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Chemical Geothermometry and Fluid-Mineral Equilibria for the Ömer-Gecek Thermal Waters, Afyon Area, Turkey

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ABSTRACT

Thermal waters of the Ömer-Gecek geothermal field, Turkey, with temperatures ranging from 32 to 92ºC vary in chemical composition and total dissolved solid (TDS) contents. They are generally enriched in Na-Cl-HCO_3 and suggest deep water circulation. Silica and cation geothermometers applied to the Ömer-Gecek thermal waters yield reservoir temperatures of 75-155ºC. It is concluded that the solubility of silica in most of the waters is controlled by the chalcedony phase. Equilibrium states of the Ömer-Gecek thermal waters were studied by means of Na-K-Mg triangular diagram, activity diagram and saturation index (SI) diagrams. Most of the spring and low-temperature well waters in the area are classified as shallow or mixed waters which are likely to be equilibrated with calcite, chalcedony and kaolinite at predicted temperature ranges. Temperatures calculated using the chemical geothermometers are in the same range. It was also observed that mineral equilibrium in the Ömer-Gecek waters is largely controlled by CO_2 concentration.

1. INTRODUCTION

The Afyon area is one of the most extensive geothermal fields in Turkey. The current studies in the area are directed towards the utilization of the thermal waters for district heating. This study presents the geochemical evaluation of thermal waters in the Ömer-Gecek field of the Afyon area on the basis of chemical geothermometry and mineral equilibrium calculations. The purpose of investigation is also to determine the processes affecting the chemical composition and mineral equilibrium of the waters collected in this field.

The Ömer-Gecek field is located 15 km northwest of the city of Afyon. Most of the hot springs are concentrated in three sites: Uyuz Bath, Ömer Bath, and Gecek Bath (Figure 1). The basement in the Ömer-Gecek field is represented by mica schist and marbles of Paleozoic age. Neogene deposits composed of conglomerate, sandstone, clayey limestone-sandstone, and volcanic glass-trachyandesitic tuff unconformably overlie the Paleozoic basement. The area was affected by the volcanic activity which prevailed between upper Miocene and Pliocene. Quaternary deposits are mostly found in flat plains and stream beds. The travertine deposits, which are currently precipitating, are observed dominantly in the western part of the field and predominantly around the Ömer and Gecek baths (Figure 1).

The General Directorate of Mineral Research and Exploration of Turkey (MTA) drilled 13 wells (AF-1 through AF-12 and R-260) in the Ömer-Gecek field from 1971 to 1996 within the framework of the Afyon Geothermal Energy Project. In addition, two wells (HGF and UH) were drilled in the area by the private sector. Current discharge rate of all these wells is estimated to be more than 500 l/s. Previous studies reported that there were many hot springs in the area prior to the drillings (Erişen, 1976). Neogene limestone, silicified limestone, and Paleozoic schist and marbles are thought to be the probable reservoir rocks of the Ömer-Gecek field. Sandy clay, silt, marl, and tuffs of Neogene age and phyllite and mica schists of Paleozoic age are the main cap rocks in the area.

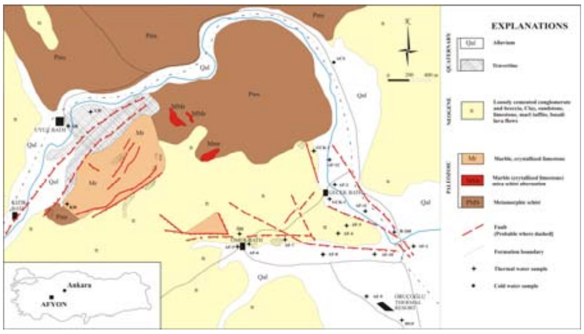


Figure 1: Geological map of the Ömer–Gecek field. Simplified from Erişen et al. (1984).

2. MATERIALS AND METHOD

A total of 12 thermal and one cold water samples were collected from geothermal wells and springs in the Ömer-Gecek field. The locations of the water sampling points are shown in Figure 1. Only five of the wells of MTA (AF-1, AF-4, AF-8, AF-9, and R-260) could be sampled at the time of the study due to carbonate scaling encountered within the pipes of the other wells. Two other samples in the field were taken from HGF (Hayat geothermal facilities) and UH (Uyuz bath) wells. A total of six spring waters was sampled in the Ömer-Gecek field. Five of them are thermal springs, namely ÖH (Ömer bath), GCK-1, GCK-2 (Gecek bath), AB (Askeri bath), and KH (Kızık bath). Water from a fountain on the Afyon-Kütahya road was sampled (ACS) to represent the cold water component in the whole Ömer-Gecek field (Figure 1).

Water samples were collected into 500-ml polyethylene containers. All water samples were collected as two filtered batches. 5 ml concentrated HCl was added into one of the batches for cation analyses. The other batch taken for anion analyses was untreated. A 50-ml special sample was diluted in a ratio of 1/1 with distilled water to bring the silica concentration levels below 100 ppm. This treatment prevented polymerization of silica as a jelly deposit. Temperature and pH measurements were conducted at the sampling sites. Na and K concentrations were determined with flame photometry. The titration method was used for Ca, Mg, Cl, and alkalinity (HCO_3) analyses. SO_4 concentrations were determined with ion chromatography. Atomic absorption spectrophotometry was used for Fe, Al and SiO_2, analyses. Chemical analyses of waters were conducted at the laboratories of MTA.

3. CHEMISTRY OF THE WATERS

The results of chemical analyses of waters from the Ömer-Gecek field are presented in Table 1. The pH values in the waters are between 6.25 and 7.70. Excluding the sample ACS, TDS (total dissolved solids) contents of the thermal waters range from 2807 to 6018 mg/l. Temperatures of the thermal springs range from 32ºC (sample KH) to 62.5ºC (sample AB). Among the wells, AF-4 has the hottest water with a measured temperature of 92ºC.

All the samples listed in Table 1 are plotted in the Cl-SO_4-HCO_3 ternary diagram (Figure 2). It is shown that waters of Ömer-Gecek plot between HCO_3 and Cl fields yielding a mixing along the line between peripheral and mature water fields, but they never attain maturity.

4. GEOTHERMOMETRY

4.1. Chemical Geothermometers

The results of chemical geothermometers applied to the thermal waters of the Ömer-Gecek field are given in Table 2. The quartz geothermometers of Fournier and Potter (1982b) and Arnórsson (1985) yield reservoir temperatures ranging from 105 to 180ºC. Compared with quartz geothermometers, the chalcedony geothermometers of Fournier (1977) and Arnórsson et al. (1983b) display relatively lower reservoir temperatures between 75 and 158ºC. Since chalcedony, rather than quartz, controls silica saturation at temperatures less than 180ºC (Fournier, 1991), it appears that the chalcedony geothermometers better reflect the reservoir temperatures for the Ömer-Gecek field, but this is further checked with cation geothermometers.

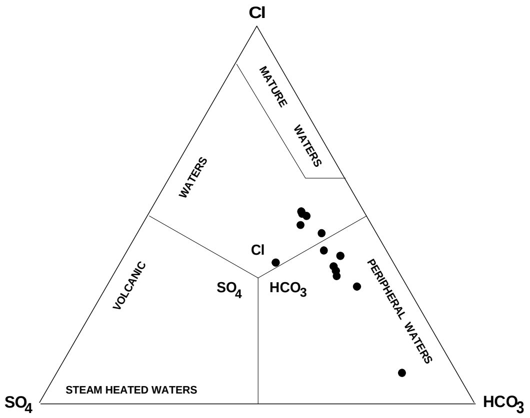
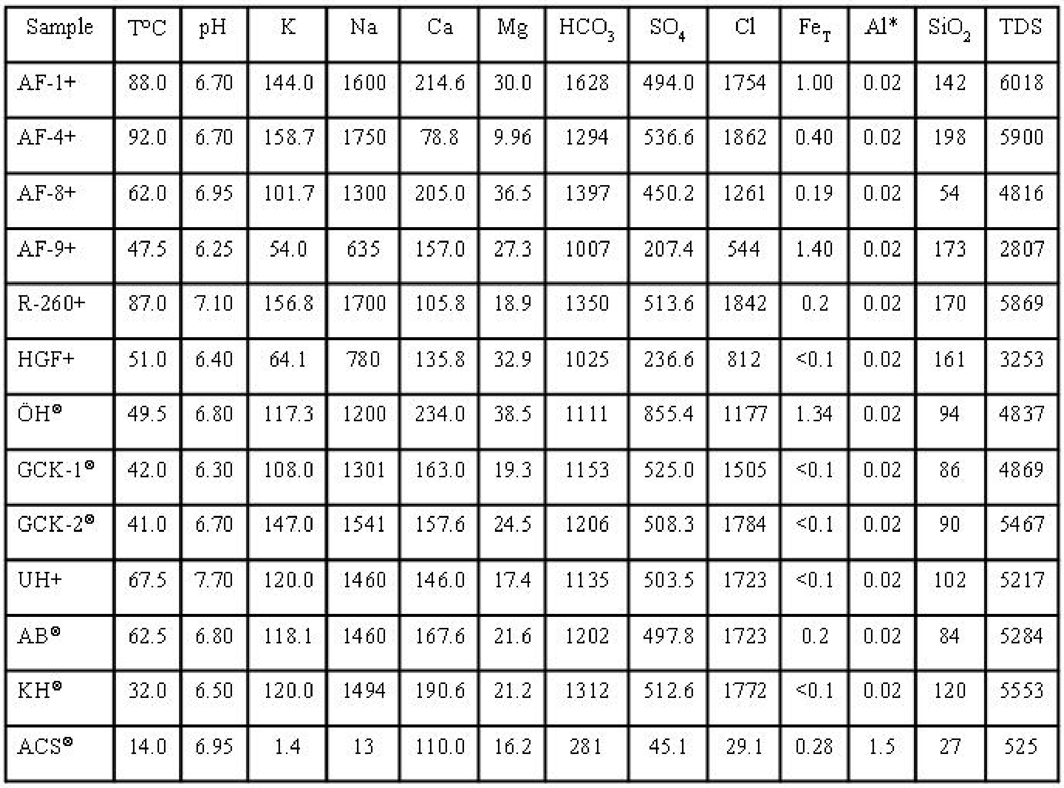


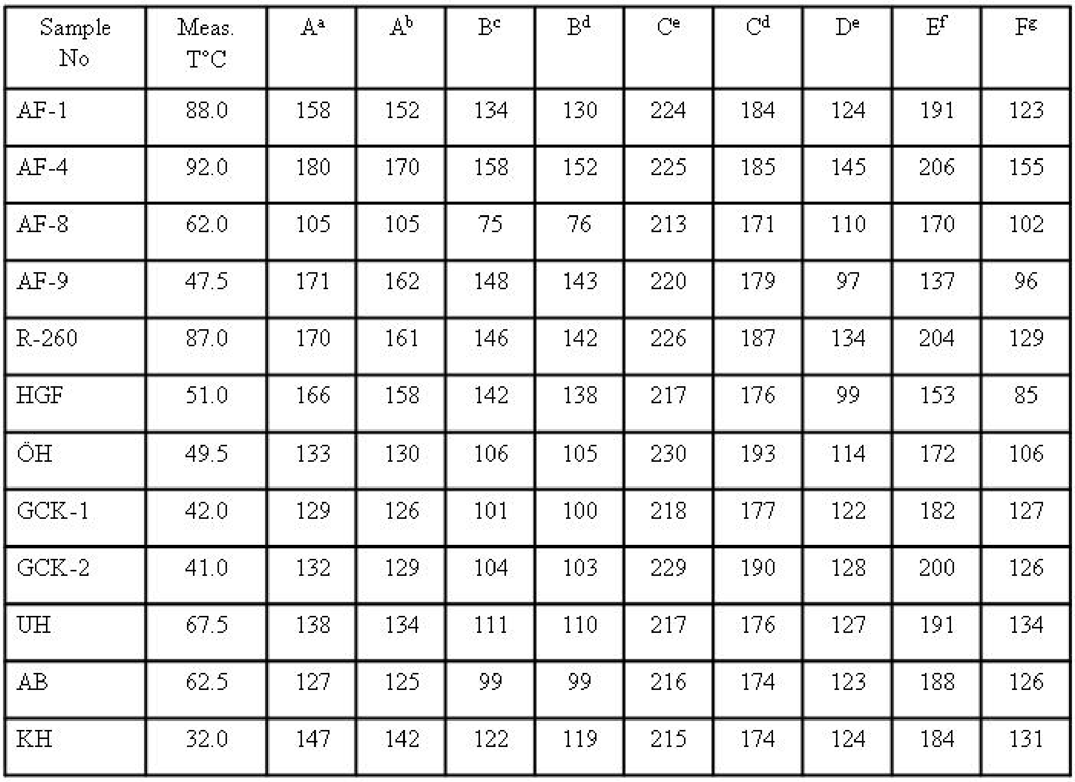
Figure 2: Relative Cl, SO4, and HCO3 contents of the Ömer-Gecek thermal waters on weight (mg/kg) basis. Fields from Giggenbach (1988).

Table 1: Chemical analyses of the Ömer-Gecek thermal waters. +wells, ⊙springs. Concentrations are in ppm. *Calculated by the SOLVEQ program (Reed and Spycher, 1990).



Sample	T°C	pH	K	Na	Ca	Mg	HCO_3	SO_4	Cl	Fe_T	Al*	SiO_2	TDS
AF-1+	88.0	6.70	144.0	1600	214.6	30.0	1628	494.0	1754	1.00	0.02	142	6018
AF-4+	92.0	6.70	158.7	1750	78.8	9.96	1294	536.6	1862	0.40	0.02	198	5900
AF-8+	62.0	6.95	101.7	1300	205.0	36.5	1397	450.2	1261	0.19	0.02	54	4816
AF-9+	47.5	6.25	54.0	635	157.0	27.3	1007	207.4	544	1.40	0.02	173	2807
R-260+	87.0	7.10	156.8	1700	105.8	18.9	1350	513.6	1842	0.2	0.02	170	5869
HGF+	51.0	6.40	64.1	780	135.8	32.9	1025	236.6	812	<0.1	0.02	161	3253
ÖH⊙	49.5	6.80	117.3	1200	234.0	38.5	1111	855.4	1177	1.34	0.02	94	4837
GCK-1⊙	42.0	6.30	108.0	1301	163.0	19.3	1153	525.0	1505	<0.1	0.02	86	4869
GCK-2⊙	41.0	6.70	147.0	1541	157.6	24.5	1206	508.3	1784	<0.1	0.02	90	5467
UH+	67.5	7.70	120.0	1460	146.0	17.4	1135	503.5	1723	<0.1	0.02	102	5217
AB⊙	62.5	6.80	118.1	1460	167.6	21.6	1202	497.8	1723	0.2	0.02	84	5284
KH⊙	32.0	6.50	120.0	1494	190.6	21.2	1312	512.6	1772	<0.1	0.02	120	5553
ACS⊙	14.0	6.95	1.4	13	110.0	16.2	281	45.1	29.1	0.28	1.5	27	525

Table 2: Chemical geothermometers for the Ömer-Gecek thermal waters (ºC).



Sample No	Meas. T°C	A[a]	A[b]	B[c]	B[d]	C[e]	C[d]	D[e]	E[f]	F[g]
AF-1	88.0	158	152	134	130	224	184	124	191	123
AF-4	92.0	180	170	158	152	225	185	145	206	155
AF-8	62.0	105	105	75	76	213	171	110	170	102
AF-9	47.5	171	162	148	143	220	179	97	137	96
R-260	87.0	170	161	146	142	226	187	134	204	129
HGF	51.0	166	158	142	138	217	176	99	153	85
ÖH	49.5	133	130	106	105	230	193	114	172	106
GCK-1	42.0	129	126	101	100	218	177	122	182	127
GCK-2	41.0	132	129	104	103	229	190	128	200	126
UH	67.5	138	134	111	110	217	176	127	191	134
AB	62.5	127	125	99	99	216	174	123	188	126
KH	32.0	147	142	122	119	215	174	124	184	131

A:Quartz, B:Chalcedony, C:Na-K, D:K-Mg, E:Na-K-Ca, F:Na-K-Ca Mg corrected. [a]Fournier and Potter (1982b); [b]Arnórsson (1985); [c]Fournier (1977); [d]Arnórsson et al. (1983b); [e]Giggenbach (1988); [f]Fournier and Truesdell (1973); [g]Fournier and Potter (1979).

The reservoir temperatures computed from the cation geothermometers for each water are generally higher than those of silica geothermometers (Table 2). The Na-K geothermometers of Arnórsson et al. (1983b) and Giggenbach (1988) give temperature ranges of 171-193ºC and 213-230ºC, respectively. It is obvious that Na-K geothermometers applied to the Ömer-Gecek field give anomalously high temperatures and suggest a deeper reservoir. The K-Mg geothermometer of Giggenbach (1988), however, yields a maximum temperature of 145ºC (Table 2).

In order to eliminate the possible effects of Ca concentration on the Na-K geothermometer, the Na-K-Ca geothermometer of Fournier and Truesdell (1973) was used. The reservoir temperatures calculated from this geothermometer range from 137 to 206ºC, which are lower than those of the Na-K geothermometers but still higher than those of the quartz and chalcedony geothermometers.

Reservoir temperatures computed from the Na-K-Ca-Mg geothermometer of Fournier and Potter (1979) are consistent with those of silica geothermometers. The overall reservoir temperature range is 85-155ºC.

4.2. Na-K-Mg Diagram

A further evaluation of the cation geothermometers is made on the Na-K-Mg diagram proposed by Giggenbach (1988). Figure 3 shows that none of the Ömer-Gecek waters attains a water-rock chemical equilibrium. Waters of wells are close to the boundary between mature (partly equilibrated) and immature (shallow) waters. AF-4 is the only sample located at the center of mature waters area. For the samples in the region of immature waters, the application of both K-Na and K-Mg, and indeed any type of cation geothermometers, is doubtful and the interpretation of the temperature predictions of such waters should be made cautiously (Giggenbach, 1988). However, most of the data points of the Ömer-Gecek field are close to the partial equilibrium region and, therefore, temperature estimates of these waters can be performed with some degree of confidence.

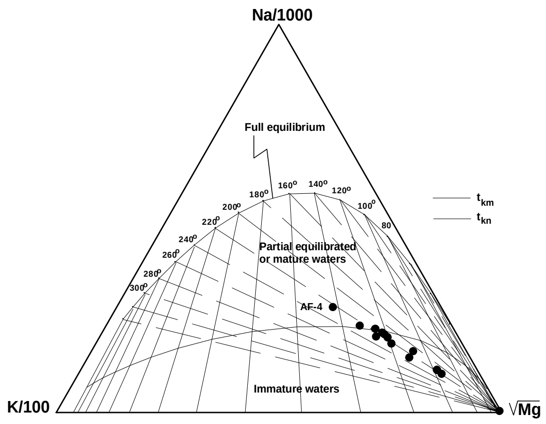


Figure 3: Graphical evaluation of the water-rock equilibration temperatures (Giggenbach, 1988) using relative Na, K, and Mg concentrations (mg/kg) of the Ömer-Gecek thermal waters.

5. FLUID-MINERAL EQUILIBRIA

Evaluation of chemical equilibria between minerals and solutions in natural water systems requires the determination of aqueous species activity and the knowledge of solubility of the minerals found in the altered rocks. The large number of ions, ion pairs and complexes in the solution, particularly at elevated temperatures, necessitates the use of a computer program for the calculation of individual species activitiy from the analytical data. In this study, the WATSPEC computer program (Wigley, 1977) was used to calculate the ion activitiy and SI of minerals with respect to given water compositions. In order to get more reliable results for high temperatures, thermodynamic data of WATSPEC on mineral and aqueous species were replaced with those of Arnórsson et al. (1982).

In the calculation of activity coefficient, the temperature effect was also handled using the temperature-dependent form of the b_i parameter in the Debye-Hückel equation. Therefore, the program WATSPEC with its new form was considered to be a powerful tool for computing the equilibrium states of the Ömer-Gecek thermal waters. The SUPCRT-92 (Johnson et al., 1992) and SOLVEQ (Reed and Spycher, 1990) computer programs were also used in constructing the activity diagrams and mineral equilibria calculations, respectively.

5.1. Activity Diagrams

To investigate the fluid-mineral equilibria in the Ömer-Gecek geothermal field, an activity (stability) diagram (Figure 4) was constructed at the reservoir temperature which was calculated to be around 125ºC from the chemical geothermometers in the previous section. The mineral boundaries in Figure 4 were drawn at 100, 125 and 150ºC. In producing the activity diagram, 5 pure minerals, kaolinite, muscovite, K-feldspar, albite and paragonite, were considered.

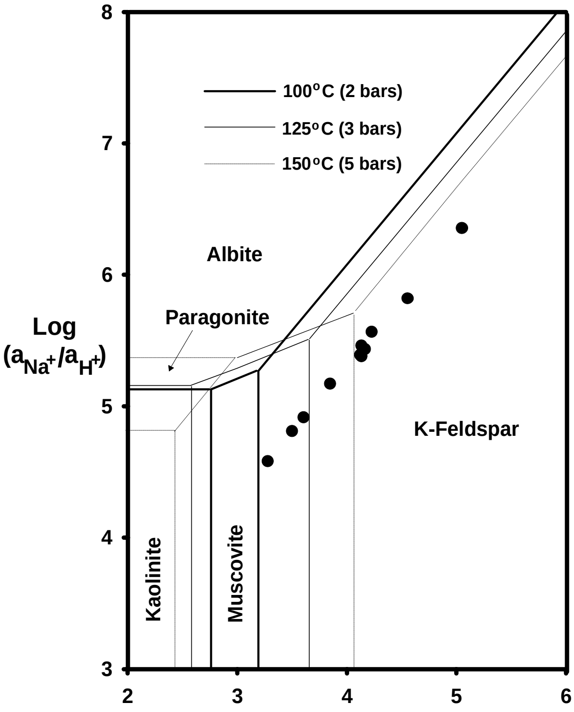


Figure 4: Activity diagram for the Ömer-Gecek thermal waters at 100, 125, and 150ºC in the system of Na_2O-K_2O-Al_2O_3-SiO_2-H_2O.

The SUPCRT-92 computer program (Johnson et al., 1992) was used for calculating the equilibrium constants (K_{eq}) of the reactions of minerals which have common boundaries in the diagram. The computations were performed at 100, 125, and 150ºC and at pressures of 2, 3, and 5 bars, respectively. In the calculations, the activities of water (a_{H2O}) and solid phases (minerals) were assumed to be unity (1), and activity of silicic acid (a_{H4SiO4}) or SiO_2 was fixed at the average silica value of the Ömer-Gecek waters (log a_{H4SiO4}= -2.69). The activities of Na^+, K^+, H^+, H_4SiO_4 and other species were computed with the program WATSPEC (Wigley, 1977) and plotted on the same diagram (Figure 4).

It was observed that the activities of the species do not significantly change as the temperature of the solution varies, unlike the stability fields of minerals. In other words, the positions of the water samples in the activity diagrams remain unchanged. Duchi et al. (1995) used the WATEQ4F program to calculate the activities of species in the thermal waters of the Campania region in southern Italy. They stated that the ion activity values computed at a temperature range between 150 and 250ºC remain the same. Therefore, it is concluded that the activity coefficients, and hence the ion activities calculated are not significantly affected by the changes in temperature. However, it should be noted that the value assigned for the activity of silicic acid may significantly affect the boundaries between the minerals.

Considering that a temperature range of 100-125ºC best represents the reservoir temperature of the Ömer-Gecek field as a whole, all waters generally define an equilibrium trend between albite, muscovite, and K-feldspar minerals. Some spring and deep well waters have a tendency to be equilibrated with K-feldspar rather than muscovite (Figure 4). Unexpected positions of some waters in the center of K-feldspar field, such as UH and R-260, are due to their high pH values.

Since, except for small amounts of K-feldspar, albite and muscovite are not found in the cutting samples from the wells, it is believed that the Na/K ratio of the waters may be controlled by the equilibrium between a sodic clay (Na-montmorillonite) and K-feldspar. The Na/K ratio of the waters at depth could also remain unchanged during the rise to the surface without precipitating or dissolving any Na- and K-bearing mineral.

5.2. Thermodynamic Saturation States

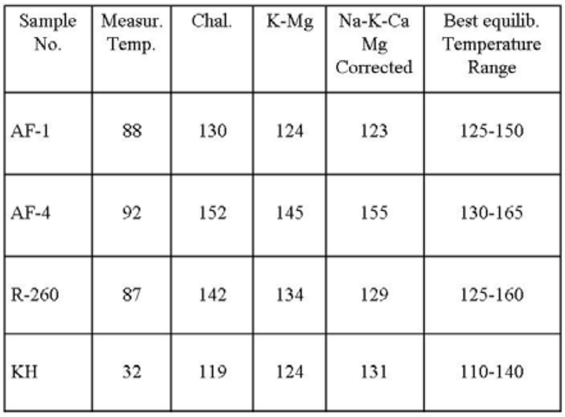
This is a different approach to the geothermometry which is not based on the assumption of predetermined mineral/solute equilibrium or the use of empirically calibrated geothermometers. It is related to the evaluation of the saturation state of a water composition at different temperatures with respect to various minerals which are likely to equilibrate with the water of interest. If a group of minerals is close to equilibrium at a particular temperature, it can be concluded that the water is equilibrated with these minerals and the temperature resembles the reservoir temperature. However, mixed waters and non-equilibrated waters, such as shallow or immature waters, show no equilibrium saturation with hydrothermal minerals at a given temperature.

The WATSPEC program (Wigley, 1977) was used to calculate saturation indices (SI) of 16 most common hydrothermal minerals some of which were identified as alteration minerals in the reservoir (e.g. calcite, kaolinite, and chalcedony). Since the aluminum concentration in all the thermal waters of the Ömer-Gecek field (except the sample ACS) is less than 0.02 ppm (Table 1), the Al concentration in each water was calculated by the SOLVEQ computer program (Reed and Spycher, 1990). In the calculations, the Al concentration in waters was fixed to that of the equilibrium with respect to K-feldspar, muscovite, and kaolinite minerals. The Al concentrations, computed for the Ömer-Gecek thermal waters at their corresponding reservoir temperatures and at the equilibrium with the mineral phases, were found to be generally between 0.002 and 0.02 ppm and do not exceed the analyzed values. In the present study, the Al concentration of 0.02 ppm was used for the mineral equilibrium calculations. The geothermometer results obtained, therefore, represent only the maximum temperatures that the reservoir waters can attain.

Possible reservoir temperatures estimated with the mineral equilibrium calculations for the selected waters of Ömer-Gecek field (AF-1 and spring KH) are presented in Figure 5 and 6, respectively. The reservoir temperatures determined from the equilibrium calculations agree well with the temperature estimations of the chemical geothermometers and other geochemical techniques. For a given water sample, the curves of different minerals tend to move closer to the equilibrium line (log SI=0) at almost the same temperature, which is around the temperature estimate obtained through the chemical geothermometers.

Table 3 summarizes the temperature ranges at which most minerals appear to reach equilibrium for such water compositions. The measured temperatures, and temperatures computed from the chalcedony, K-Mg, and Na-K-Ca with Mg correction geothermometers, are also given in the same table for comparison. The temperature range at which most of the minerals intersect the equilibrium line (log SI=0) was accepted to be the best equilibrium temperature range. Due to the fact that waters of the Ömer-Gecek area have high carbonate contents, and hence the temperatures obtained from the equilibration of carbonate minerals may yield misleading results. The saturation states of minerals such as calcite, dolomite, and aragonite were ignored in determining the best equilibrium temperatures.

Table 3: Summary of geothermometry results (°C) for some of the Ömer-Gecek thermal waters.



Sample No.	Measur. Temp.	Chal.	K-Mg	Na-K-Ca Mg Corrected	Best equilib. Temperature Range
AF-1	88	130	124	123	125-150
AF-4	92	152	145	155	130-165
R-260	87	142	134	129	125-160
KH	32	119	124	131	110-140

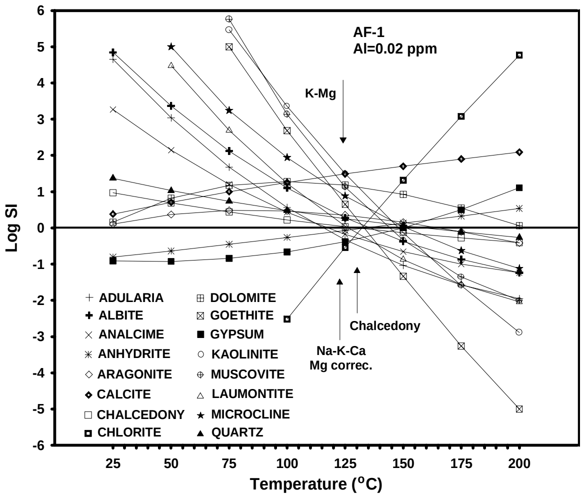


Figure 5: Mineral equilibrium diagram for AF-1 well.

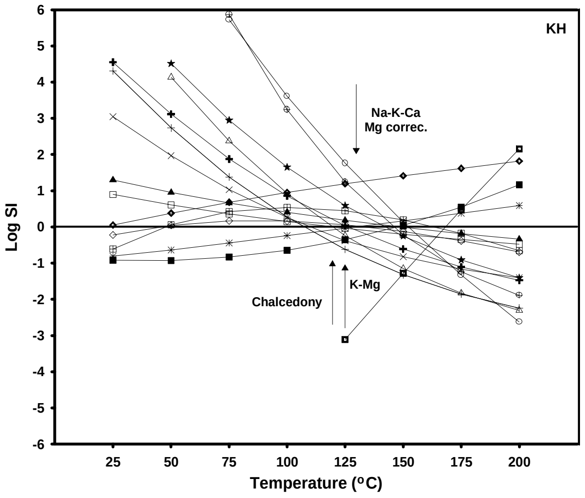


Figure 6: Mineral equilibrium diagram for sample KH. Mineral symbols are same as in Figure 5.

Equilibrium calculations presented in Figure 5 and 6 reveal that all the waters become oversaturated with respect to carbonate (calcite, aragonite, and dolomite) and sulfate (gypsum and anhydrite) minerals as the temperature increases. However, due to their thermodynamic properties, dolomite and aragonite show a decrease in the saturation level beyond a temperature of 100ºC. All the silicate minerals are likely to precipitate at lower temperatures. As the temperature increases, they tend to dissolve and stay in solution as ions. However, among the silicate minerals, chlorite presents an opposite saturation trend, that is, it is precipitated at high temperatures. This is an expected feature of this mineral since chlorite contains Mg, unlike the other silicate minerals that bear Na and K ions as cations in their structural forms.

Overall inspection of the figures reveals that saturation trends of most minerals are closely intersected on the equilibrium line only for high temperature waters or for waters that have been less affected by the mixing processes (e.g. sample AF-1) (Figure 5).

CONCLUSIONS

Thermal waters of the Ömer-Gecek field in the Afyon area are generally enriched in Na-Cl-HCO_3. Significantly high Cl contents may suggest that the circulation of water is deep and that water has a long residence time in the reservoir.

Chalcedony, K-Mg, and Na-K-Ca-Mg geothermometers suggest the reservoir temperature around 155ºC. Although a low-temperature mineral assemblage is found in the area, activity diagrams indicate a deeper reservoir for the system. The results of cation geothermometers (especially Na-K) should be carefully evaluated. Equilibrium temperature ranges obtained from the saturation index vs. temperature diagrams constructed for selected waters of the Ömer-Gecek field generally fit the reservoir temperatures computed from the chemical geothermometers (chalcedony, K-Mg, and Na-K-Ca-Mg). All geothermometry and mineral equilibrium calculations also lead to the conclusion that application of these techniques to low temperature waters (particularly CO_2-rich) fails unless one has a good knowledge of processes affecting the chemistry of the reservoir water.

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