

Updated geochemical and geothermometry study on Ömer-Gecek geothermal area (Afyonkarahisar/Turkey)

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Received: 10.01.2022 • Accepted/Published Online: 21.05.2022 • Final Version: 07.07.2022

Abstract: The Ömer-Gecek region, one of the most critical geothermal areas of Afyonkarahisar, together with Western Anatolia, serves as a model for the integrated use of geothermal waters. As a result of the analysis made on the samples collected from the newly drilled wells, the chemical composition of the Ömer-Gecek geothermal waters, with a max temperature of 125 °C, has been determined as Na-Cl. The primary hydrochemical process affecting the chemical composition is silicate weathering. All the applied geothermometer methods showed that the water's maximum reservoir temperature was 120–130 °C. The calcite, dolomite, and aragonite minerals tend to precipitate. When compared with the previous studies in the region, it is seen that the chemical compositions of the waters have not changed, but they have become relatively more mature and closer to reaching their calculated reservoir temperature.

Key words: Ömer-Gecek, geothermal, silicate weathering, hydrochemistry, Afyonkarahisar

1. Introduction

The most important geothermal fields in Turkey are mostly located in Western Anatolia such as Denizli, Aydın, Manisa, Uşak, Kütahya, and Afyonkarahisar. Associated with the active Afyon-Akşehir graben faults (Sultandağı-Işıklar-Gecek-Gazlıgöl faults; Özkaymak and Sözbilir, 2020), there are many geothermal areas around Afyonkarahisar (Figure 1). Ömer-Gecek region, which has the highest temperature and the most used area in Afyonkarahisar, sets an example of the integrated use of geothermal energy. For the last ten years, under the leadership of AFJET (Afyon Geothermal Tourism and Trade Inc.), depending on the increasing interest in geothermal energy and the intended sustainable management, the geothermal field has been greatly improved. The Afjet Inc., which was established in 1996 with a capacity of 5000 equivalent houses capacity, currently has a capacity of ~25,000 equivalent houses, electricity production (~3mV), greenhouse (~100,000 m²), district heating, and thermal tourism (~6000 beds). To achieve these capacities, renovation and development studies have been initiated, water pipelines were replaced, old wells were made functional for pumping, reinjection and monitoring wells were activated, and new wells were drilled (Başaran et al., 2015). The AF24 and AF25 wells are used for electricity production, and the others are used for the district, greenhouse heating, and thermal tourism.

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The geothermal waters are first deposited into the storage pools, and city water is heated with them in the primary heating center. The heating of houses and greenhouses is carried out with heated city water. Then the temperature of geothermal waters reduces to 55 °C, and it is reinjected. Since the system works with a closed circuit and 90% of used geothermal waters are reinjected, hydrogeochemical or hydrogeologic changes do not occur. Previous studies have been carried out by different researchers in the Ömer-Gecek region. Mutlu (1998) stated the Ömer-Gecek geothermal waters have Na-Cl-HCO₃ type with 92 °C max temperature and give reservoir temperatures of approximately 125 °C. Akan (2002) worked on geothermal system modeling and aimed to show the effect of current operating conditions (district-greenhouse heating etc.) on the hot water system. Ulutürk (2009) stated that the waters with a temperature of 80–105 °C have Na-Cl-HCO₃ composition and meteoric origin. Yıldız et al., 2018 tried to determine the permeable tectonic zones of the geothermal system using radon, carbon dioxide concentrations, and soil temperature measurements in the Ömer-Gecek geothermal area. Özkaymak and Sözbilir (2020) focused on the structural evidence of Ömer-Gecek and Gazlıgöl geothermal areas. Their field-based studies reveal that geothermal fields in Afyon-Akşehir Graben develop on active faults' interactions in the extensional domain type

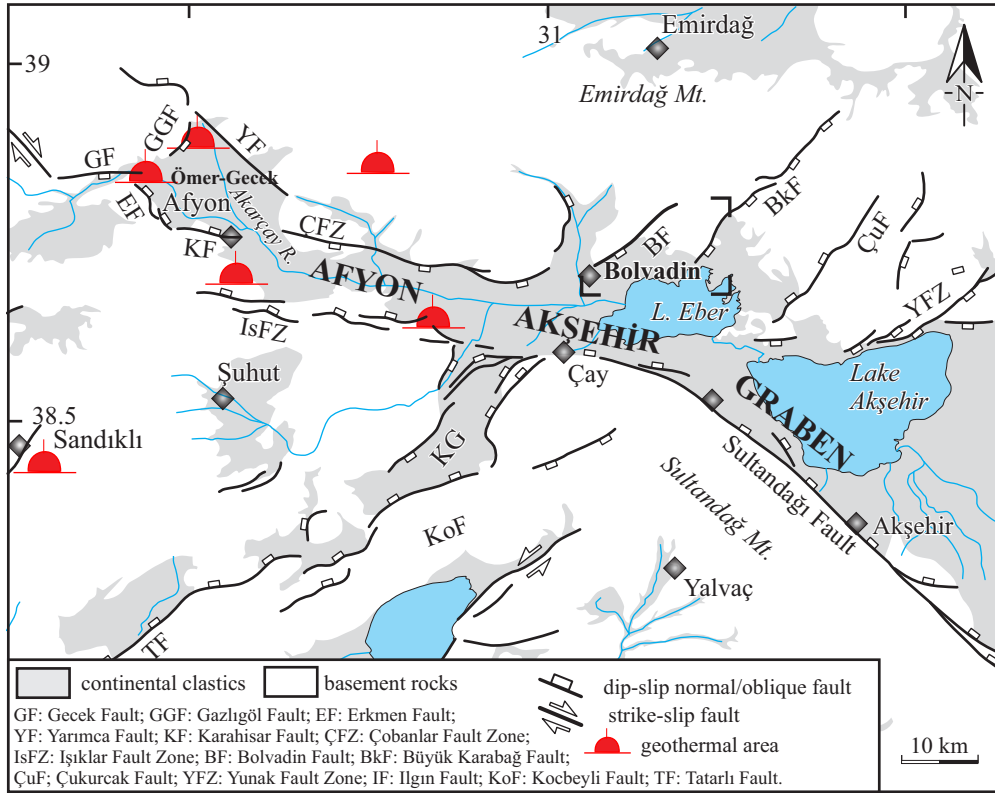


Figure 1. Geothermal areas in the Afyon-Akşehir graben system (modified from Özkaymak et al., 2019).

of geothermal play without active volcanism coming to the surface.

As a result of all these developments, studies, and resampled waters, it is crucial to reevaluate the region from a chemical point of view and to reveal the current situation.

2. Materials and methods

2.1. Geology and hydrogeology of the study area

Afyonkarahisar is located in Anatolide belt and in Afyon Zone (Ketin, 1966; Okay, 1984; Okay and Tüysüz, 1999). The basement rocks of the Afyon zone are Paleozoic aged Afyon metasedimentary group consisting of schist, quartzite, and marble. This group was unconformably covered by Triassic sediments. Neogene aged young volcanic, pyroclastic series, and the alluvium are the youngest lithologies (Tolluoğlu et al., 1997). In Afyonkarahisar, there is a NW-SE-trending normal fault system named as Akşehir Simav Fault System (ASFS) (Koçyiğit and Deveci, 2007; Özkaymak et al., 2019; Özkaymak and Sözbilir, 2020) and Afyon-Akşehir Graben is a part of ASFS. Most of the geothermal areas in Afyonkarahisar are associated with edge faults of the graben and secondary faults cutting across them (Figure 1).

Paleozoic aged Afyon metamorphic rocks (schists and marbles) are the basement of the study area. The Bayramgazi schists are of the albite-chlorite-muscovite-

biotite-quartzite schist type. The Oyuklutepe marbles are composed of calcite and dolomite and secondary chlorite, sericite, quartz, and magnetite minerals (Ulutürk, 2009). Miocene aged lithologies (marl, limestone, tuff, conglomerate, silica layers) overlie the basement rocks. Upper Miocene volcanic units characterize the volcanism in the region. Quaternary alluviums are the youngest units in the study area (Ulutürk, 2009; Başaran et al., 2020) (Figure 2).

Western Anatolia has abundant geothermal activity due to the significant extension. The faults are the primary parameters that control the geothermal systems in this region (Faulds et al., 2009; Karaoğlu et al., 2019; Uzelli et al., 2021). The geothermal activity in the Ömer-Gecek region is primarily controlled by the Gecek fault system. The geothermal wells are located on normal fault segments of the Gecek fault (Figure 2). Paleozoic calcschist and marbles have reservoir rock features in the study area. Miocene lithologies and alluvium are the caprock. The waters that feed the Ömer-Gecek geothermal system reach the reservoir rock by filtering through crack zones. The filtered waters react with environment rocks and gain Na-Cl type. The meteoric waters filtering underground warm up along the geothermal gradient and flow along fracture and fault zones (Figure 2; Ulutürk, 2009; Özkaymak and Sözbilir, 2020; Can et al., 2021).

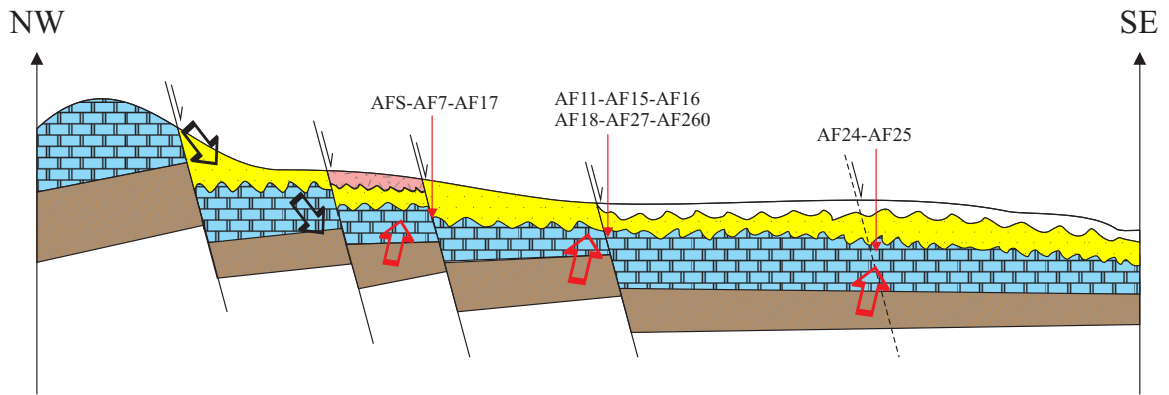
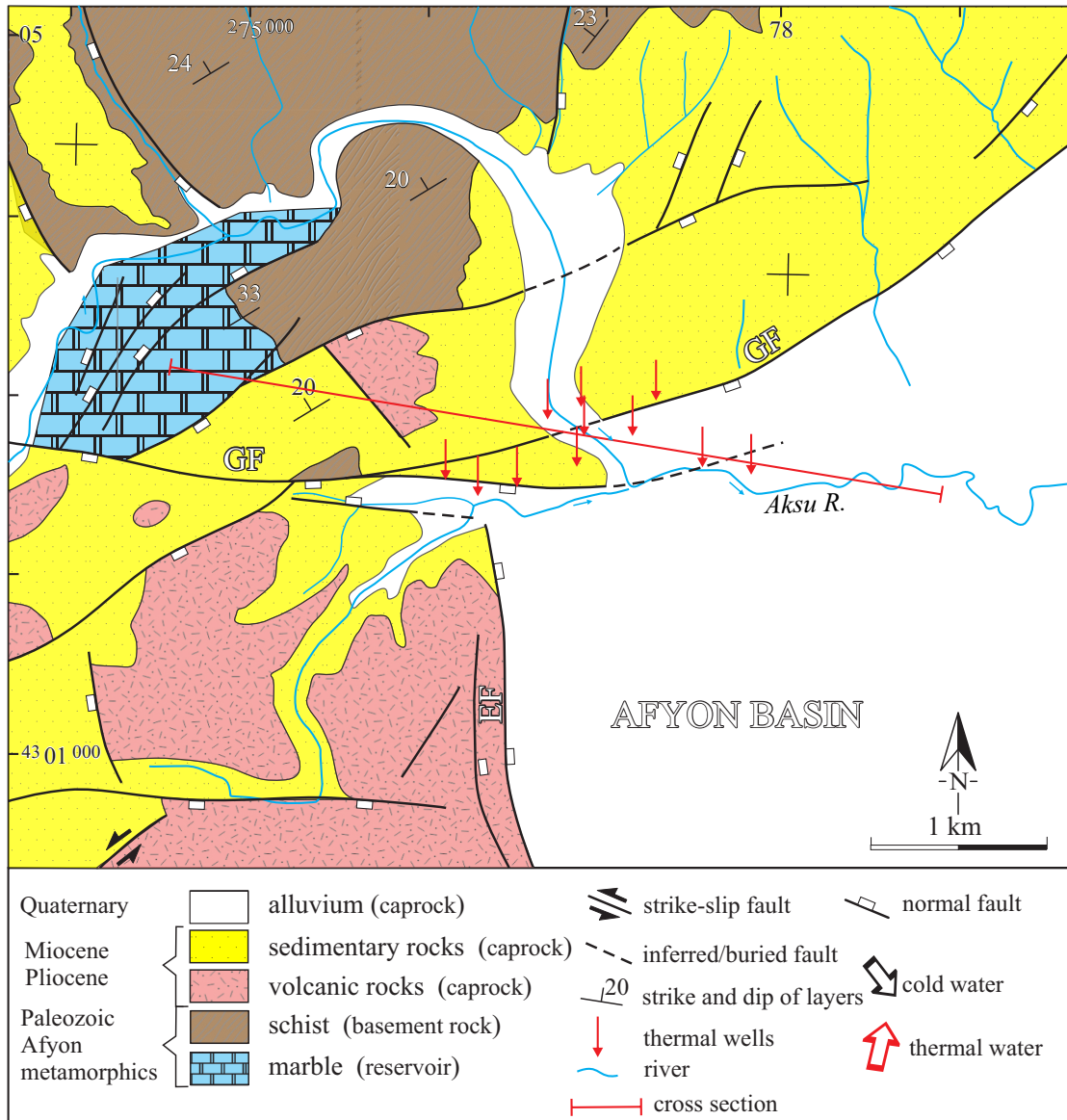


Figure 2. Geology map and conceptual geothermal model of the study area (modified after Özkaymak and Sözbilir, 2020).

2.2. Sampling and analyses

Within the scope of the study, field studies were carried out to determine the regional geology and previous studies recorded for the area. Eleven thermal water samples were collected to determine the chemical compositions in October 2021 (Figure 2). In-situ parameters (temperature °C, electrical conductivity (EC), and pH) were measured by using the HQ40D measuring tool (-10-110 °C and 0–200 ms/cm) and analog thermometer (up to 160 °C). Water samples were filtered into high-density polyethylene bottles. One bottle was acidified with ultrapure nitric acid for cations, B, and Li. The other was hermetically sealed and left unacidified for anion analyses. Major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and Li were analyzed using atomic absorption spectroscopy (Perkin Elmer Model 2280), B analysis realized as spectrometric, and the major anions (SO_4^{2-} , F^- , and Cl^-) were analyzed by ion chromatography (Dionex lc25). The detection limits for analyzed cations and anions were as follows: Na^+ (0.001 mg/L), K^+ (0.001 mg/L), Ca^{2+} (0.001 mg/L), Mg^{2+} (0.001 mg/L), SO_4^{2-} (0.001 mg/L) and Cl^- (0.01 mg/L). Alkalinity was determined with a titrimetric method. SiO_2 concentrations were determined by spectrophotometer, and 100 mL of acid-free sample was taken for the experiment. All the analyses were realized in Hacettepe University-Water Chemistry Laboratory. The hydrogeochemical properties and aqueous speciation were established using Aquachem (v 9.0 Waterloo Hydrogeologic), and saturation states and activities of sampled waters are established by Phreeqc computer programs (Parkhurst and Appelo 2013). For further investigation, chloro-alkaline indice (CAI) was calculated (Schoeller 1977).

$$CAI = \frac{Cl - (Na + K)}{Cl} \quad 1$$

The negative CAI values indicate forward ion exchange, and the positive values show reverse ion exchange.

3. Analytical results and discussion

3.1. Physicochemical characterization

The in-situ measurements and some general information about boreholes are given in Table 1. The temperatures of the geothermal waters are 80–125 °C. The thermal waters' electrical conductivities (EC) vary between 6726–8133 $\mu\text{s}/\text{cm}$, and the pH of the waters is generally neutral between 7.32–8.07.

3.2. Hydrochemistry

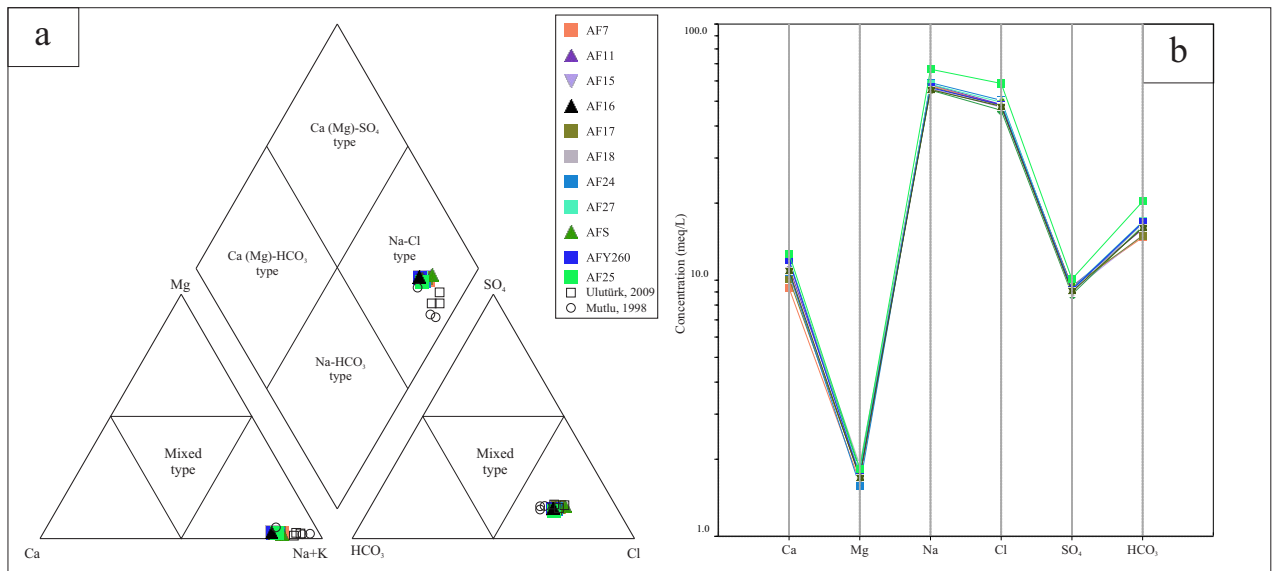
The chemical analysis results are presented in Table 2. For a holistic assessment, some values from previous studies (Mutlu, 1998; Ulutürk, 2009) were also used in some diagrams for the general chemical situation. All the sampled waters are located in the Na-Cl type waters area in Figure 3a. Schoeller's semilogarithmic diagram shows the major anions and cations substances as meq/L (Figure 3b). The hydrogeochemistry of the waters in Ömer-Gecek is characterized by sodium as the dominant cation and chlorine and bicarbonate as a dominant anion. According to IAH (1979) the dominance of cations (meq/L) is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and anions is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$, respectively. The Na^+ and K^+ content of the waters is probably due to the dissolution of alkali feldspar minerals, whereas Ca^{2+} , Mg^{2+} , and HCO_3^- contents may refer to carbonate aquifer and/or carbonic acid weathering. The molar Na/Cl ratio is a useful tool for assessing the salinity source in groundwater (Cartwright et al., 2004, 2010). The sampled waters' Na/Cl molar ratios are between 1.13 and 1.20. If the Cl originated from marine origin or halite dissolution, the Na/Cl ratios would be expected to be <1 and equal to 1, respectively (Vengosh et al., 2002; Birkle, 2005; Şanlıyüksel Yücel et al.,

Table 1. Descriptive data and information on the Ömer–Gecek geothermal wells.

Sample	EC ($\mu\text{s}/\text{cm}$)	T °C	pH	Depth (m)	Discharge (L/s)	Usage
AF7	6783	92	7.65	230	60	Heating
AF11	6825	90	7.54	210	60	Heating
AF15	6790	96	7.7	185	75	Heating
AF16	6754	82	7.61	240	60	Heating
AF17	6902	87	7.49	218	60	Heating
AF18	6726	90	7.41	430	60	Heating
AF24	7245	118	7.63	700	75	Electricity Production
AF27	7170	104	8.07	630	40	Heating
AFS	6849	91	7.57	??	60	Heating
AFY260	6871	80	7.48	210	60	Heating
AF25	8133	125	7.32	840	100	Electricity Production

Table 2. Chemical analysis results (mg/L).

Sample	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	F ⁻	Li	B
AF7	186.7	19.9	1323.7	94.0	1708.4	452.2	896.3	62.2	5.74	1.73	6.80
AF11	226.2	22.2	1334.9	95.3	1722.0	453.5	964.8	78.3	5.34	1.72	5.49
AF15	211.8	20.8	1287.1	92.0	1678.8	435.2	915.0	55.7	5.45	1.60	4.85
AF16	239.3	22.1	1269.6	92.7	1634.0	422.3	989.7	68.5	5.48	1.64	4.42
AF17	203.3	20.9	1309.5	94.6	1702.7	450.4	908.7	72.0	5.81	1.64	5.78
AF18	235.9	23.1	1281.5	91.6	1692.1	428.6	1014.5	66.3	5.05	1.63	5.56
AF24	215.3	19.1	1357.8	95.5	1786.7	439.0	1020.8	89.4	5.96	1.50	5.69
AF27	242.0	21.4	1336.9	94.3	1756.7	445.0	1033.2	100.3	5.21	0.90	5.58
AFS	183.5	16.8	1297.1	92.7	1775.2	459.3	796.7	53.8	6.26	1.59	5.17
AF260	239.1	20.9	1298.1	93.3	1716.2	441.7	1027	72.3	4.77	1.58	5.76
AF25	254.5	22.3	1532.5	109.9	2079.6	484.6	1238.6	79.6	4.96	1.86	6.42

**Figure 3.** (a) Piper (1944) and (b) Schoeller diagram.

2021). Strong water-rock interactions in the geothermal system can result in high Na/Cl ratios (Chen et al., 2016). The Na/Cl ratios of thermal waters are higher compared to seawater and halite, thus confirming that their salinity is controlled by water-rock interactions (Dotsika et al., 2021). The high Na/Cl ratios in these geothermal water samples can be explained by Na derived predominantly from water-rock interactions at high temperatures. As there is no sea or halite formation in the area, thus, the closest approach to the Cl⁻ source is the long and deep circulation of waters.

3.3. Silicate weathering

Silicate weathering is one of the most critical geochemical processes controlling the water's major ionic chemistry.

Figure 4a, shows forward ion exchange and silicate weathering are the main hydrochemical process. The forward ion-exchange releases more sodium ions, rather than calcium in water (Appelo and Postma, 2005; Barzegar et al., 2018; Kumar et al., 2009; Mgbenu and Egbueri, 2019; Das et al., 2021). An excess of Na⁺ may be due to the exchange of Ca²⁺ or Mg²⁺ in the water by Na⁺ in clay materials (Cartwright et al., 2007).

Figure 4b also shows that samples are on the SO₄²⁻ + HCO₃⁻ side, indicating silicate weathering is the dominant hydrogeochemical process. Figure 4c demonstrates that silicate weathering by carbonic acid and cation exchange releases Ca²⁺ and HCO₃⁻ into the waters (Fisher and Mullican 1997; Li et al., 2018).

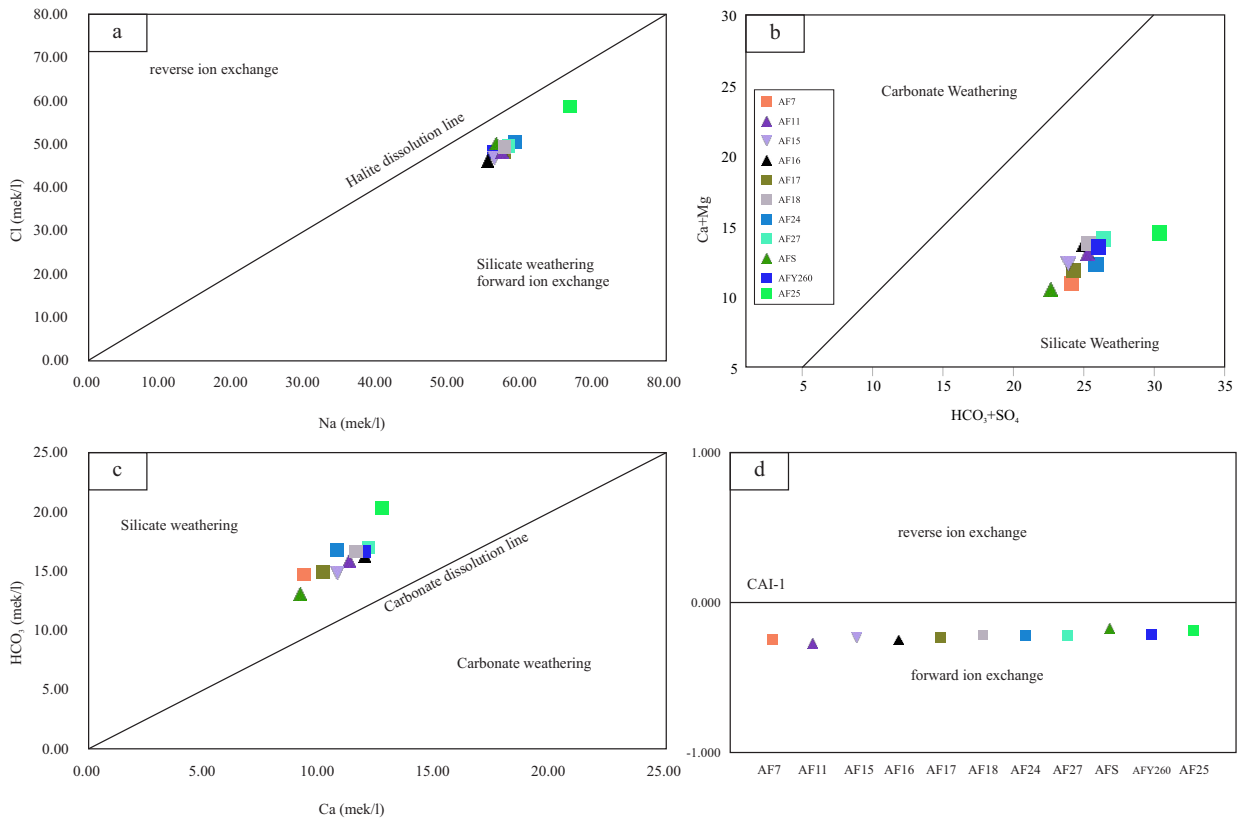


Figure 4. (a) Cl⁻ versus Na⁺, (b) Ca²⁺+Mg²⁺ versus HCO₃⁻+ SO₄²⁻, (c) HCO₃⁻ versus Ca²⁺ and (d) CAI values.

The CAI values of thermal waters (Figure 4d) showed and confirmed the existence of forwarding ion exchange offering the exchange of Mg_{aq}⁺⁺ and Ca_{aq}⁺⁺ with Na_{rock}⁺ and K_{rock}⁺ (Schoeller 1977; Nagaraju et al., 2006; Mahmoudi et al., 2017; Agyemang 2020, Yasin and Kargin 2021).

Relatively low HCO₃⁻/Cl⁻ ratios of waters (0.30–0.34) refer to the long water cycle and deeper reservoir (Han et al., 2010). On the other hand, according to Arnórsson and Andrésdóttir (1995), chlorides and boron are released from the rock during water-rock interaction in high-temperature waters. The high boron and chloride contents of water are due to deep circulation and water-rock interaction.

3.4. Mineral saturation and activity diagrams

Determining the scaling tendencies is very important to predict the reactive mineralogy and to evaluate the production characteristics. Calcite and amorphous silica are the most common scaling minerals in the World (Arnórsson, 1989). Saturation indices of anhydrite, aragonite, calcite, dolomite, chalcedony, gypsum, fluorite, amorphous silica, and quartz were calculated for discharge temperatures and pH. The saturation index values for quartz, calcite, aragonite, and especially dolomite for all groundwater samples are greater than zero (Figure 5), indicating oversaturation and precipitation of these

carbonate minerals and quartz. Dolomite and calcite may be the primary carbonate minerals in the study area. It is quite compatible with the publication reported by Bağcı et al., (2020) showing that the reservoir rock of Ömer-Gecek area is composed of calcite and dolomite. The samples are relatively in equilibrium with chalcedony whereas anhydrite, gypsum, and amorphous silica are undersaturated.

Activity diagrams were also used to investigate the fluid–mineral equilibria in the Ömer–Gecek geothermal field. The calculated activity values (based on the wellhead temperatures) were marked on activity diagrams from Mutlu (1998). All the waters were equilibrated with K-feldspar and relatively muscovite minerals between 100–150 °C as shown in Figure 6a and 6b. There are Afyon metamorphics in the region, which are very rich in muscovite and feldspar (Bağcı et al., 2020). The Na/K ratio of the waters is most likely controlled by the forward ion exchange and waters-Afyon metamorphics interaction like any other graphics.

4. Geothermometry

4.1. Na-K-Mg diagram

The Na-K-Mg diagram (Giggenbach, 1988) is very useful for both seeing the general condition of the waters and

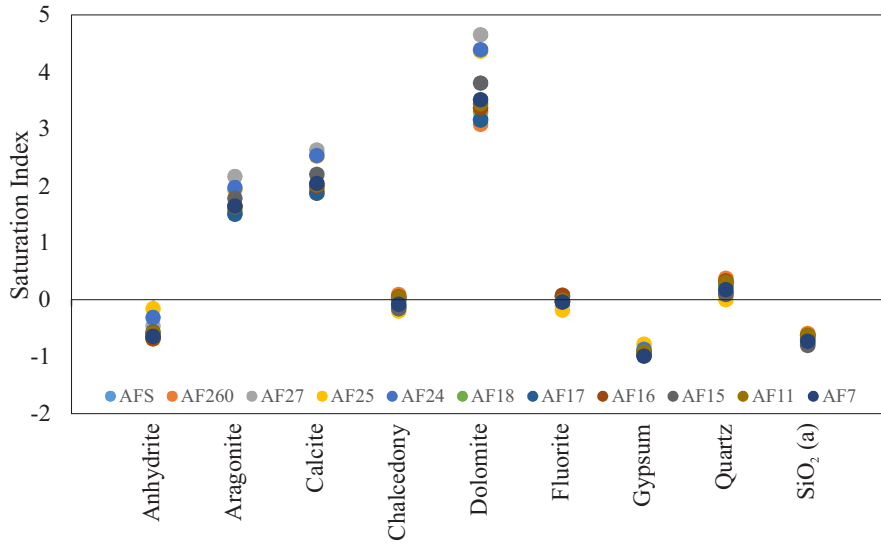


Figure 5. Saturation indices.

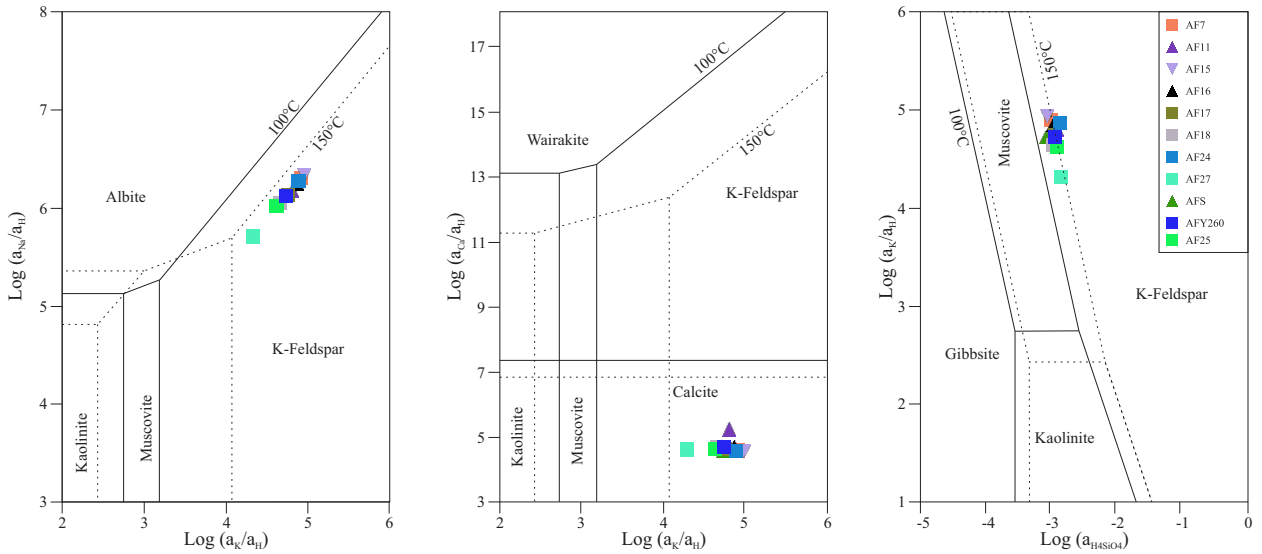


Figure 6. Activity diagrams (borders from Mutlu, 1998).

calculating the reservoir temperatures. It is important to consider that the mixing produces samples plotting in the field of partial-equilibrated waters and/or dilution and concentration displace the composition of original samples (Romano and Liotta, 2020). Figure 7 shows the plot of the whole water on the border of the immature and mature water. There is an ongoing water-rock interaction, but they have not yet reached maturity. The diagram also gives 120–130 °C reservoir temperature for these waters.

4.2. K-Mg-Ca diagram

Ömer-Gecek thermal water’s partial CO₂ pressures can be evaluated in the K–Mg–Ca geothermometer (Giggenbach and Goguel, 1989) if the waters are in equilibrium with calcite (Figure 8; Mutlu, 1998). In

Figure 9, waters locate in the calcite formation area. The compositions of the waters at their discharge temperatures are controlled by CO₂ and calcite appears as a newly formed mineral between 110–120 °C (Mutlu, 1998; Martinez-Florentino et al., 2019).

4.3. K-Mg-Quartz diagram

K-Mg and the quartz (conductive) geothermometer (Giggenbach and Goguel, 1989), which combine two low temperatures, give both silica solubility and reservoir temperature. The reservoir temperatures of Ömer-Gecek thermal waters were determined to be about 120 °C (Figure 9). The diagram also shows that the SiO₂ solubility in sampled thermal waters is controlled by quartz and/or chalcedony.

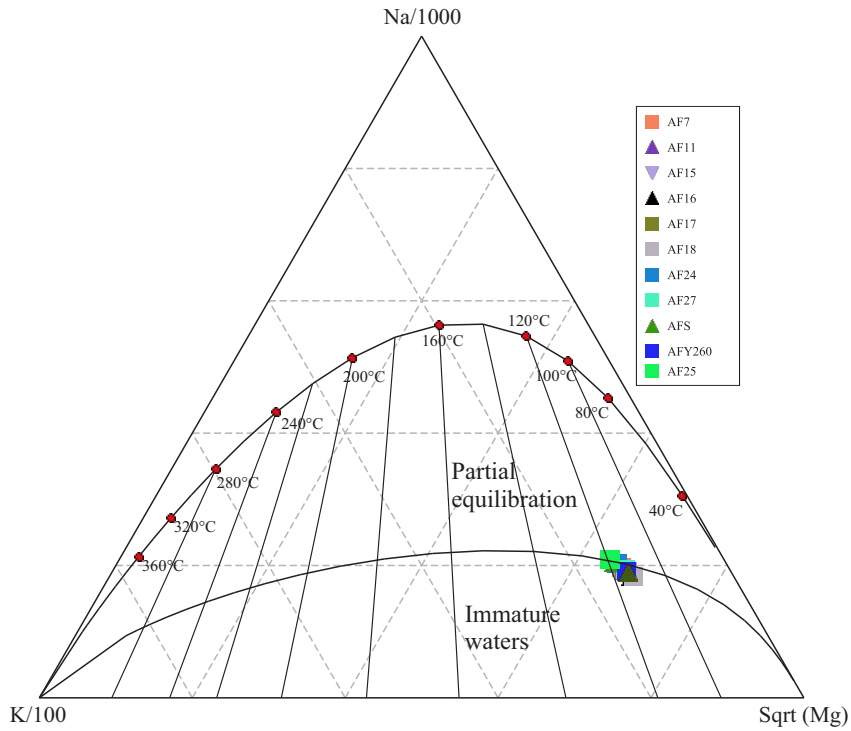


Figure 7. Na-K-Mg diagram.

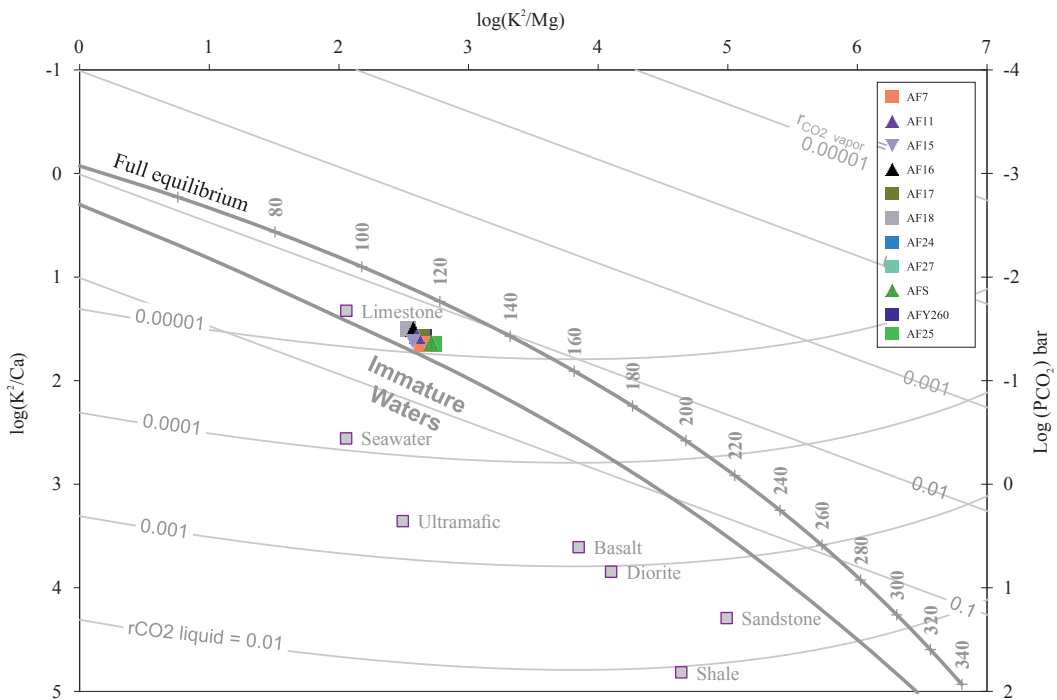


Figure 8. K-Mg-Ca geothermometer diagram (Giggenbach and Goguel, 1989).

4.4. Chemical geothermometers

Calculated chemical geothermometer results of the Ömer-Gecek field are given in Table 3. The quartz geothermometer

is generally more suitable for reservoir conditions >150 °C. Below this temperature, chalcedony controls the dissolved silica content (Karingithi, 2009). However, as chalcedony

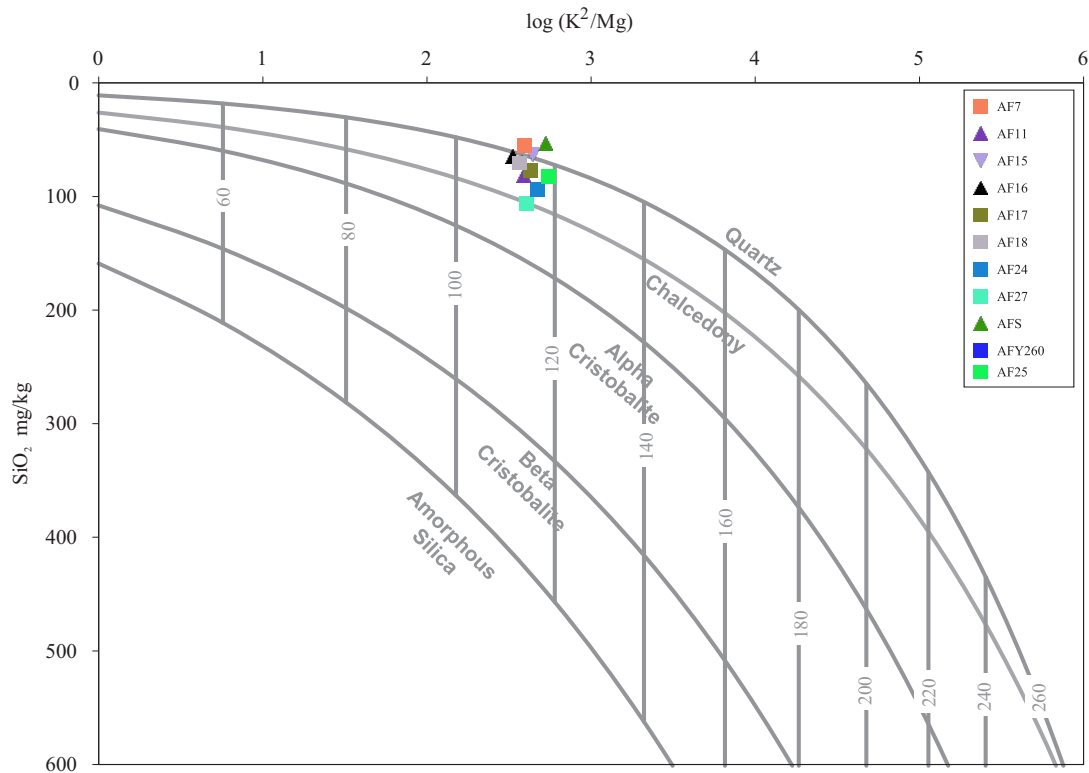


Figure 9. The cross plot of silica versus K^2/Mg geothermometer for thermal wells (Giggenbach and Goguel, 1989).

geothermometers give lower temperatures than measured, and Figure 9 shows that quartz controls the silica content, the quartz geothermometers have been evaluated. Silica geothermometry results may be lower due to the loss of silica during ascent, degassing by CO_2 , conductive cooling, mixing with saline waters, dilution, or meteoritic recharge (Arnórsson et al., 1982; Arnórsson, 2000; Nitschke et al., 2018). Considering that the SiO_2 content is not affected by these conditions the quartz geothermometers yield reservoir temperatures ranging from 102 to 137 °C. The cation geothermometers results are generally higher than silica geothermometers; since the water-rock interaction continues and the waters are immature and/or partially equilibrated, the use of cation geothermometers can be misleading (Table 3). The Na–K geothermometers give a temperature range of 147–208 °C, K/Mg, Mg/Li, and Na/Li results are very close to measured temperatures.

In general, all the geothermometry diagrams and quartz geothermometers give a reservoir temperature of approximately 120 °C. In this case, it can be said that the waters are about to reach their maximum temperature. The obtained values reflect the current conditions.

5. Conclusions

The usage of geothermal energy is becoming widespread and is encouraged. Afyonkarahisar province is very important in terms of geothermal since it is spread over a

wide usage area as electricity production, residential and greenhouse heating, and thermal baths. There are 7 different geothermal areas with different temperatures, usage areas, and chemical characteristics. The cation contents of other geothermal regions in Afyonkarahisar vary between Na–Ca/Ca–Na, and most of them are rich in bicarbonate as the dominant anion (Can et al., 2021). Due to its high temperature, silicate weathering process, and deeper wells, the waters of the Ömer Gecek region have Na^{2+} as the dominant cation and Cl^- as the dominant anion. As a result of scientific and technological studies carried out in the last ten years, water with a temperature of ~125 °C, which can also be used in electricity generation, has been obtained from the Ömer-Gecek geothermal area. The waters have Na–Cl type, with 6726–8133 $\mu s/cm$ conductivity values. The most important chemical process that determines the composition of waters is silicate alteration and forward ion exchange. Saturation indices showed that the carbonate minerals and quartz are oversaturated, relatively with silicate weathering and carbonate aquifer. All the calculated and evaluated geothermometers gave a reservoir temperature of approximately 120 °C. When the new analysis results are compared to the studies conducted by Mutlu (1998) and Ulutürk (2009), although the same well samples were not analyzed and may be analytical errors, it is seen that the general chemical composition of the geothermal system and the main chemical process

Table 3. Estimated reservoir temperatures by chemical geothermometers.

Jeotermometre	References	AF7	AF11	AF15	AF16	AF17	AF18	AF24	AF27	AFS	AFY260	AF25
Measured (°C)		92	90	96	82	87	90	118	104	91	80	125
SiO ₂	(Verma, 2000)	108	121	102	113	116	111	128	135	100	116	122
SiO ₂	(Fournier, 1977)	112	124	107	117	120	115	131	137	105	120	125
SiO ₂	(Verma and Santoyo, 1997)	113	124	107	117	120	116	131	137	106	120	125
SiO ₂	(Fournier, 1977)	112	122	107	116	118	114	128	133	106	118	122
SiO ₂ (Chalcedony)	(Fournier, 1977)	83	96	77	88	91	87	104	111	76	91	97
SiO ₂ (Chalcedony)	(Arnorsson et al., 1983)	84	95	78	89	91	87	103	109	77	91	96
SiO ₂	(Arnorsson et al., 1983)	102	114	96	107	109	105	122	128	94	110	115
Na/K	(Arnorsson et al., 1983)	163	163	163	165	164	163	162	162	163	164	163
Na/K	(Arnorsson et al., 1983)	190	190	190	192	191	191	189	190	190	191	190
Na/K	(Fournier and Truesdell, 1973)	147	148	148	150	149	148	146	146	148	148	148
Na/K	(Verma and Santoyo, 1997)	193	194	194	195	195	194	193	193	194	194	194
Na/K	(Fournier, 1979)	189	190	190	191	191	190	189	189	190	190	190
Na/K	(Nieva and Nieva, 1987)	177	177	177	179	178	177	176	176	177	178	177
Na/K	(Giggenbach, 1988)	206	207	207	208	208	207	206	206	207	207	207
K/Mg	(Giggenbach, 1988)	117	116	116	115	116	114	118	116	119	116	116
Mg/Li	(Kharaka and Mariner, 1989)	101	99	98	98	99	97	98	83	101	98	96
Na/Li (mol)	(Verma and Santoyo, 1997)	101	100	98	100	99	99	92	66	97	97	94

have not changed. Depending on the ongoing water-rock interaction and higher temperatures, the waters in the region relatively tended towards the mature waters area. In these waters where water-rock interaction continues, it would be misleading to consider cation geothermometers. According to silica geothermometer calculations, the geothermal system is close to reaching the previously calculated reservoir temperatures by Mutlu, 1998 and Ulutürk, 2009, and the new calculations support this situation. According to Karaoğlu (2021) the presence of a hot magma chamber with a temperature between 600

°C and 800 °C, residing at either 5 km or 7.5 km depth. In order to discover warmer waters in the Ömer-Gecek region, perhaps the deeper second and third reservoirs should be explored.

Acknowledgment

This study is a part of the project titled “Investigation of Lithium Potential and Origin of Geothermal Waters of Ömer-Gecek Region (Afyonkarahisar)”, and is supported by Afyon Kocatepe University-Scientific Research Project, 21.TEMATİK.01.

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