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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 92°C vary in chemical composition and 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 75–155°C. The enthalpy–chloride mixing model, which approximates a reservoir temperature of 125°C for the Ömer–Gecek field, accounts for the diversity in the chemical composition and temperature of the waters by a combination of processes including boiling and conductive cooling of deep thermal water and mixing of the deep thermal water with cold water. It is also determined that the solubility of silica in most of the waters is controlled by the chalcedony phase. Equilibrium states of the Ömer–Gecek thermal waters studied by means of the Na–K–Mg triangular diagram, Na–K–Mg–Ca diagram, K–Mg–Ca geoindicator diagram, activity diagrams in the systems composed of Na_2O–CaO–K_2O–Al_2O_3–SiO_2–CO_2–H_2O phases, log SI diagrams, and finally the alteration mineralogy indicate that most of the spring and low-temperature well waters in the area can be classified as shallow or mixed waters which are likely to be equilibrated with calcite, chalcedony and kaolinite at predicted temperature ranges similar to those calculated from the chemical geothermometers. It was also observed that mineral equilibrium in the Ömer–Gecek waters is largely controlled by CO_2 concentrations. © 1998 Elsevier Science B.V.

Keywords: geothermometry; thermal waters; Ömer-Gecek geothermal field; fluid–mineral equilibrium

1. Introduction

The Afyon area is known as 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 greenhouse and house heating purposes as well as for bathing. There are a total of four geothermal fields in the Afyon area. These are the Ömer–Gecek, Gazlıgöl, Sandıklı, and Heybeli–Karaburun fields (Fig. 1). 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, remarkable for its many hot springs, is located 15 km northwest of the city of Afyon (Fig. 1). Most of the hot springs are concen-

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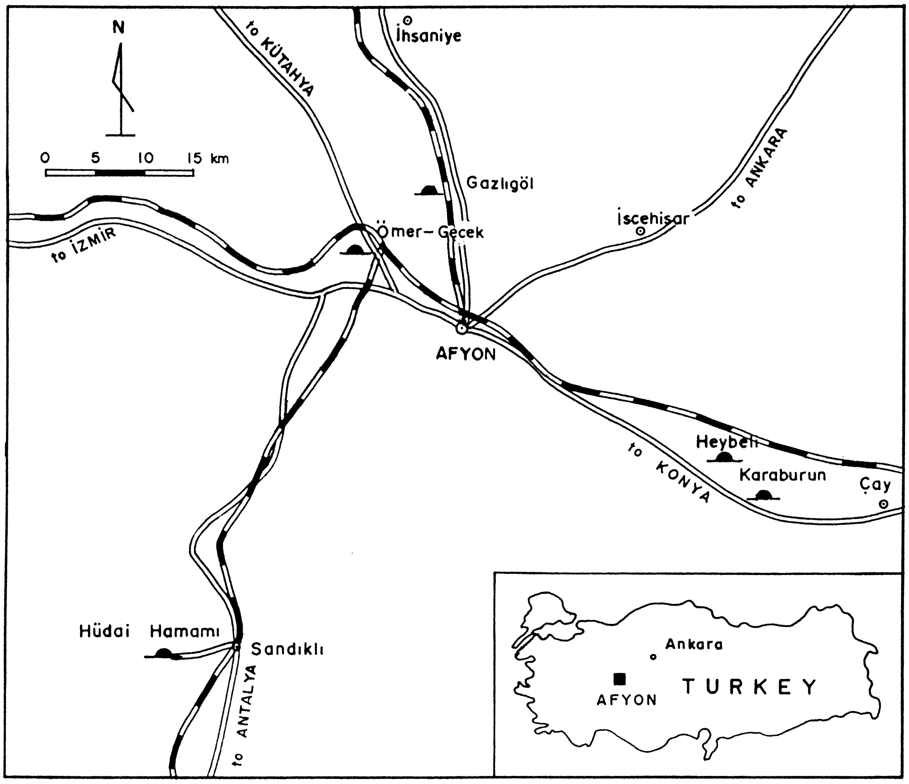

Fig. 1. Location map of the Afyon geothermal area, Turkey.

trated in three sites which are, from west to east, the Uyuz Bath, Ömer Bath, and Gecek Bath (Fig. 2). The basement in the Ömer–Gecek field is represented by mica schist and marbles of Paleozoic age. In a general sequence, from bottom to top, they are observed as: (1) muscovite–biotite–calc–quartz schist; (2) marble; and (3) albite–chlorite–muscovite–sericite schist. In addition, meta-conglomerate and meta-sandstones are recognized as big lenses and bands in the schists (Metin et al., 1987). 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 Late Miocene and Pliocene times. As a result of this activity, tuffs, agglomerates, and lava flows of andesitic, trachytic, trachyandesitic and basaltic compositions are widespread not only in the Ömer–Gecek field but also throughout the Afyon area (Keller and Villari, 1972). 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 (Fig. 2; Metin et al., 1987; Çevikbaş et al., 1990).

The General Directorate of Mineral Research and Exploration of Turkey (MTA) drilled thirteen 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. The current discharge rate of all these wells is estimated to be more than 500 l/s (Koçak, pers. commun., 1996). Table 1 lists some information about these wells including depth, production level, temperature and discharge of the reservoir waters, type of reservoir rock, and the time of drilling. Because no information is available for the UH well, it is not included in Table 1. Previous studies report

Table 1
Data relevant to the Ömer–Gecek geothermal wells

Well No.	Well depth (m)	Production level[a] (m)	Reservoir rock	Well head temp. (°C)	Discharge (l/s)	Year	Ref.
AF-1	902.0	640.0	quartz–mica schist	97.4	20	1974	Erişen, 1976
R-260[b]	165.0	158.0	marble schist	95.0	18	1971	Erişen, 1976
AF-3	250.0	185.0	mica–calc schist	97.0	50–60	1975	Erişen et al., 1985
AF-4	125.7	60.0	limestone–marble schist	95.0	6	1982	Erişen et al., 1985
AF-5	270.4	125.0	marble schist	79.0	4	1982	Erişen et al., 1985
AF-6	211.4	137.0	quartzite–mica schist	92.0	6	1982	Erişen et al., 1985
AF-7	210.0	152.0	marble–schist cong.	93.0	5–6	1984	Erişen et al., 1984
AF-8	250.0	165.0	marble–mica schist	60.0	5–10	1984	Erişen et al., 1984
AF-9	320.0	165.0	basalt–sandstone cong.	51.0	62	1990	Tamgaç and Kalkan, 1990
AF-10	318.4	280.0	marble schist	96.0	73	1990	Kalkan and Uzel, 1990
HGF	250.0	—	basalt–sandstone cong.	54.0	15	1990	Hayat Geothermal Facilities, 1995 (pers. commun.)
AF-2	56.80	40.0	marble schist	96.0	> 150	1996	Tamgaç et al., 1996
AF-11	185.0	120.0	marble schist	98.0	150	1996	Tamgaç et al., 1996
AF-12	58.70	53.0	marble schist	86.0	not prod.	1996	Tamgaç et al., 1996

[a] approximated.
[b] exploratory well.

that there were many hot springs in the area prior to the drillings (Erişen, 1976). Today, a few of them are observed in places as leakages with moderate temperatures (50–60°C). They mostly issue through an E–W-trending normal fault (Fig. 2). 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.

2. Materials and method

A total of twelve thermal and one cold water samples were collected from the geothermal wells and hot springs in the Ömer–Gecek field in August 1995. The locations of the water samples are shown in Fig. 2. 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 (Fig. 2).

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 pure 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. Water analyses were performed using standard methods reported in Fishman and Friedman (1989). 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, SiO_2 and Li analyses. B concentrations were obtained with spectrophotometry. Chemical analyses of waters and the

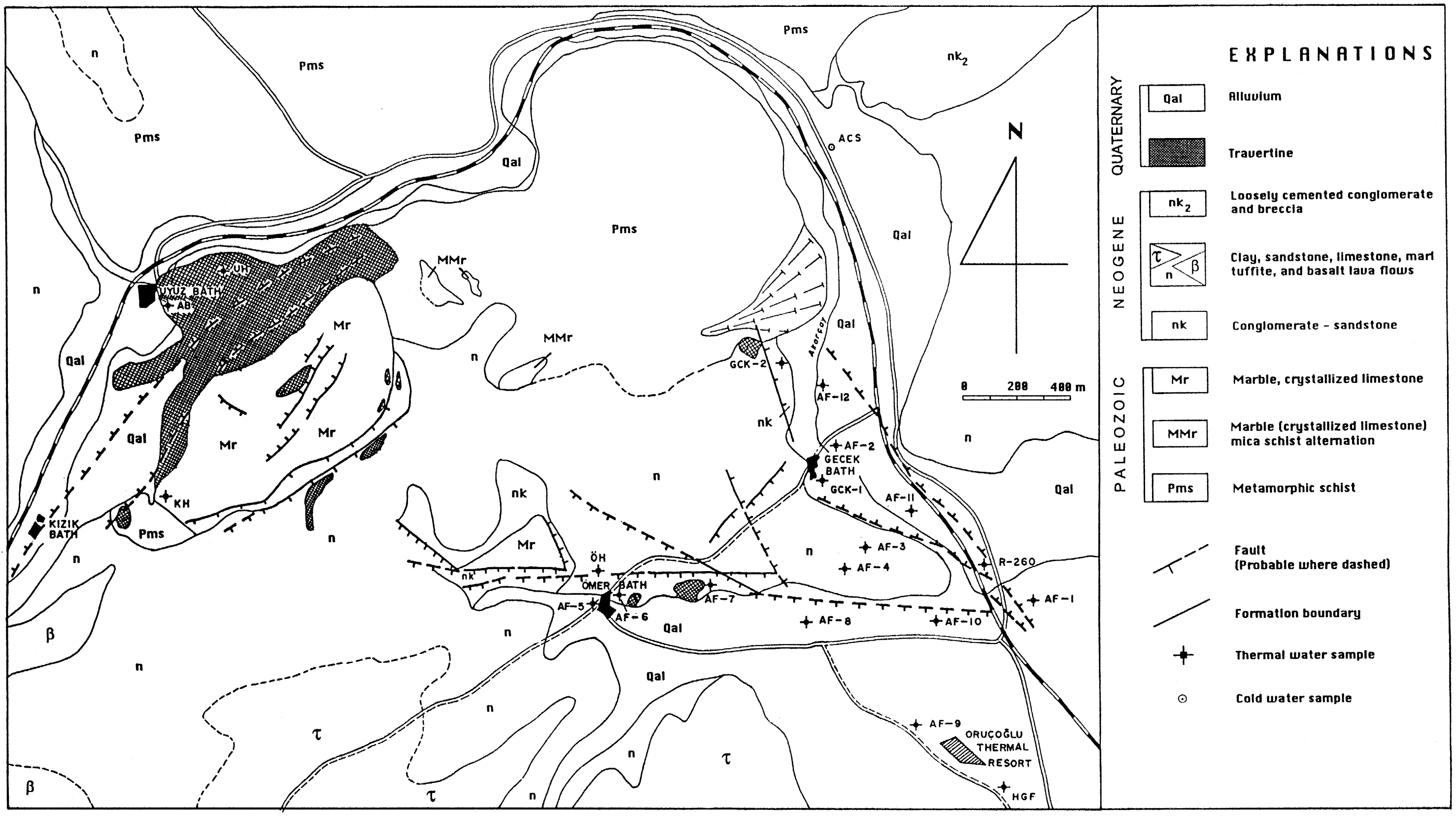

Fig. 2. Geological map of the Ömer–Gecek field. Simplified form Erişen et al. (1984).

Table 2
Chemical analyses of waters from the Ömer–Gecek field of the Afyon area

Sample No.	*T* (°C)	pH	K	Na	Ca	Mg	HCO_3	SO_4	Cl	Fe_T	Al	SiO_2	B_T	Li	TDS	C.B.%
AF-1[a]	88.0	6.70	144.0	1600	214.6	30.0	1628	494.0	1754	1.00	< 0.02	142	8.6	1.5	6018	0.16
AF-4[a]	92.0	6.70	158.7	1750	78.8	9.96	1294	536.6	1862	0.40	< 0.02	198	10.0	1.6	5900	0.17
AF-8[a]	62.0	6.95	101.7	1300	205.0	36.5	1397	450.2	1261	0.19	< 0.02	54	8.2	1.9	4816	3.79
AF-9[a]	47.5	6.25	54.0	635	157.0	27.3	1007	207.4	544	1.40	< 0.02	173	< 0.1	1.1	2807	4.57
R-260[a]	87.0	7.10	156.8	1700	105.8	18.9	1350	513.6	1842	0.2	< 0.02	170	9.6	1.6	5869	0.15
HGF[a]	51.0	6.40	64.1	780	135.8	32.9	1025	236.6	812	< 0.1	< 0.02	161	4.4	0.9	3253	0.66
ÖH[b]	49.5	6.80	117.3	1200	234.0	38.5	1111	855.4	1177	1.34	< 0.02	94	6.6	1.8	4837	0.54
GCK-1[b]	42.0	6.30	108.0	1301	163.0	19.3	1153	525.0	1505	< 0.1	< 0.02	86	7.7	1.4	4869	2.30
GCK-2[b]	41.0	6.70	147.0	1541	157.6	24.5	1206	508.3	1784	< 0.1	< 0.02	90	6.5	1.6	5467	0.15
UH[a]	67.5	7.70	120.0	1460	146.0	17.4	1135	503.5	1723	< 0.1	< 0.02	102	8.2	1.5	5217	1.57
AB[b]	62.5	6.80	118.1	1460	167.6	21.6	1202	497.8	1723	0.2	< 0.02	84	8.2	1.5	5284	1.24
KH[b]	32.0	6.50	120.0	1494	190.6	21.2	1312	512.6	1772	< 0.1	< 0.02	120	8.5	1.6	5553	1.76
ACS[b]	14.0	6.95	1.4	13.1	110.0	16.2	281	45.1	29.1	0.28	1.5	27	< 0.1	< 0.1	525	7.51

Concentrations are expressed in ppm; all CO_3 concentrations are below the detection limit (0.01 ppm); C.B. = charge-balance of the water. [a]Wells, [b]springs.

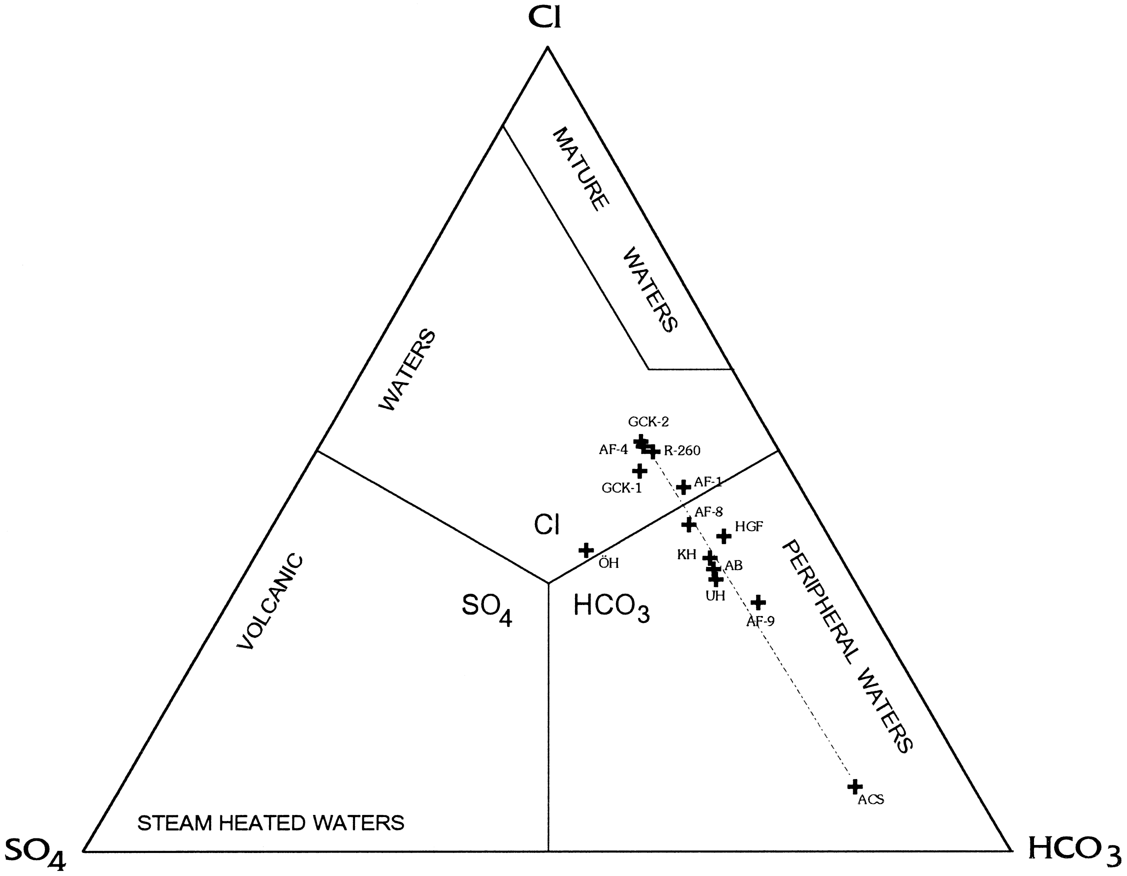

Fig. 3. Relative Cl, SO_4 and HCO_3 contents of the Ömer–Gecek thermal waters on weight (mg/kg) basis. Fields from Giggenbach (1988).

mineralogic investigations of the cutting samples 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 2. 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 32°C (sample KH) to 62.5°C (sample AB). Among the wells, AF-4 has the hottest water with a measured temperature of 92°C.

All the samples listed in Table 2 are plotted in the Cl–SO_4–HCO_3 ternary diagram (Fig. 3). 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. Alteration mineralogy

Unfortunately, there is no sufficient core sample available for the wells drilled in the Ömer–Gecek field since the purpose of drilling in the Afyon area is only to exploit the thermal water commercially. Therefore, the study of alteration mineralogy in this research is mainly based on the cutting samples collected from the AF-11 and AF-12 wells during the drilling operation. Mineralogic determinations of the samples were carried out by the X-ray powder diffraction method.

Travertine currently precipitates all around the Ömer–Gecek field (Fig. 2). A sudden drop in the pressure and the decreasing temperature accompanied by CO_2 loss cause calcite to precipitate mostly at shallow depths and also in the drilling pipes. The thickness of travertine deposits ranges from 25 to 30 m. Dolomite and aragonite in minor amounts are the other carbonate minerals found in association with travertines. Mineralogical analyses of the cutting samples from the AF-11 and AF-12 wells drilled in the vicinity of Gecek Bath reveal chalcedony, quartz, kaolinite, illite and little amounts of montmorillonite, K-feldspar and pyrite. The alteration mineral assemblage indicates that Ömer–Gecek is a low-temperature geothermal field in which CO_2 concentration controls the water chemistry.

5. Geothermometry

5.1. Chemical geothermometers

The results of chemical geothermometers applied to the thermal waters of the Ömer–Gecek field are

Table 3
Chemical geothermometers for the Ömer–Gecek thermal waters (°C)

Sample No.	Meas. disc. *T* (°C)	Quartz[a]	Quartz[b]	Chal.[c]	Chal.[d]	Na–K[e]	Na–K[d]	K–Mg[e]	Na–K–Ca[f]	Na–K–Ca Mg correc.[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] Fournier and Potter (1982b); [b] Arnórsson (1985); [c] Fournier (1977); [d] Arnórsson et al. (1983); [e] Giggenbach (1988); [f] Fournier and Truesdell (1973); [g] Fournier and Potter (1979).

given in Table 3. Among the silica geothermometers, the quartz geothermometers of Fournier and Potter (1982b) and Arnórsson (1985) yield reservoir temperatures ranging from 105 to 180°C. Compared with quartz geothermometers, the chalcedony geothermometers of Fournier (1977) and Arnórsson et al. (1983) display relatively lower reservoir temperatures between 75 and 158°C. Since chalcedony, rather than quartz, controls silica saturation at temperatures less than 180°C (Fournier, 1991), it appears that among silica geothermometers, chalcedony geothermometers better reflect the reservoir temperatures for the Ömer–Gecek field, but this should be further checked with cation geothermometers.

The reservoir temperatures computed from the cation geothermometers for each water are generally higher than those of silica geothermometers (Table 3). The Na–K geothermometers of Arnórsson et al. (1983) and Giggenbach (1988) give temperature ranges of 171–193°C and 213–230°C, 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 145°C (Table 3).

In order to eliminate the possible effects of Ca concentrations on the Na–K geothermometer, the Na–K–Ca geothermometer of Fournier and Trues-

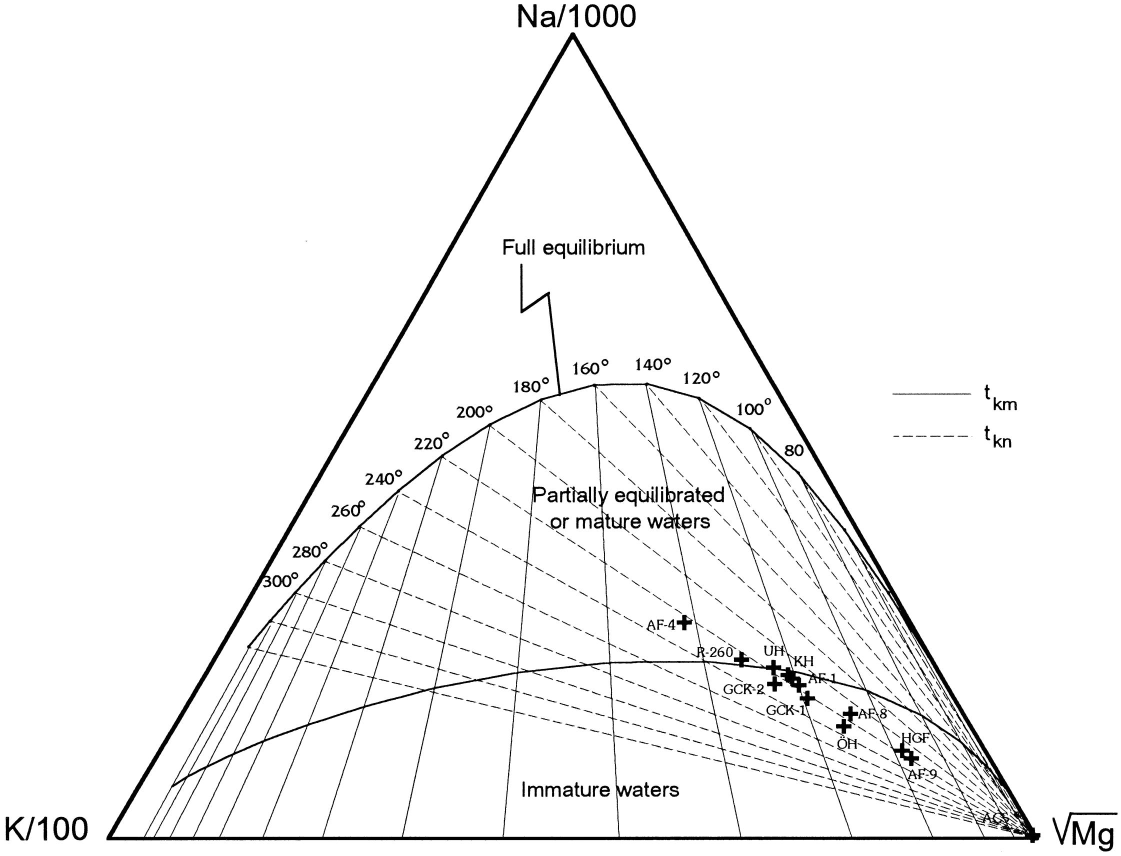

Fig. 4. Graphical evaluation of the water–rock equilibration temperatures (Giggenbach, 1988) using relative Na, K and Mg concentrations (mg/kg) of the Ömer–Gecek thermal waters.

dell (1973) was used. The reservoir temperatures calculated from this geothermometer range from 137 to 206°C which are lower than those of the Na–K geothermometers but still higher than those of the quartz and chalcedony geothermometers.

When the Na–K–Ca–Mg geothermometer of Fournier and Potter (1979) is applied to the thermal waters of the Ömer–Gecek field more realistic results are obtained. The new reservoir temperature range now becomes 85–155°C, which is in agreement with the quartz and chalcedony temperature ranges of 105 to 180°C and 75 to 158°C, respectively.

5.2. Na–K–Mg diagram

A further evaluation of the cation geothermometers is made on the Na–K–Mg diagram (Fig. 4) proposed by Giggenbach (1988). The model is based on the following geothermometers assuming that activities of minerals are close to unity:

$$t_{\mathrm{kn}} = 1390/\left[1.75 - \log(C_{\mathrm{K}}/C_{\mathrm{Na}})\right] - 273.15 \quad (1)$$

$$t_{\mathrm{km}} = 4410/\left[14.0 - \log\left(C_{\mathrm{K}}^2/C_{\mathrm{Mg}}\right)\right] - 273.15 \quad (2)$$

Fig. 4 shows that none of the Ömer–Gecek waters attains a water–rock chemical equilibrium. Waters of

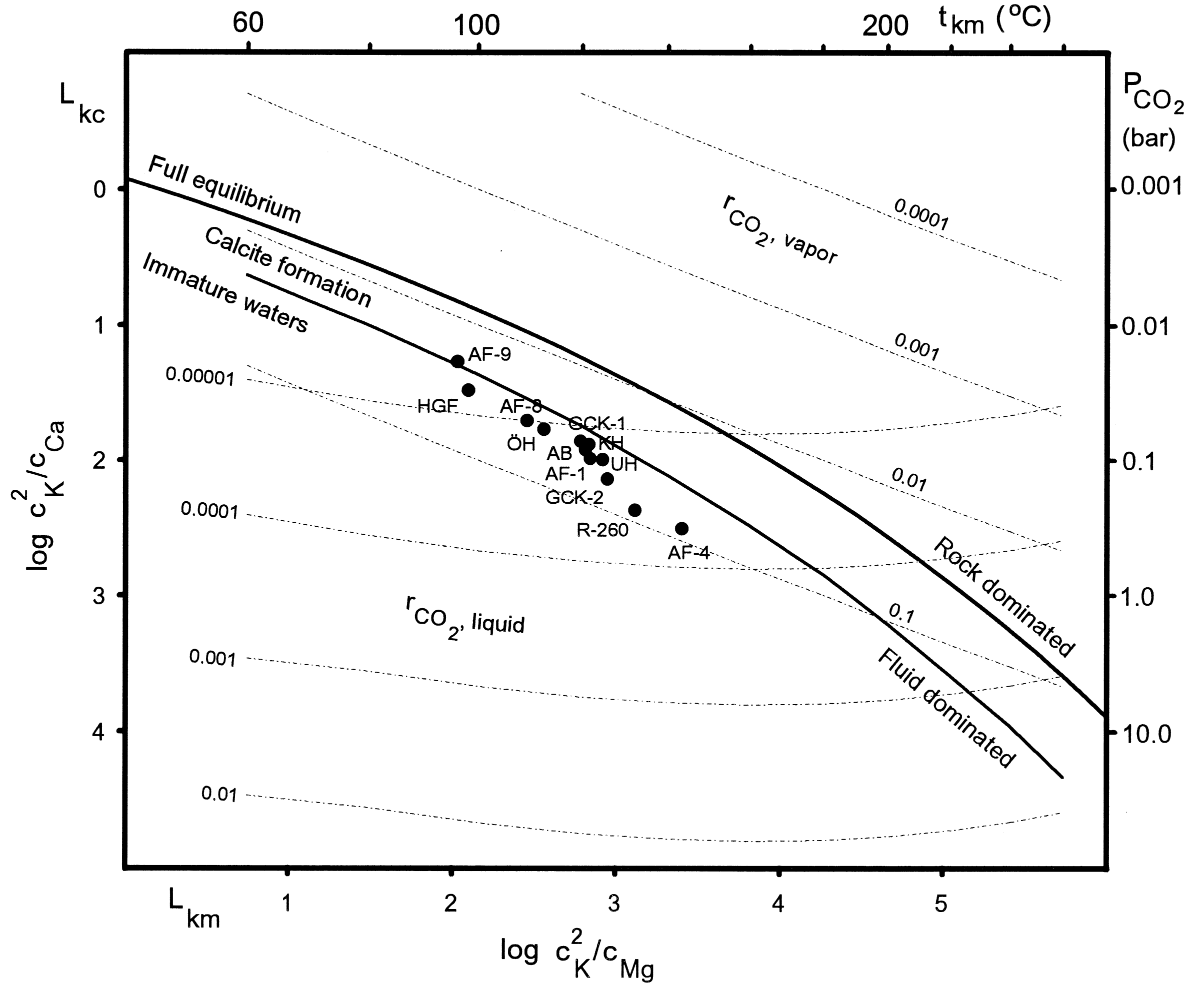

Fig. 5. K–Mg–Ca geoindicator diagram (Giggenbach, 1988) for the Ömer–Gecek thermal waters.

wells plot closely on the boundary between mature waters (partly equilibrated) and immature waters (shallow waters). AF-4 is the only sample plotting towards the center of the mature waters field. For the samples plotting in the immature waters field, 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 plot close to the partial equilibrium field and, therefore, temperature estimates of these waters can be performed with some degree of confidence.

5.3. K–Mg–Ca geoindicator diagram

Assuming equilibrium with calcite, CO_2 partial pressures (P_{CO_2}) of the Ömer–Gecek thermal waters

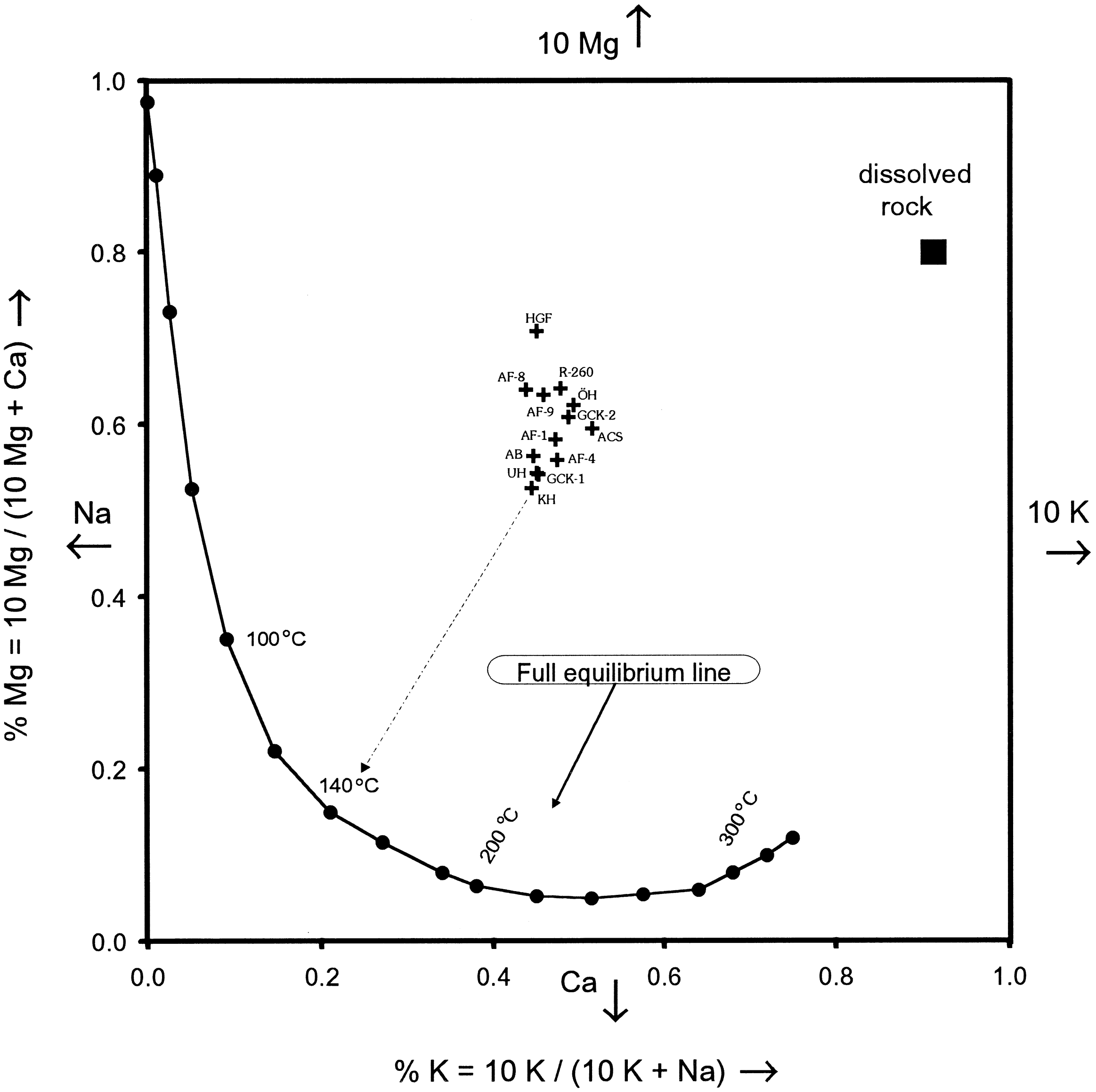

Fig. 6. Plot of 10K/(10K + Na) vs. 10Mg/(10Mg + Ca) (Giggenbach, 1988) of the Ömer–Gecek thermal waters (mg/kg).

can be evaluated in the K–Mg–Ca geoindicator diagram (Fig. 5). Equations to construct the diagram are given by Giggenbach (1988) as:

$$L_{\mathrm{kc}} = \log\left(C_{\mathrm{K}}^{2}/C_{\mathrm{Ca}}\right) \tag{3}$$

$$L_{\mathrm{kc}} = \log P_{\mathrm{CO_2}} + 3.0 \tag{4}$$

$$L_{\mathrm{km}} = \log\left(C_{\mathrm{K}}^{2}/C_{\mathrm{Mg}}\right) \tag{5}$$

In the diagram, all the waters fall below the full equilibrium line but plot on the line between calcite formation and immature water fields. This indicates that the compositions of the waters at their last equilibration temperatures (t_{km}) are exclusively controlled by CO_2.

5.4. Na–K–Mg–Ca diagram

The plot of 10Mg/(10Mg + Ca) versus 10K/(10K + Na) (Giggenbach, 1988) for waters of the Ömer–Gecek field is presented in Fig. 6. Like the models given in Figs. 4 and 5, the positions of the samples do not indicate any equilibration between the rock and waters. Another result deduced from the diagram is that the waters of the Ömer–Gecek field have not been produced through the dissolution of average crustal rock or they have gained their salinity by simple rock leaching or mixing. The variations in the 10K/(10K + Na) ratio are much less than those of 10Mg/(10Mg + Ca). This may indicate that the K/Na ratios of the waters are not affected so much by the precipitation–dissolution processes, if there is any. The Ca/Mg ratios of the waters, on the other hand, show a rather wide range suggesting the precipitation–dissolution processes of Ca- and Mg-bearing minerals (most probably carbonates). Although Ömer–Gecek waters do not attain a full equilibrium, if a trend encompassing most of the data points of this field (including some of the well waters) is extended to the full equilibrium line, it intersects this line at a temperature of about 140°C agreeing with the computed temperature ranges of the silica and cation geothermometers. (Fig. 6).

5.5. Enthalpy–chloride mixing model

The reservoir temperature of thermal waters and the processes controlling the chemical composition of well and spring waters in the Ömer–Gecek field are further examined with the enthalpy–chloride diagram (Truesdell and Fournier, 1975). The enthalpy values used in the diagram (Fig. 6) that correspond to discharge, boiling and reservoir temperatures are taken from the Steam Tables in Henley et al. (1984).

As a first approach, the water of AF-4, which has the highest chloride content and enthalpy value, is joined to the cold spring water (ACS) (line M1). The fluids of HGF, AF-8, AF-1 and R-260 nearly coincide with this mixing line at different positions (Fig. 7). It is possible that these samples originated by a mixing between ACS and AF-4. A second mixing line (M2) is also obtained between samples UH-AB and ACS. The water of ÖH is most probably formed by the mixing of these two fluids (Fig. 7).

In order to find the origin of AF-4 and KH samples, it was assumed that the water of AF-4 was boiled and then conductively cooled to its discharge temperature before mixing occurred. In constructing this model, first, the original data point of AF-4 water was projected upwards to 100°C (boiling temperature), which corresponds to an enthalpy value of 419 J/g. Then the new point at 100°C was connected with a boiling line (B1) to point S which represents the steam at 100°C (0 mg/l chloride and 2676 J/g enthalpy). A mixing line (M3) crossing the most dilute water (AF-9) was drawn from cold water to boiling line B1. The intersection point, R, on B1 line yields a reservoir temperature of 125°C for the Ömer–Gecek field. The water of AF-4 could thus have been derived from the boiling and subsequent conductive cooling of a less saline but hotter water. The water of KH has most probably originated from the conductive cooling of reservoir fluid without further boiling and/or mixing. The same origin can also be suggested for the waters of GCK-2 and AF-1.

In the model given above, sample KH is believed to be the most likely water representing the deep reservoir fluid (R). There are several reasons to make this postulation. First, although it has the lowest temperature (32°C) in the field, KH is one of the waters having high Cl contents. In addition, the same water has the closest position to the full equilibrium line in the Na–K–Mg–Ca diagram (Fig. 6). The chalcedony geothermometers of Fournier (1977) and Arnórsson et al. (1983) for the sample KH yield 122 and 119°C, respectively. The K–Mg geothermometer of Giggenbach (1988) and the Na–K–Ca geothermometer of Fournier and Truesdell (1973) with the Mg correction of Fournier and Potter (1979) also yield similar temperatures for the same water: 124 and 131°C, respectively. Thus, the reservoir temperature estimated for the Ömer–Gecek field in the Afyon area through the use of chemical geothermometers agrees well with the results of the enthalpy–chloride diagram of Truesdell and Fournier (1975) which yields a reservoir temperature of 125°C.

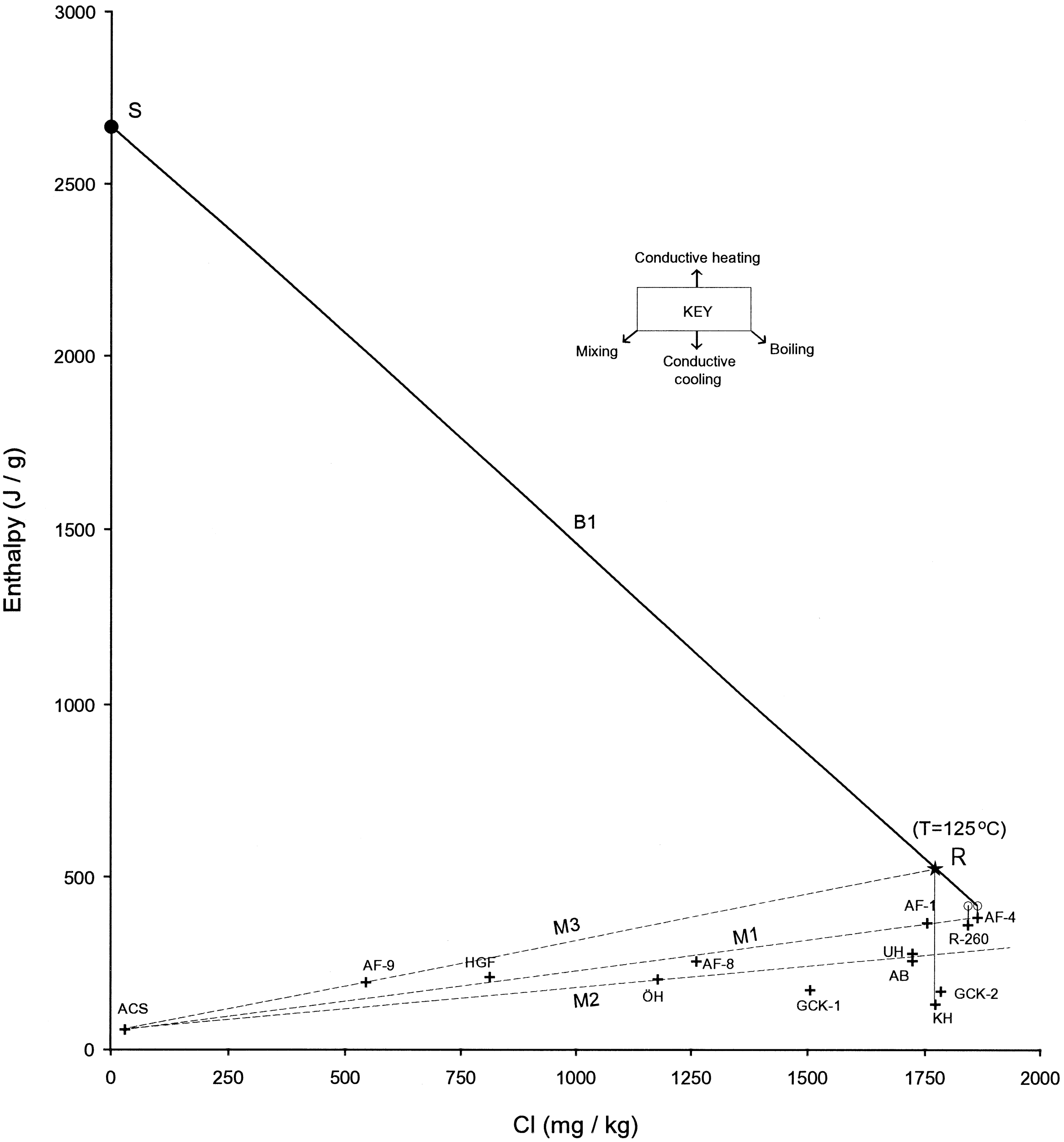

Fig. 7. Enthalpy–chloride diagram for the Ömer–Gecek waters.

6. Fluid–mineral equilibria

Evaluation of chemical equilibria between minerals and solutions in natural water systems requires determination of the activities of aqueous species and knowledge of the solubilities 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 derivation of the activities of individual species from the analytical data. In this study, the WATSPEC computer program (Wigley, 1977) was used to calculate the ion activities and saturation indices 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 calculations of activity coefficients, 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.

6.1. *Activity diagrams*

To investigate the fluid–mineral equilibria in the Ömer–Gecek geothermal field, activity (stability) diagrams (Fig. 8a–c) were constructed at the reservoir temperature which was calculated to be 125°C from the chemical geothermometer calculations and enthalpy–chloride model deduced in the previous section. In order to show the temperature effect on the mineral boundaries, the diagrams in Fig. 8 were also drawn at 100 and 150°C. In producing the activity diagrams, three different systems and eight pure minerals were considered. The systems are Na_2O–K_2O–Al_2O_3–SiO_2–H_2O, CaO–K_2O–Al_2O_3–SiO_2–CO_2–H_2O, and K_2O–Al_2O_3–SiO_2–H_2O. The minerals under investigation are kaolinite, muscovite, K-feldspar, albite, paragonite, gibbsite, wairakite and calcite.

The SUPCRT-92 computer mode (Johnson et al., 1992) was used for calculating the equilibrium constants (K_{eq}) of the reactions of minerals which have common boundaries in the diagrams. The computations were performed at 100, 125, and 150°C and at pressures of 2, 3 and 5 bar, respectively. In the calculations, activity of water (a_{H_2O}) and activity of solid phases (minerals) were assumed to be unity (1), and activity of silicic acid ($a_{H_4SiO_4}$) or SiO_2 was fixed at the average silica value of the Ömer–Gecek waters ($\log a_{H_4SiO_4} = -2.69$). The activities of Na^+, K^+, Ca^{2+}, H^+, H_4SiO_4 and other species were computed with the program WATSPEC (Wigley, 1977) and plotted on the same diagrams (Fig. 8a–c).

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. In a recent study, 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 250°C 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 ($a_{H_4SiO_4}$) may significantly affect the boundaries between the minerals.

Considering that a temperature range of 100–125°C 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 (Fig. 8a and b). 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, 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

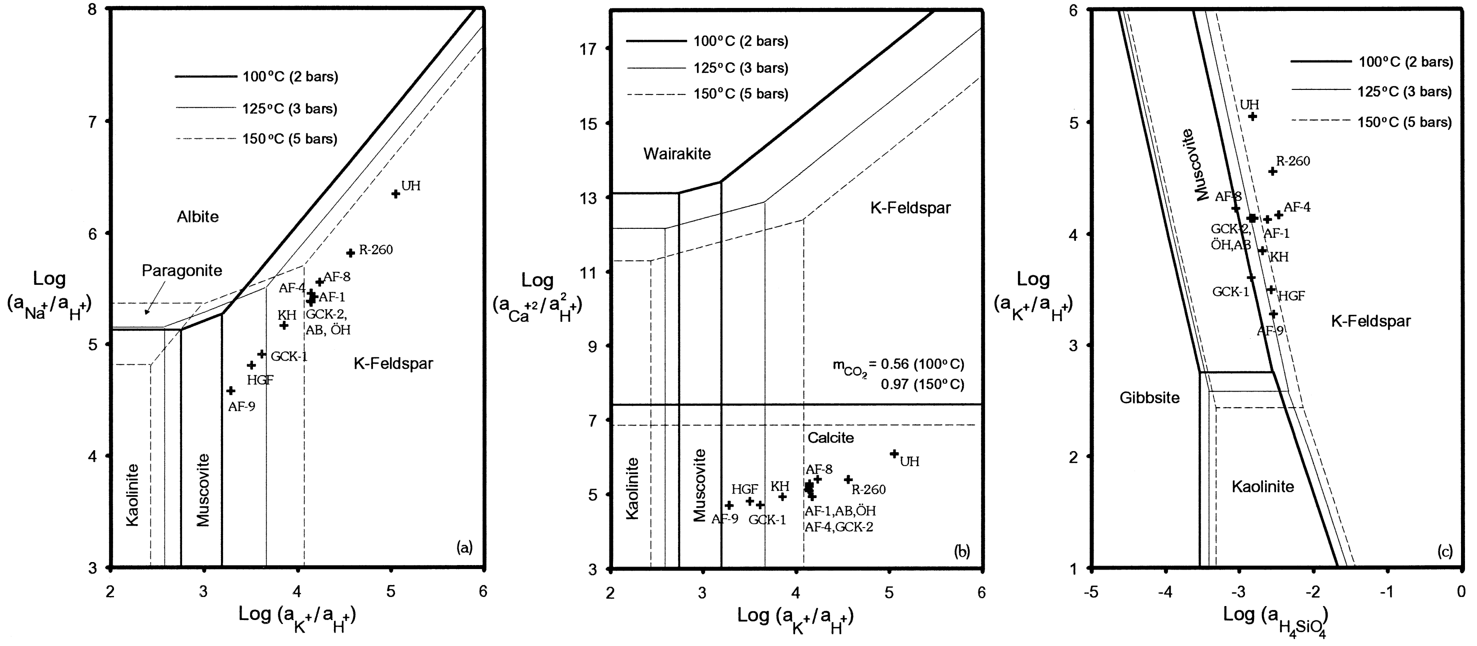

Fig. 8. Activity diagrams for the Ömer–Gecek thermal waters at 100, 125 and 150°C in the systems of (a) Na_2O–K_2O–Al_2O_3–SiO_2–H_2O, (b) CaO–K_2O–Al_2O_3–SiO_2–CO_2–H_2O and (c) K_2O–Al_2O_3–SiO_2–H_2O.

without precipitating or dissolving any Na- and K-bearing mineral.

Also shown in Fig. 8b are the equilibrium lines of calcite at 100 and 150°C and at corresponding the CO_2 concentrations (0.56 and 0.97 bar) which were computed by the WATSPEC program using the average water composition of the Ömer–Gecek geothermal field. In the model, solubility of calcite was computed using the equation:

$$CaCO_3 + 2H^+ \Leftrightarrow Ca^{2+} + CO_{2,aq} + H_2O \tag{6}$$

If the fugacity coefficient of CO_2 (α_{CO_2}) is assigned to be unity (Henley et al., 1984), the equilibrium constant of the reaction in Eq. (6) can be arranged as:

$$\log\left(a_{Ca^{2+}}/a^2_{H^+}\right) = m_{CO_2} - pK_{eq} \tag{7}$$

Like the model illustrated in Fig. 5, Ömer–Gecek waters plot close to the calcite equilibrium line (Fig. 8b). It is also concluded that more accurate results could be obtained if the complete CO_2 concentrations of the waters were known.

6.2. Thermodynamic saturation states

This is a different approach to the geothermometry and 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, as also stated by Tole et al. (1993), since this method of temperature estimation is essentially based on the state of saturation with respect to pure end-members in solid solution minerals, the results obtained cannot be regarded as more than an approximation. Furthermore, 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 sixteen most common hydrothermal minerals some of which were identified as alteration minerals in the reservoir (e.g. calcite, kaolinite and chalcedony). Since all the aluminum concentrations in the thermal waters of the Ömer–Gecek field (except the sample ACS) are less than 0.02 ppm (Table 2), the detection limit of Al analysis with the atomic absorption method performed at the laboratories of MTA, the following criteria were employed to estimate the Al concentrations in thermal waters:

(1) Minerals selected for the equilibrium calculations are K-feldspar, muscovite, and kaolinite.

Table 4

Al^{3+} concentrations (ppm) of the Afyon waters calculated by SOLVEQ through the use of forced equilibria with various minerals at temperatures between 75 and 150°C

Mineral:	K-feldspar				Muscovite				Kaolinite			
T (°C):	75	100	125	150	75	100	125	150	75	100	125	150
AF-1	1.E − 4	0.002	0.010	0.042	0.002	0.009	0.025	0.053	0.005	0.023	0.077	0.181
AF-4	5.E − 5	5.E − 4	0.003	0.014	0.001	0.006	0.017	0.028	0.003	0.017	0.055	0.095
AF-8	0.003	0.039	0.254	1.073	0.008	0.036	0.105	0.223	0.021	0.109	0.356	0.839
AF-9	2.E − 4	0.002	0.013	0.052	0.001	0.005	0.013	0.027	0.001	0.007	0.021	0.049
R-260	7.E − 5	9.E-4	0.006	0.023	0.003	0.013	0.038	0.061	0.009	0.049	0.163	0.282
HGF	2.E − 4	0.002	0.013	0.056	0.001	0.006	0.017	0.035	0.002	0.010	0.032	0.075
ÖH	6.E − 4	0.007	0.042	0.178	0.004	0.016	0.046	0.097	0.009	0.044	0.143	0.338
GCK-1	8.E − 4	0.009	0.058	0.242	0.002	0.008	0.023	0.050	0.003	0.015	0.049	0.117
GCK-2	5.E − 4	0.006	0.038	0.161	0.003	0.013	0.039	0.082	0.007	0.037	0.120	0.284
UH	5.E − 4	0.006	0.041	0.178	0.014	0.062	0.180	0.390	0.067	0.346	1.146	2.737
AB	8.E − 4	0.009	0.058	0.246	0.004	0.018	0.052	0.109	0.009	0.049	0.162	0.382
KH	3.E − 4	0.003	0.019	0.082	0.002	0.008	0.023	0.048	0.003	0.017	0.057	0.134

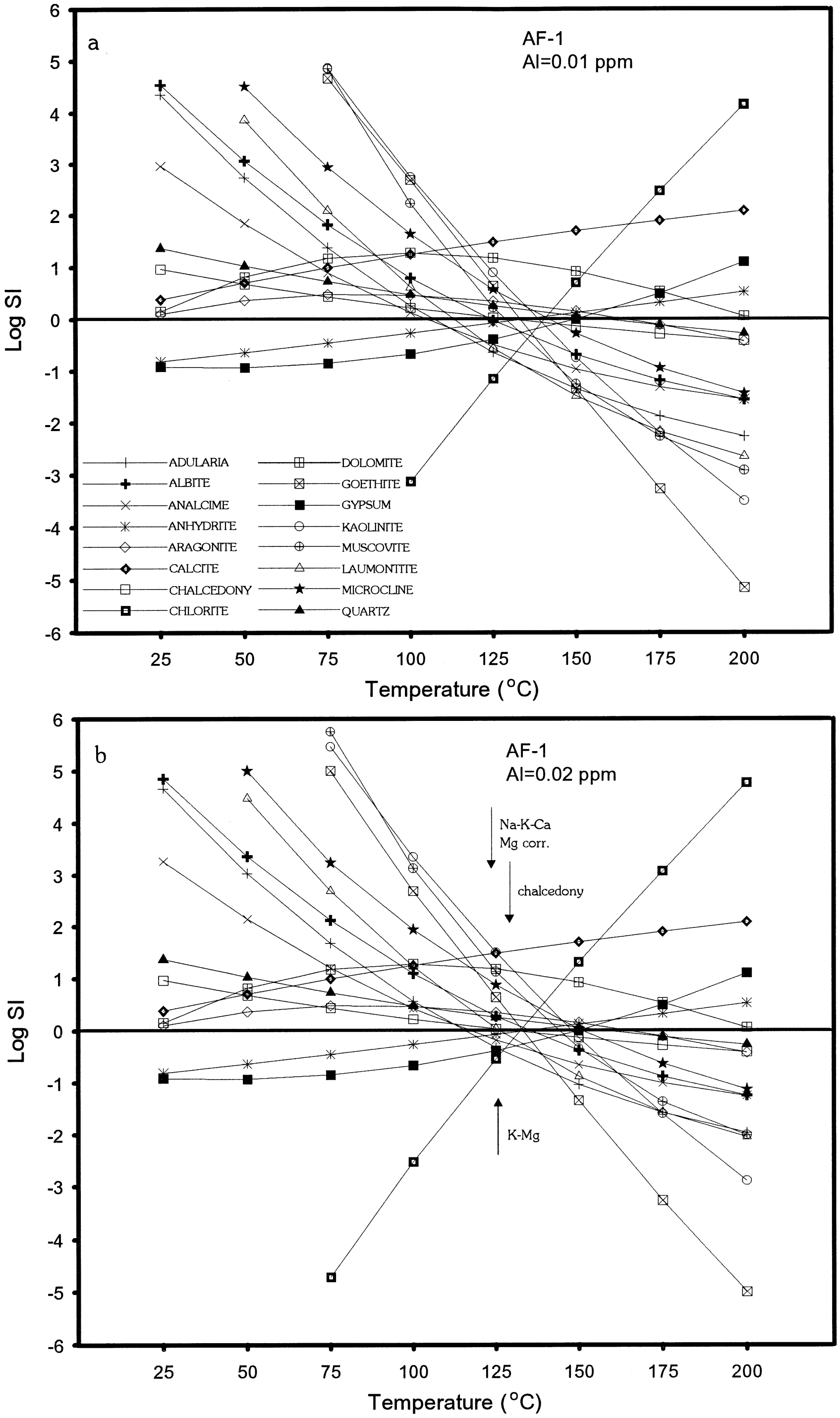

Fig. 9. Mineral equilibrium diagrams for AF-1 well. (a) Al = 0.01 ppm. (b) Al = 0.02 ppm.

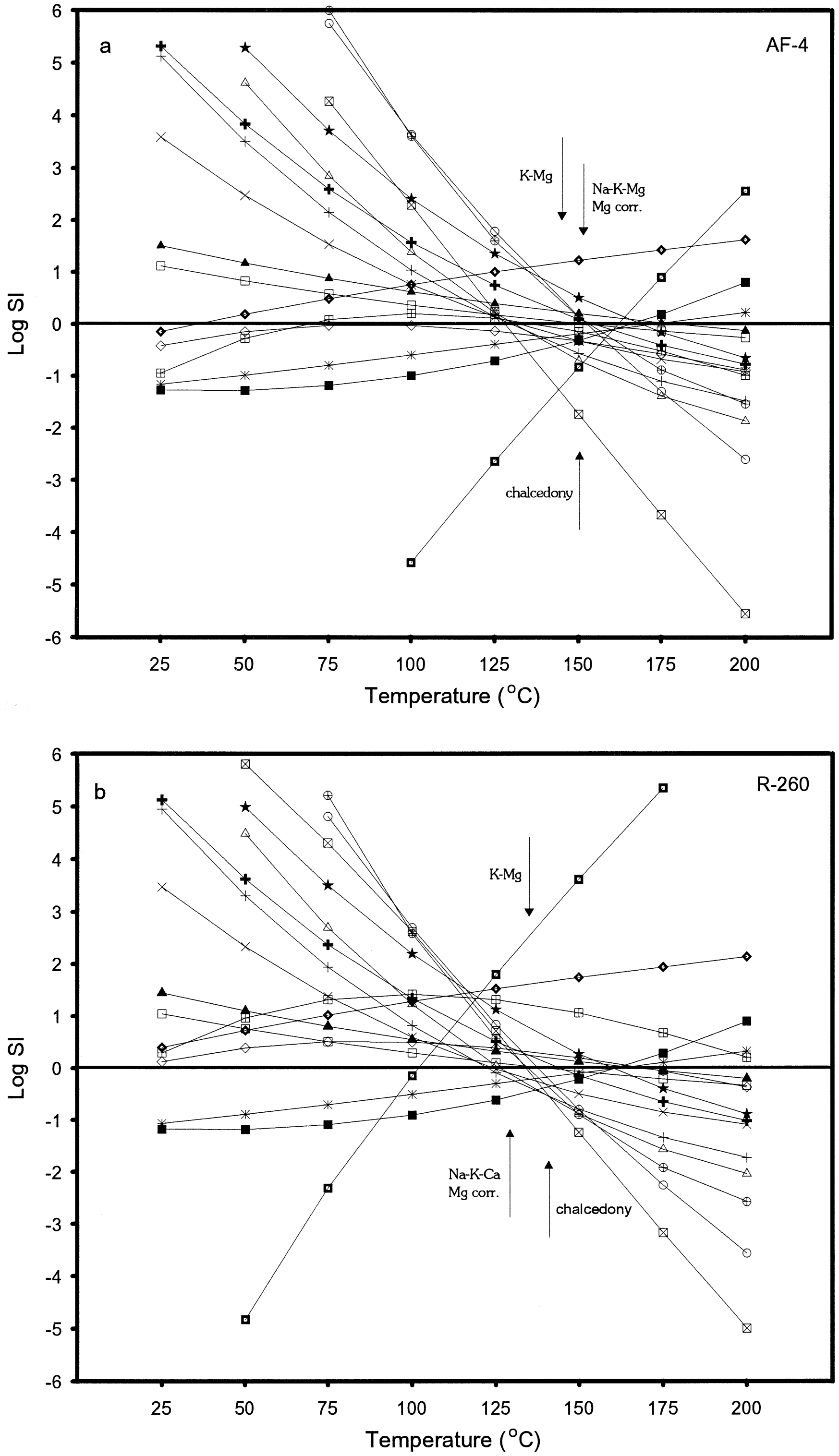

Fig. 10. Mineral equilibrium diagrams for (a) AF-4 well, (b) R-260 well and (c) sample KH.

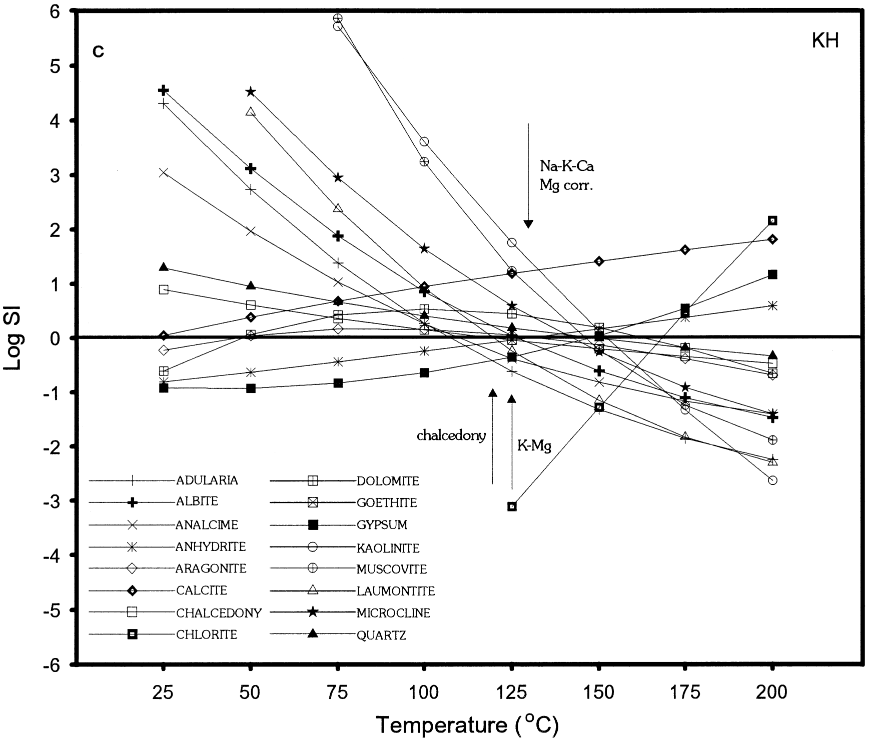

Fig. 10 (continued).

(2) The Al concentration in each water was fixed to equilibrium with respect to one of these minerals by the forced equilibria option (that is, all the Al in solution was assumed to be in equilibrium with the specified mineral) of the SOLVEQ computer program (Reed and Spycher, 1990).

(3) During the computations, temperatures calculated from the chemical geothermometers were assigned for the equilibrium temperature.

The results of the calculations are given in Table 4. For most of the Ömer–Gecek waters, Al concentrations lower than 0.02 ppm were obtained at temperatures between 100 and 150°C.

Careful examination of Table 4 also reveals that the Al concentrations, computed for the Ömer–Gecek thermal waters at their corresponding reservoir temperatures and at equilibrium with the mineral phases, are generally between 0.002 and 0.02 ppm and do not exceed the analyzed values (e.g. sample KH).

Fig. 9 demonstrates the mineral equilibrium states of sample AF-1 at elevated temperatures based on two different aluminum concentrations, 0.01 ppm (Fig. 9a) and 0.02 ppm (Fig. 9b). The ranges of possible intersection temperatures in the diagrams constructed with these two Al concentrations are similar. Higher aluminum values yield higher equilibrium temperatures, the shift in equilibrium temperatures being only about 5 or 10°C depending on the equilibrating mineral. It is also noticeable that analytical precision becomes poor at very low aluminum concentrations and this may cause discrepancies in the results of equilibrium calculations as stated by Tole et al. (1993). In the present study, an aluminum concentration of 0.02 ppm was used for the mineral equilibrium calculations of selected waters of the Ömer–Gecek field. The results obtained, therefore, represent only the maximum temperatures that the reservoir waters can attain.

Possible reservoir temperatures of the selected well waters of Ömer–Gecek field (AF-4, R-260 and spring KH), estimated with the mineral equilibrium calculations, are presented in Fig. 10a, b and c, respectively. The diagrams imply that the reservoir temperatures determined from the equilibrium calcu-

Table 5
Summary of the mineral equilibrium results for some of the Ömer–Gecek thermal waters

Sample No.	Meas. disc. *T* (°C)	Chalcedony (°C)	K–Mg (°C)	Na–K–Ca Mg corr. (°C)	Best equil. temp. range (°C)
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

lations agree well with the temperature estimations of the chemical geothermometers and other geochemical techniques. That is, for a given water sample, the curves of different minerals tend to move closer to the equilibrium line ($\log \mathrm{SI} = 0$) at almost the same temperature, which is around the temperature estimate obtained through the chemical geothermometers.

Table 5 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 ($\log \mathrm{SI} = 0$) 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, saturation states of minerals such as calcite, dolomite and aragonite were ignored in determining the best equilibrium temperatures.

Equilibrium calculations presented in Figs. 9 and 10 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 100°C. 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; Fig. 9).

7. Results

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.

Among the chemical geothermometers applied to the Ömer–Gecek field, chalcedony, K–Mg, and Na–K–Ca–Mg geothermometers yield reservoir temperatures agreeing well with each other and not exceeding 155°C. Another geochemical technique, the Na–K–Mg–Ca diagram of Giggenbach (1988), gives a reservoir temperature of about 140°C which is within the temperature range estimated from the chemical geothermometers. The enthalpy–chloride diagram constructed for the Ömer–Gecek field approximates a reservoir temperature of 125°C which is also in good agreement with the results of chemical geothermometers. Based on this diagram, the variations in the temperature and chemical composition of the waters can be accounted for by a combination of processes including mixing, boiling and conductive cooling.

Although a low-temperature mineral assemblage is found in the area, activity diagrams indicate a deeper reservoir for the system. Therefore, 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) and enthalpy–chloride model.

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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