Πρακτικά	6ου Συνεδρίου		Μάϊος 1992
Δελτ. Ελλ. Γεωλ. Εταιρ.	Τομ. XXVIII/3	σελ. 629-645	Αθήνα 1993
Bull. Geol. Soc. Greece	Vol.	pag.	Athens

HYDROGEOCHEMICAL AND ISOTOPIC INVESTIGATIONS IN ÇEŞME (IZMIR) REGION

S.FILIZ, G.TARCAN

ABSTRACT

The study area is located in the western parts of the Karaburun Peninsula. The rocks observed in the study area are divided into three groups. These are Mesosozoic karstic limestones, Neogene tuffs and Neogene lacustrine sediments. Mesozoic karstic limestones have been overlain by the Neogene tuffs and Neogene lacustrine sediments with an unconformity. The Neogene lacustrine sediments consist of conglomerate, sandstone, clay, marl and limestone intercalations.

Mesozoic karstic limestones are an aquifer of the hot springs. It is understood from the geochemical and isotopic data that the origin of the hot waters is sea water. Sea water percolates through the fractures and karstic voids, and is heated at depth and is also through percolation brought up to the surface. These hot waters are mixed with different proportions of cold sea water and cold fresh water as they travel to the surface. The proportions of cold sea water in the hot (mixing) mixture waters could have varied from 36 % to 79 %. The proportions of fresh water in the hot and cold mixed waters could have ranged at least from 32 % to 79 %. The isotopic compositions of the hot waters are about similar to the modern sea water of Aegean sea. The circulation velocities of them are very fast.

Results obtained from different chemical geothermometers are unreliable because of the sea water origins of them and mixing phenomena. Application of Fournier's silica enthalpy warm spring mixing model gave the temperature of the hot water in the reservoir before mixing as the variation about 85°C and 130°C.

D.E. University, Dept. of Geological Engineering, Bornova-İzmir-TURKEY

1. INTRODUCTION

The hydrogeological studies on the geothermal springs, which are important for energy, health and touristic purposes, have been started in the years of 1960 in Turkey. Çeşme is one of the major important tourism centers of Turkey. This tourism center is also one of the known important geothermal field on the Aegean Region. The study area, which covers Çeşme and surrounding area, is located in the western parts of the Karaburun Peninsula, and is about 80 km away from İzmir on the Aegean Region (Figure 1).

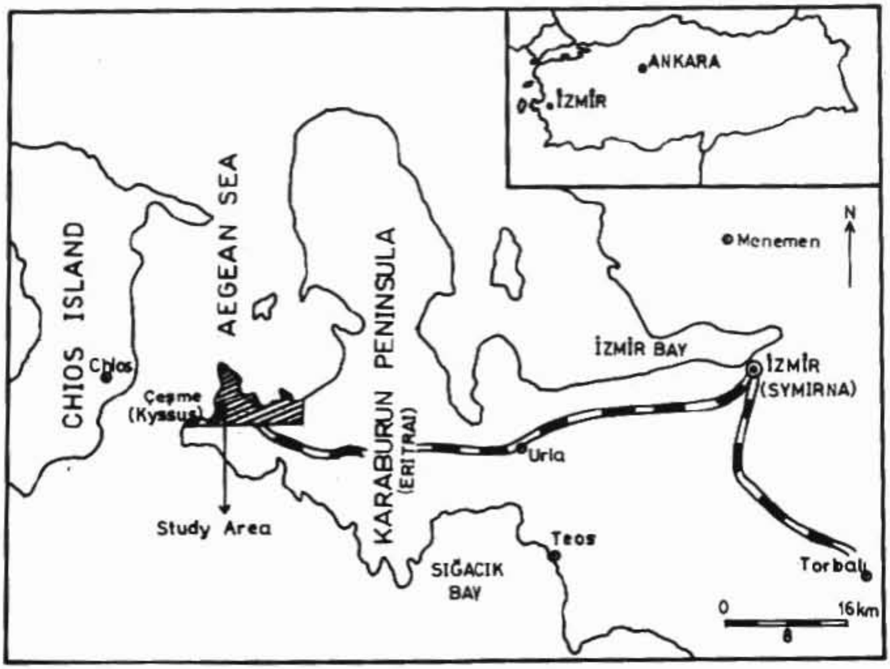

Figure 1. Location Map

In this area, hydrogeological, hydrogeochemical and isotopic studies were carried out. Geological survey of 60 km^2 at 1: 25.000 scale was conducted in 1990. Some of the chemical analyses and isotopic analyses of the sampled water points in 1978, 1979 and 1980 were done at Thonon-Les-Bains Geodynamic Research Center and Saclay Nuclear Energy Laboratory in France. Water samples were collected in plastic bottles with double covers. The Oxygen-18 and Deuterium ($D = {}^2H$) were measured with CH-7 Mass Spectrometer. The Tritium ($T = {}^3H$) analyses were made with Nuclear Chicago radioactive counter. The measurements were made before and after enriching with electrolyse.

Some of the chemical analyses were done in the Mineral Research and Investigations (MTA) General Directory Laboratory and in the States Hydraulic Works (DSİ) Laboratory and in the D.E.Ü. Geological Engineering, Geochemistry Laboratory in Turkey. Analyses were made using methods described in TS-266 (1970).

2. GEOLOGY

The rocks observed in the study area are divided into three groups. These are Mesozoic karstic limestones, Neogene tuffs and Neogene lacustrine sediments (Figure 2).

The oldest unit of the study area is Middle-Upper Triassic limestones, which contain many fractures and karstic voids. Lower contact of these limestones has not been seen in the study area. These limestones have been overlain by an unconformity of the Neogene tuffs and lacustrine sediments. Neogene lacustrine sediments consist of conglomerate, sandstone, claystone, marl and limestone intercalations.

3. HYDROGEOLOGY

Mesozoic karstic limestones are the aquifer of the hot waters such as Topan Ilıca Hot Spring and Şifne Hot Spring, and of the some mineral waters such as Şifne İçmeler Spring and Şifne Büyük İçmeler Spring. This unit contains generally hot waters of fresh waters, which are contaminated by the sea water. Neogene tuffs are the locally aquifer. Clay levels of the Neogene lacustrine sediments are impermeable rocks. Conglomerates, and marl, and limestone levels of the lacustrine sediments are the aquifers, which are not very important. These aquifers, which are situated in the seaside, have been locally contaminated from the sea because of the excessive pumping of ground

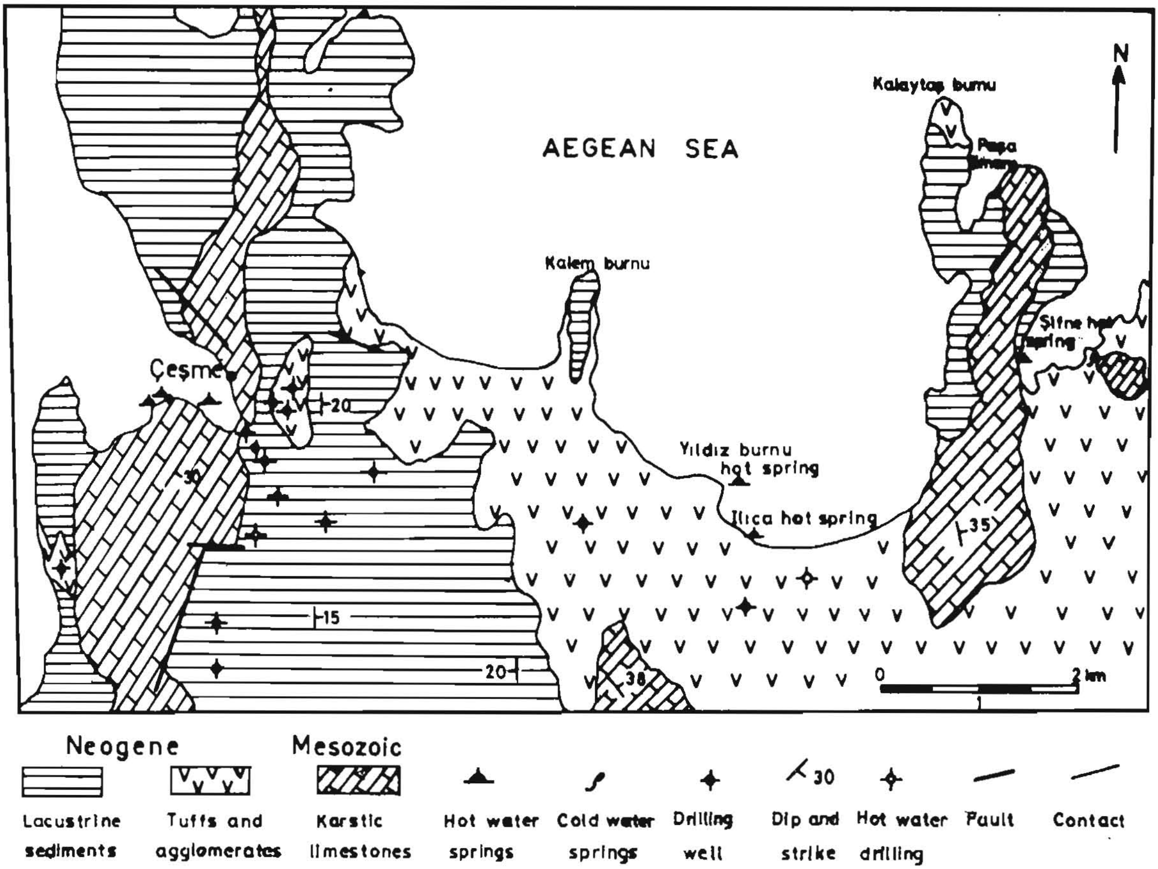

Figure 2. Simplified Geological Map of the Study Area and Locations of the Sampled Water Points.

water. Since the clay levels of the lacustrine sediments are also the cap rocks of the geothermal system, a heat convection trend occurs.

3.1. HYDROGEOCHEMICAL AND ISOTOPIC INVESTIGATIONS

Selected chemical analyses of water points and some of their geochemical properties are given in tables 1, 2, 3, 4, 5 and 6. Some symbols and explanations in these tables are shown as follows.

Na+ = sodium, K+ = potassium, Ca++ = calcium, Mg++ = magnesium, Cl- = chloride, HCO3- = bicarbonate, SO_4= sulfate, Sr++ = strontium, pH = negative log activity of hydrogen, EC = electrical conductivity,

Table 1. Geochemical properties of Topan Ilıca Hot Spring

SAMPLE NAME : TOPAN ILICA HOT SPRING
DATE OF SAMPLING : MAY 1980 LAB NR :T100 FRANCE

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	6310	274.47	0.27447	0.27447	0.1372	0.1917	0.70	77.54
K+	283	7.26	0.00726	0.00726	0.0036	0.0051	0.70	2.05
Ca++	718	35.83	0.01791	0.07166	0.0358	0.0043	0.24	10.12
Mg++	443	36.43	0.01822	0.07286	0.0364	0.0043	0.24	10.29
Cl-	11600	327.04	0.32704	0.32704	0.1635	0.2285	0.70	92.41
HCO3-	203	3.33	0.00333	0.00333	0.0017	0.0023	0.70	0.94
SO4=	1130	23.53	0.01176	0.04705	0.0235	0.0028	0.24	6.65

TOTAL CATION AMOUNT (meq/l)	: 353.98	PH	: 7.10
TOTAL ANION AMOUNT (meq/l)	: 353.89	EC(mmho/cm)	: 28250
TOTAL ION AMOUNT (meq/l)	: 707.87	Si(mg/l)	:10.750
IONIC STRENGTH	: 0.402	HARDNESS(FR)	:361.30
SAR (SODIUM AD.RATIO)	: 45.66	Sr++(mg/l)	: 4.00
Cl/(SO4+HCO3)	: 12.18	Ca/Mg	: 0.98

Table 2. Geochemical properties of Şifne Hot Spring

SAMPLE NAME : ŞIFNE HOT SPRING
DATE OF SAMPLING : MAY 1980 LAB NR :T101 FRANCE

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	7990	347.54	0.34754	0.34754	0.1738	0.2410	0.69	77.81
K+	348	8.92	0.00892	0.00892	0.0045	0.0062	0.69	2.00
Ca++	786	39.22	0.01961	0.07844	0.0392	0.0045	0.23	8.78
Mg++	620	50.99	0.02549	0.10197	0.0510	0.0059	0.23	11.41
Cl-	15580	439.24	0.43924	0.43924	0.2196	0.3045	0.69	97.85
HCO3-	191	3.13	0.00313	0.00313	0.0016	0.0022	0.69	0.70
SO4=	313	6.52	0.00326	0.01303	0.0065	0.0008	0.23	1.45

TOTAL CATION AMOUNT (meq/l)	: 446.67	PH	: 6.90
TOTAL ANION AMOUNT (meq/l)	: 448.89	EC(mmho/cm)	: 33435
TOTAL ION AMOUNT (meq/l)	: 895.57	Si(mg/l)	:10.280
IONIC STRENGTH	: 0.496	HARDNESS(FR)	:451.04
SAR (SODIUM AD.RATIO)	: 51.75	Sr++(mg/l)	: 6.00
Cl/(SO4+HCO3)	: 45.53	Ca/Mg	: 0.77

Table 3. Geochemical properties of the sea water in Aegean sea

SAMPLE NAME : SEA WATER(AEGEAN SEA)
DATE OF SAMPLING : 1987(ANNUAL AVERAGE) LAB NR :DEU 89

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	12423	540.37	0.54037	0.54037	0.2702	0.3756	0.70	78.77
K+	520	13.33	0.01333	0.01333	0.0067	0.0093	0.70	1.94
Ca++	591	29.49	0.01475	0.05898	0.0295	0.0034	0.23	4.30
Mg++	1250	102.80	0.05140	0.20559	0.1028	0.0120	0.23	14.99
Cl-	23090	650.97	0.65097	0.65097	0.3255	0.4525	0.70	90.09
HCO3-	108	1.77	0.00177	0.00177	0.0009	0.0012	0.70	0.25
SO4=	3355	69.85	0.03492	0.13970	0.0698	0.0082	0.23	9.67

TOTAL CATION AMOUNT (meq/l)	: 685.99	PH	: 8.15
TOTAL ANION AMOUNT (meq/l)	: 722.59	EC(mmho/cm)	: 36320
TOTAL ION AMOUNT (meq/l)	:1408.58	SiO2(mg/l)	: 6.42
IONIC STRENGTH	: 0.805	HARDNESS(FR)	:661.44
SAR (SODIUM AD.RATIO)	: 66.44	TOTAL HARDNESS	:661.95
Cl/(SO4+HCO3)	: 9.09	Ca/Mg	: 0.29

Table 4. Geochemical properties of the cold water in the study area

SAMPLE NAME : COLD (FRESH) WATER AVERAGE
DATE OF SAMPLING : 1984(ANNUAL AVERAGE) LAB NR :DSi 84

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	390	16.96	0.01696	0.01696	0.0085	0.0141	0.83	54.20
K+	6	0.15	0.00015	0.00015	0.0001	0.0001	0.83	0.49
Ca++	121	6.04	0.00302	0.01208	0.0060	0.0014	0.48	19.29
Mg++	99	8.14	0.00407	0.01628	0.0081	0.0019	0.48	26.01
Cl-	750	21.14	0.02114	0.02114	0.0106	0.0176	0.83	68.01
HCO3-	401	6.57	0.00657	0.00657	0.0033	0.0055	0.83	21.14
SO4=	162	3.37	0.00169	0.00675	0.0034	0.0008	0.48	10.85

TOTAL CATION AMOUNT (meq/l)	: 31.30	PH	: -
TOTAL ANION AMOUNT (meq/l)	: 31.09	EC(mmho/cm)	: -
TOTAL ION AMOUNT (meq/l)	: 62.39	Si(mg/l)	: -
IONIC STRENGTH	: 0.040	HARDNESS(FR)	: 70.90
SAR (SODIUM AD.RATIO)	: 6.37	TOTAL HARDNESS	: 70.95
Cl/(SO4+HCO3)	: 2.13	Ca/Mg	: 0.74

Table 5. Geochemical properties of Şifne B. İçmeler spring

SAMPLE NAME : ŞiFNE BÜYÜK iÇMELER MINERAL WATER
DATE OF SAMPLING : AUGUST 1976 LAB NR :MTA 2988

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	3013	131.06	0.13106	0.13106	0.0655	0.0933	0.71	57.03
K+	111	2.85	0.00285	0.00285	0.0014	0.0020	0.71	1.24
Ca++	585	29.19	0.01460	0.05838	0.0292	0.0037	0.26	12.70
Mg++	811	66.69	0.03335	0.13339	0.0667	0.0086	0.26	29.02
Cl-	7050	198.76	0.19876	0.19876	0.0994	0.1415	0.71	86.64
HCO3-	727	11.92	0.01192	0.01192	0.0060	0.0085	0.71	5.19
SO4=	900	18.74	0.00937	0.03747	0.0187	0.0024	0.26	8.17

TOTAL CATION AMOUNT (meq/l) : 229.79
TOTAL ANION AMOUNT (meq/l) : 229.41
TOTAL ION AMOUNT (meq/l) : 459.20
IONIC STRENGTH : 0.287
SAR (SODIUM AD.RATIO) : 18.93
Cl/(SO4+HCO3) : 6.48

PH : 6.52
F-(mg/l) : 0.60
SiO2(mg/l) :27.000
HARDNESS(FR) :479.43
Fe(Total)(mg/l): 0.66
Ca/Mg : 0.44

Table 6. Geochemical properties of Şifne İçmeler spring

SAMPLE NAME : ŞiFNE iÇMELER MINERAL WATER
DATE OF SAMPLING : AUGUST 1976 LAB NR :MTA 2988

IONS	mg/l	meq/l	mol/l	CZ2	.5CZ2	AC	F	%
Na+	2730	118.75	0.11875	0.11875	0.0594	0.0866	0.73	69.35
K+	79	2.03	0.00203	0.00203	0.0010	0.0015	0.73	1.18
Ca++	566	28.24	0.01412	0.05649	0.0282	0.0040	0.28	16.50
Mg++	270	22.20	0.01110	0.04441	0.0222	0.0031	0.28	12.97
Cl-	5450	153.65	0.15365	0.15365	0.0768	0.1120	0.73	88.07
HCO3-	351	5.75	0.00575	0.00575	0.0029	0.0042	0.73	3.30
SO4=	723	15.05	0.00753	0.03010	0.0151	0.0021	0.28	8.63

TOTAL CATION AMOUNT (meq/l) : 171.22
TOTAL ANION AMOUNT (meq/l) : 174.46
TOTAL ION AMOUNT (meq/l) : 345.68
IONIC STRENGTH : 0.206
SAR (SODIUM AD.RATIO) : 23.64
Cl/(SO4+HCO3) : 7.38

PH : 6.90
F-(mg/l) : 0.20
SiO2(mg/l) :35.000
HARDNESS(FR) :252.24
Fe(Total)(mg/l): -
Ca/Mg : 1.27

Si = silisium, Fe = iron, F- (mg/l) = fluorine, mg/l = milligrams per liter, meq/l = milliequivalents per liter, mol/l = molarities per liter, % = percentages of cations and anions, F = ionic activity coefficient, AC = ionic activities, .5CZ2 = ionic strengths of ions. Debye-Huckel and Davies equations (Garrels and Christ, 1965), were used in the calculating of the ionic activity coefficient (F) of ions.

In the study area, some waters were investigated with oxygen-18 (^{18}O), deuterium (^{2}H = D) and tritium (^{3}H = T) natural isotopes (Tables 7 and 8). The stable isotopic variations are expressed as $\mp \delta$ values in parts per thousand (permil) differences in the measured isotopic ratios in a sample and in appropriate standard: Standard Mean Ocean Water (SMOW) for oxygen ($\delta^{18}O$) and hydrogen (δ D) in water. If R is the absolute content, relative deviation is given by the following equation :

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 10^{3}$$

Tritium is measured by tritium unit (TU) = 1 TU = $\frac{\text{Tritium atom}}{\text{Hydrogen atom}} \cdot 10^{18}$

The tritium is used in the determination of the relative age of the waters and of the rate of water movements under the ground. ^{18}O and D are used in the tracing the origin of the ground water. Results of the analyses for this study are given in tables 7, 8. Figure 2 shows the locations of the sampled wated points.

The little differences in the annual $\delta^{18}O$ variations of the water points are related with different recharges and evaporations which varied montly.

The enriched tritium values of the hot springs are about similar to the modern sea water of Aegean sea. The circulation velocities of these waters are very fast at under ground. The tritium centent of the sea water is small. Cold fresh waters, which are the meteoric origin, contain lighter isotopic molecules than both the hot waters and sea waters. Therefore, sea water and the hot waters are lie over the right (+) side of the meteoric water lines (Figure 3).

Table 7. The Variations of $\delta\,^{18}O$ (permil) $\delta^{18}O$ = standart expression of the ratio of the ^{18}O ion with respect to the ^{16}O ion.

Sampled Water Point Date of Sampling	Yıldız Burnu Hot Spring	Topan Ilıca Hot Spring	Şifne Hot Spring	Şifne Büyük İçmeler Spring
14.8.1978	+ 0.99	- 2.35	- 1.04	- 3.75
14.9.1978	+ 1.15	- 1.38	- 1.04	- 3.75
16.10.1978	+ 0.99	- 2.05	- 0.87	- 3.93
10.11.1978	+ 0.99	- 1.89	- 3.92	- 3.75
2.2.1979	+ 0.99	- 1.89	- 0.54	-
12.4.1979	+ 0.82	- 1.89	- 0.61	-
15.5.1979	+ 1.32	- 2.00	- 0.88	-
17.7.1979	+ 1.32	- 2.05	- 0.21	- 3.75
10.5.1980	-	- 2.05	- 1.05	-

Table 8. Analyses of natural isotopes (^{18}O, D, T) in water from selected water points sampled for this study and temperature of these waters. (*): enriched tritium value

	Date of Sampling	Topan Ilıca Hot Spring	Şifne Hot Spring	Yıldız Burnu Hot Spring	Şifne Büyük İçmeler Spr.	Sea Water (Aegean Sea)
$\delta^{18}O$ (permil)	17.7.1979	- 2.05	- 0.21	+ 1.32	- 3.75	+ 0.96
δD (permil)	17.7.1979	- 7.6	+ 1.8	+ 8.5	- 19.4	-
Tritium (TU)	17.7.1979 10.8.1980	$13 \leq TU \leq 26$ 8 ∓ 1 (*)	39 ∓ 9 9 ∓ 1(*)	29 ∓ 9 -	$TU \leq 13$	10 ∓ 1(*)
Temperature (^{o}C)	17.7.1979	60	42	57	20	18

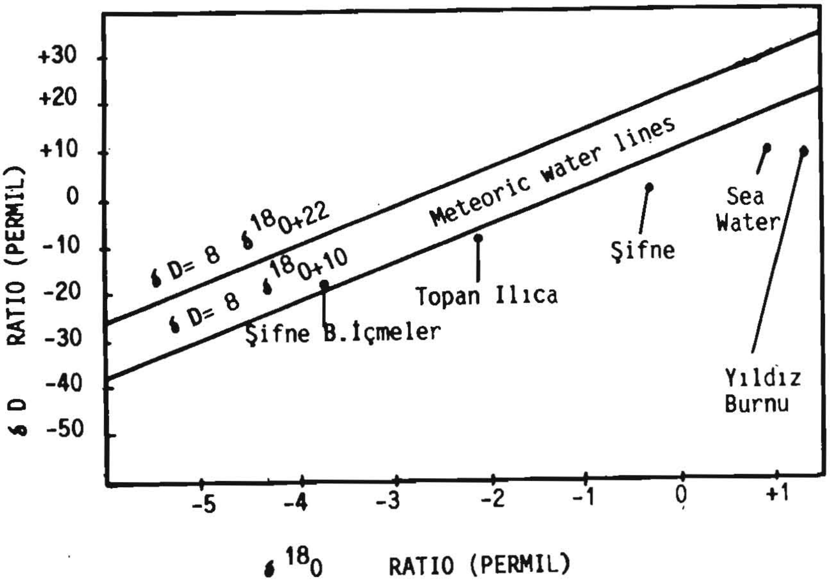

Figure 3. $\delta^{18}O - \delta D$ relationship of waters in the study area.

Isotopic analyses show that Yıldız Burnu Hot Spring is the natural heated water.

Mesozoic karstic limestones are the reservoir of the hot springs. It is interpreted from the geochemical studies (Tables 1-4, Figure 4) and isotopic data (Tables 7, 8 and Figure 3) that the origin of the hot waters is sea water. The sea water percolates through the fractures and karstic voids, and is heated at depth and also through the percolation brought up to the surface. These hot waters are mixed with the different proportions of cold fresh water and cold sea water as they travel to the surface (Figure 4,5).

Mesozoic karstic limestones are also the aquifer of the Şifne İçmeler and Şifne Büyük İçmeler Springs. The origin of these springs known as "mineral water" is meteoric, but these waters are mixed with the sea water (Figure 4).

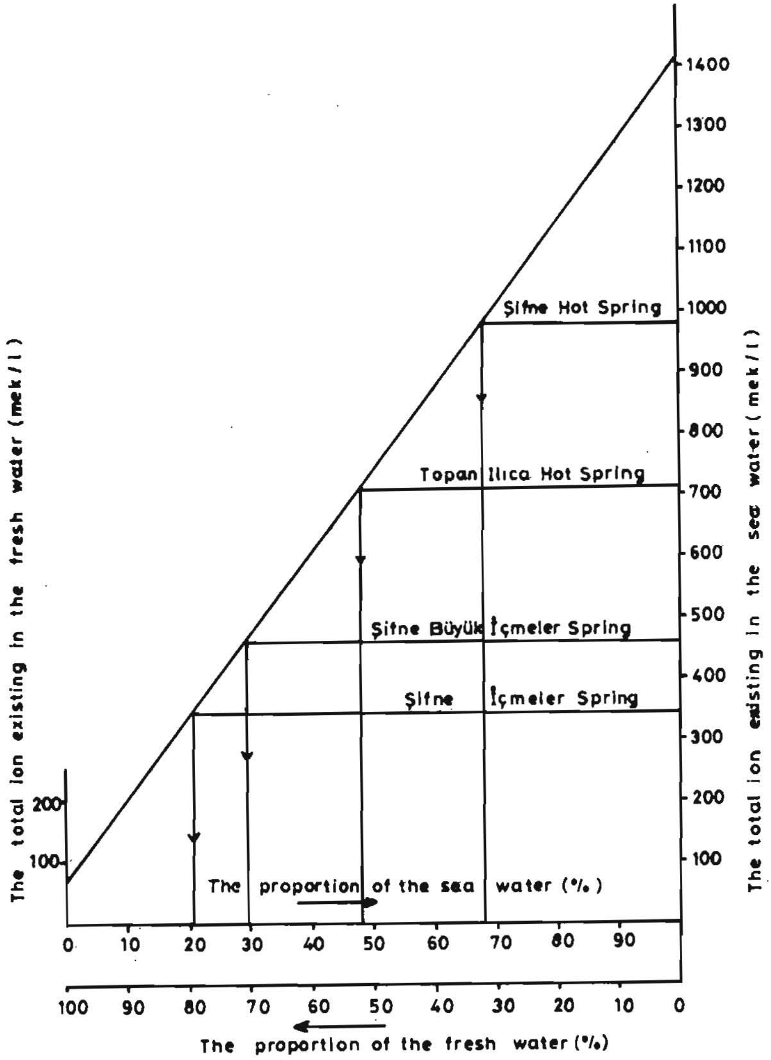

Figure 4. Proportions of sea water and Fresh Water in mixture waters.

It is important to know the aquifer temperature of a geothermal system during the exploration stages in order to determine the kind of use to be obtained from it such as electricity generation, district heating etc. Temperature can be determined quantitatively by using geothermometers.

Many chemical geothermometers have been developed during the past two decades (Arnorsson, 1975, Fournier, 1977, Truesdel, 1975). In this study, the reservoir temperature of the field was estimated by using the following equations (Table 9).

Table 9. Geothermometric Equations used for this study. All concentrations are in mg/l.

	Geothermometer	Equation
1-	Amorphous silica	$t = 731/(4,52-\log SiO_2) - 273,15$
2-	Chalcedony	$t = 1032/(4,69-\log SiO_2) - 273,15$
3-	Quartz	$t = 1309/(5,19-\log SiO_2) - 273,15$
4-	Quartz (after steam loss)	$t = 1522/(5,75-\log SiO_2) - 273,15$
5-	Quartz (adiabatic cooling)	$t = 1533,5/(5,768-\log SiO_2) - 273,15$
6-	Quartz (conductive cooling)	$t = 1315/(5,205-\log SiO_2) - 273,15$
7-	Chalcedony(conductive cooling)	$t = 1015,/(4,655 - \log SiO_2) - 273,15$
8-	Na^+/K^+	$t = 1319/(\log Na/K+1.699) - 273,15$

The results of the geothermometry applications are given in table 10.

Table 10. Geothermometry Results in Şifne Hot Spring and Topan Ilıca Hot Spring

	Şifne Hot Spring	Topan Ilıca Hot Spring
1	- 43.1	- 41.4
2	35	36.9
3	67	68.8
4	72.2	73.7
5	73.4	74.9
6	67.3	69.0
7	33.3	35.1
8	157.9	159.7

As it is seen Table 10, results are unreliable.

The chemical characteristics of warm mixed waters are different than unmixed waters. Therefore, chemical geothermometers do not indicate the temperature of the unmixed water and are unreliable. Fournier's silica enthalpy warm spring mixing model between cold sea water and hot mixed waters was applied for this study (Table 11). The following equations have been used for these calculations

$$x_t = (H_h-H_s)/H_h-H_c) \;,\; X_{Si} = (Si_h-Si_s)/(Si_h-Si_c) \quad \text{where,}$$

x_t = the theoretical proportion of the cool sea water, X_{si} = the theoretical SiO_2 amount in the reservoir, H_h= the theoretical enthalpy of the reservoir, H_s and H_c = the enthalpies of the warm spring and cold sea water, Si_h = the theoretical SiO_2 amount in the reservoir, Si_s and Si_c = the amount of SiO_2 in the warm spring and in the cold sea water.

Table 11. X_t and X_{si} values in Topan Ilıca Hot Spring and Şifne Hot Spring according to the theoretical reservoir temperature.

			Şifne Hot Spring		Topan Ilıca Hot Spring	
t°C	H_h(cal/g)	Si_h(mg/l)	X_t	X_{Si}	X_t	X_{si}
75	75	26.6	0.59	0.23	0.26	0.18
100	100.09	48	0.71	0.63	0.49	0.60
125	125.41	80	0.78	0.79	0.61	0.77
175	177.055	185	0.85	0.91	0.74	0.91
200	203.61	265	0.87	0.94	0.77	0.94
225	225.52	367	0.88	0.96	0.80	0.95
250	259.2	490	0.90	0.97	0.83	0.97
275	289	615	0.91	0.97	0.85	0.97
300	321	692	0.92	0.97	0.86	0.98

The following values were used for these calculations

H_c = 18 cal/g, Si_c = 6.42 mg/l, H_s = 42 cal/g (Şifne), H_s = 60 cal/g (Topan Ilıca) Si_s = 22 mg/l (Şifne) Si_s = 23 mg/l (Topan Ilıca)

The reservoir temperatures and the proportions of the cold sea water have been shown in figure 5.

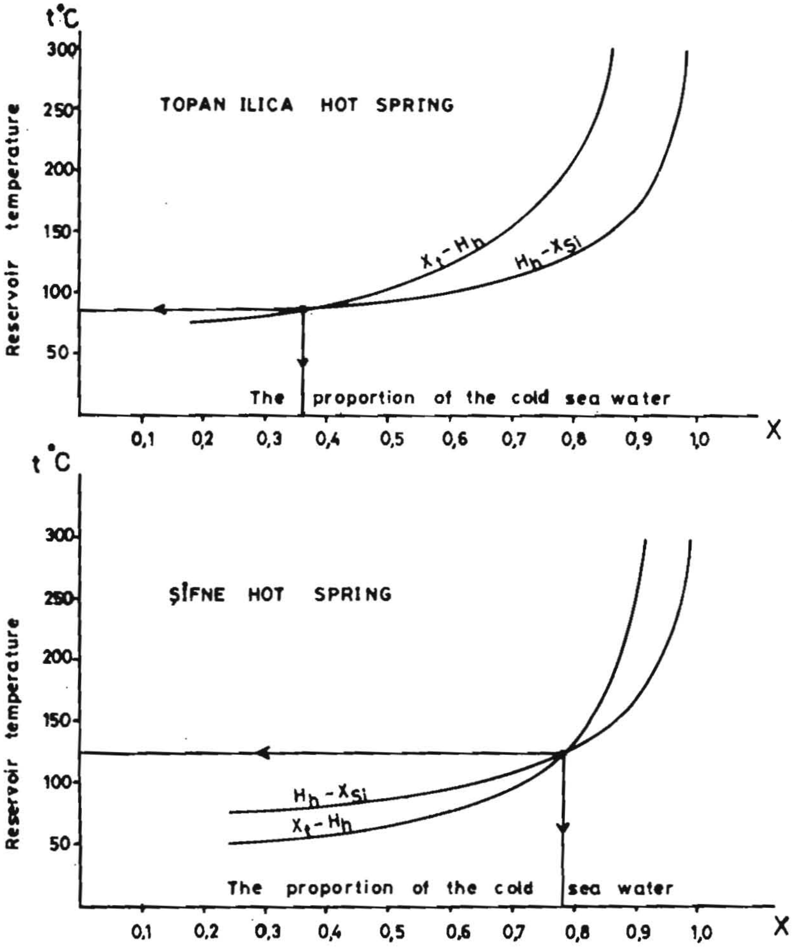

Figure 5. The reservoir temperatures and the proportions of the cold sea water in Şifne and Topan Ilıca Hot Spring according to the silica enthalpy warm spring model.

4. RESULTS AND CONCLUSIONS

1. Mesozoic karstic limestones are the reservoir of the hot waters in the study area. Tectonic and young magmatic activities cause the heating of waters at depth. Since the clay levels of the Neogene lacustrine sediments are cap rocks of the Çeşme geothermal systems, a heat convection trend occurs.

2. It is understood from the hydrogeological, geochemical and isotopic studies that the origin of the hot waters is sea water. Sea water percolates through the fractures and karstic voids, and is heated at depth and is also through percolation brought up to the surface. These waters mixed at different proportions of meteoric waters. The proportions of the meteoric waters mixed with the sea water in these thermal springs, have been estimated to be 30-80 %.

3. The enriched tritium values of the hot springs are about similar to the modern sea water of Aegean sea. The circulation velocities of these waters are very fast at under ground. Both sea water and hot waters are lie over the right (+) side of the meteoric water lines in the $\delta^{18}O - \delta D$ diagramme. These hot waters are the natural heated and metamorphosed sea waters.

4. In this study, the reservoir temperatures of the field were estimated by using different chemical geothermometers such as quartz, Na^+/K^+, etc. But the results of these geothermometry applications are unreliable and unfeasible because of the sea water origins and mixing phenomena.

5. Application of Fournier's silica enthalpy warm spring mixing model between cold sea water and hot mixed waters, gave the temperature of the hot waters in the reservoir before mixing as the variation about 85°C and 130°C. According to this model, the proportions of the cold sea water in the hot mixing waters could have varied from 36 % to 79 %.

6. The geothermal fluids in this area, are not appropriate for electricity production. The other uses such as heating, drying, cooling and for balneological and touristic purposes etc., have to be considered instead of electrical power production.

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