesozoic carbonates are other reservoir rocks of the geothermal system in Western Turkey. Impermeable Neogene terrestrial sediments, which are made up mainly of sandy and clayey conglomerates, occur in different facies in the northern and southern parts of the grabens, since these rocks cap the geothermal systems. High concentrations of As (up to 1.42 mg/l) can be seen in these geothermal fluids as well as a close correlation between increasing concentration and elevated temperature. In addition trace elements indicating intense, high-temperature fluid-rock interaction-such as B (up to 67 mg/l) and Li (up to 12.2 mg/l) are found in high concentrations in geothermal fluids in western Turkey. B and Li exhibit a close correlation in the thermal waters as function of increasing temperature (Table 2).

6.1. Biga peninsula

The Biga peninsula is located in the northwestern part of Turkey and characterized by significant neotectonic activity. Regionally, the Biga Peninsula is closely related to the active tectonic zones of the North Anatolian Fault Zone and the West Anatolian Graben Systems (WAGS). For this reason, there are several geothermal springs with temperatures ranging from 30 to 174 °C in this peninsula. High-level granodiorite intrusions include the Kestanbol, Eybek, Ilıca, Kozak, Karabiga, and Evciler intrusions found here. The major geothermal regions of the Biga Peninsula are Tuzla, Kestanbol, and Hıdırlar. The measured reservoir temperature of Tuzla is 174 °C. The surface temperatures of Kestanbol and Hıdırlar are 76 °C and 84 °C, respectively. The Kocabaşlar, Kırkgeçit, Kulcüler, Palamutoba, Çan, Alibeykoy, Karaılıca, Bardakçılar, and Akçakeçili geothermal sites can be seen all around the Biga Peninsulla where the surface temperature of geothermal fluids ranges between 33 and 52 °C in springs (Table 2). Except for Tuzla and Kestanbol, the water types of this geothermal system are the $Na\text{-}SO_4$ type (Fig. 4a and b). However, Tuzla and Kestanbol water types are of the Na-Cl type (Fig. 4c and d). Isotopic composition studies show that the Tuzla, Kestanbol and other geothermal fluids in Biga Peninsula have different origins (Fig. 5). These results indicate that the hot saline waters (brine) in the Tuzla geothermal field originate from connate water along faults (Baba et al., 2009a, 2009b). Kestanbol water samples, depicted by oxygen ($\delta 1^8O$) and deuterium (δ^2H) show that mixing of meteoric or cold water and sea water occurs. Other geothermal fluids (from Hıdırlar, Kocabaşlar, Kırkgeçit, Kulcüler, Palamutoba, Çan, Alibeykoy, Karaılıca, Bardakçılar) have the same recharge area, shallow circulation, and are meteoric in origin as depicted by their $\delta^{18}O$ (‰) and δ^2H (‰) contents (Fig. 5). Ages of these three geothermal fluids are more than 50 years old, as determined by tritium (^3H) data. The other geothermal systems of the Biga Peninsula show properties similar to those seen at the Hıdırlar geothermal site. The highest concentration of As can be seen in Alibeyköy where the arsenic concentration ranges from 1 μg/l to 251.9 μg/l in Biga Peninsula (see Table 2).

6.2. Gediz graben

The Gediz graben is 140 km long and 3–40 km wide and has a WNW–ESE trending structure bounded by active normal faults. The Gediz detachment, which is located along a discontinuous trace along the fault for more than 100 km from Turgutlu to Alaşehir district, is one of several crustal-scale detachment faults that were formed at the edge of the southern basin of the Gediz graben (Koçyiğit et al., 1999; Sözbilir 2001, Fig. 3). The footwall of the Gediz detachment comprises mylonitic gneiss, marble, and schist of the Menderes metamorphic core complex as well as Miocene synextensional granite. The hanging wall of the detachment fault comprises Miocene to Quaternary sedimentary units reaching up to 2500 m thick.

Many geothermal resources occur along the Gediz Graben starting from the Alaşehir to the Sarıgöl Region in the east. The measured reservoir temperature has been found to be as high as 287 °C in this graben. The major geothermal sites of the Gediz Graben are Turgutlu (Urganlı), Salihli, and Alaşehir. The measured reservoir temperatures of Salihli, Alasehir and Urganlı are 287 °C, 215 °C, and 85 °C, respectively. The thermal waters of Alaşehir, Salihli, and Urganlı geothermal systems are alkaline, where carbonate alkalinity is greater than non-carbonate alkalinity (Yılmazer et al., 2010). The Kursunlu, Caferbey, Göbekli, Ufuruk, and Sart-Çamur geothermal sites are found in the Salihli Region where the surface temperature of geothermal fluid changes from 30 to 55 °C in springs and from 51 °C to 287 °C in

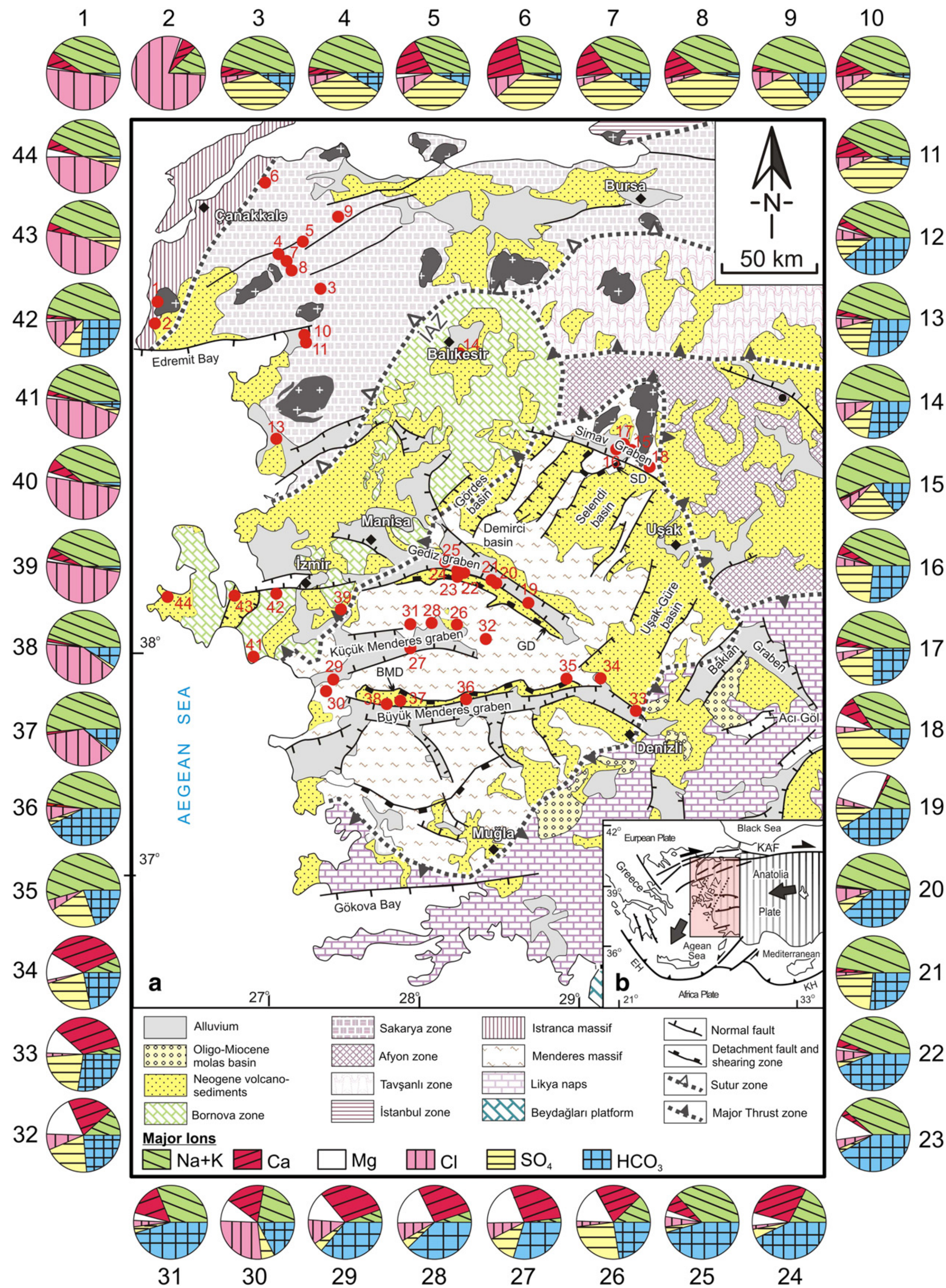

Fig. 3. General map of western Turkey and location of geothermal area.

wells. However, their discharges are between 2 and 80 l/s from either springs or wells (Ozen et al., 2010). The geothermal fluid of the Gediz Graben geothermal site has surface temperatures of 25–95 °C and has electrical conductivity of 874–6020 µS/cm. Mineralization is mostly dominated by Na^{+} (188–2027 mg/l) and HCO_3^{-} (544–2950 mg/l) (Tarcan et al., 2005). The chemical composition of Kursunlu, Caferbey,

Table 2
General data on geothermal systems from western Turkey.

Region	No	Location	pH	T	EC	Na	K	Ca	Mg	Cl	SO_4	HCO_3	As	B	Li	Water type	References
				°C	µS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l		
Biga Peninsulla	1	Kestanbol	6.4	74	3002	6529.6	759.21	902.3	65.63	12,929	112.5	334.2	184.3	7787	6367	Na-Cl	Baba and Deniz (2008)
	2	Tuzla	6.5	87	80300	5893	1979.2	2636	75.2	58,220	201	134	136	32000	nd	Na-Cl	Baba and Deniz (2008)
	3	Hıdırlar	7.9	75.5	1087	200.13	7.33	18.89	0.13	15	277.65	162	2.2	193	78.8	$Na-SO_4$	Baba and Deniz (2008)
	4	Alibeyköy	7.48	21	2460	612.49	13.91	38.07	3.84	83	970	290	251.8	2029	607.2	$Na-SO_4$	Baba and Deniz (2008)
	5	Çan	6.93	45.5	3160	606.99	27.42	259.8	22.12	201	1298	274	101.6	4050	1146.8	$Na-SO_4$	Baba and Deniz (2008)
	6	Koçabaşlar	7.4	31	1301	167.94	0.88	118.8	0.27	78	425	48.8	17.8	485	102.3	$Na-SO_4$	Baba and Deniz (2008)
	7	Karaılıca	6.76	43.3	2470	489.13	20.89	183	7.05	87	980	317.2	55.7	1991	1082.6	$Na-SO_4$	Baba and Deniz (2008)
	8	Bardakçılar	8.08	49.1	1689	298.52	5.71	86.13	0.24	25	672	48.8	0.8	360	113	$Na-SO_4$	Baba and Deniz (2008)
	9	Kırkgeçit	8.95	49	669	140.56	1.74	5.88	0.15	35	173	122	<0.5	760	98.6	$Na-SO_4$	Baba and Deniz (2008)
Edremit Graben	10	Edremit	7.83	57.6	1354	272.7	5.2	50.2	0.8	59.6	506.9	48.8	4.3	1190	305	$Na-SO_4$	Mutlu (2007)
	11	Derman	7.1	57.8	857	246	4.6	49.8	1.6	52	498	67.1	nd	nd	nd	$Na-SO_4$	Yalcın (2007)
Dikili-Bergama Graben	12	Pasha	6.52	46	2320	598	16.7	45.38	10.6	105	295	1523	690	4210	370	$Na-HCO_3-SO_4$	Tarcan and Gemici (2010)
	13	Dikili Ilıcası	7.3	65	2900	660	42	37	7.4	97.7	564	1090	nd	nd	nd	$Na-HCO_3-SO_4$	MTA-JICA (1987)
Bigadiç	14	Hisarköy	7.29	94.6	2820	706.4	74	8.4	11.7	206.7	381.5	1051.6	1265.5	8896	1501	$Na-HCO_3-SO_4$	Mutlu (2007)
Simav Graben	15	Eynal	9.51	96	2940	600	61	2	1	73	483	425	1020	5400	1000	$Na-SO_4-HCO_3$	Erisen et al. (1989), Palabiyik (2006)
	16	Çitgöl	7	83	1757	340	44	34	5.3	57	376	573	90	4200	–	$Na-HCO_3-SO_4$	Erisen et al. (1989), Palabiyik (2006)
	17	Naşa	6.57	63.5	1621	395	42	39	9.6	52	344	604	240	3400	800	$Na-HCO_3-SO_4$	Erisen et al. (1989), Palabiyik (2006)
	18	Gediz	7.3	74.4	3290	661.0	86.0	139.2	65.8	95.0	1153.5	1023.4	nd	nd	nd	$Na-SO_4-HCO_3$	Güneş (2006)
Gediz Graben	19	Alasehir	6.82	30.5	2240	231.5	15.9	2.8	192.3	60	276	1477	5	18,710	1229	$Mg–Na-HCO_3$	Bulbul (2009)
	20	Kavaklıdere	8.14	21	4450	1289.7	17.6	5	1.8	342	280	2929	260	15,001	643	$Na-HCO_3$	Bulbul (2009)
	21	Göbekli	8.31	95	6020	2027	78.9	12.8	3.1	165	1843	2950	nd	nd	nd	$Na-HCO_3-SO_4$	Bulbul (2009)
	22	Kurşunlu	7.43	55	2780	539	60	35	11	98	58	1449	nd	nd	nd	$Na-HCO_3$	Tarcan and Gemici (2005)
	23	Caferbeyli	7.8	90	2700	680	70	42	100	115	34	1983	nd	67000	nd	$Na-HCO_3$	Karamanderesi (1997)
	24	Sart	6.33	43	1506	155.3	24.99	197.7	24.63	27	71.9	976.3	23.39	14	230	$Ca–Na-HCO_3$	Ozen et al. (2010)
	25	Urganlı	6.93	60	2630	511	49	91	23	84	69	1679	nd	6000	1451	$Na-HCO_3$	Tarcan and Gemici (2005)
Küçük Menderes Graben	26	Odemiş	7.04	17	472	27	1.67	42	22	12	123	140	nd	50	120	$Ca–Mg-HCO_3-SO_4$	Yildirim et al. (2010b)
	27	Çayırlı	7.21	16.8	869	11	2.3	99	37	43	101	323	nd	320	890	$Ca–Mg-HCO_3$	Yildirim et al. (2010b)
	28	Kayaköy	7.39	18.5	468	11	0.7	49	19	27	15	211	nd	nd	nd	$Ca–mg-HCO_3$	Yildirim et al. (2010b)
	29	Belevi	7.3	19.7	890	21	2.9	108	27	65	34	375	nd	80	370	$Ca-HCO_3$	Yildirim et al. (2010b)
	39	Selçuk	7.4	18.2	1615	153	12.5	100	38	290	77	328	nd	100	970	$Na–Ca-HCO_3$	Yildirim et al. (2010b)
	31	Bayındır	7	38	1231	159	13.8	61	8	21	29	597	nd	700	400	$Na-HCO_3$	Yildirim et al. (2010b)
	32	Beydağı	7.32	18	907	53	3.9	77	44	48	185	280	nd	100	650	$Ca–Mg-HCO_3-SO_4$	Yildirim et al. (2010b)
Büyük Menderes Graben	33	Pamukkale	6.68	33	2520	40	5.2	450	86	12.2	610.1	1049	nd	nd	nd	$Ca–Mg-HCO_3$	Dilsiz (2006), Tokçaer (2007)
	34	Karahayıt	7	60	2900	116.8	23.6	505.2	117.2	24.5	863	964	7	120	nd	$Ca–Mg-HCO_3$	Dilsiz (2006), Gokgoz et al. (2010)
	35	Kızıldere	8.9	102	5080	1337	147	1.5	0.2	156	964	1306	1080	nd	nd	$Na-HCO_3$	Ozgur (2002)
	36	Salavatlı		167		1260	105	6	1	250	150	2900	nd	51.100	nd	$Na-HCO_3$	Vengosh et al. (2002),
	37	Germencik	8.7	231		1600	145	6	1.2	1700	24	900	nd	nd	nd	Na-Cl	Gemici and Tarcan (2001); Simsek (2003)
	38	Gümüşköy	8.2	80	11,560	2650	208	32	11	3456	70	1482	nd	nd	nd	Na-Cl	Simsek (2003), Yildirim et al. (2010a)
Seferihisar	39	Cumalı	6.25	66	30200	6058	1034	651	71	11,050	363	469	172	16,600	12,230	Na-Cl	Conrad et al. (1995), Tarcan and Gemici (2003)
	40	Tuzla spring	6.28	65	34,200	6328	759	794	225	12,200	602	466	75	12,800	9550	Na-Cl	Conrad et al. (1995), Tarcan and Gemici (2003)
	41	Doğanbey	6.9	72	7515	2750	130	128	38	4320	332	515	78	9800	5030	Na-Cl	Tarcan and Gemici (2003).
	42	Balçova	7.77	129	1842	459.5	36.5	13.22	2.19	200	186	664	1419	21,333	1873	$Na-HCO_3-Cl$	Aksoy et al. (2009), Simsek (2010a, 2010b), Tarcan and Gemici (2010)
	43	Urla	7.39	37	34,390	11468	469	1383	835	19,877	2865	140	24	4237	333	Na-Cl	Tarcan (2000)
	44	Çeşme	6.5	58	26,600	7108	631	677	367	11,530	1665	195				Na-Cl	Gemici and Filiz (2001)

nd: no data.

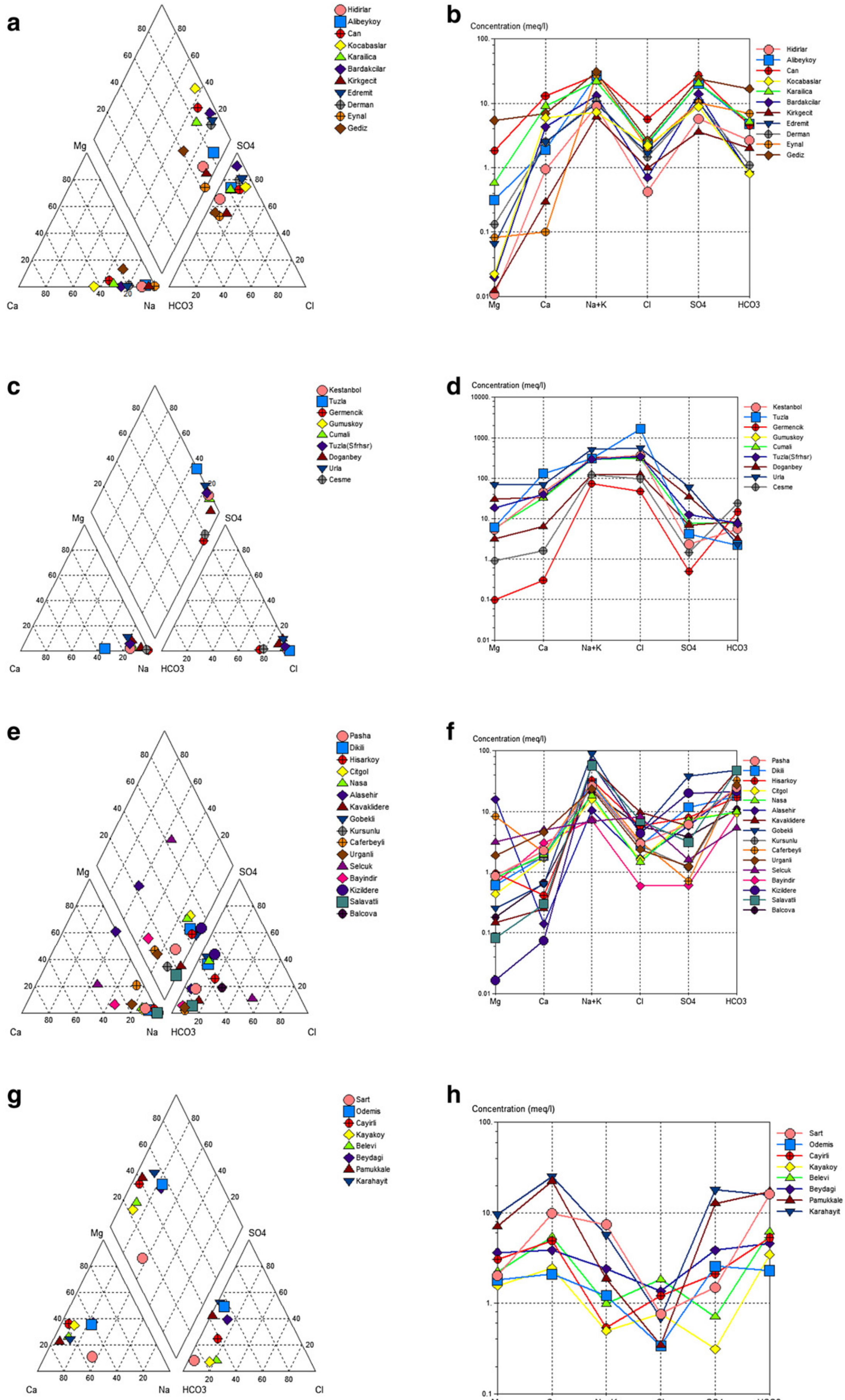

Fig. 4. Chemical analysis of water in the study area plotted on Piper and Schoeller diagrams.

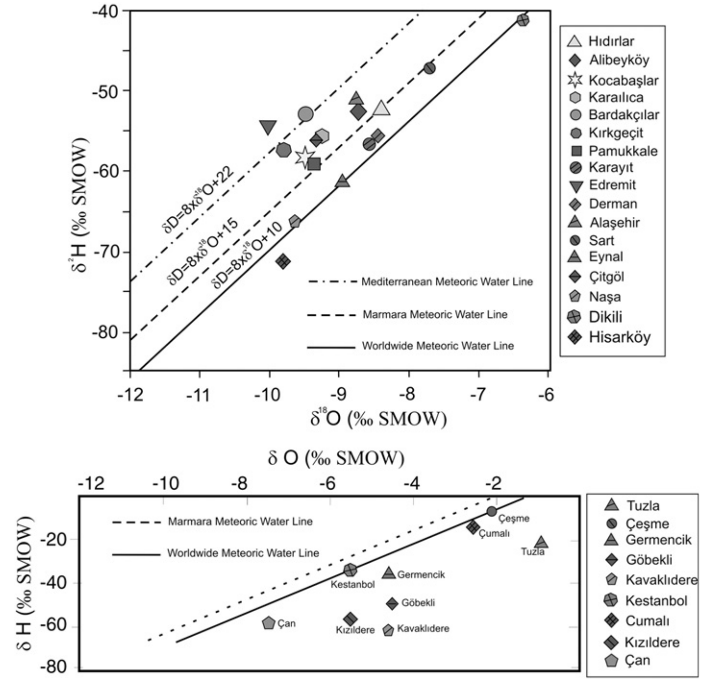

Fig. 5. Stable isotope compositions of the geothermal reservoir fluids in western Turkey.

and Sart-Çamur is of the Na-HCO_3, Na-HCO_3 (Fig. 4e and f), and Ca–Na-HCO_3 types (Fig. 4g and h), respectively.

According to isotopic ($\delta^{18}O$–$\delta^{2}H$) results, the geothermal fluid from Gediz Graben is fed by meteoric waters (Tarcan and Filiz, 1997) (Fig. 5). The Sart-Çamur Geothermal field is located in the southeastern part of the ancient city of Sardes, located in the Gediz region on the Kavaklıdere River, where the highest As values (260 μg/l) were measured in the thermal spring (Ozen et al., 2010). These thermal springs are located on the detachment fault of the Gediz Graben.

6.3. Buyuk menderes graben

Buyuk Menderes Graben contains the valley of the Buyuk Menderes River, which is 150 km long and 10–20 km wide. The graben is bordered by well-developed normal fault systems along its length. Rock units exposed in the vicinity of Buyuk Menderes Graben can be classified into two groups as the basement and basin fill units. Metamorphic rocks belonging to the Menderes Massif constitute the pre-Neogene basement units, which is an extensional metamorphic core complex in the Western Anatolian extensional province (Bozkurt, 2001b). The basin fill consists of four sedimentary packages that formed on the metamorphic rocks of the Menderes Massif (e.g. Sözbilir and Emre, 1990; Bozkurt, 2000). These are, from bottom to top, the early-middle Miocene Haskoy Formation, late Miocene Gokkırantepe formation, late Pliocene–Pleistocene Asartepe formation and Quaternary alluvium (Sözbilir and Emre, 1990). Detailed descriptions of the sequence stratigraphic units are given in Sözbilir and Emre (1990), Seyitoğlu and Scott (1992), Cohen et al. (1995) and Bozkurt (2000).

Büyük Menderes Graben is one of the most developed regions in Western Anatolia for geothermal energy research. The geothermal system is controlled by the active graben faults in the region. The reservoir rocks in the geothermal field are limestone in a Neogene complex, while marbles and quartzite schist exist in the Paleozoic basement complex. Most of the important geothermal systems can be seen between the Denizli and Aydın regions. Kızıldere, Gölemezli, and Yenice located in Denizli. Germencik, Ömerbeyli, Salavatli, Yilmazköy, Imamköy, and Ilıcabasi are located in the Aydın region. These geothermal sites have medium and high enthalpy fluid. The first electric power plant in Turkey, having an output capacity of 20.4 MWe was constructed in the Kızıldere (Denizli) geothermal site (200–242 °C). Turkey has six electric power plants that produce a total output capacity of 100 MWe via geothermal sources. Research on geothermal energy has been carried out at the Germencık-Aydın (200–232 °C), Sultanhisar-Aydın (145 °C) Salavatlı-Aydın (171 °C), Yilmazköy-Aydın (142 °C), Atca-Aydın (124 °C), Nazili-Aydın (155 °C), Umurlu-Aydın (155 °C), and Ilıcabasi-Aydın (101 °C), Gölemezli (75–88 °C) and Yenice (36–63 °C) sites in Denizli. Other important geothermal fields are the Tekkehamam, Buldan, Karakova, and Karahayit-Pamukkale sites in the Denizli region where the geothermal fields are located along the edges of the Menderes and Gediz Graben and the Germencik Camur-Bozköy-Alangüllü, Nazilli Basin (Güvendik-Gedik-Nazilli), and Söke fields in the Aydın region (Simsek, 2003). The results of analyses show that geothermal waters in the Aydin region change from site to site. Examples of high temperature wells of Gümüşköy are characterized by higher mineralization with the predominant ions being Na^{+}, K^{+} and Cl^{-}, and HCO_3^{-}. On the other hand, the mineralization of the "low temperature" springs of Argavlı and Sazlıköy is much lower and dominated by the presence of Ca^{2+}, Mg^{2+}, and HCO_3^{-}. The natural artesian discharge of Gümüşköy shallow mixture water displays intermediate mineralization between the two main groups, both of which are of the NaCl-type (Yildirim et al., 2010a). Also Germencik geothermal mixture water is mainly of the NaCl type (Fig. 4c and d) and of the Na-HCO_3 type (Fig. 4e and f) in the Salavatlı site. Thermal waters from Pamukkale springs are dominated by Ca–Mg-HCO_3 (Fig. 4g and h). The Karahayit geothermal site is located at the intersection of the Buyuk Menderes and Gediz grabens in the Denizli Province of Western Turkey. The reservoir rocks at the site are Paleozoic marble, various schist, and quartzite, all of which have high secondary permeability. The impermeable sediments of Neogene have good cap rock characteristics. The temperatures of thermal waters at the site range from 33 to 61.5 °C. The thermal waters are of the Ca-SO_4-HCO_3 type and of meteoric origin (Gokgoz et al., 2010). The chemistry of these thermal waters is probably dominated by a combination of mixing with cold waters, mineral dissolution–saturation reactions, and ion exchange reactions. Ion concentrations of hot waters from deep wells are higher than those of hot springs. However, their minor constituents are variable. Arsenic concentrations (1080 μg/l) of thermal waters at the Kızıldere geothermal sites are high. The tritium contents of the geothermal waters in Kızıldere, Aydın, and Germencik indicate that the residence time of recharging water in the geothermal system is more than 50 years while at the Pamukkale and Söke sites the thermal waters appear to be younger. There is a clear $\delta^{18}O$ shift from MMWL in the Kızıldere, Aydın, and Germencik high temperature fields (Simsek, 2003) (Fig. 5).

6.4. Küçük menderes graben

The Küçük Menderes Graben (KMG) is part of the horst-graben system of Southwestern Anatolia, Turkey. It is bounded by the Bozdağ horst in the north and by the Aydın horst in the south. The E–W-trending KMG is 80-km long and 3–10 km wide. It was developed over the pre-Miocene basement rocks comprising metamorphic rocks of the Menderes Masif, cut by the Miocene andezitic, basaltic rocks, and the Upper Cretaceous–Palaeocene Bornova melange. It is filled with Miocene–Quaternary continental deposits. The Miocene–Quaternary sequences are composed of five distinct rock types, from bottom to top: Miocene–Pliocene continental deposits, Pliocene fluvial clastics, Plio(?)–Quaternary elevated fluvial clastics, Quaternary alluvial fans and Quaternary alluvium. The Miocene–Pliocene continental deposits are widespread to the north of Torbalı and west of Selçuk. Other limited examples are seen in the northeast of Kiraz, as well as in the east and west of Tire.

Many springs can be seen in the Küçük Menderes Graben starting from towns of Ödemiş to Selçuk in the west. But most of these springs have low temperatures. The highest temperature (48 °C) of these geothermal fluids was measured in Bayındır, near Ödemiş. Except for the Bayındır spring, Çayırlı, Kayaköy, Beydağ and Ödemiş water samples fall into the earth-alkaline (Ca–Mg)-bicarbonate waters category, which is linked to shallow circulation. The Bayındır spring is of the Na-HCO_3 type (Fig. 4e and f). There have not been any analyses performed concerning arsenic and isotopes in the water resources of the Küçük Menderes Graben.

6.5. Seferihisar region

The Seferihisar region is located at the western termination of the Küçük Menderes Graben, close to the southeastern part of the İzmir–Balıkesir Transfer zone. The stratigraphy of the study area is considered within three main groups: (1) the basement rock units, which consist of Palaeozoic—Mesozoic metamorphic rocks of the Menderes Massif and the Upper Cretaceous—Paleocene rocks of the Bornova mélange; (2) Neogene volcano-sedimentary units (ancient basin fill units); and (3) Plio–Quaternary units (modern basin fill units). The metamorphic rocks of the Menderes Massif consist of schists and marbles with local phyllite intercalations (Güngör and Erdoğan, 2002). The Bornova mélange is made up of a deformed and locally metamorphized flysch-like matrix from the Maastrichtian–Paleocene age in which blocks of Mesozoic limestones, serpentinites, and submarine volcanics occur (Erdoğan, 1990). The Menderes Massif and tectonically overlying Bornova mélange are unconformably overlain by the Neogene volcano-sedimantary successions.

The Seferihisar Geothermal system is located south of the city of Izmir where several geothermal sites have been investigated since 1970. This geothermal system is characterized by an average heat flow of 110 mW m^{-2} (Ilkisik, 1995; Sari and Salk, 2003) and abundant geothermal activity controlled by strike-slip faults. The strike-slip and normal faults break into several splays along which natural hot springs form (Magri et al., 2010). The Na–Cl thermal waters of Seferihisar have measured surface temperatures of 66–72 °C. The reservoir temperature of this region reaches 153 °C. Bornova melange rocks, which consist of sandstone shale intercalations, conglomerate, mafic submarine volcanics, limestone lenses, serpentinite and limestone bodies, and their complexes, through the intersection of faults in this region. The clay-rich zones of the overlying Neogene terrestrial sediments cap the system. The heat source is the high geothermal gradient caused by the graben tectonics of the area. Na^+ and Cl^- ions mainly dominate the chemistry of these thermal waters, thus the thermal waters of the Seferihisar area appear to be mixtures of groundwaters and seawater (Tarcan and Gemici, 2003). The concentrations of As range from 78 to 172 μg/l in the Seferihisar geothermal field (see Table 2).

6.6. İzmir bay region

İzmir Bay is a typical depression for the Aegean back-arc domain undergoing N–S extension which is accommodated by active dip- to oblique-slip normal faults and strike-slip faults. The major part of the modern depression is flooded by the waters of Aegean Sea, forming the bay of İzmir.

The southern edge of the bay is characterized by the Balçova geothermal system, which is one of the most important geothermal locations for the city of İzmir, and supplies hot water to the Balçova district heating system. The geothermal fluid of this region is rich in terms of Na^+ and HCO_3^-. The Balçova geothermal sites are fed by meteoric groundwater seeping into the reservoir unit from terrains at elevations of about 500 m above sea level (Yılmazer, 1989; Aksoy, 2001; Aksoy et al., 2009). The highest concentration of arsenic (1419.8 μg/l) was measured in the Balçova district geothermal fluid (see Table 2).

6.7. Simav graben

Simav graben is a E–W trending Pliocene to Quaternary asymmetric depression that developed on the older NE–SW trending Miocene basins in Western Anatolia (Seyitoğlu, 1997). The graben is bounded from the south by an active oblique-slip normal fault, the Simav fault. The Graben fill associated with the Simav fault is composed of semlithified boulder conglomerate and sandstone. The northern part of the Simav graben is known as the Akdere basin, which consists of coarse clastics and Naşa volcanics.

The Simav geothermal field, one of the most important geothermal fields, is located in Kütahya's Simav graben system of Western Anatolia. The geothermal fluid of this region is rich in terms of Na-HCO_3-SO_4 (Fig. 4a and b) and Na-SO_4-HCO_3 (Fig. 4e and f) and is affected by groundwater which is low in the concentration of Cl^-. The water is of meteoric origin and belongs mostly to the immature water group (Palabiyik and Serpen, 2008). The concentration of As ranges from 90 to 1020 μg/l in the Simav geothermal site. The highest concentration of arsenic was measured in Eynal geothermal fluid (Palabiyik and Serpen, 2008).

6.8. Edremit graben

The Edremit graben which is 80 km long and 5 km wide, is an offshore graben of Western Anatolia. The northern margin of the graben is bounded by the Kazdağı Mountain, which rises from sea level to over 1000 m. The major faults bounding the Edremit gulf forms western branches of the North Anatolian fault Zone (Yılmaz et al., 2000). The most prominent topographic feature of the region is the Kazdağı horst formed in the late Paleozoic–Triassic period with exposed metamorphic rocks. The late Oliocene-Early Miocene Karaköy, Evciler and Kestanbol granodioritic plutons are intruded into the metamorphic basement. This unit is overlain by Miocene volcanosedimentary units (Siyako et al., 1989). Many geothermal springs have been seen in this graben. The surface temperature of these springs changes from 55 to 65 °C. The geothermal fluid of this region is rich in terms of Na-SO_4 as a result of the fault. The geothermal fluids of this region do not contain arsenic.

6.9. Dikili-bergama graben

The Bergama graben is one of the major depressions of western Anatolia. It is a V-shaped depression trending NE–SW along the Bergama district and NW–SE along the Dikili district. The faults along both sides of the grabens indicate oblique-slip normal faults.

The Kozak horst consisting of metamorphic (Triassic Karakaya formation), plutonic (latest Oligocene–Early Miocene Kozak granite) and volkanosedimentary units, rises to over 1000 m with respect to the Bergama and Dikili grabens. The region is mainly delineated by two sets of oblique-slip faults trending in the NE–SW and NW–SE directions (Karacık et al., 2007). All the products of the calc-alkaline Miocene volcanism of Western Anatolia crop out in this area. The Dikili-Candarlı high consists essentially of volcanic rocks. Two major rock groups have been distinguished: the Dikili and the Candarlı groups (Karacık and Yılmaz, 2000). The Dikili group is Early–Middle Miocene in age and consists mainly of pyroclastic rocks, lavas, and associated sedimentary rocks. The Candarlı group consists of Upper Miocene–Pliocene sediment association and volcanic rocks, which are rhyolitic domes and basaltic andesite-basalt lavas-dikes. The contact between Dikili and Candarlı groups is an unconformity surface.

The Dikili Bergama geothermal site is one of the most important geothermal sites, and is located in the north of Izmir. Many geothermal springs are exposed in this region. Geothermal fluids of this region are rich in terms of Na-HCO_3-SO_4 as a result of faults. The water is of meteoric origin. The highest concentration of arsenic for this region (690 μg/l) was measured in the Pasha geothermal fluid.

6.10. Karaburun Peninsula

The Neogene stratigraphy of the Karaburun Peninsula is represented by a volcano-sedimentary succession, including several sedimentary and volcanic units. These units rest on a basement comprising non-metamorphic and intensely sheared Paleozoic to Mesozoic rocks of the Karaburun belt (e.g., Erdoğan, 1990; Robertson and Pickett, 2000; Tatar-Erkül et al., 2008). The Neogene volcano-sedimentary units begin at the Bozköy Formation consisting of conglomerates of alluvial fans of fluvial origin. The unit laterally and vertically passes into the Urla limestone that is composed of mainly white-colored fresh-water limestones. In the Karaburun Peninsula, several volcanic units interfinger with the Urla limestone. These are Karaburun, Armağandağ, Kocadağ, and Yaylaköy volcanics, which were emplaced contemporaneously with deposition of the Urla limestone during latest early Miocene. These units are unconformably overlain by the Urla volcanics and finally the Ovacık basalt. The Urla volcanics have been dated by Borsi et al. (1972) to be 11.7 and 11.9 Ma (K–Ar ages). The overlying Ovacık basalt crops out in three different localities around the Urla village as small basaltic lava flows and have been dated by Borsi et al. (1972) to be 11.3 Ma (K–Ar age).

There are some geothermal springs venting on the onshore areas of the Karaburun Peninsula. Çeşme and Gülbahçe are placed in the western part of the İzmir city, where there is a hot water resource of high potential. The waters of this region have surface temperature values ranging between 30 and 60 °C. Çeşme and Gülbahçe water types are of the Na-Cl type. The concentration of arsenic (24 μg/l) was measured in the Gülbahçe geothermal fluid in this field.

7. Discussion

The Aegean region is well known for its geothermal resources and numerous hot springs. A crustal-scale metamorphic core complex, the Menderes Massif, dissects the approximately east–west grabens to form the most prominent features of the region. In the regional framework, the majority of west Anatolian geothermal waters are of either the Na-HCO_3 or the Na-Cl types, although Na-SO_4-type waters are also present. The waters are weakly acidic to alkaline with pH values ranging from 6.1 to 9.6, and have total dissolved solids (TDS) contents ranging between 550 and 54,884 ppm (Mutlu and Güleç, 1998). Thermal systems of western Turkey exhibit a wide range of chemical composition that reflects the complex nature and different sources of thermal waters (Table 1). Generally, the four major groups are separately reflecting different origins and mechanisms of water–rock interactions in western Turkey. The first group is an Na-Cl type of marine origin found in places such as Cesme, Urla, Seferihisar, and Kestanbol; the second group is an Na-HCO_3 type which is associated with metamorphic rocks of the Menderes Massif. The third group is an Na-SO_4 type that is also associated with metamorphic rocks of the Kazdağı and Menderes Massif and volcanic rocks. The last group is a Ca–Mg-HCO_3-SO_4 type that results from interactions with carbonate rocks at shallow depths (Vengosh et al., 2002).

Isotopic composition studies have shown that Tuzla, Kavaklıdere, Göbekli, Germencik, and other geothermal fluids in Western Turkey have different origins (Fig. 5). These results also indicate that the hot saline waters (brine) in the Tuzla and Germencik geothermal fields originated from connate water along the faults. Kestanbol, Urla, and Çeşme water samples are easily depicted in Oxygen ($\delta^{18}O$) and Deuterium (δ^2H) diagrams to show a mixing type of meteoric or cold water, and sea water. Water from these systems is deep circulated seawater. There is a clear ($\delta^{18}O$) shift from the MMWL. This suggests that the water–rock interaction is an important process for geothermal fluids according to the effect of deep circulation and high temperature of the waters of Tuzla and Germencik. Other geothermal fluids have the same recharge area, shallow circulation, and meteoric in origin as depicted by their $\delta^{18}O$ (‰) and δ^2H (‰) data. The age of these all geothermal fluids is more than 50 years as determined by Tritium (^3H) data.

The circulation of the thermal and mineral waters is closely related to major faults and fracture zones. Due to its neotectonic structure and the influence of volcanism, the Anatolian Plate contains various altered rock types that contain elevated levels of arsenic and other trace elements. Most of the thermal waters in Western Turkey are enriched in As with concentrations ranging from 1 to 1419.8 μg/l. High arsenic content is attributed to deep water circulation from a deeply seated magma body. The water–rock interaction is the most important source for arsenic. Generally As is attributed to the dissolution of ferromanganese minerals within the Late Miocene sediments in Western Turkey. For example; the high As concentration in the hot-saline waters of the Tuzla Geothermal Field results from the rapid evolution of anoxic conditions in brines (Drever, 1997) and the reduction of the sulfite (SO_3) formed by reactions with trace elements, followed by release of trace elements during oxidation of the metal sulfides via bacterial processes. Mixing of thermal water and shallow groundwater, (the latter providing the opportunity for oxidation processes to occur), provides an easy pathway for the dissolution of As in an aquatic environment (Baba et al., 2009a, 2009b). The As content may also be elevated, due to the dissolution of As in rhyolite tuff (Stauffer and Thompson, 1984) that is seen in different parts of the study area. Because of factors arising from active tectonics, many ore deposits are exposed along fault systems, where dense alterations can outcrop. Arsenopyrite, orpiment, and realgar can been seen in these zones. For example, Salihli, which is in Gediz Graben, is also known for its mineralized mercury of hydrothermal origin, where small mining operations have been carried out intermittently for several years. The site is currently under reconsideration as a prospect for epithermal mineralized Au–Sb (Larson and Erler, 1993). These ore deposits have arsenopyrite minerals. In the Salihli geothermal field hot springs are concentrated in the Kurşunlu, Kükürtlü, and Sart areas. Therefore high concentrations of As can be seen in the Kurşunlu thermal springs (Yılmazer et al., 2010).

8. Conclusion

Most of the geothermal fluids in western Turkey originated from the Menderes Massif Metamorphic, which discharges from the rims of the east–west-trending faults that form the Büyük Menderes, Küçük Menderes, Gediz, and Simav grabens. In addition to some thermal springs that originated from Kazdağı Massive in Northwestern Turkey, the circulation of the geothermal fluid is closely related to major faults and fractured zones in these regions. Some of the best known granitoids which are heat sources of the geothermal systems in western Turkey, from north to south, include the following: Karabiga, Kapıdag, Armutlu, Kestanbol, Evciler, Eybek, Orhaneli, Topuk, Tepeldag, Kozak, Egrigoz, and Baklan granitoids. Due to its neotectonic structure and the influence of volcanism, the Anatolian Plate contains various altered rock types that contain elevated levels of arsenic. The concentration of arsenic in geothermal waters in many places around western Turkey is found to exceed the maximum allowable limits (10 μg/l) set by national and international standards for drinking water. It is important to monitor arsenic in all geothermal systems and to study in detail the waterrock interactions within each geothermal system in western Turkey.

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