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HYDROGEOCHEMISTRY OF KIZILDERE GEOTHERMAL SYSTEM AND NEARBY REGION

Massimo Guidi (1) Luigi Marini (1) and Claudia Principe (2)

(1) Geotermica Italiana, Lungarno Mediceo 16, Pisa, ITALY
(2) Istituto di Geocronologia e Geochimica Isotopica, CNR-Pisa; Gruppo Nazionale Vulcanologia, CNR-Roma, ITALY

ABSTRACT

The sodium bicarbonate waters of Kizildere geothermal system are close to equilibrium with hydrothermal minerals at 220 °C and P_{CO2} of 30-50 atm.

The main upflow zone of these deep waters is probably north of the geothermal field, where they undergo a limited steam separation. Then they infiltrate at shallow levels moving southwards and mixing progressively with shallow waters.

Both the chemical features of the sodium bicarbonate thermal end member involved in the feeding of the other main surface manifestations (Tekke Hamam, Kokar Hamam, Demirtas and Golemez) and the thermodynamic conditions at depth under these sites are very similar to those of Kizildere. Hence it seems likely that a unique sodium bicarbonate thermal water feeds all these sites.

INTRODUCTION

Between 1968 and 1973 sixteen wells have been drilled in the Kizildere geothermal field and six of them are used to feed a 20.6 MW geothermal power plant (Simsek, 1985). Recently the Turkish Electrical Company (TEK) and the Italian Electrical Company (ENEL) have begun a project to minimize calcium carbonate scaling, to dispose of wastewater and to assess the horizontal and vertical boundaries of the geothermal field, in order to optimize its economical exploitation. In particular a geochemical survey was carried out in the geothermal field zone and nearby areas within the framework of this project.

The aim of this paper is to present the hydrogeochemical features of this peculiar geothermal system and nearby hot and cold springs, in order to elaborate a qualitative model of the water circulation in the region. Only the chemical composition of the hot springs and geothermal wells is given in table 1, for brevity; the complete set of newly acquired hydrogeochemical data is reported by Guidi et al. (1988).

The geological framework of Kizildere region is well understood thanks to a number of geological and geophysical studies (e.g. Simsek, 1982 and Duprat, 1970).

Kizildere geothermal field is located in the northern sector of the Buyuk Menderes graben, an important tectonic structure of Quaternary age (fig. 1). Quaternary alluvia outcrop in the central part of the graben, where they reach a maximum thickness of some hundred meter. Both a Neogene series and the underlying Paleozoic basement outcrop in the horsts. The basement is made up of gneisses and micaschists with lenses of marbles. The prevalently clastic Neogene series is characterized by the local occurrence of gypsum and anhydrite and by a Middle-Lower Miocene sequence made up of limestones and marly limestones.

Between the Kizildere geothermal field and Tekke Hamam, the basement made up a sort of threshold within the graben; here the limestones of Middle-Lower Miocene are found at a depth of 700-800 m, as shown by gravimetric and geoelectric data. In the area of the drilled geothermal field, the metamorphic basement and the overlying Neogene cover are dissected into a series of blocks by two tectonic systems with NW-SE and NE-SW bearings; here the depth of the Middle-Lower Miocene limestones is between 250 and 600 m. These limestones and the metamorphic basement exhibit good permeability, particularly where fractured. Other Neogene deposits are instead impervious.

THERMAL MANIFESTATIONS

The only thermal manifestations present in the area of the geothermal field are the wet fumaroles located at the northern boundary of the drilled zone, where hot springs were once found (Dominco and Samilgil, 1970). This change indicates a substantial deepening of the piezometric surface, likely caused by exploitation.

Spectacular and widespread hot springs, with temperature up to the boiling point and a total discharge in the order of 20 l/s, are located at Tekke Hamam (fig. 2).
Figure 1. Simplified hydrogeological cross sections across the Buyuk Menderes graben, through the Kizildere geothermal field and Tekke Hamam-1 well (from Guidi et al., 1988).

Figure 2. Location map of main surface manifestations (from Guidi et al., 1988).
Guidi et al.

0.09 and 0.13 eq/l. Calcium and magnesium are very low and chloride is low. Measured CO2 partial pressure is from 30 to 50 atm. The relatively high sulfate content of these waters is probably due to the infiltration of meteoric recharge. Infiltrating waters dissolve calcium sulfate from the Neogene sediments and bring it to depth; even though calcium sulfate and calcium carbonate precipitate upon heating, a remarkable amount of sulfate is still present in the geothermal aqueous solutions circulating within the metamorphic rocks of the basement. Mixing of shallow waters (with sodium magnesium sulfate composition) takes place at the margins of the geothermal field: this process is particularly evident in well KD-9, whose maximum in-hole temperature is 172 °C only.

The hot springs of Tekke Hamam (samples 1, 2, 3, 4, 5, 14, 15, 17) show variable sodium bicarbonate sulfate to sodium sulfate bicarbonate composition and TDS between 0.08 and 0.12 eq/l. These waters have higher sulfate and lower bicarbonate than those of Kizildere, while the TDS is very close in both sites. Tekke Hamam waters could originate from the Kizildere waters through leaching of calcium sulfate from the Neogene sediments, upon cooling, and subsequent precipitation of calcium carbonate upon CO2 loss. The total compositional change is described by the following reaction:

\[ 2 \text{NaHCO}_3 + \text{CaSO}_4 (s) = \text{Na}_2\text{SO}_4 + \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O} \]

The thermal springs of Kamara Yenice (samples 8, 9, 10) and Ortakci (samples 6, 7) have sodium calcium bicarbonate composition and TDS of 0.03 to 0.09 eq/l, while the thermal springs of Golemez (sample 11), Demirtas (sample 18), Kokar Hamam (sample 19) and well TH-1 (sample 16) have sodium calcium sulfate composition and TDS of 0.06 to 0.11 eq/l. The intermediate composition of all these waters is explained by mixing of a thermal sodium bicarbonate component, a cold calcium sulfate component and a cold calcium bicarbonate component in different proportions; alternatively the sodium bicarbonate thermal water could dissolve calcium sulfate from the Neogene sediments and mix with cold calcium bicarbonate water to originate these intermediate waters.

Finally two shallow wells (samples 30 and 31) located close to the Kizildere field exhibit sodium magnesium sulfate composition and high TDS (0.14 and 0.22 eq/l). The genetic mechanism of these waters implies the infiltration of sodium bicarbonate thermal waters into shallow environments, where leaching of Neogene sedimentary rocks and calcium carbonate precipitation take place; anyway the details of this process are poorly understood.

**MINERAL-SOLUTION EQUILIBRIA AND GEOTHERMOMETRY**

The availability of physico-chemical data on the geothermal reservoir of Kizildere allows one to investigate the mineral-solution equilibria in such an environment and to test the dependability of geothermometric functions.

A mineral-solution equilibria model, based upon the approach by Michard et al. (1981), is used to calculate the composition of the aqueous solution in equilibrium with a specified mineral paragenesis at known temperature, CO2 partial pressure and concentrations of mobile species. The following 36 aqueous species are taken into account: H+, OH−, Na+, Mg2+, Ca2+, K+, Cl−, KClO3, KHSO4, Ca2+, CaSO4, CaCO3, CaHCO3, CaF2, CaOH+, Mg2+, MgSO4, Mg3(CO3)2, Mg(HCO3), Mg2+, Mg(SO4), MgF2, MgOH+, Mg(OH), SO42−, HCO3−, HCO2−, H2CO3, CO32−, CO2, SiO2, H3SiO4, Al(OH)4−, Al(H+)3, Al(OH)−, Al(OH)2−.

Activity coefficients of charged aqueous species are calculated by means of the extended Debye-Hückel equation (Helgeson, 1969), while those of uncharged species and water are taken equal to 1.

As no reliable information is presently available on the hydrothermal paragenesis existing in depth in the Kizildere geothermal field, it is assumed that the mineral phases controlling the activity of Na+, K+, Ca2+, Mg2+, SO42−, F−, H4SiO4− and Al(OH)4 are low-albite, microcline, calcite, chlorite, anhydrite, fluorite, chalcedony and illite, respectively. Such hypothesis is based upon the general knowledge gathered in the explored active geothermal systems, where a monotonous stable hydrothermal mineral assemblage develops, in the 150–300 °C range, independently on the original lithology, if chemical equilibrium is attained (e.g. Browne, 1978; Fournier, 1981; Giggenbach, 1981, 1984).

Chalcedony instead of quartz is considered the silica controlling phase, as suggested by Giggenbach (1984).

In most of such geothermal systems a Ca-Al-silicate controls calcium ion activity and the Ca-Al-silicate/calcite pair acts as an "internal" buffer of the CO2 partial pressure (Giggenbach, 1981, 1984). At the high CO2 partial pressures measured at Kizildere this buffer does not seem to be effective, as the CO2 partial pressure is probably fixed externally to the system by a deep important source. Hence it seems reasonable to consider calcite the calcium controlling phase and to introduce the measured CO2 partial pressure into the mineral-solution equilibria model.

In order to take into account the incorporation of clinohore and muscovite into the chlorite and illite phases present in nature, their activities are
Two main clusters of springs are recognized. Travertine deposits, locally dissected by active faulting, are present. Gas emission is strong.

A 615.5 m deep borehole (well TH-1) was drilled at Tekke Hamam between the two clusters of springs in the late sixties (Simsek, 1985). It struck Paleozoic rocks just a few meter before well bottom, but the casing end was set in the middle of the Miocene limestones (fig. 1), which act as an important path for cold water inflow. This is responsible for the mixed character of produced fluids and for the low measured in-hole temperature (maximum value 116 °C). Today the remnants of this borehole act as a sort of spring; its flow rate is only 0.05 l/s; outlet temperature is 69.5 °C; gas emission is strong.

At Demirtas (fig. 2), between Kizildere and Tekke Hamam, only a mud pool with no apparent discharge was found (temperature 62.4 °C).

All the other hot springs of the region have temperature lower than 60 °C. Travertine deposits are observed at Kamara Yenice, Kirmizi Su, Ortakci and Pamukkale. In the latter site the volume of these deposits is unusually large. Gas emission is strong everywhere.

CHEMICAL CLASSIFICATION OF THE WATERS

The square plots by Langelier and Ludwig (1942), e.g. fig. 3, the relevant cross-sections of the related compositional pyramids (e.g. fig. 4) and other pertinent diagrams (not shown) have been used to classify the waters of the region.

Most cold waters related to shallow hydrogeological circuits have alkaline earth bicarbonate composition and low TDS (<0.03 eq/l); these features reflect interaction with Paleozoic gneisses and/or Tertiary limestones.

Only few waters show calcium sulfate composition and high TDS (close to 0.1 eq/l), owing to leaching of gypsum-anhydrite-bearing Neogene sedimentary rocks.

Nevertheless many waters with variable alkaline earth sulfate bicarbonate to alkaline earth bicarbonate sulfate composition and intermediate TDS are present in the region; these waters could have been originated either through mixing of bicarbonate waters with sulfate waters or through leaching of different lithotypes. The water of the Buyuk Menderes river (samples 42 and 43) display this composition. Input of small amounts of sodium bicarbonate thermal waters is evident in some of these waters, such as the thermal spring of Kirmizi Su (sample 12).

The thermal waters of Kizildere geothermal field (wells KD-1A, KD-6, KD-9, KD-13, KD-14 and KD-16) exhibit sodium bicarbonate composition and TDS between

![Figure 3. Langelier-Ludwig square plot with the bicarbonate as isolated anion. Symbols are as follows: open triangles, alkaline earth bicarbonate waters; open squares, calcium sulfate waters; open diamonds, waters with variable alkaline earth sulfate bicarbonate to alkaline earth bicarbonate sulfate composition; black squares, sodium bicarbonate waters; black circles, waters with variable sodium bicarbonate sulfate to sodium sulfate bicarbonate composition; black diamonds, sodium calcium bicarbonate waters; black triangles, sodium calcium sulfate waters; open circles, sodium magnesium sulfate waters.](image)

![Figure 4. N-S cross-section of the Langelier-Ludwig compositional pyramid whose base is the square plot of fig. 3. Symbols are as in fig. 3.](image)
Thermodynamic data are taken from the EQ3/6 software package (Wolery, 1983) for all aqueous species and minerals.

Geothermal wells

The calculated concentrations of aqueous species involved in geothermometric functions are compared with the concentration range observed in geothermal wells KD-1A, KD-6, KD-13, KD-14 and KD-16 in fig. 5. Calcium is not considered as calcite precipitation strongly reduces observed contents, with respect to equilibrium values, thus preventing the use of calcium bearing geothermometers.

Measured in-hole temperatures span the 195-212 °C range, while the mixing/boiling relationships in the enthalpy vs sodium plot (not shown) imply the existence of a unique geothermal end member with sodium content slightly lower than 1100 mg/l and temperature close to 220 °C.

If this is taken as the most likely equilibrium temperature, it can be concluded that the observed concentrations match satisfactorily with the predicted ones or, in other terms, that the waters of Kizildere geothermal system are close to equilibrium with the assumed paragenesis at 220 °C approximately, under a CO₂ partial pressure of 30 to 50 atm.

Nonetheless observed sodium, potassium and fluoride contents are somewhat higher than calculated values, while observed silica, sulfate and magnesium contents are somewhat lower than predicted values. Besides the discrepancies between observed and predicted values are small for sodium, potassium and fluoride, not so small for sulfate and silica and quite large for magnesium. These discrepancies are probably caused by different reasons, such as uncertainties in the thermodynamic data and in the analysis of wells effluents, occurrence of mixing, boiling and minor precipitation of solid phases in the natural system, etc.

These discrepancies reflect in the behaviour of geothermometric functions. In fact:

(i) Na/K temperatures are in the 221-229 °C range and may be considered dependable;
(ii) both K'/Mg and SO₄/F⁻ temperatures (up to 260 °C) are too high, likely due to the occurrence of some interfering processes; considering that these geothermometers re-equilibrate much faster than the Na/K one, they can not give a temperature higher than the Na/K one, unless some interfering processes take place, e.g. precipitation of a Mg bearing mineral; both the K'/Mg and the SO₄/F⁻ temperatures amplify the discrepancies in fluoride and magnesium contents, as their squares appear in the geothermometric functions;
(iii) chalcedony temperatures (176-190 °C) is too low, considering that quartz solubility gives reasonable values, in the 199-213 °C range.

Therefore the only geothermometers which can be used with confidence for surface manifestations are the Na/K and the quartz functions.

![Figure 5. Calculated molal concentrations of aqueous species at different temperatures and CO₂ partial pressures (curves) are compared with the concentration range observed in Kizildere geothermal wells KD-1A, KD-6, KD-13, KD-14 and KD-16 (shaded areas). Silica concentration is independent upon CO₂ partial pressure.](image)
Surface manifestations

Only the surface manifestations less affected by mixing of shallow waters (Tekke Hamam, Demirtas, Kokar Hamam and Golemez) provide consistent geothermometric evaluations and are considered hereunder.

Na/K temperatures (table 1) of Tekke Hamam (samples 1, 2, 3, 4, 5, 14, 15, 17), Demirtas (sample 18) and Kokar Hamam (sample 19) hot springs are in the 208 to 221 °C interval; only Golemez hot spring (sample 11) and well TH-1 (sample 16) exhibit a somewhat higher Na/K temperature: 226 and 232 °C, respectively. The similarity between these values and the Na/K temperature of Kizildere wells (221-229 °C) suggests that the sodium bicarbonate geothermal waters tapped by Kizildere wells take also part in the feeding of these other thermal sites. The slightly lower Na/K temperature of most hot springs is probably due to the longer time of circulation along the less direct flowpath towards the surface.

The quartz temperature (table 1) of surface manifestations is somewhat lower than the Na/K temperature, probably due either to mixing with shallow low silica waters or to the fact that quartz function re-equilibrates faster than Na/K geothermometer.

The log Si02 vs log SO4 plot (fig. 6) provides some additional information. The equilibrium condition with respect to quartz and anhydrite at different temperatures and CO2 partial pressures is shown for reference. Most Kizildere wells are close to simultaneous saturation with respect to both solid phases at about 220 °C, as expected; only well KD-9 departs significantly from this condition due to mixing with high sulfate low silica shallow waters, as already discussed. Many hot springs of Tekke Hamam (samples 3, 4, 5, 14, 15 and 17) are also close to simultaneous saturation with respect to quartz and anhydrite, but at temperature values somewhat lower than Kizildere wells. This suggests that, under natural conditions, the sodium bicarbonate thermal waters cool relatively slowly until 195-205 °C in the Tekke Hamam subsoil, precipitating some silica and dissolving some calcium sulfate, before they uprise to the surface. Other hot springs and well TH-1 depart significantly from the quartz plus anhydrite saturation line due either to mixing or other processes.

CONCLUSIONS

The Kizildere geothermal system is fed by meteoric waters that percolate slowly through and interact with the Neogene sedimentary rocks and the underlying metamorphic basement. They must reach a depth sufficient to acquire their enthalpic content, as no anomalous

Figure 6. Log Si02 vs log SO4 plot. The equilibrium condition with respect to quartz and anhydrite at different temperatures and CO2 partial pressures is shown for reference. Symbols are as in fig. 3.
"shallow" heat source has been recognized in the region so far. Besides they must circulate for a time sufficient to approach equilibrium with a hydrothermal paragenesis comprehending low-albite, microcline, calcite, anhydrite, fluorite, illite and a silica mineral (quartz or chalcedony) at 220 °C approximately, under a CO2 partial pressure of 30 to 50 atm.

These geothermal waters uprise quickly along the important active tectonic structures which dissect Kizildere area. The main uprising zone is probably underneath the large fumaroles located a few hundred meter north of the field, where the geothermal waters undergo a limited steam separation. Then they infiltrate at shallow levels moving southwards and mixing progressively with shallow waters.

In spite of the complex mixing and leaching processes occurring in the region, available data show that the deep originated sodium bicarbonate thermal waters involved in the feeding of Tekke Hamam, Kokar Hamam, Demirtas and Golmez hot springs and well TH-1 are very similar to those tapped by geothermal wells at Kizildere. Furthermore the thermodynamic conditions present at depth underneath these thermal sites are very similar to those of Kizildere. Hence it seems likely that a unique sodium bicarbonate thermal water feeds all these sites.

REFERENCES


Guidi et al.


### Table 1. Hydrogeochemical data. Well data are referred to bottom-hole conditions

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