THE EFFECTS ON HUMAN HEALTH AND HYDROGEOCHEMICAL CHARACTERISTICS OF THE KIRKGEÇIT AND OZANCIK HOT SPRINGS, ÇANAKKALE, TURKEY

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Abstract. This investigation was carried out to determine the hydrogeochemical characteristics of the Kirkgeçit and Ozancik hot springs. The study areas are located northeast and southwest of the town of Çan, Çanakkale. During the investigation, geological maps of the hot springs and its surroundings were prepared, and hot waters and rock samples were collected from the study sites. The Paleogene–Neogene aged andesite, trachyandesite, andesitic tuff, silicified tuff and tuffites form the basement rocks in the Ozancik hot spring area. In the Kirkgeçit hot spring area, there are Lower Triassic aged mica and quartz schists at the basement rocks. The unit is covered by limestones and marbles of the same age. They are overlain by Quaternary alluvial deposits. A chemical analysis of the Kirkgeçit hot water indicates that it is rich in SO_4^{2-} (1200.2 mg L^{-1}), Cl^- (121.7 mg L^{-1}), HCO_3^- (32.5 mg L^{-1}), Na^+ (494 mg L^{-1}), K^+ (30.2 mg L^{-1}), Ca^{2+} (102 mg L^{-1}), Mg^{2+} (15.2 mg L^{-1}), and SiO_2 (65.22 mg L^{-1}). Chemical analysis of the Ozancik hot water indicates that it is rich in SO_4^{2-} (575 mg L^{-1}), Cl^- (193.2 mg L^{-1}), HCO_3^- (98.5 mg L^{-1}), Na^+ (315 mg L^{-1}), K^+(7.248 mg L^{-1}), Ca^{2+} (103 mg L^{-1}), Mg^{2+} (0.274 mg L^{-1}), and SiO_2(43.20 mg L^{-1}). The distribution of ions in the hot waters on the Schoeller diagram has an arrangement of $r(Na^+ + K^+) > rCa^{2+} > rMg^{2+}$ and $r(SO_4^{2-}) > rCl^- > r(HCO_3^-)$. In addition, the inclusion of Fe^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+} and Hg^{2+} in the hot water samples indicates potential natural inorganic contamination. The water analysis carried out following the ICPMS-200 technique was evaluated according to the World Health Organisation and Turkish Standards. The use and the effects of the hot water on human health are also discussed in the paper.

Key words: hot spring, hydrogeochemistry, lithogeochemistry

1. Introduction

The study areas are the villages of Bardakçilar and Kaynarca, town of Çan in Çanakkale city (Figure 1). Kaaden (1957), Wedding (1960), Brinkman (1971), Bingöl *et al.* (1975), and Ercan (1981) carried out geological studies and Okay *et al.* (1990) did geological and tectonic studies in this area and its surroundings. Similarly, geomorphological studies were carried out by Erol (1992), and geological and hydrogeochemical studies by Pehlivan (1996, 1999).

The aim of this study is to discuss the types of geological litologies effects that hot springs discharge from different geologic rocks, the changes in surrounding rocks in mineralogy and geochemistry, the quality of hot springs, and the effects of water analysis results by comparing with different standards.

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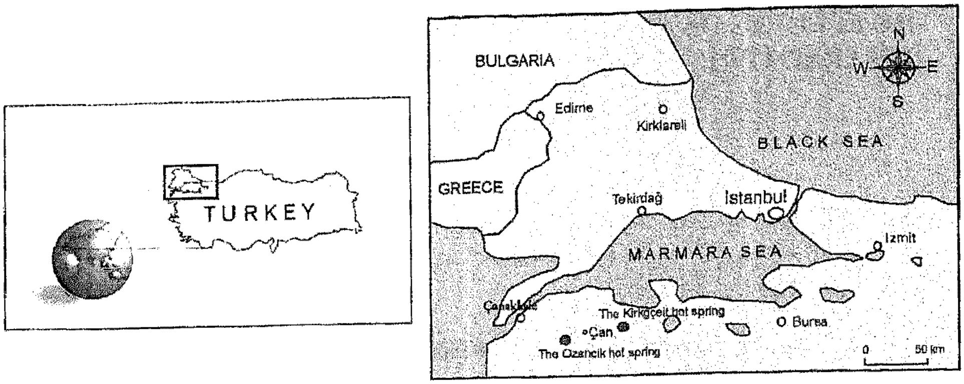

Figure 1. Location map of the study areas.

The major element analysis of the rock samples was done in the laboratories of the Geological Engineering Department, Hacettepe University, Turkey. Trace element studies were carried out at the same place by applying the ICP-30 technique in SGS-XRAL. In addition, the ultra trace element analysis of the hot water samples was carried out using the ICPMS-200 technique at the detection limit of $0.01\,\mu g\,L^{-1}$ in SGS-XRAL Laboratories of Canada. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^- and HCO_3^- analysis of the hot water was performed at the Geochemistry Laboratory of Istanbul University.

2. Geological setting

Owing to the proximity of the North Anotolia Fault Zone (NAFZ), the study areas are ramified by southwest–northwest trending faults, and an active fault (i.e. the Etili Fault) also lies in the north.

2.1. AREA OF THE OZANCIK HOT SPRING

The Çan volcanities occur in most of the study areas and consist of andesite, trachyandesite, andesitic tuff, and silicified tuff and tuffite (Figure 2(a)). The Eocene–Upper Miocene Çan volcanities are the products of the calc-alkaline volcanism.

At the andesite outcrop location ORP6, hydrothermal activity was not noticed. Trachyandesite is hard but its feldspar is altered to kaolinite. Andesitic tuff consists of plagioclase, biotite, and seconder quartz. Silicified tuff is formed by the extreme silicification of andesites. Tuffite contains volcanic material, which is replaced in places by thin-to-medium layers and lamina of clay and silt.

2.2. AREA OF THE KIRKGEÇIT HOT SPRING

In the Kirkgeçit hot spring area there are Biga metamorphics. Biga metamorphics that were Lower Triassic aged belong to the Kazdağ group rocks (Figure 2(b)). Biga

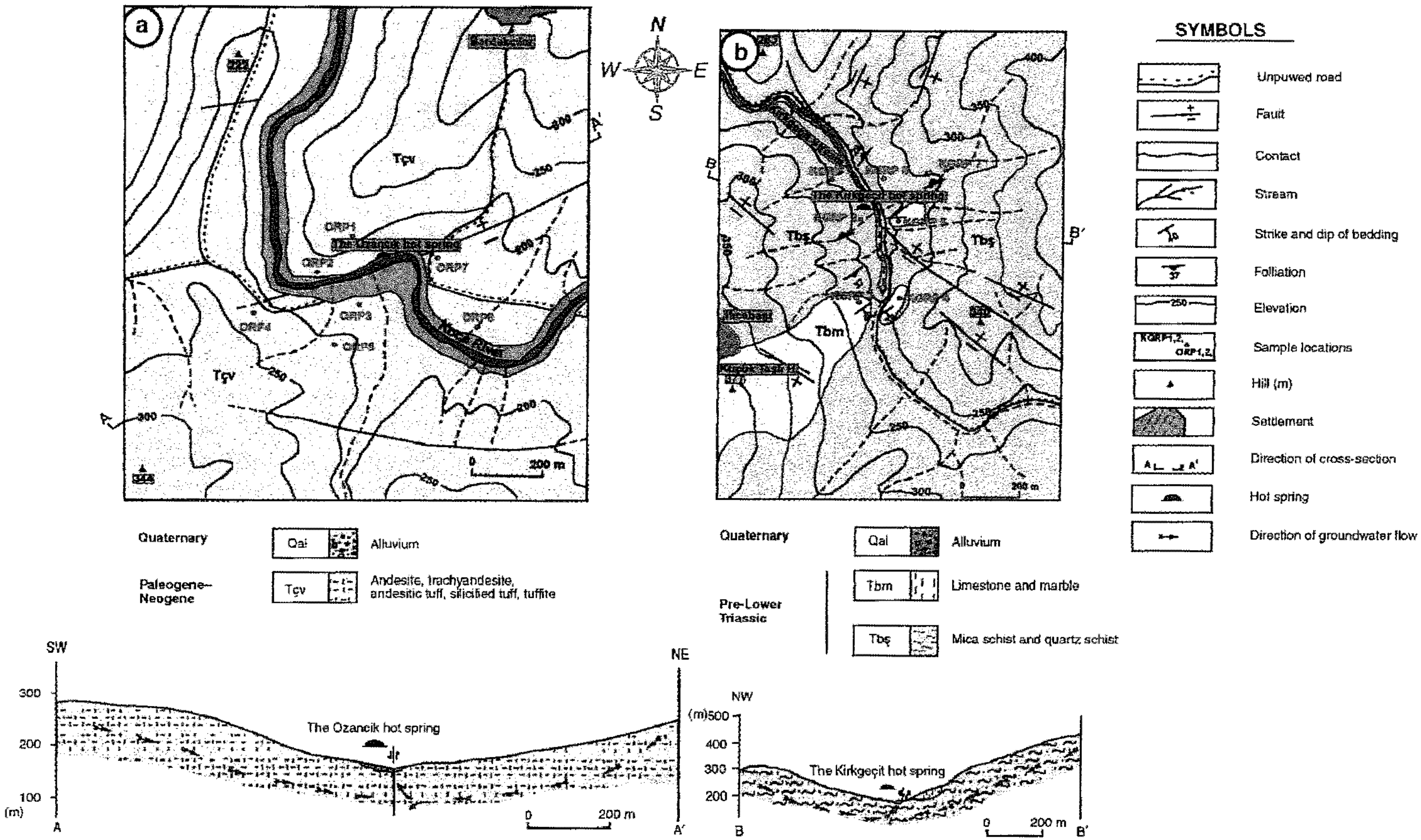

Figure 2. Geological maps and cross-sections of the study areas: (a) the Ozancik hot spring, (b) the Kirkgeçit hot spring.

metamorphics in study area are the products of green schist, and their patterns have been observed around the Kirkgeçit hot spring; they are composed of quartz mica schist and quartz schist that show good foliation. In the upper part there are lens-shaped marbles and in some parts limestones.

The sample KGRP1 taken from the rock samples in the study area is made up of quartz, muscovite and calcite; the sample KGRP2 is made up of mica, quartz, dolomite, and calcite and plagioclase minerals. The samples KGRP3 and KGRP consist of calcite minerals. The sample KGRP5 limestone consists of calcite and quartz minerals. KGRP6 and KGRP7 numbered rock samples are named quartz schist. Rock samples are formed of quartz muscovite and opaque minerals.

3. Hydrogeology and hydrogeochemical characteristics

3.1. HYDROGEOLOGY

The Koca River's tributaries drain the Ozancik hot spring area. The drainage network is developed on permeable rock units formed by the alteration of the Çan volcanites. Therefore, there are no good aquifers in the region. The hot water system is formed in the Çan volcanites including rocks such as andesite, andesitic tuff, silicified tuff, and tuffite. Circulation of groundwater in the study area takes place within the volcanic rocks, outcropping near the springs. The hot water emerges from a fracture zone after passing through a heat resource underground. The temperature of the Ozancik hot spring at the mouth of the fault zone is 65°C and its discharge (average flow) is $5.0\,L\,s^{-1}$.

The water basin of the Kirkgeçit stream is developed over the Biga Metamorphics. Since the limestones around the Kirkgeçit hot spring have many cracks and karstic, they carry a good aquifer specification for the hot spring. The basement rock of the hot spring system is Biga metamorphics that is formed of mica schist and quartz schist. The circulation of groundwater in the Kirkgeçit hot spring area is also realised in volcanic rocks in the surface basin of the hot spring. The temperature of the Kirkgeçit hot spring at the mouth of the fault zone is 52°C and its discharge (average flow) is $3.5\,L\,s^{-1}$.

3.2. HYDROGEOCHEMISTRY

The results of the chemical analysis of the Ozancik hot spring are presented in Table I. The hot spring contains mainly the following ions: Na^+ ($315\,mg\,L^{-1}$), Ca^{2+} ($103\,mg\,L^{-1}$), K^+ ($7.248\,mg\,L^{-1}$), Mg^{2+} ($0.724\,mg\,L^{-1}$), SO_4^{2-} ($575\,mg\,L^{-1}$), Cl^- ($193.2\,mg\,L^{-1}$), HCO_3^- ($98.5\,mg\,L^{-1}$), and SiO_2 ($43.20\,mg\,L^{-1}$).

These values (Table I) were also plotted in the Schoeller diagram (Schoeller, 1962). The diagram (Figure 3) depicts the following arrangement of anions and cations: $r(Na^+ + K^+) > rCa^{2+} > rMg^{2+}$ and $r(SO_4^{2-}) > rCl^- > r(HCO_3^-)$, and

TABLE I
Chemical analysis results of the Kirkgeçit and Ozancik hot springs (mg L^{-1})

Ions	The Kirkgeçit hot spring			The Ozancik hot spring		
	mg L^{-1}	meq L^{-1}	meq L^{-1} (%)	mg L^{-1}	meq L^{-1}	meq L^{-1} (%)
Na^+	494	21.47	74.96	315	13.70	71.91
K^+	30.2	0.77	2.69	7.248	0.18	0.94
Ca^{2+}	102	5.10	17.80	103	5.15	27.03
Mg^{2+}	15.2	1.26	4.39	0.274	0.02	0.10
Fe^{2+}	0.5	0.018	0.06	0.049	0.002	0.02
Cr^{3+}	0.021	0.001	0.003	0.0009		
Mn^{2+}	0.002	0.0001	0.0003	0.0003		
Cl^-	121.7	3.4330	11.85	193.2	5.44	28.60
$SO_4{}^{2-}$	1200.2	25.0040	86.36	575	11.97	62.93
$NO_3{}^-$	0.015	0.0002	0.0006	0.08	0.001	0.005
$HCO_3{}^-$	32.5	0.5327	1.83	98.5	1.61	8.46
Co^{2+}	0.0001			0.0002		
Ni^{2+}	0.0002			0.0068		
Cu^{2+}	0.0017			0.0029		
Pb^{2+}	0.00002			0.00001		
Zn^{2+}	0.0027			0.0079		
As^{3+}	0.0004			0.0001		
Rb^+	0.0112			0.036		
Sr^{2+}	0.174			1.652		
Ag^{3+}	0.0001			0.0009		
Cd^{2+}	0.00001			0.00001		
Sn^{2+}	0.0001			0.00001		
Sb^{3+}	0.0001			0.0001		
Ba^{2+}	0.013			0.018		
Se^{4+}	0.0007			0.0014		
Th^{3+}	0.00001			0.00001		
Hg^{2+}	0.0091			0.0016		
U^{3+}	0.00001			0.00001		
SiO_2	65.22			43.20		
pH	7.4			7.2		
T (°C)	52			65		
Ec (μmho cm^{-1})	1900			1000		

it conforms to the following arrangement for the volcanic rocks: ($r(Na^+ + K^+) > rCa^{2+} > rMg^{2+} > r(SO_4{}^{2-}) > rCl^- > r(HCO_3{}^-)$] as given by Şahinci (1991). But, from the Kirkgeçit hot spring analysis results (Table I), the following arrangement of cations and anions has been determined: ($r(Na^+ + K^+) > rCa^{2+} >$

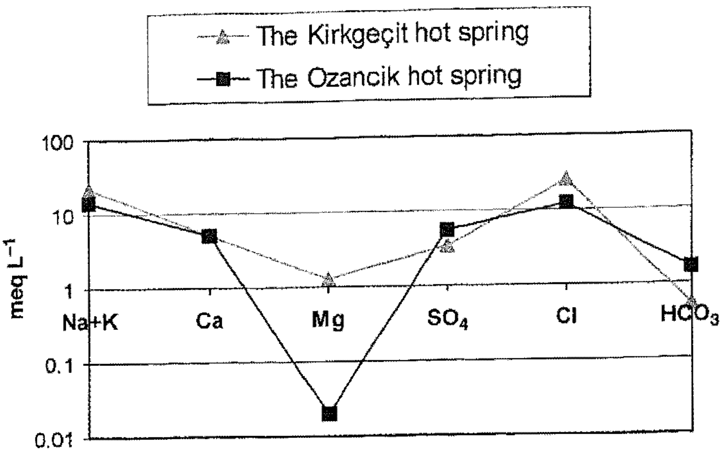

Figure 3. Schoeller diagram of the Kirkgeçit and Ozancik hot springs.

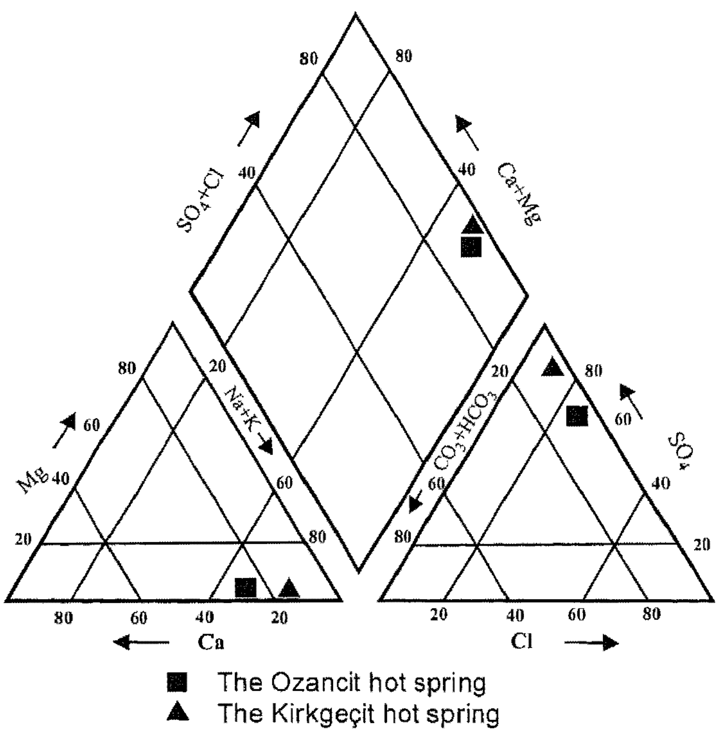

Figure 4. Piper diagram of the Kirkgeçit and Ozancik hot springs.

$rMg^{2+} > r(SO_4{}^{2-}) > rCl^- > r(HCO_3{}^-)$], and it is not similar to ($rCa^{2+} > rMg^{2+} > r(Na^+ + K^+)$, $r(HCO_3{}^-) > rCl^- > rSO_4{}^{2-}$)], the arrangement of cations and anions of the hot springs discharged from metamorphic rocks.

The Piper diagram of the hot springs in terms of meq L^{-1}(%) is depicted in Figure 4. In the Piper diagram, hot and mineralised springs are generally arranged as $Na^+ + K^+ > Ca^{2+} + Mg^{2+}$ and $SO_4^{2-} + Cl^- > HCO_3^- + CO_3^{2-}$, and the present hot spring also depicts a similar trend. The results derived from the Piper diagram are compatible with those obtained from the Schoeller diagram.

Although the Kirkgeçit hot spring discharges from volcanic rocks, the Kirkgeçit hot spring discharges from metamorphic rocks, and although there is a distance of exactly 40 km between the two springs, it has been determined that the arrangement of cations and anions of both is the same. This means that the hot springs are in interaction with the same geological units.

TABLE II

Major oxides (%) and trace elements (mg kg^{-1}) in the selected rock samples

Component	KGRP 1 (Quartz schist)	KGRP 5 (Limestone)	ORP 1 (Silicified tuff)	ORP 2 (Andesite)	ORP 3 (Andesitic tuff)
SiO_2	69.62	6.36	97.70	57.43	64.25
Al_2O_3	14.04	1.69	0.24	20.20	16.77
Fe_2O_3	2.25	0.79	0.64	6.50	6.39
MnO	2.02	0.02	0.003	0.20	0.01
MgO	0.85	0.99	>0.01	2.04	0.96
CaO	2.18	49.59	0.09	4.25	0.98
Na_2O	2.95	0.17	>0.01	2.75	0.73
K_2O	3.60	0.41	0.03	1.08	2.97
TiO_2	0.41	0.12	0.68	0.78	0.88
P_2O_5	0.04	0.02	0.05	0.05	0.06
LOI	1.98	39.80	0.12	4.32	5.81
Total	99.94	99.96	99.57	99.60	99.81
Cr	166	40	152	80	138
Mn	39	155	21	91	63
Co	12	2	5	3	5
Ni	98	26	113	37	43
Cu	21	7	17	25	32
Zn	8	16	6	12	14
Pb	33	8	53	71	110
As	21	2	60	–	–
U	14	4	10	26	48

3.3. LITHOGEOCHEMISTRY

Major and trace element analysis of some rocks samples obtained from the surroundings of the Ozancik hot spring was carried out to determine the influence of hydrothermal activities in the area. Alteration (decomposition in plagioclase and micas) development has been determined in the sample KGRP2 taken from the surroundings of the Kirkgeçit hot spring (Table II). With reference to the major element analysis, the rocks are considered to have been transformed into quartzite because the rock sample ORP1 contains 97.6% of SiO_2.

The rocks sample ORP2 falls into the andesite field (Figure 5) based on the $Na_2O + K_2O - SiO_2$ relation in the volcanic rocks nomenclature diagram (Le Maitre, 1989), and it has a calc-alkaline affinity (Figure 6) as per Irvine and Baragar (1971) $Na_2O + K_2O - SiO_2 - FeO^*$ triangle diagram. The sample ORP3 is rich in SiO_2.

In terms of trace and the major element analysis, the silicified tuff samples are enriched with As and Ni, whereas the andesitic tuff samples are enriched with Pb and U. In addition, the sample ORP3 has a high SiO_2 content (Table II).

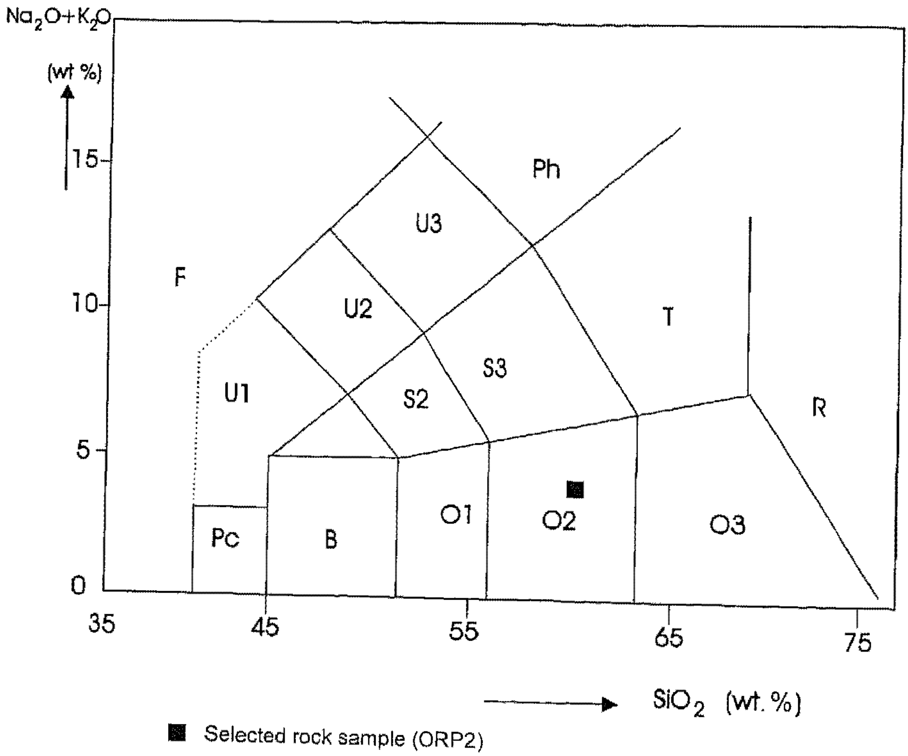

Figure 5. Nomenclature of the Çan volcanite according to Le Maitre (1989).

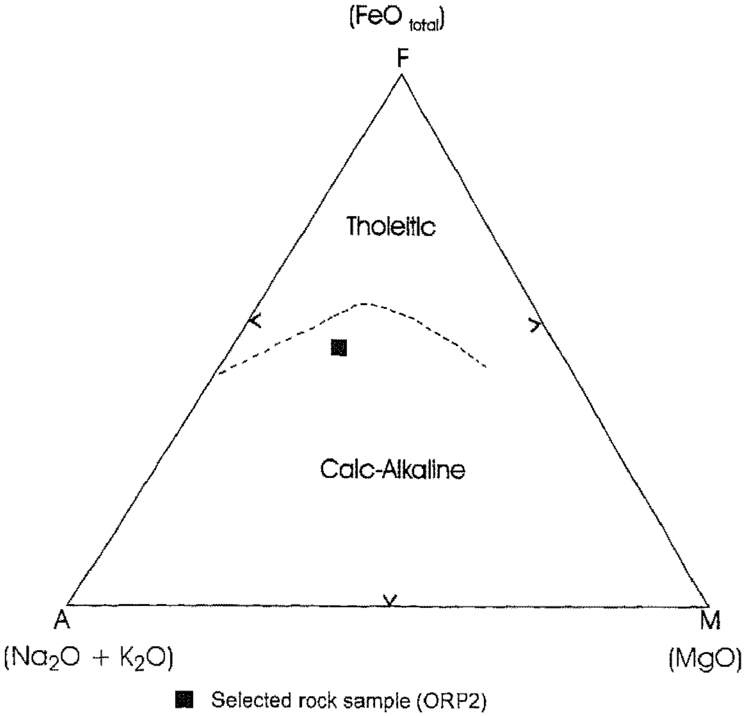

Figure 6. Classification of the Çan volcanite according to Irvine and Baragar (1971).

4. Utilisation of the hot water

4.1. WATER QUALITY

Present data on water chemistry of the Kirkgeçit and Ozancik hot springs were evaluated as per the Environmental Regulations for Water Pollution Control (Turkey Environment Regulation, 1992). It has been determined that the hot springs have different water quality classes (Table III). For example, the Kirkgeçit hot spring belongs to Quality Class 2 based on Cr^{3+}, Fe^{2+} and Cl^-; and to Quality Class 3 based on Hg^{2+}; and to Quality Class 4 based on Na^+ concentration. The Ozancik hot spring belongs to Quality Class 2 based on Cl^-; Quality Class 3 based on Hg^{2+}; Quality Class 4 based on Na^+ and $SO_4{}^{2-}$ concentration. The water belonging to Quality Classes 1 and 2 can be made fit for drinking after disinfection and purification. Similarly, that of Quality Class 3 can be used as industrial water after purification, and the water belonging to Quality Class 4 should be taken as excessively polluted water not suitable for any purpose.

4.2. THE EFFECTS ON HUMAN HEALTH

Hot and mineralised springs can cause positive or adverse effects on human health. Limit values (Table IV) for drinking, mineral, and spring water permitted by the

TABLE III

Water quality classes of the Kirkgeçit and Ozancik hot springs according to the Water Quality of Water Contamination Control Regulation, classification (Turkey Environment Regulation, 1992)

	Quality Class 1	Quality Class 2	Quality Class 3	Quality Class 4	The Kirkgeçit hot spring		The Ozancik hot spring	
					($\mu g L^{-1}$)	(Quality Class)	($\mu g L^{-1}$)	(Quality Class)
Hg	0.1	0.5	2	>2	9.1	4	1.6	3
Cd	3	5	10	>10	0.01	1	0.01	1
Pb	10	20	50	>50	0.02	1	0.01	1
As	20	50	100	>100	0.4	1	0.1	1
Cu	20	50	200	>200	1.7	1	2.9	1
TCr	20	50	200	>200	21	2	0.9	1
Co	10	50	200	>200	0.1	1	0.2	1
Ni	20	50	200	>200	0.2	1	6.8	1
Zn	200	500	2000	>2000	2.7	1	7.9	1
CN	10	50	100	>100				
F	100	1500	2000	>2000				
Cl_2	10	10	50	>50				
S	2	2	10	>10				
Fe	300	1000	5000	>5000	500	2	49	1
Mn	100	500	3000	>3000	2	1	0.3	1
B	1000	1000	1000	>1000				
Se	10	10	20	>20	0.7	1	1.4	1
Ba	1000	2000	2000	>2000	13	1	18	1
Al	300	300	1000	>1000	75	1	49	1
Na	125 000	125 000	250 000	>250 000	494 000	4	315 000	4
Cl	25 000	200 000	400 000	>400 000	121 700	2	193 200	2
SO_4	200 000	200 000	400 000	>400 000	350 200	3	575 000	4
NH_4–N	200	1000	2000	>2000				
NO_2–N	2	1000	2000	>2000				
NO_3–N	5000	10 000	20 000	>20 000	15	1	80	1
PO_4–P	20	160	650	>650				

World Health Organisation (WHO) (Uyar, 1985; Gray, 1994) and the Turkish Standards (TS) (1984, 1991) as well as for swimming water allowed by the Turkish Standards (1993) are compared with the analysis results (Tables I and III). It can be seen that in the Kirkgeçit and Ozancik hot springs, Hg, Na and SO_4 ions exceed the limit values.

TABLE IV

The limits permitted by World Health Organisation (WHO) and the Turkish Standards (TS) for drinking, mineral, spring, and swimming waters

Ions	Drinking water		Mineral water (TS) (mg L^{-1})	Spring water (TS) (mg L^{-1})	Swimming water (TS) (mg L^{-1})
	(WHO) (mg L^{-1})	(TS) (mg L^{-1})			
Pb	0.05	0.05	0.05	X	0.01
Cr	0.05	0.05	0.05	X	X
As	0.01	0.05	0.05	X	0.02
Se	0.01	0.01	0.01	X	0.003
CN	0.01	0.01	0.01	X	0.01
Cd	0.01	0.005	0.005	X	X
Ag	0.05	0.05	X	X	X
Hg	0.001	X	0.001	X	X
Fe	1	1	X	0.3	X
Mn	0.05	0.5	0.5	0.1	X
Cu	1	1.5	1	1	X
Zn	5	15	3	5	X
Ca	200	200	X	25	X
Mg	125	150	X	10	X
Ba	1	X	1	X	X
Cl	600	600	X	500	X
F	1	2.4	1.5	1	X
SO_4	400	400	X	20	X
NH_3	X	X	X	X	0.2
NH_4	X	X	0.05	X	X
NO_2, NO_3	45	45	25	25	5

X = Data not available.

5. Conclusions

The conclusions drawn from the present study can be summarised as follows:

The Ozancik hot spring exhibits the following anion and cation arrangement: $r(Na^+ + K^+) > rCa^{2+} > rMg^{2+}$ and $r(SO_4{}^{2-}) > rCl^- > r(HCO_3{}^-)$, and it is compatible with the following arrangement reported from the volcanic rocks: $(r(Na^+ + K^+) > rCa^{2+} > rMg^{2+}$ and $r(SO_4{}^{2-}) > rCl^- > r(HCO_3{}^-)]$. But in the Kirkgeçit hot spring the arrangement of cations and anions does not resemble $(rCa^{2+} > rMg^{2+} > r(Na^+ + K^+)$, $r(HCO_3{}^-) > rCl^- > rSO_4{}^{2-})]$, the arrangement of cations and anions of the hot springs discharged from metamorphic rocks. This shows that the Kirkgeçit hot spring is in interaction with volcanic

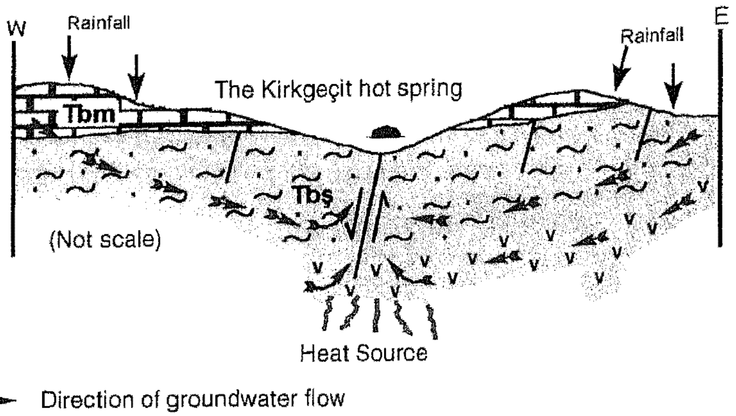

Figure 7. Schematic cross-section of the Kirkgeçit hot spring.

rocks and limestones through the circulation in the surface and underground (Figure 7).

Like the Ozancik hot spring, the Kirkgeçit hot spring is rich in K^+, Mg^{2+}, $SO_4{}^{2-}$, Na^+ and SiO_2. The increase in the K^+, Mg^{2+}, $SO_4{}^{2-}$, Na^+ and SiO_2 concentration in the Kirkgeçit hot spring can be explained by the hot spring–volcanic rock interaction. These data make us feel that although the Kirkgeçit hot spring discharges from metamorphic rocks, the decomposition in the surrounding rocks affects it. Also, the inclusion of Fe^{2+}, Cr^{3+}, Mn^{2+} and Hg^{2+} in both the hot water samples indicates a potential natural inorganic contamination.

The Kirkgeçit and Ozancik hot springs can be used for swimming. However, the water cannot be used for drinking because it contains mercury.

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