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Distribution of geothermal arsenic in relation to geothermal play types: A global review and case study from the Anatolian plate (Turkey)

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ABSTRACT

Arsenic has a natural cycle as it travels underground. It can mix with geothermal fluid in different ways under the control of magmatic and tectonic processes. Geogenic arsenic is present in many geothermal fields in the world at concentrations above the limits set for human health. The arsenic content of geothermal fluids is also related to the concept of geothermal play type, which forms geothermal systems, because the natural processes that form the geothermal system also control the arsenic cycle. In this study, an attempt is made to explain the relationship between the geothermal play type concept and geothermal arsenic circulation. For this purpose, geothermal field examples are given from around the world and Turkey. The result shows that arsenic concentrations can reach significant levels along with plate tectonic boundaries in the world. When arsenic concentrations were evaluated, the effect of major faults on the Anatolian Plate was clearly seen. Also, in the Anatolian plate where volcano-sedimentary units are common, geothermal fluids caused more effective alteration along with structural control and increased arsenic concentrations in geothermal systems. This interaction between structural elements, geothermal fluid, and the arsenic cycle shows that the concept of play type in geothermal systems should also be taken into consideration. It was determined that the places with high arsenic values are located within the convective-non-magmatic extensional geothermal play types such as Western Anatolian Extensional System and the North Anatolian Fault. The concept of play type in geothermal systems includes all systematic and external factors that make up these processes. For this reason, it is very important to evaluate the play type classification together with the arsenic cycle.

1. Introduction

Globally-occurring catastrophic natural phenomena, pandemic virus outbreaks, and climate change have begun to change our perspective on lifestyle, natural resources, and energy resources in the world. In recent years, many studies and were carried out in areas such as energy transition, the importance of water resources, and the evaluation of environmental impacts.

As a renewable energy, geothermal energy, which has been used for thousands of years in some countries for cooking and heating, is contained in rock mostly as hot fluids and steam within the Earth's crust. When magma comes near the earth's surface, it heats reservoir rock, geothermal fluid heats up and reaches the surface along fractures and faults (Dickson and Fanelli, 2004). For this reason, the most active geothermal resources are usually found along major tectonic plate boundaries. Also, economically important alteration zones and hydrothermal minerals were recognized in and around these active geothermal systems (e.g., Browne, 1970; 1978; Browne and Ellis, 1970; Reyes, 1990; Simmons and Browne, 2000; Simpson and Christie, 2019).

There are other integrated and practical applications of geothermal energy called "direct use," as well as use in electricity production. Greenhouse and space heating, cooling, thermal pools, drying, aquaculture, and other industrial applications are among the areas where geothermal resources have been used in recent years (Lindal, 1973). Different features of the geothermal fluid used in all these areas enable different applications. Fluid temperature and flow rate are the most important physical parameters in determining the usage area. For chemical parameters, element concentrations are the most critical factor controlling operating problems such as corrosion, scaling and environmental pollution effects. Especially higher element concentrations of

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arsenic, boron, and mercury, for example, which may be harmful to health and environment have become a natural pollution factor to be considered during the use of geothermal fluids (Baba and Ármannsson, 2006; Baba, 2010; 2015; Axtmann, 1975). However, with developing technology and research, it is possible to recover and extract these elements together with implementations called geothermal fluid mining/mineral extraction.

Previous studies have shown that geothermal fields have high concentrations of arsenic primarily originating from geothermal fluid (Ellis and Mahon, 1967; 1977; Pimentel et al., 1978; Birkle, 1998; Sakamoto et al., 1988; Gonzalez et al., 2000; Romero et al., 2003; Chandrasekharam and Bundschuh, 2008; Mukherjee et al., 2009; Birkle et al., 2010; Nordstrom, 2010; Baba and Sozbilir, 2012; López et al., 2012; Bundschuh and Prakash Maity, 2015). This is quite natural because arsenic is found in the continental crust of the earth, in most minerals, usually in combination with sulfur and metals or as a pure elemental crystal. Also, the arsenic concentrations associated with the rock cycle may differ depending on the hosting geological environments. Many researchers have reported high arsenic concentrations in geothermal fluids in different parts of the world (e.g., USA, Japan, Chile, Philippines, Iceland, Indonesia, and Turkey).

Within this study's scope, an attempt was made to establish a relationship between the geothermal play type concept and arsenic concentrations in important geothermal systems in the world, especially in the Anatolian Plate (Turkey).

2. Geothermal systems in the world

Geothermal energy sources have different usage areas today. In parallel with technological developments electricity generation has become a rapidly developing sector with new power plant types and applications, especially in recent years. The world total installed power capacity, which was around 10,000 MW_e in 2000, approached 20,000 MW_e in 2020 and has increased approximately twice (Fig. 1a). The top five countries for geothermal electricity production are the USA (3700 MW_e), Indonesia (2289 MW_e), the Philippines (1918 MW_e), Turkey (1549 MW_e), and Kenya (1193 MW_e) (Huttrer, 2020), while New Zealand, Mexico, Italy, Iceland, and Japan are other countries that use geothermal power plants for electricity generation.

The term "direct use of geothermal resources" includes space/residential heating, thermal pool & spa, cooling, drying, greenhouse heating, aquaculture, and industrial applications. Today, geothermal sources can be used directly if they have sufficient temperature, if not, they can be supported by heat pumps. While direct use rates increase every year (Fig. 1b), the top 5 countries for direct use (with heat pumps) are China, the USA, Sweden, Germany and Turkey, while the top 5 countries in direct use (without heat pumps) are China, Turkey, Japan, Iceland, and Hungary (Lund and Toth, 2020).

With developments in the geothermal energy sector, unfortunately, wrong and mistaken applications and some problems are also experienced. Conditions such as discharge of geothermal resources without reinjection, corrosion, scaling, accidents, and blow-outs damage living environments in the impacted area. Environmental effects will be inevitable, especially without reinjection and with discharge of geothermal fluids rich in arsenic and boron (Baba and Ármannsson, 2006). It is planned that development will continue in the geothermal sector, excepting the effect on global economic dynamics by the pandemic and other processes. Thus, special attention should be paid to geothermal applications where the arsenic concentration of the geothermal fluid is high.

3. Concept of geothermal play types and arsenic relationship

3.1. Main factors controlling the arsenic cycle

On a global scale, plate tectonics is the strongest control mechanism for lithospheric structure that controls the location, deformation, and physicochemical properties of rocks together with the distribution of fault zones and volcanism in the Earth (Wegener, 1912; Oliver and Isacks, 1967). Regional morphological structures such as orogenic mountain belts, volcanic systems, mid-ocean ridges, and deep trenches are formed and vanish under the control of plate tectonics for millions of years. The areas in which earthquakes and mass movements are the most intense are also crucial for water resources, mineral deposits, and geothermal resources. For this reason, tectonic plate boundaries are highly important as they reflect the inner dynamics of the planet Earth.

Different plate boundary types have been determined in the world with respect to plate tectonic theory. These are; subduction zones (SUB), oceanic spreading ridges (OSR), oceanic transform faults (OTF), oceanic convergent boundaries (OCB), continental rift boundaries (CRB), continental transform faults (CTF) and continental convergent boundaries (CCB). Plate boundary types in the world are shown in Fig. 2 (Bird, 2003). Volcanoes and their impact areas in the world are also included in the figure (Global Volcanism Program, 2013).

While geologically different environments can occur at passive or active plate boundaries, basins and orogenic belts associated with plate boundaries will be favorable environments for geothermal sources (Muffler, 1976; Acharya, 1983; Ravenscroft et al., 2009; Moeck, 2013, 2014; Chi and Lin, 2015; Mukherjee et al., 2014; 2019). A tectonically active zone creates secondary permeability and porosity in rocks. All these processes are associated with heat transfer in the mantle that forces the plates to move. In tectonically active regions where heat

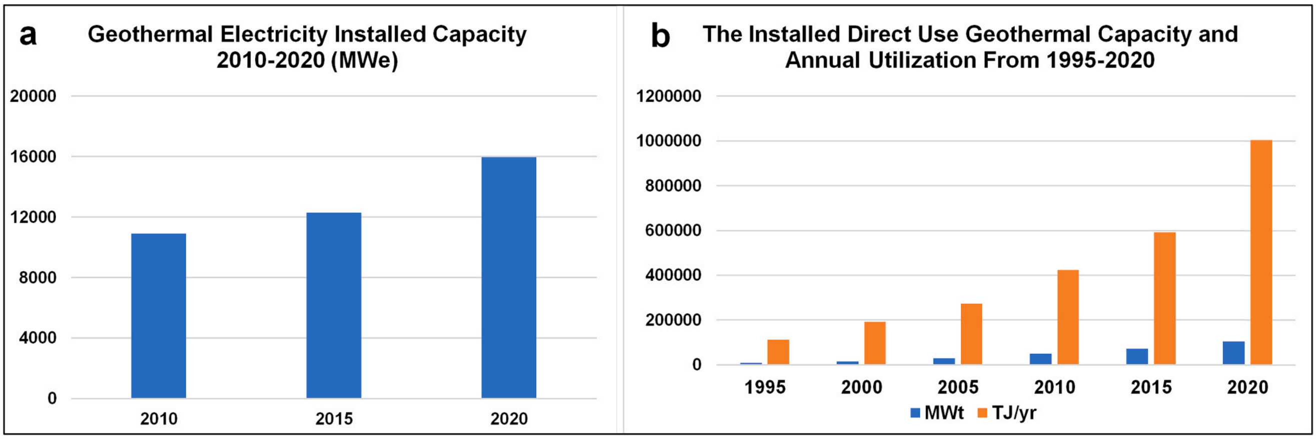

Fig. 1. (a) Geothermal electricity installed capacity changes between 2010 and 2020 (Huttrer, 2020), (b) the installed direct use geothermal capacity and annual utilization between 1995 and 2020 (Lund and Toth, 2020).

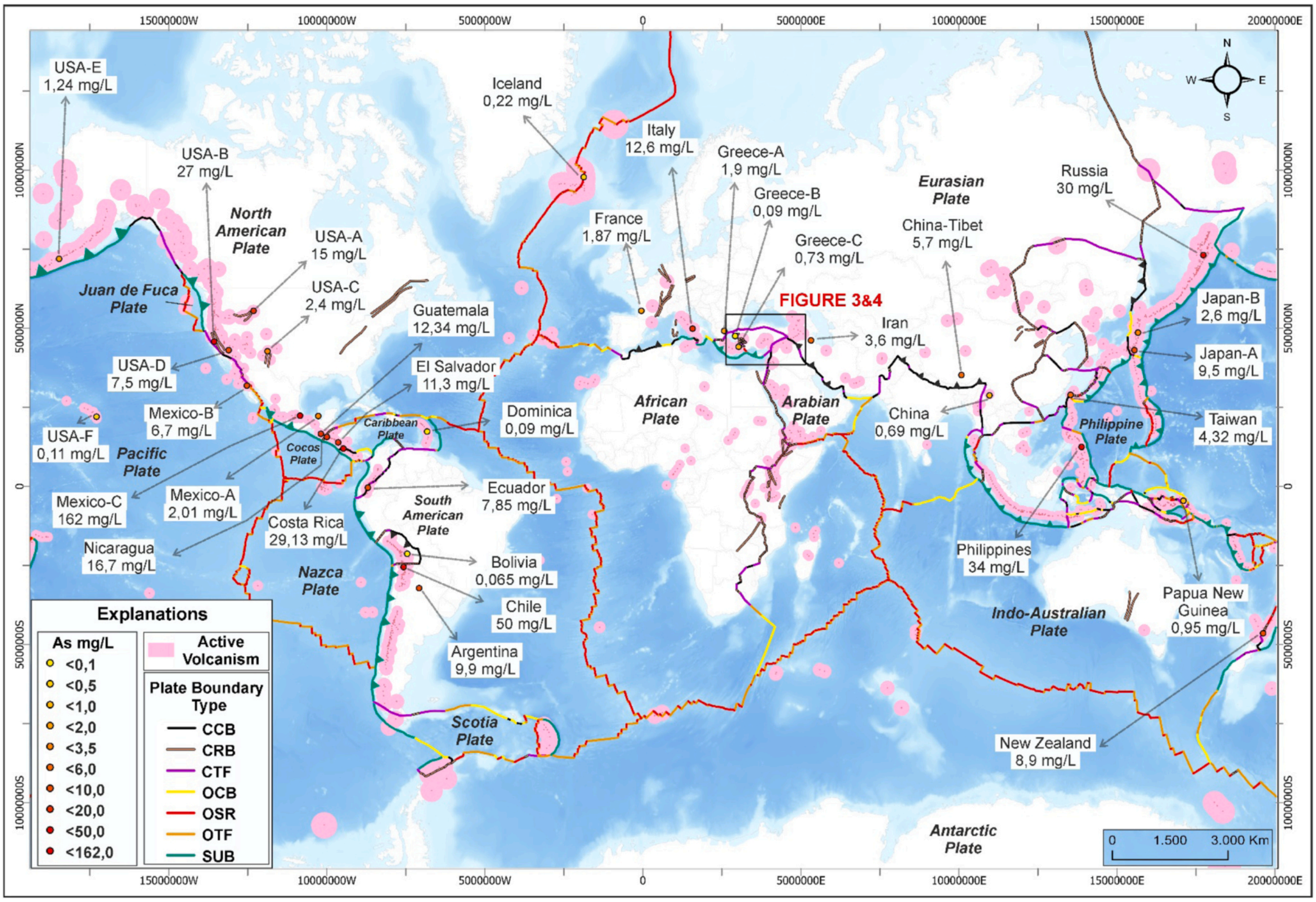

Fig. 2. Global maximum arsenic concentrations of geothermal fluid data (references there in Table 1) with plate boundary types (Bird, 2003) and volcanic fields (Global Volcanism Program, 2013; Base map: Esri, Garmin, GEBCO, NOAA NGDC, and other contributors).

transfer occurs intensely, arsenic in rocks can simultaneously pass into geothermal fluid (Chandrasekharam and Bundschuh, 2008).

Geogenic arsenic, which passes from geological formations into the hydraulic cycle, is affected by different physicochemical processes. The predominant geothermal play type (geothermal system, fluid chemistry, temperature, lithological properties, aquifer-reservoir conditions, etc.) and external factors (climate, biological and anthropogenic activities) shape this process (Ellis and Mahon, 1977; Yokoyama et al., 1993; Aiuppa et al., 2006; Giroud, 2008; Mukherjee et al., 2009, 2014, 2019; Cumbal et al., 2009; Nicolli et al., 2010; Ormachea et al., 2010, 2015; López et al., 2012; Maity et al., 2012; Liu et al., 2016; Wang et al., 2018; Morales-Simfors et al., 2020; Quezada et al., 2020; Tomaszewska et al., 2020).

Climate and atmospheric conditions directly affect the hydraulic system. This effect may differ depending on the different climatic conditions in the world. The infiltration process in the geothermal system is controlled by atmospheric precipitation composition, evaporation and precipitation regimes. Natural processes such as weathering of rocks, evapotranspiration, deposition due to wind, leaching from soil, run-off due to hydrological factors, and biological processes change the water quality (Du Laing et al. 2009; Frohne et al., 2010; Khatri and Tyagi, 2015; Shaheen et al., 2016; LeMonte et al., 2017; Mensah et al.,2020). As well as other pollutants, arsenic can be transported in atmospheric conditions by evaporation of surface ponds (which host intense biological activity), volcanic lakes, and ocean waters (Smedley and Kinniburgh, 2002). Similarly, arsenic with different origins can be carried with dust particles (Maity et al., 2012).

Apart from all these factors, arsenic circulation in geothermal systems is mainly controlled by geological properties. Lithology and rock composition are the most important controls of the geogenic arsenic cycle. Minerals and rock type/composition are the first parameters to be considered in determining the origin of geogenic arsenic during the water-rock interaction. High concentrations of dissolved ions determined in fluids generally interact with the related mineral assemblages in rocks (Hem, 1985; Robinson, 1997; Ayotte, 1999). Also, arsenic deposition generally results from alteration processes, iron-sulfur cycle and reactions between arsenic with iron-hydroxides, iron-monosulfides, and pyrite in general (Edenborn et al., 1986; Moore et al., 1988; Giroud, 2008).

As geothermal systems are studied in more detail every day, new ideas about formation, origin, internal mechanisms, and dynamics of the system have been obtained. The origin of geothermal fluid has been reshaped with new studies. It was observed that magmatic/meteoric shallow circulating waters and fluids coming from deeper can form mixed water in systems. In this case, porosity, permeability, secondary permeability, and fault-fracture systems are of great importance along with the concepts of heat source, cover rock and reservoir rock in the geothermal system (Bell and Ramelli, 2007; Coolbaugh et al., 2002; Curewitz and Karson, 1997; Faulds et al., 2006; 2010; 2011; Gunnarsson and Aradóttir, 2015, Moeck, 2014; Moeck and Beardsmore, 2014; Siler et al., 2015).

In contrast to shallow circulating surface waters, geothermal fluid circulates to deeper depths (nearly 3000 m; Minetto et al., 2020) for a longer time in the geothermal system and water-rock interaction time becomes longer. Lower dissolved oxygen ratio, higher pH values, high temperatures and more reduced redox conditions represent deeper aquifer environments with geothermal fluids (Ayotte, 1999).

Additionally, active magmatism and volcanism increase the world's internal heat at shallower levels, acts as a heat source in the geothermal system and may cause differences in arsenic concentrations. There are important studies about the effects of pH and temperature variations on the release and mobilization of As from rocks. According to Casentini et al. (2010), in some cases, significant increases in arsenic release in proportion to the decrease in pH and temperature increase were determined in experiments performed on volcanic rocks. Bundschuh and Prakash Maity (2015) stated that arsenic is in the form of arsenopyrite (FeAsS) at temperatures higher than 250 degrees, while it is in the form of pyrite (FeS_2) containing arsenic at lower temperatures, and that arsenic concentrations are higher especially in volcanic rocks and NaCl-type fluids.

Determination of arsenic species is very important for geogenic arsenic mobilization and circulation. Arsenic in geothermal fluids exists as inorganic As (III) or As (V). While As (V) is predominantly observed in natural hot springs at the surface, As (III) is dominant in deeper reservoir conditions (Webster and Nordstrom, 2003). This situation may differ according to depth, microorganism oxidation and Eh values (Wilkie and Hering, 1996; Cumbal et al., 2009).

In previous research and studies on arsenic, the focus has been on plate boundaries and magmatic-volcanic areas. Active volcanic areas, continental-continental collision zones & orogenic belts, rift systems, volcanic regions that have been active in the past, foreland and other sedimentary basin systems are the geological environments that have been extensively studied in terms of arsenic (Stauffer and Thompson, 1984; Webster and Nordstrom, 2003; Saunders et al., 2005; Zheng, 2006, 2007; Ravenscroft et al., 2009; Birkle et al., 2010; López et al., 2012; Nordstrom, 2012; Mukherjee et al., 2014; Bundschuh and Prakash Maity. 2015). There are critical studies about geogenic arsenic in recent years. Morales-Simfors et al. (2020) studied about 423 sites in 15 Latin countries related to the relationship between arsenic and volcanic emissions and hydrogeochemistry. Mukherjee et al. (2019) conducted a comprehensive study examining the relationship between the geogenic arsenic cycle in water sources in Himalayan and Andean basin aquifers with respect to plate tectonics. These studies show that evaluating all these geological environments with a more comprehensive evaluation system such as geothermal play type classification can be very useful for arsenic-based studies of geothermal fluids.

By evaluating tectonics, magmatism-volcanism, fluid circulation, and lithology, Moeck (2014), who classified geothermal systems in a similar way to petroleum systems, provided a unique infrastructure and methodology for geothermal studies. In the geothermal play type classification of Moeck, geothermal systems are divided into two different groups as “conduction (CD)” and “convection (CV)” dominated considering the heat transfer regime. While systems in convection dominant play types have very active fluid dynamics, conduction systems are more passive in terms of fluid circulation, volcanism, and tectonics. Convection-dominated systems have volcanic, plutonic, and extensional domain play types, while conduction-dominated systems have intracratonic basin, orogenic belt, and basement types. Fig. 2 shows the geothermal fields containing geothermal fluids, whose arsenic concentrations reach significant levels in the world, and the plate tectonics they are related to. Some of the areas that may be relevant are mentioned under play type titles, but many geothermal fields need to be studied all around the world. Especially with studies to be carried out under the concept of play type, more than one type of play can be defined, and hybrid fields can be defined in areas with complex geological structures associated with many plate boundaries.

While conduction and convection dominated systems are concentrated in plate boundaries and tectonically active areas, some essential classification methods are used to determine these systems (Moeck, 2014; Moeck and Beardsmore, 2014). This classification is based on the definition of play fairway, "the geographic area over which the play is believed to extend; for example, the size of an intrusion in diameter and depth, or a fault zone hosting vast volumes of circulating fluids". Moeck (2014) stated that the definition of igneous or non-magmatic play type is very useful in distinguishing the conduction-convection system. There are both conduction and convection systems in igneous play systems. However, to distinguish between these systems, it is necessary to look at heat source and tectonic activity. While conduction dominant systems require heat sources such as granitic intrusions, convective dominant systems have magma chamber heat sources due to tectonic and volcanic activity. Being able to make this distinction is the basis of the concept of geothermal play type.

3.2. *Geothermal arsenic in convection-dominant geothermal plays*

Convection-dominant play types are generally observed in tectonically and volcanically active geological environments with higher reservoir temperatures. These environments are; subduction zones and magmatic arcs associated with convergent plate boundaries, oceanic spreading ridges and continental rift systems, transform plate boundaries, and mid-ocean hot-spot zones (Moeck and Beardsmore, 2014; Moeck, 2014).

3.2.1. *Magmatic geothermal plays–volcanic field (CV-1)*

The concept of magmatic geothermal play type generally describes geothermal systems under the control of intrusive and extrusive magmatic systems. Geothermal fluid circulation is controlled by magma chambers located at shallow levels and related fault, fracture, and crack systems. Structural controls can be characterized by large-scale plate tectonics. The oceanic and continental crust has to be thinned or faulted for the magma to form a chamber close to the surface. Such geological environments are usually found at divergent plate boundaries, where the plates move away from each other. Consequently, active volcanism, island arcs, and intrusive systems are typical geological environments of magmatic geothermal plays. The best examples are Iceland, Taiwan, the South American Andes, and New Zealand (Moeck, 2014).

3.2.1.1. Extrusive magmatic play type. Located between two different subduction zones, the Taiwan geothermal system is characterized by magmatic activity that enabled the formation of dominant geothermal systems in the region. There are areas with a high concentration of arsenic, especially in Beitou and Yangbajing geothermal fields. The origin of these fluids is known to be Pleistocene andesitic volcanism, and fluids in these fields generally have acidic character and $H\text{-}SO_4$ water type (Maity et al., 2012). In the analysis made in previous studies in Taiwan, the highest arsenic value measured at nine different sites was determined at the Yangbajing site with 5.7 mg/L (Wang, 2005; Guo et al., 2008; Chiang et al., 2010).

Active igneous and tectonic conditions have led to a different geological environment in Iceland where the Eurasian and the North American plates are separated from each other along the Mid-Atlantic Ridge. Dominant lithology is oceanic basalts in Iceland, and the reservoir is made up of basalts influenced by fault-crack systems. Arsenic values in geothermal fluids have reach a concentration of 0.22 mg/L in the Bjarnarflag power plant at an average of 0.15 mg/L (Weaver et al., 2019). As a result of the water-rock interactions, arsenic forms from the hydrothermal alteration of the basalts, and mixes into the geothermal fluid (Weaver et al., 2019).

Another example is the subduction event around the North American and Caribbean plates, which forms a unique geological environment including an intra-arc rift-depression and volcanic region. The geothermal fields where the subduction event is directly effective are the Los Humeros and Los Azufres sites in Mexico. In these fields, exposure to rock leaching with high temperatures and arsenic-bearing volcanic units in connection with the subduction event caused high As concentrations in the geothermal fluid. Arsenic concentrations reach up to 50 mg/L in Los Azufres and 162 mg/L in Los Humeros (Birkle, 1998; Gonzalez et al., 2000; Arellano et al., 2003; Birkle et al., 2010; López et al., 2012). The foreland examples of Poopo Lake (Bolivia) and El Tatio (Chile) fields are located near the thrust zone (Banks et al., 2004; Ormachea et al., 2010, 2015; Tomaszewska et al., 2020; Cusicanqui et al., 1976; Ellis and Mahon, 1977; Romero et al., 2003; Mukherjee et al., 2009; López et al., 2012). In these regions, arsenic concentrations reach up to 50 mg/L levels (Table 1).

The subduction zone within intra-arc rift-depression zone around Nicaragua includes volcanoes, local extensional zones, and large-small lakes and lagoon environments. Notably, Central American Volcanic Arcs and accompanying tectonic activity increased arsenic values in lakes and geothermal fluid in this region. The maximum arsenic values for Nicaragua are 16.7 mg/L; for Costa Rica are 29.13 mg/L (Hammarlund, 2009; Hammarlund et al., 2009; López et al., 2012); for El Salvador are 11.3 mg/L (DiPippo, 1980; López et al., 2012); and for Guatemala are 12.3 mg/L (López et al., 2012) (Table 1).

Table 1
Geothermal fields with high arsenic concentrations around the world (abbreviations: GGS: Geothermal fluid mixed with shallow groundwater or surface water, GHS: Geothermal Hot Spring, GW: Geothermal Well, GF: Geothermal Fluid, GPP: Geothermal Power Plant Wastewater & Evaporation Pond, GHSG: Geothermal Geiser Water).

Country	Field	As Concentration (mg/L-mg/kg)	Related Plate Boundary Type	Reference
Argentina	Chaco Pampean Plain	1,66 (GGS), 9,9 (GHS)	SUB	Nicolli et al. (2010, 2012)
Bolivia	Coipasa a Uyuni-Altiplano Poopó Lake	0,03–0,06 (GHS)	SUB, CRB, CCB	(Banks et al., 2004; Ormachea et al., 2010, 2015; Tomaszewska et al., 2020)
Chile	El Tatio	50 (GW-GHS)	SUB, CRB, CCB	(Cusicanqui et al., 1976; Ellis and Mahon, 1977; Romero et al., 2003; Mukherjee et al., 2009; López et al., 2012)
China	Rehai Yunnan	0,68 (GHS)	CCB, CTF	Zhang et al. (2008)
China-Tibet	Yangbajing GTP	5,7 (GW)	CCB	Guo et al. (2008)
Costa Rica	Miravalles, Rincón de la Vieja	29,13 (GF), 4,65–10,9 (GHS), 13 (GW)	SUB, CCB	(Hammarlund, 2009; Hammarlund et al., 2009; López et al., 2012)
Dominica	Dominica (Lesser Antilles)	0,09 (GF)	SUB	McCarthy et al. (2005)
Ecuador	Papallacta & Tambo River	7,85 (GHS)	SUB, CCB, CTB	(Bundschuh et al., 2009; Cumbal et al., 2009; López et al., 2012)
El Salvador	Ahuachapan- Coatepeque	11,3 (GF), 3,1(GHS)	SUB, CRB	(DiPippo, 1980; López et al., 2012)
France	Aquitaine Basin	1,87 (GHS)	CRB	(Criaud and Fouillac, 1989; Chery et al., 1998; Grossier and Ledrans, 1999)
Greece-A	Chalkidiki- Kalikratia	1,9 (GF), 0,04(GW)	CTF	(Kouras et al., 2007; Katsoyiannis et al., 2007; 2015; Aloupi et al. 2009)
Greece-B	Kalloni Lesvos	0,09 (GGS)	CTF CRB	Aloupi et al. (2009)
Greece-C	Kos Island	0,73 (GHS)	SUB, CRB	(Varnavas and Cronan, 1991; Gamaletos et al., 2013; Winkel et al., 2013; Katsoyiannis et al., 2015)
Guatemala	Zunil	12,34 (GF)	SUB, CRB	(López et al., 2012)
Iceland	Bjarnarflag Power Plant	0,22 (GW)	OSR, OTF	Weaver et al. (2019)
Iran	Mt. Salaban	0,89 (GHS), 3,6 (GW)	CCB, CTF	Haeri et al. (2011)
Italy	Phlegraean Fields, Larderello	12,6 (GHS)	CCB, SUB	(Celico et al., 1992; Chandrasekharam and Bundschuh, 2008; Bundschuh and Prakash Maity, 2015)
Japan-A	Obama Nagazaki,Oita and National Surveys	0,55–9,5 (GHS)	SUB, CRB	(Sakamoto et al., 1988; Yoshizuka et al., 2010)
Japan-B	Tamagawa Onsen	2,6 (GHS)	SUB	Noguchi and Nakagawa (1969)
Mexico-A	Cactus Sitio Grande, Jujo-Tecominoacán, Luna-Sen, Pol Chuc Abkatún	0,05–2,01 (GW)	SUB	(Birkle, 2003; Birkle et al., 2010)
Mexico-B	Cerro Prieto, Les Tres Virgenes	2,24 (GPP), 5,18 (GW), 6,7 (GF)	CTF- OTF-CRB	(Birkle et al., 2010; Armienta et al., 2014; Tomaszewska et al., 2020)
Mexico-C	Los Azufres, Los Humeros	49,6–162 (GW), 73,6 (GF)	SUB	(Birkle, 1998; Gonzalez et al., 2000; Arellano et al., 2003 Birkle et al., 2010; López et al., 2012)
New Zealand	Broadlands, Kawerau, Orakei Korako, Waikato-Waiotapu, Wairakei	4,86–8,9 (GW), 5,1–8,5 (GHS)	CTF,CRB, OSR, SUB	(Brown and Simmons, 2003; Ellis and Mahon, 1977; Ewers and Keays, 1977; Grimmett and McIntosh, 1939; Mroczek, 2005; Papke et al., 2003; Ritchie, 1961; Webster and Nordstrom, 2003; DiPippo, 1980; Piper and Kim, 2006)
Nicaragua	Monte Galán Lagoon, Apoyeque Lagoon, Asososca León lagoon, Xiloá Lagoon; Tipitapa; Managua Lake, Telica; Momotombo	0,01–0,72 (GHS), 0,05–2,65 (GF), 16,7 (GPP)	SUB, CCB	(Lacayo et al., 1992; Parello et al., 2008; López et al., 2012;Diaz et al., 2016; Quezada et al., 2020; Tomaszewska et al., 2020)
Papua New Guinea	Tutum Bay	0,95 (GF)	OCB, OTF,CTF	Pichler et al. (1999)
Philippines	Mt. Apo, Tongonan	6,2 (GHS), 34 (GW)	SUB	(Kingston, 1979; Darby, 1980; Webster, 1999)
Russia	Kamchatka, Ebeko Volcano Kuril Island	max 28 (GW), max 30 (GHS)	SUB	Goleva (1974); Khramova (1976); Belkova et al. (2004)
Taiwan	Antung, Bao-Lai, Beitou, Chung-Lun, Jiben, Kuan-Tzu-Ling, Tai-Pu, Yang Min Shan	0,04–4,32 (GHS), 0,06–1,46 (GF)	SUB, CCB, CTF, OTF	(Wang, 2005; Chiang et al., 2010; Jean et al., 2010; Maity et al., 2011; Maity et al., 2012; Kao et al., 2013; Liu et al., 2016)
USA-A	Yellowstone (Y.N.P.),Norris Geyser Basin, Madison River Valley, Bath Spring	1,56–2,5 (GF), 3,6 (GHSG), 15 (GHS)	CRB	(Stauffer and Thompson, 1984; Bauder, 1995; Nimick, 1998; Nimick et al., 1998; Langner et al., 2001; Smedley and Kinniburgh, 2002 Webster and Nordstrom, 2003; Planer-Friedrich et al., 2006; Planer-Friedrich et al., 2007; Nordstrom et al., 2009)
USA-B	California - Brawley, East Mesa, Heber; Salton Sea, Imperial Valley, San Joaquin Valley, Lassen National Park	0,1–2,6 (GF), 12 (GHS), 15–27 (GF), max 2 (GW)	CRB, CTF, CCB	(Pimentel et al, 1978; Thompson, 1985; Welch et al., 1988, 2000; Klinchuch et al., 1999; Mukherjee et al., 2009)
USA-C	Rio Grande Rift, Ojo Caliente, Soda Dam-Valles Caldera	1,5–2, (GF), 2,4 (GHS)	CRB	(Criaud and Fouillac, 1989, Stanton et al., 2001;Reid et al., 2003; Webster and Nordstrom, 2003, Bexfield and Plummer, 2003; Planer-Friedrich et al., 2006; Planer-Friedrich et al., 2007)
USA-D	Coso Hot Springs, Honey Lake Basin, Hot Creek, Eastern Sierra, Long Valley, Southern Carson Desert, Steamboat Springs	max 7,5 (GHS), 1,4–3,5 (GF)		(Welch et al., 1988, 2000; Welch and Lico, 1998; Wilkie and Hering, 1996; Mukherjee et al., 2009)
USA-E	Alaska Akutan Island	max 1,24 (GHS)	SUB	Dasher et al. (2012)
USA-F	Kilauea-Hawaii	max 0,11 (GW)	OHS	De Carlo and Thomas (1985)

3.2.1.2. Intrusive magmatic play type. Influenced by active faulting, deep rooted magmas can intrude beneath flat terrain with no volcanism, but with an upflow of liquids and form geothermal surface manifestations (Moeck, 2014). New Zealand is a unique example of this play type and the arsenic concentrations reach nearly 8.9 mg/L (Grimmett and McIntosh, 1939; Ewers and Keays, 1977; Ellis and Mahon, 1977; DiPippo, 1980; Webster and Nordstrom, 2003; Brown and Simmons, 2003; Papke et al., 2003; Mroczek, 2005; Piper and Kim, 2006).

3.2.2. Magmatic geothermal plays–plutonic type (CV-2)

In plutonic magmatic systems, the heat source is crystalline rocks or young crystalline intrusion masses. Since, volcanism can accompany these as it has a magmatic system. Examples of areas where volcanism is not observed are passive subduction zones in continental crust and associated fold-thrust belts and arcs. In systems with volcanism, intrusions are generally fault-controlled, and volcanism accompanies the system regionally or locally. The best examples of plutonic type systems are the California Geysers and Italy Larderello geothermal fields (Moeck, 2014).

When the arsenic values obtained from these regions are examined, while the Phlegraean Fields (Italy) has concentrations around 12.6 mg/L (Celico et al., 1992; Chandrasekharam and Bundschuh, 2008; Bundschuh and Prakash Maity, 2015), California and Yellowstone (USA) values reach 15–27 mg/L levels (Stauffer and Thompson, 1984; Bauder, 1995; Nimick, 1998; Nimick et al., 1998; Langner et al., 2001; Smedley and Kinniburgh, 2002 Webster and Nordstrom, 2003; Planer-Friedrich et al., 2006, 2007; Nordstrom et al., 2009; Pimentel et al, 1978; Thompson, 1985; Welch et al., 1988, 2000; Klinchuch et al., 1999; Mukherjee et al., 2009).

In plutonic systems, geothermal fluid is largely associated with surface waters of meteoric origin. This interaction is under the control of volcanism and fracture systems. However, it is present in more mature systems that contain a small amount of fluid without fault systems. Different fluid characters can be observed according to the lithological properties of the cover rock, weathering, and alteration processes. While acid sulfate water can be seen in the central parts of the plutonic systems, NaCl and more mixed type fluids can be seen moving away from the center. This situation may differ even further in environments where plutonic and volcanic systems work together (Moeck and Beardsmore, 2014; Moeck, 2014).

3.2.3. Non-magmatic geothermal plays – extensional domains (CV-3)

In extensional domains where magmatism is not the primary control, structural controls ensure fluid circulation. Here, the continental crust is thinned, and thus the asthenosphere is close to the surface due to tectonic regime, and extensional systems become responsible for deformation. Continental rift and graben-horst systems are the most typical examples of this type where the meteoric waters, flowing deep down along the faults, heat up at depth, follow a similar path and reach the surface. Secondary permeability and porosity are significant in such domains. The best examples of such fields are Western Anatolia, Western USA, and other rift systems (Moeck, 2014). Geothermal sources with higher arsenic concentrations in Nevada and California, especially east of the San Andreas Fault and Basin & Range region are located in extensional basins behind subduction zone.

Reservoir rocks may vary regionally in extensional domains. While reservoirs can be formed in volcanic, plutonic, and sedimentary basin deposits, relatively high Cl concentrations are characteristic because deep circulating fault-controlled systems are dominant and high carbonate values can be seen in areas containing carbonate basement (Moeck and Beardsmore, 2014; Moeck, 2014). The transport of geogenic arsenic in basement rocks (e.g., granites) in the regions generally occurs where the faults reach deep in the graben and half-graben systems (Baba and Sozbilir, 2012).

The geothermal fields in Western Anatolia (Turkey) and Great Basin (USA) are characterized by currently inactive Miocene volcanism (except for Manisa-Kula region). However, the absence of active volcanism in these regions does not mean that there will be no arsenic in the system. The arsenic circulation within the geothermal fluids is predominantly controlled by extensional tectonics where meteoric waters flow deeply along the faults and mix with geothermal fluids at shallow continental crust levels. Geothermal fluids, especially interacting with altered Miocene volcanics, altered basement units, arsenic-enriched old-marine units, volcano-sedimentary basin fills and evaporites are candidates to form high concentrations in CV3 play type in geothermal systems.

Another example is the continental extensional system called the East African Rift System. The recently developed geothermal sector in Kenya and Ethiopia in this region will be considered in terms of arsenic (Rango et al., 2010; Ahoulé et al., 2015). The rift system, which began developing approximately 25 million years ago, shapes the fluid circulation in the region. The fact that geothermal activity is also fault-controlled in extensional systems makes interactions during the circulation of surface waters and groundwater inevitable. Especially the high arsenic values in surface water (10,000 μg/L) shows that it should be used carefully in the geothermal resources in the region (Rango et al., 2010; Ahoulé et al., 2015). In geothermal systems with meteoric infiltration, arsenic water-rock interactions in arsenic-enriched sediments can create high concentrations in the geothermal fluid.

3.3. Geothermal arsenic in conduction-dominant geothermal plays

In conduction dominant geothermal systems, there is no actively circulating fluid or this circulation is quite limited or short-term (Moeck, 2014). For this reason, geological formations are very important in these systems. Generally, volcanic and tectonic activity is no longer active, and heat conduction is under the control of stratigraphy in these systems located in the central parts of old continents. This situation causes the geothermal gradient to be more prominent in the system. Unlike convection-dominant systems, the temperature in the geothermal system provides more favorable conditions at deeper levels. However, the absence of fluid is the most significant handicap of these systems. Fluid production can be achieved with applications such as hot dry rocks and enhanced geothermal systems (EGS). Suitable tectonic environments are continental extension and subsidence areas, foreland basins related to orogenic belts, and basins located near crystalline bedrock.

3.3.1. Non-magmatic geothermal plays – intracratonic basins (CD-1) and orogenic belts (CD-2)

According to Moeck (2014), Moeck and Beardsmore (2014), the first of the systems where magmatism is not seen is the intracratonic basin play type. These systems, which are affected by past tectonic activities and have very thick sedimentary basin fills, can contain locally produced reservoirs with lithological and structural controls. In conductional systems associated with foreland basin and orogenic belts, the location and deformation of the basin strata become important. As a result of erosion of the mountain belts, sediments in the foreland basins tilt and gain inclination and local extensional regions may occur. Geothermal reservoirs formed like oil traps can be observed in such locations. However, the excessive deformation of the orogenic belts and environmental conditions will affect the system's feeding, heat flow and parameters of the potential reservoir.

Due to limited fluids to be obtained from intracratonic basins, the reservoir will generally have quite high concentrations of Cl and HCO_3. This is because the fluid mass is low in the system and potential basin fills are deep-sea related sediments and carbonates (Moeck, 2014). In orogenic belts, factors such as erosion, precipitation regime, flow path, infiltration type, and reservoir geometry are more effective on the physical and chemical properties of the fluid in the system.

Sampling and observations are very difficult in such systems due to the lack of fluid. Since there is not enough fluid to affect water resources and newly defined geothermal systems, existing studies are very few.

However, geogenic arsenic found outside the fluid (as in basement units) may cause long-term problems in these areas.

3.3.2. Igneous geothermal plays– basement type (CD-3)

In systems with basement play type, a fractured-cracked crystalline basement can be converted into a highly efficient heat source with techniques such as EGS (Moeck, 2014; Moeck and Beardsmore, 2014). However, the physical and chemical properties of the fluid to be sent into such fields, crack-fracture systems to develop and therefore, regional stress regimes are very important.

There is a different situation in terms of arsenic in basement type geothermal plays. There is no geothermal fluid in the system under normal conditions. For this reason, fluid is sent into the system by external intervention. In this case, besides the physical properties such as pH, temperature, and flow rate, the chemical composition will affect the whole geothermal system. Apart from the fluid sent to the system, the geological units in the region will affect the water chemistry. While volcano-sedimentary units can be arsenic sources, basement rocks may have the potential to form different concentrations in the fluid in terms of radiogenic elements, heavy metals and arsenic. It is possible to find higher concentrations in terms of arsenic if there is a small amount of fluid in the basement type geothermal plays because the fluids in the aquifers associated with the basement are exposed to water-rock interaction for longer, so higher concentrations can be reached (Rogers, 1989). For this reason, arsenic studies should be monitored carefully and continuously in EGS systems.

4. Case study: the Anatolian plate (Turkey)

Turkey is located on the Anatolian plate between the Eurasian and Arabian-African plates. The 'Neotectonic Period' in Anatolia is characterized by the compressional tectonic regime in East Anatolia and westward motion of the Anatolian Plate. The neotectonic deformation of the Anatolian Plate has formed different provinces (Barka, 1992; Bozkurt, 2001, 2003; Kocyigit and Ozacar, 2003; McKenzie et al., 2001; Sengor and Dyer, 1979; Sengor, 1980).

Along with the West Anatolian Extensional Fault Systems (WAES), the three most important transform faults in Anatolia are: the North Anatolian Fault (NAF), the East Anatolian Fault (EAF) and the Northeast Anatolian Fault (NEAF). The NAF and EAF are the largest examples of the impact of strike-slip fault systems (intra-continental transform fault) in the region, controlling the escape movement of the Anatolian Plate to the west (McKenzie, 1972, 1978; Sengor, 1979; Dewey and Sengor, 1979; Sengor et al., 1985). To the east of these fault systems, there is a complex region under the influence of reverse faults and strike-slip faults. The Anatolian Plate also contains the Bitlis-Zagros Suture Zone (BZSZ) in the southeast and an active volcanism area in the east. This situation enriched the region in geothermal resources and other geological phenomena.

The volcanic activity observed in most of the geological time, the presence of active fault zones with different characters and the distribution of water resources offer different dynamics in terms of geothermal fluid character and properties. It is possible to see Quaternary, Neogene, Paleogene, Cretaceous, and Jurassic-Triassic volcanics and granitoids all over the country (Fig. 3). According to McCoy-West et al. (2011), active magmatism related to volcanism is accepted as

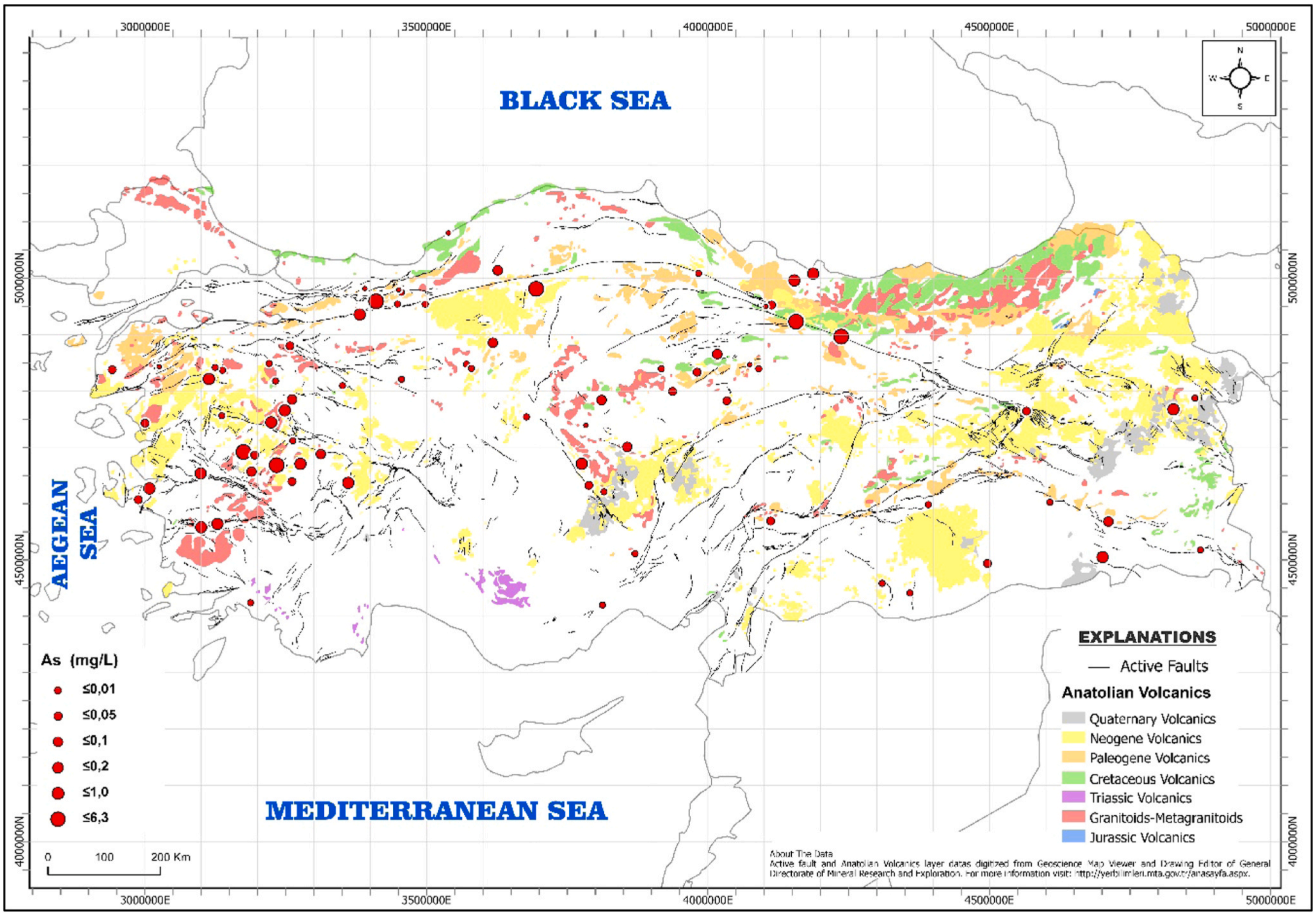

Fig. 3. Arsenic distribution map of the Turkey with active faults.
Arsenic data obtained and modified from Akkus et al. (2005), Baba and Sozbilir (2012); tectonic structures digitized from MTA (2016)

<500 years old, recent magmatism related to volcanism is accepted as 500–50,000 years old, and inactive or extinct magmatism related to volcanism accepted as >50,000 years old. Based on these assumptions, the existence of recent magmatism has been accepted in some regions containing Quaternary volcanism. For this reason, it can be locally seen in the magmatic play type in some areas with non-magmatic extensional play type. Kula in Western Anatolia, Hasan Mountain in Central Anatolia, Erciyes and Karacadag in Southeastern Anatolia, Suphan, Tendurek, Nemrut, and Agri volcanoes in Eastern Anatolia were active in the Holocene that covers the period up to 11,000/12,000 years ago. This situation has led to the definition of hybrid systems in some fields such as Aksaray, Nigde, Nevsehir, Diyarbakır, Manisa and Usak (Table 2).

All the geothermal resources in the Anatolian plate are distributed under the control of active tectonics and volcanism. Among the 81 provinces in Turkey, 63 have at least one geothermal resource with 274 geothermal fields identified across the country. According to Akkus et al. (2005), 710 geothermal resources (wells or hot springs) were identified in Turkey. All these areas are affected by volcanism of different ages and fault zones. It is possible to make some definitions under the play type classification for areas where there is no sharp difference between arsenic distributions (Table 2). While the sources in the western regions can be given as examples of convection-dominated non-magmatic extensional systems, in the central and eastern regions, convective systems where magmatism-volcanism and tectonic controls work together, and orogenic belt type systems with relatively less fluid can be seen in some regions.

Within the scope of this study, an attempt was made to reveal the general situation in the country by examining the arsenic values determined in previous studies (Akkus et al., 2005; Baba and Ármannsson, 2006; Baba and Sozbilir, 2012; Bundschuh et al., 2013). However, in most of these studies, only total arsenic concentrations in the geothermal fluid were measured.

Bundschuh et al. (2013), an important study detailing arsenic species (As, As(III) and As(V)), investigated geothermal fluids especially in Western Anatolia. According to the results of this study, reduced As (III) was determined as the dominant species in most of the sampled geothermal fluids. The highest concentrations of this naturally-occurring arsenic (As) in geothermal fluid were generally related to the extensional tectonic regime in western Anatolia.

4.1. Western Anatolia: non-magmatic geothermal plays-extensional domains (CV-3)

Western Anatolia is tectonically active and is located in an area where frequent earthquakes occur. The approximate N-S continental extension caused the formation of Neogene and Quaternary basins striking E-W and NE-SW (Sengor et al., 1985; Yilmaz et al., 2000; Seyitoglu, 1997; Bozkurt, 2003; Baba and Sozbilir, 2012). These basins and tectonic systems correspond to one of the most important neotectonic regions in the Anatolian plate, the West Anatolian Extensional Province. The main tectonic structures are the Gediz and Buyuk Menderes Grabens. Normal faults bounding these grabens and basins caused the formation of a geothermally active environment. The Menderes metamorphic core complex forms the reservoir rocks for the geothermal systems (Bozkurt and Park, 1994).

The reason for the high arsenic concentrations in Western Anatolia is

Table 2

Provincial arsenic distribution data of geothermal fluids above WHO (1993) limits (0,01 mg/L) with related regional tectonic structures and volcanics (cities with "*" symbol have also recent Quaternary magmatism-volcanism. The data obtained and modified from Akkuş et al., 2005; Baba and Sozbilir, 2012 and this study).

Play type	City (sample number)	Concentration of Arsenic (mg/L)			Related Regional Tectonic Structure	Related Volcanism and Magmatism
		Min	Max	Average		
CV3-(CV1*)	Afyon (19)	0,1	2,8	0,88	WAES	Neogene
	Aydın (10)	0,1	0,9	0,42	WAES	Granitoids-Metagranitoids
	Balıkesir (18)	0,02	1,5	0,22	WAES NAF	Neogene, Paleogene, Granitoids-Metagranitoids
	Denizli (10)	0,2	4,1	0,87	WAES	Granitoids-Metagranitoids
	Eskişehir (3)	0,02	0,03	0025	WAES NAF	Neogene, Granitoids-Metagranitoids
	İzmir (37)	0,02	1,42	0,22	WAES	Neogene
	Kütahya (30)	0,02	0,9	0,16	WAES	Neogene, Cretaceous, Granitoids-Metagranitoids
	Manisa (21)*	0,01	3,34	0,33	WAES	Quaternary, Neogene, Granitoids-Metagranitoids
	Uşak (4)*	0,1	1,5	0,48	WAES	Quaternary, Neogene, Granitoids-Metagranitoids
	Kahramanmaraş (2)	0,02	0,1	0,06	BZSZ EAF	Paleogene, Granitoids-Metagranitoids
	Ankara (16)	0,02	0,5	0,13	NAF	Neogene, Cretaceous, Granitoids-Metagranitoids
	Bolu (5)	0,02	0,09	0,04	NAF	Neogene, Paleogene, Granitoids-Metagranitoids
	Bursa (6)	0,02	0,1	0,07	NAF	Neogene, Paleogene, Granitoids-Metagranitoids
	Çanakkale (9)	0,01	0,25	0,07	NAF WAES	Neogene, Paleogene, Granitoids-Metagranitoids
	Karabük (1)	0,2	0,2	0,2	NAF	Neogene, Paleogene, Cretaceous, Granitoids-Metagranitoids
	Kırşehir (3)	0,1	0,3	0,17	SLF	Cretaceous, Granitoids-Metagranitoids
	Sivas (4)	0,02	1,4	0,39	NAF	Neogene, Paleogene, Cretaceous, Granitoids-Metagranitoids
	Yozgat (6)	0,02	0,1	0,06	NAF	Neogene, Paleogene, Cretaceous, Granitoids-Metagranitoids
	Çankırı (3)	0,09	6,3	2,16	NAF	Neogene, Paleogene
	Düzce (2)	0,01	0,02	0,01	NAF	Paleogene-Cretaceous
	Sakarya (10)	0,02	1,2	0,3	NAF	Paleogene
	Tokat (5)	0,03	1,52	0,36	NAF	Neogene, Paleogene, Cretaceous
CV1	Ağrı (1)	0,04	0,04	0,04	NEAF	Quaternary, Neogene, Granitoids-Metagranitoids
	Bingöl (1)	0,06	0,06	0,06	BZSZ EAF NAF	Quaternary, Neogene, Cretaceous, Granitoids-Metagranitoids
	Van (2)	0,5	0,9	0,7	BZSZ	Quaternary, Neogene, Cretaceous, Granitoids-Metagranitoids
CD2	Batman (1)	0,05	0,05	0,05	BZSZ	Paleogene
	Hakkari (1)	0,05	0,05	0,05	BZSZ	Cretaceous, Granitoids-Metagranitoids
CV3-(CV1*)	Diyarbakır (1)*	0,02	0,02	0,02	BZSZ	Quaternary, Neogene, Paleogene
	Mardin (1)*	0,1	0,1	0,1	BZSZ	Quaternary, Neogene
	Siirt (4)*	0,1	0,28	0,18	BZSZ	Quaternary, Paleogene
	Şanlıurfa (3)*	0,02	0,1	0,05	BZSZ	Quaternary, Neogene
	Şırnak (2)*	0,33	0,34	0,33	BZSZ	Quaternary
CD2	Ordu (3)	0,02	0,58	0,23	NAF	Neogene, Paleogene, Cretaceous, Granitoids-Metagranitoids
	Samsun (3)	0,02	0,1	0,07	NAF	Neogene, Paleogene, Cretaceous
CV3-(CV1*)	Aksaray (4)*	0,04	1,8	0,74	SLFZ	Quaternary, Neogene, Granitoids-Metagranitoids
	Nevşehir (4)*	0,04	0,18	0,12	SLFZ	Quaternary, Neogene, Granitoids-Metagranitoids
	Niğde (3)*	0,02	0,02	0,02	SLFZ	Quaternary, Neogene, Granitoids-Metagranitoids

the alteration of volcano-sedimentary units deposited in the basins, weathering of basement rocks, arsenic-bearing carbonates and geothermal fluids reaching the surface through faults from the deep. Deformation caused by intense alteration and fracturing is the primary factor controlling the arsenic circulation. While the reservoir temperature of the geothermal fluids in the Gediz graben can reach 287 °C, temperatures reaching 250 °C in the Buyuk Menderes Graben have been measured. Circulation of high temperature fluids with abundant faults causes hydrothermal alteration. Hydrothermal alteration of argillic, phyllic and silica-hematitic character and weathering are widely observed in the geothermal fields in Western Anatolia (Ozgur et al., 1997; Baba, 2010; Gunduz et al., 2010; Baba and Sozbilir, 2012). Afyon (up to 2.8 mg/L), Aydın (up to 0.9 mg/L), Denizli (up to 4.1 mg/L), İzmir (up to 1.42 mg/L) and Manisa (up to 3.34 mg/L) are geothermal fields containing significant amounts of arsenic concentrations in the geothermal fluid (Table 2).

4.2. Eastern Anatolia: magmatic geothermal plays–volcanic field (CV-1)

The eastern part of the Anatolian Plate is a natural laboratory for geology, volcanism, and tectonics. The reason for this is that the Anatolian Plate influenced by Alpine orogenesis is one of the regions where continent-continent collision tectonics are seen most clearly (Sengor and Kidd, 1979; Dewey et al., 1986). The deformation that took place along the collision zone of the Eurasian and Arabian Plates known as the Bitlis-Zagros Suture Zone (BZSZ) caused an elevated topography in the Anatolian plate and active volcanism. Volcanism, with increasing activity especially after the uplifting process, caused fissures, dykes, calderas, domes, and sill formations in more than 20 volcanic centers in the region (Pearce et al., 1990; Keskin et al., 1998; Yilmaz et al., 1998; Keskin, 2003). As a result of calc-alkaline to alkaline volcanism in the region, andesite, basalt and rhyolites were formed and spread all over the region.

The NEAF, the BZSZ, the EAF, and other minor structural elements that control volcanism in the region created suitable environments for geothermal fluid circulation. The BZSZ, which corresponds to the convergent continental boundary, divides the Eastern Anatolia region into two regions. North of the BZSZ, fractures and faults around the volcanoes (Suphan Mt., Agrı Mt., Tendurek Mt., etc.) and calderas (Nemrut Caldera, Bingol Caldera, etc.) and the surrounding areas control the magmatic arsenic circulation. As a result of the alteration of the volcano-sedimentary units, and old-arc units, fluid circulation chemistry becomes more complex. Areas with high arsenic values such as Agrı (up to 0.04 mg/L), Bingol (up to 0.06 mg/L) and Van (up to 0.9 mg/L) are in accordance with geothermal fields with magmatic play type created by volcanism together with tectonism (Table 2).

South of the BZSZ, the Karacadag volcanism with mildly alkaline basaltic character affects geothermal systems in the region. Volcanism originated in the Arabian lithosphere and reached the surface along N-S directional fissures and local extension zones (Saroglu et al., 1987; Pearce et al., 1990). There are many geothermal resources related to volcanism and tectonism in the region (Baba et al., 2019). Geothermal fields with high arsenic concentrations, especially around Sanlıurfa (up to 0.1 mg/L), Kahramanmaras (up to 0.1 mg/L), Siirt (up to 0.28 mg/L) and Batman (up to 0.05 mg/L), are associated with Karacadag volcanism (Table 2).

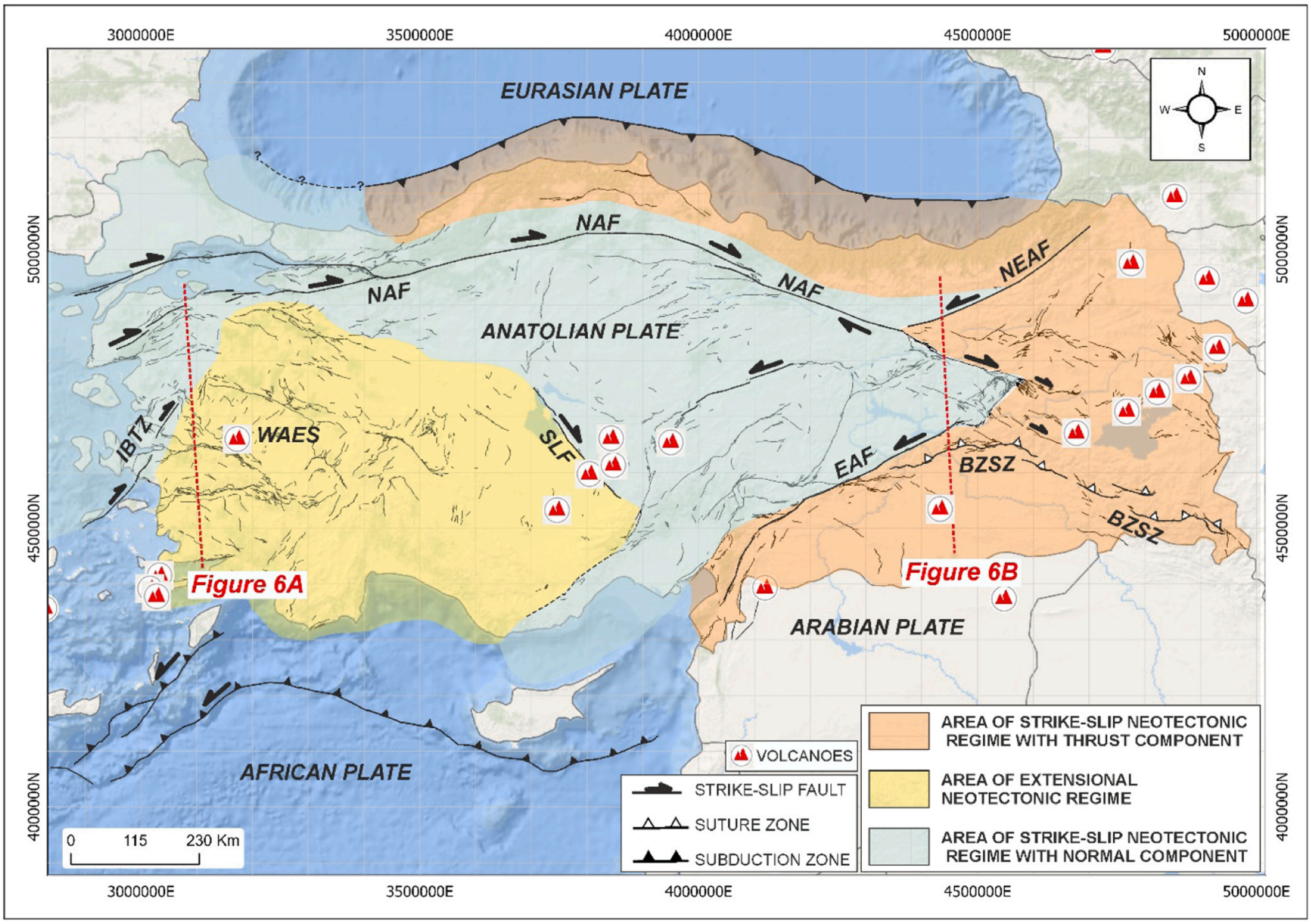

Fig. 4. Neotectonic structures and provinces of the Anatolian Plate.
Modified from Sengor and Dyer (1979), Sengor (1980), Barka (1992), Bozkurt (2001), Kocyigit and Ozacar (2003); tectonic structures and volcanic data is digitized from MTA (2016); Base map: Esri, Garmin, GEBCO, NOAA NGDC, and other contributors

4.3. Central Anatolia: non-magmatic geothermal plays-extensional domains (CV-3) and Magmatic geothermal plays–volcanic field (CV-1)

The central part of Anatolia is bounded by the NAF and EAF and forms an area of strike-slip neotectonic regime with normal component (Fig. 4). Geothermal systems around Ankara (up to 0.5 mg/L) and Bolu (up to 0.09 mg/L) are systems that contain geogenic arsenic in fluids under the influence of the NAF and inactive Neogene volcanism (Table 2).

Another important region is Cappadocia (Aksaray, Nevsehir, Nigde) where Quaternary volcanism is effective. Active tectonism and volcanism, with climate, affected morphology to form beautiful landscapes (e.g., fairy chimneys, canyons, maars, travertines). Geothermal fields within the borders of Nevsehir, Nigde and Kayseri are affected by this volcanic system. The arsenic concentrations of geothermal fields reaches up to 0.02 mg/L in Nigde and up to 0.18 mg/L in Nevsehir. These fields are examples of places where both recent magmatism and extensional systems are seen as hybrids. In areas where Quaternary volcanism is not observed, extensional-CV3 systems related to tectonic activity of the Salt Lake Fault (SLF) continue to exist.

There is a different situation in the geothermal systems of Central Anatolia between Kırsehir and Kayseri. The Paleozoic-Mesozoic Central Anatolian Crystalline Complex (metamorphic rocks consisting of gneiss, schist, and marble with granitoid intrusions) and the Tertiary volcano-sedimentary units above it created a geothermal system containing a limited amount of fluid (Goncuoglu et al., 1991; Sener and Baba, 2019). High arsenic values in fluids were measured in these basement play type geothermal systems around Kırsehir (up to 0.3 mg/L). The limited amount of geothermal fluid gives important clues for enhanced geothermal system projects that can be applied in the future. These fields have the potential to be classified as fields with conductive play type depending on the results of detailed studies to be carried out in the future. Metamorphic basement, granitoid and arsenic-containing minerals of volcanogenic origin in the covering rock have the potential to cause contamination that should be considered for applications.

4.4. Black Sea Region and East Anatolia: Orogenic Belt Type (CD-2)

Conduction-dominated geothermal play systems without active igneous activity encompass different types of geologic settings such as orogenic belts and associated foreland basins with no active tectonism (Moeck, 2014). Some geothermal resources are present in mountainous areas where highly permeable formations and faults allow deep circulation of meteoric water.

The Pontides between the subduction zone and the NAF on the Black Sea coast (Ordu and Samsun) and some of the sources around the BZSZ (Batman and Hakkari) formed in relation to orogenic belts. Arsenic concentrations of 0.5–0.6 mg/L (Akkus et al., 2005) were measured in these sources, which have not been studied in detail to date. It is seen that arsenic concentrations of these play type fields are relatively lower than other fields.

5. Discussion

There are many well-known geothermal systems worldwide. All these systems are located in areas related to tectonically and magmatically active regions. The systems located in active regions allow the inner heat of the world to reach the surface as well as the magma-derived fluids. Meteoric waters, groundwaters and fluids of geothermal origin generally interact with each other in these active areas. This interaction is not limited to fluids. With the water-rock interaction, minerals and heavy metals in the rocks can pass into water. Considering the arsenic cycle, volcano-sedimentary units and basement units including minerals containing arsenic are very important geological environments.

The vast majority of geothermal systems in the Anatolian Plate are convection-dominant geothermal play types. While tectonic activity is present in some fields with volcanism-magmatism effects, fluid circulation is provided only by faults in some fields. Volcanic units can be observed all over the Anatolian Plate. Geothermal systems are concentrated especially around the Quaternary, Neogene and Paleogene volcanics. These areas also correspond to areas with important fault zones.

When Fig. 3 is examined, high arsenic values are generally found in tectonically active regions. Significant arsenic concentrations were determined especially in areas with extensional neotectonic regime and strike-slip neotectonic regime with normal component (Fig. 4). A sharp geographical distribution between volcanism and arsenic concentrations could not be determined because young or old volcanic units are spread across the entire plate. The regions where the arsenic values are highest are sources around the Western Anatolian Extensional Fault System and the North Anatolian Fault. However, when we look at the average arsenic concentrations, almost all of the structural controls in the Anatolian plate are important elements for arsenic circulation (Fig. 5). For this reason, in the Anatolian Plate geothermal fluids caused more effective alteration along with structural controls and increased arsenic concentrations in geothermal systems.

Fig. 6 represents the plate tectonic environments of the Anatolian Plate. Fig. 6a shows enlarged tectonic systems in Western Anatolia. The model modified from Baba and Sozbilir (2012) shows graben systems, Neogene basins, and tectonic units in Western Anatolia and their relationships. Arsenic-bearing geothermal fluids in the extensional tectonic system generally travel through reservoirs under the control of high-angle normal faults and reach the surface. The arsenic minerals and alteration processes associated with Neogene volcano-sedimentary units, old-marine units, and granodiorites-granitoids are the most important factors affecting the arsenic cycle. The play type in this region is predominantly the convective-non-magmatic, extensional play type (CV-3).

In Fig. 6b, a comprehensive model prepared for the Eastern Anatolia region was modified for arsenic circulation (Keskin, 2003). According to the model, while the Arabian Plate moves under the Anatolian Plate, it causes Karacadag volcanism in the south. Besides, more than 20 volcanic centers in Eastern Anatolia were characterized by volcanism developing due to the asthenosphere rising towards the middle part of the section. The arsenic circulation in the convection-dominant magmatic-volcanic geothermal systems is due to tectonic activities that occur along the rising asthenosphere and subduction zone. Alterations associated with volcanism, old-arc rocks, volcano-sedimentary units, and chemical and physical weathering processes observed throughout the high topography ensure arsenic participation in the geothermal fluid in this region. The play type of this region is considered as convective-magmatic geothermal play (CV-1).

6. Conclusion

Structural controls and physical properties of rocks cause differences in all these mentioned physicochemical properties of deep circulating geothermal fluids. Also, thermal regime, heat flux, stress regime, and lithological features should be taken into account along with fluid dynamics and chemistry. For this reason, geothermal systems have characteristics depending on the concept of geothermal play type, a phenomenon that defines a wider geographical area by considering all these factors.

As is known, the concept of play type is quite new and play type classification of many fields has not been made yet. It is a classification based on fluid dynamics, active tectonism and magmatism in geothermal systems and heat transfer. Worldwide play type definition is divided into different groups based on plate tectonic boundary types and volcanic activity. However, more than one play type can be seen in local areas in Western America or in active regions such as Indonesia or along the Alpine orogeny. For this reason, it is necessary to keep previous arsenic studies together with the play type classification within the

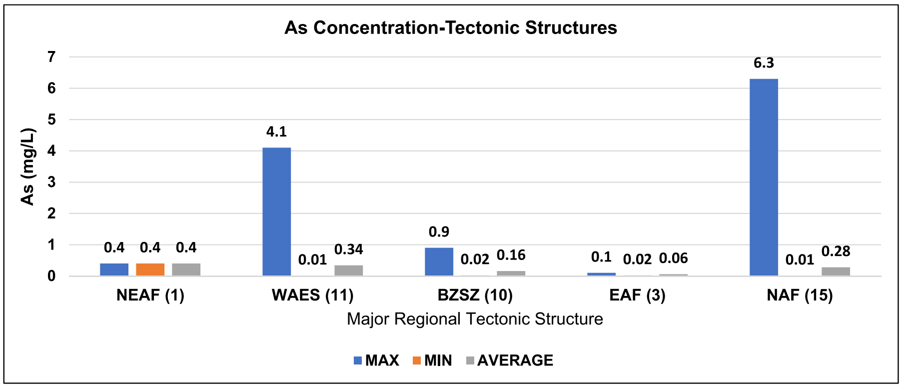

Fig. 5. The distribution of the arsenic concentration of geothermal fluids in relation with regional tectonic structure relation data (The arsenic concentration data of the provinces affected by the relevant tectonic structures are taken from Table 2 and evaluated).

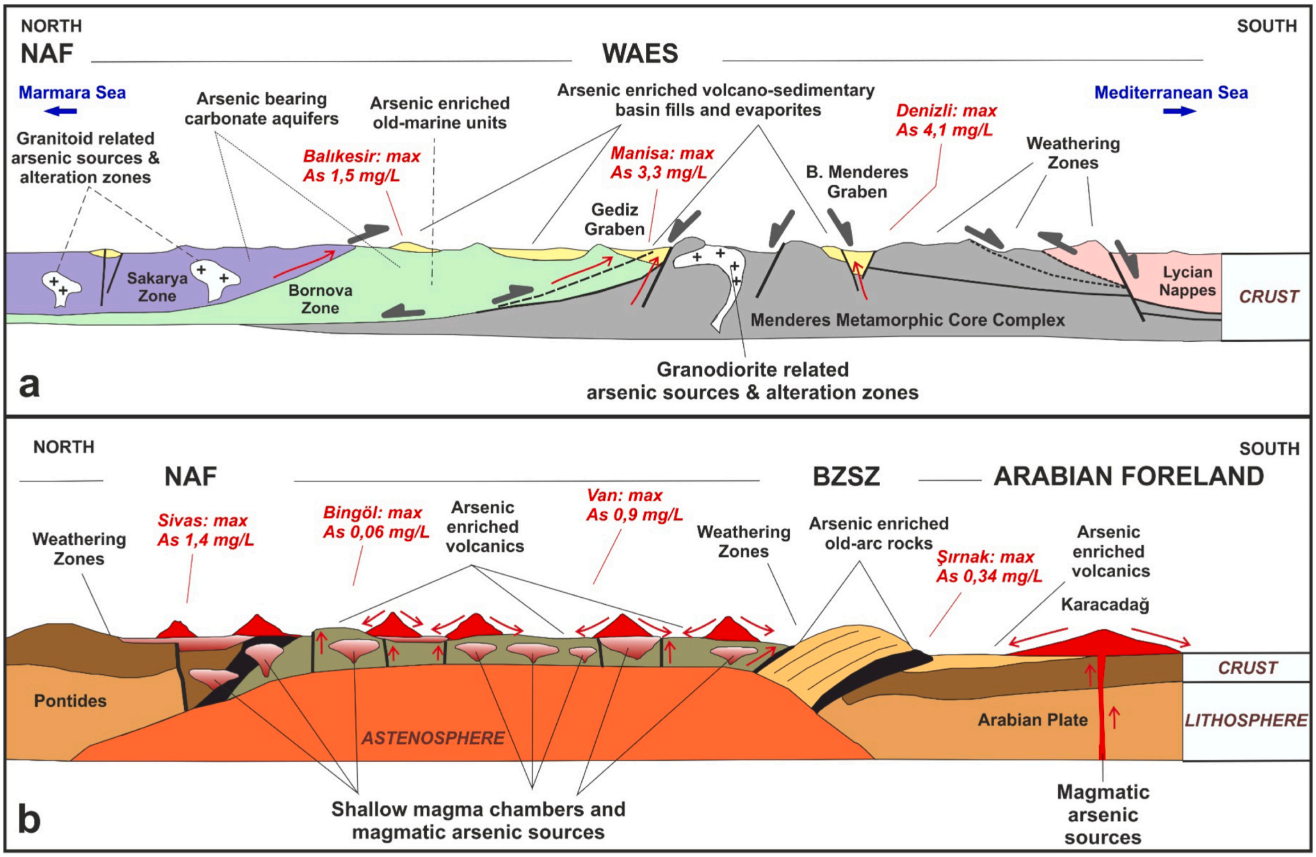

Fig. 6. Red arrows show the arsenic enriched geothermal fluid flows and please see Fig. 4 for the cross-section lines. The plate tectonic settings of the Anatolian plate with important arsenic value locations (a) a cross-section of the extensional systems of the Western Anatolia, (b) a cross-section of the recent magmatism and volcanism of the Eastern Anatolia. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
(a) Modified from Baba and Sozbilir (2012) and (b) Keskin (2003)

boundaries of the geothermal system instead of a holistic evaluation. Arsenic values in geothermal resources in America have different values, related to each other and/or independently. For example, CV-extensional systems are present in the Basin & Range (USA) fields, while active volcanic systems are present to the north. For this reason, as in some countries listed in Table 1 (e.g., USA, Greece, Mexico), it is necessary to make field-based sub-groupings and study in detail by considering the play type components of the fields.

According to the current situation in Turkey, the chemical composition of geothermal resources, especially in western regions, was investigated in detail with studies carried out in recent years. However, the number of data from sources in the east is relatively small. For this reason, more studies are recommended in these areas with important volcanic sites. With evaluation of the available data, Anatolian Plate falls under the convective-extensional play type class under the influence of extensional tectonic regime and strike-slip regime with normal component, especially in the central and western parts. In arsenic measurements made in geothermal fluids, the areas where arsenic concentrations are high are generally convective-extensional play type fields. The reason for this is that arsenic circulation and alteration occur more easily in fault zones compared to compressional regimes.

In the east, there are mostly geothermal fields in accordance with the convective-magmatic geothermal play classification. It is not be correct to reach a definitive conclusion due to the lack of data in this region. However, it is estimated that arsenic values are high, especially in regions with volcanic activity and alteration zones. In addition, together with conductive thrust-belt type fields, the existence of hybrid (CV1 + CV3) fields is evaluated as a result of the unique and complex tectonic structure of the Anatolian Plate.

With this study, an attempt was made to establish a connection between arsenic concentrations in geothermal resources and newly defined play type domains. The connection between arsenic-fluid dynamics and arsenic-play type concepts will be easier to establish with play type focused studies and new classifications of geothermal fields.

CRediT authorship contribution statement

Alper Baba: Conceptualization, Methodology, Investigation, Writing. **Taygun Uzelli**: Collect data, Visualization, Draw pictures. **Hasan Sözbilir**: Conceptualization, Writing.

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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