Hydrogeochemical Investigation of Hot and Mineral Waters of Karaada (Bodrum)

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ABSTRACT

Karaada geothermal area is located in the Kerme (Gokova) Gulf, south of Bodrum (Mugla-Turkey). Main lithostratigraphic units of the region are Triassic-Liassic aged dolomitic limestones, Liassic-Malm aged silty and marly limestones, Malm-Cenomanian aged cherty limestones, Upper Miocene aged magmatic rocks, Upper Cretaceous-Paleocene aged Bodrum flysches and Quaternary aged alluviums. Among these units, dolomitic-cherty limestones are the main groundwater bearing formations. Horst-graben systems have been developped due to active tectonism in the area. Permeability has been occurred by tectonism and karstification processes. The hot and mineral springs at the region located on the main fault lines and related segments running through cherty limestones.

The hot spring emerges from a karstic cave, located north of Karaada Island in the Aegean Sea. Temperature of the hot spring is measured between 30.6°C and 31.7°C. The flowrate of the hot spring varies between 2 and 25 l/s depending on the sea level fluctuations. The type of the hot and mineral spring is Na-Cl. The spring has high salinity due to seawater intrusion. According to the silica geothermometers, estimated temperatures are between 38°C and 60°C. Environmental isotope analyses show that the hot spring is of meteoric origin; low tritium values indicate that deep circulating waters constitute the source of spring flow. As a result of this study, Karaada conceptual hydrothermal model was established.

1. INTRODUCTION

The study area is located at the southern part of Bodrum district at the Kerme (Gokova) Gulf in Mugla province of Turkey (Figure 1). The Karaada hot spring has a potential to be used as Spa tourism. The main aim of this study is to determine chemical characteristics of spring water.

The conceptual model of the geothermal system was established based on the chemical and isotope analysis of water samples collected from the study area, as well as geological and hydrogeological assessments. As a result of the study, hydrogeochemical processes in the groundwater system, the reservoir temperature and the fluid-mineral equilibrium and heat sources were estimated. It is determined that the Karaada Spring waters are usable for Spa purposes.

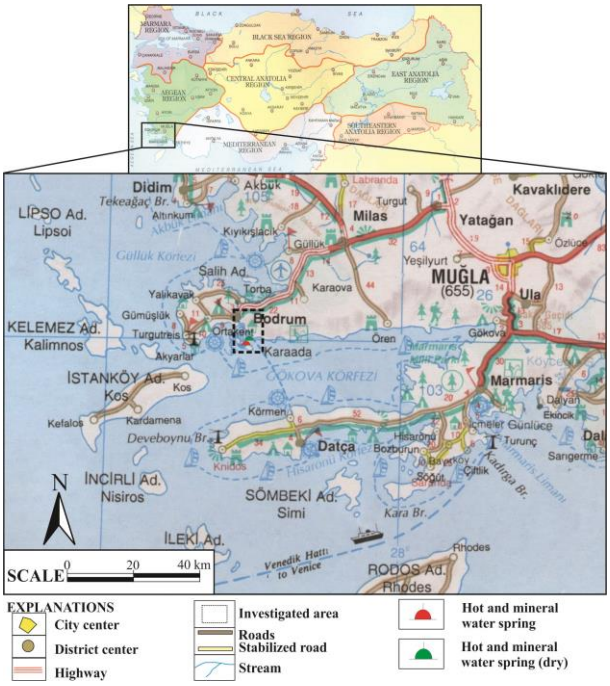

Figure 1: Location map of investigation area.

2. MATERIAL AND METHOD

In order to determine the hydrogeochemical characteristics of the hot and mineral springs in the study area, water samples were taken two times in a year, and chemical analysis were performed. The physical and chemical parameters, such as pH, total dissolved solid (TDS), electrical conductivity (EC) and temperature (T), were measured during the field work (Table 1). For sampling purposes, 250 ml specific polythene bottle was used. Diluted HNO_3 was used to preserve the cation keeping pH<2. Subsequently, samples were taken to Hacettepe University Hydrogeology Engineering Water Chemistry laboratory. Environmental isotopes of $\delta^{18}O$

and δ^2H, which were collected from 9 samples in the study area, were analyzed in the Scientific and Technological Research Council of Turkey (TUBITAK) Marmara Research Center (MAM) Environmental and Petroleum Laboratory. ^3H isotopes were analyzed in Hacettepe University Water Chemistry Laboratory in Hydrogeology Engineering Department.

3. GEOLOGY AND HYDROGEOLOGY

The basement rock in the area is composed of Paleozoic Gulluk formation which is not observed in the area. Triassic-Liassic Pazardagi Formation, which is characterized by recrystallized dolomitic limestones, conformably overlays the Paleozoic basement. The Pazardagi formation is conformably overlain by the Karadag formation which is composed of silty marly limestone. The Kisladagi formation which is composed of pelagic limestone is found conformably overlying the Karadag formation. Above this unit is the unconformably overlying Cretaceous-Paleocene Bodrum formation. The Bodrum formation is unconformably overlain by volcanic and plutonic rocks such as tuff, agglomerate, andesite, trachiandesite and latite which are formed by post Oligocene severe volcanic processes (Ercan et al., 1983). The Bodrum volcanic rocks formed during the early Pliocene volcanism are also, found in the area (Montigny and Robert, 1991). Quaternary alluvial deposit is the youngest and the uppermost unit in the area (Figure 2).

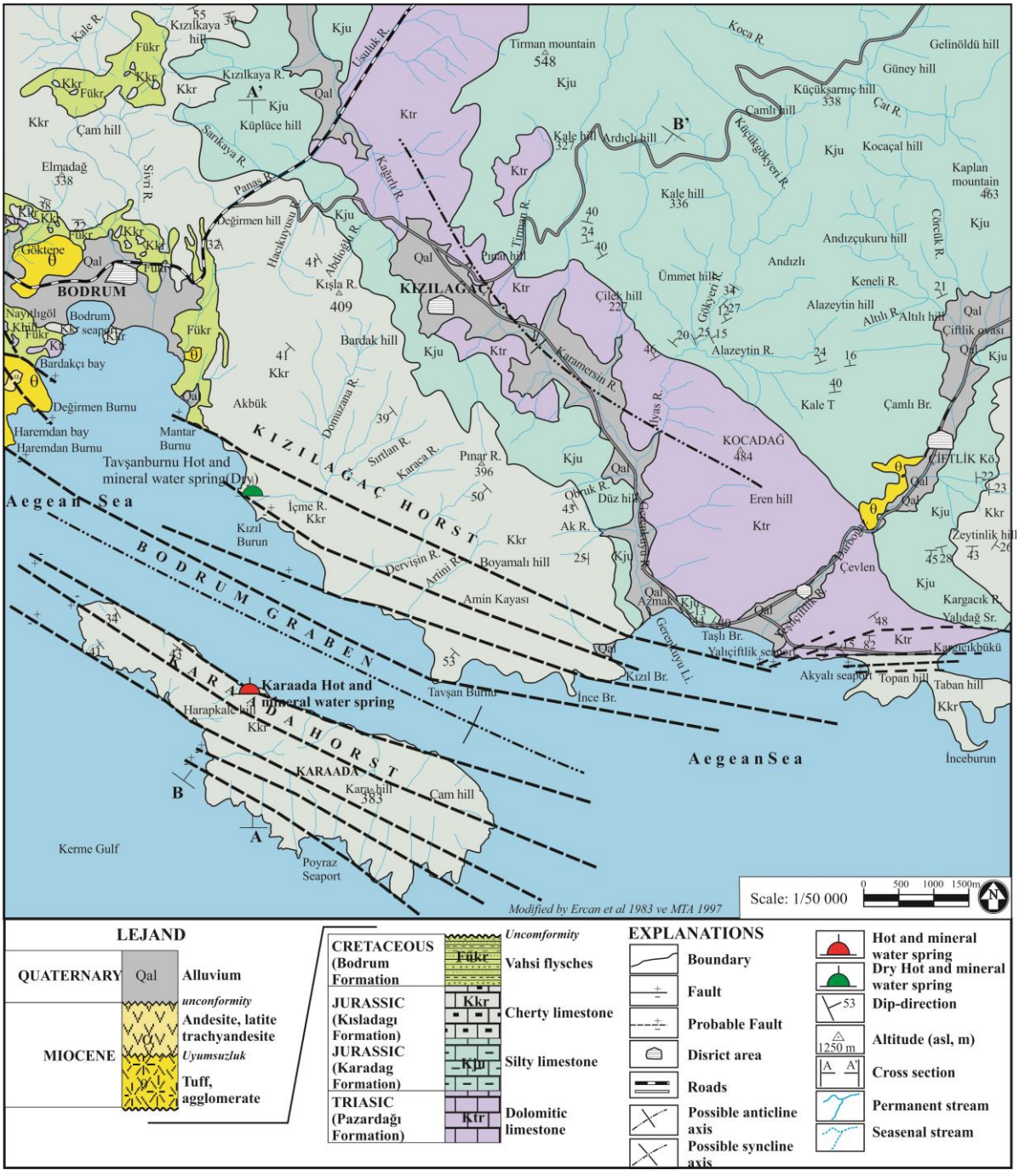

Figure 2: The geological map of Bodrum-Karaada and surrounding area.

The most important faults in the Bodrum-Karaada geothermal area are Karaada faults, Mantarburun fault Kizilburun fault, Inceburun fault and Tavsanburnu fault at the regional graben system (Figure 2, 3). Pazardagi formation (Kt) and Kisladagi formation (Kkr) are characterized by fractured and fissured zones and represent karst aquifers. The shallow alluvial aquifers have local importance. The magmatic rocks in the study area are originated from calcalkaline volcanism and the products of this volcanic activity such as andesite, latite, trachiandesite, and agglomerates (α, θ) are assessed as semi permeable units (Aquitard). Bodrum formation (Fukr) and Karadag formation (Kju) were identified as the impermeable units (Figure 2, 4).

3.1. Karaada hot and mineral water spring

Karaada hot and mineral water springs emerge from many points around the cave, along the fault lines which pass through the northern part of Karaada Island and have nearly E-W orientation (Figure 2, 4). The flowrate of the hot spring varies between 2 and 25 l/s, depending on the sea level fluctuations and the temperature was measured between 30-33°C (MTA, 2005; Caglar, 1947; Canik, 1983; Yenal et al. 1971; Piskin, 1983).

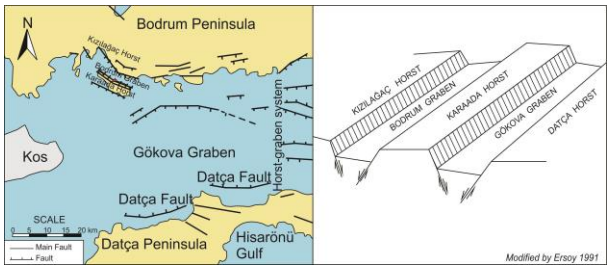

Figure 3: The fault line map of the study area and its surrounding area.

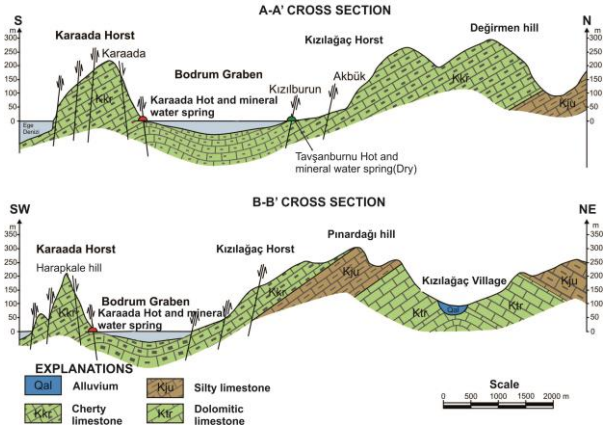

Figure 4: Hydrogeological cross-section of the study area along A-A" and B-B"

4. HYDROGEOCHEMISTRY

Water samples were taken in order to evaluate the hydrogeochemistry of the groundwater and the surface water, to understand the interaction of thermal system with cold groundwater system. In-situ measurements of physical and chemical parameters of waters were made two times in a year. A total of 13 water samples including seawater, spring water and cold water wells were taken from the field (Photo 1). The major ion analyses were conducted at the Hydrogeology Engineering Water Chemistry Laboratory in Hacettepe University. The isotope analyses were handled by TUBITAK MAM. The results of chemical analysis of the water samples taken from the study area are given in Table 1. Waters were classified into three groups based on hydrogeochemical properties by using Piper and Schoeller Diagrams (Figure 5 and 6). The first group in Piper Diagram consists of highly salty waters (Na-Cl type) including B-1, B-5, B-8, B-9 and B-10. The ionic characteristics of the wells of B-1 and B-5 are Na+K>Mg>Ca, $Cl>HCO_3>SO_4$ and for the samples B-8, B-9 and B-10 are Na+K>Mg>Ca, $Cl>SO_4>HCO_3+CO_3$. These cold waters are recharged from shallow groundwater circulation system (mixed with seawater) are classified as highly saline water group. The second group of waters is the mixed waters in the transition zone. The ionic characteristics of these waters are Na+K>Ca>Mg and $Cl>HCO_3+CO_3>SO_4$.

The third group of waters is of $CaCO_3$-HCO_3 type; consisting of the samples B-2, B-6, B-7, B-11, B-12 and B-13. The ionic characteristics of these waters are Ca>Mg>Na+K and $HCO_3+ CO_3>Cl>SO_4$.

According to Schoeller diagram, it is possible to classify the waters into three groups (Figure 6). The samples which are at the top of the diagram were classified as the first group (B-5, B-8, B-9 and B-10). The second group which is in the middle of the diagram has major ions Ca, HCO_3, Na and Cl suggesting that groundwater pumped from the wells is a mixture of sea water and freshwater (B-2, B-6, B-7, B-11, B-12 and B-13). The samples in the third group at the bottom represent shallow circulation and dominated by Ca, HCO_3. Besides limestone, dolomite, dolomitic limestone are among the geological units encountered in the recharge area of the wells.

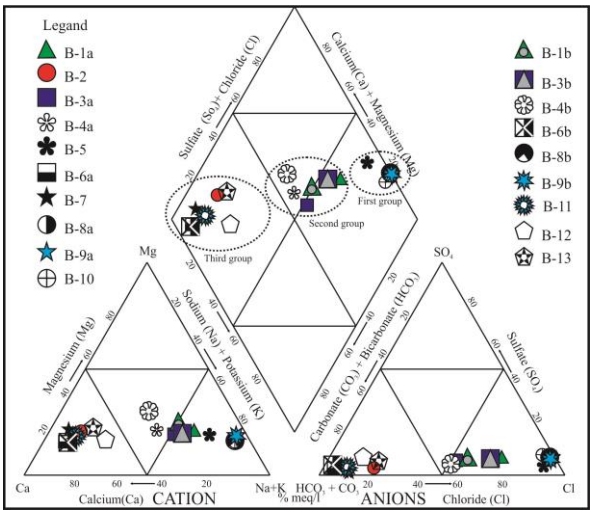

Figure 5: Piper diagram of the water samples in the study area

Table 1: Results of chemical analysis of the water samples collected from the study area (concentrations are ppm)

No	Name	pH	EC (µS/cm)	T (°C)	DO (mg/l)	Ca	Mg	Na	K	Cl	SO_4	HCO_3	CO_3	SiO_2
B-1a	Kizilagac well	7.15	3000	21.3	*	151,63	87,83	472,11	16,78	806,08	120,95	380	28,57	5.766
B-1b	Kizilagac well	7.20	1890	20.3	5.2	96,05	50,39	203,70	9,06	342,08	54,96	373	0,00	0.00
B-2	Hasan Huseyin drilling well	7.30	800	24.8	*	114,26	21,14	25,81	2,30	53,45	12,40	325	17,14	12.103
B-3a	Kizilagac sinkholes	8.10	1700	19.5	*	81,66	31,36	155,44	9,86	225,79	37,12	258	28,57	7.476
B-3b	Kizilagac sinkholes	7.38	1860	16.53	3.8	86,40	36,57	213,02	10,11	379,89	53,12	266	0,00	0.00
B-4a	Suheyla Enc drilling well	7.10	1500	20.1	*	119,11	42,91	165,03	7,75	269,40	42,73	351	20,00	8.08
B-4b	Suheyla Enc drilling well	9.4	817	18.1	*	58,71	31,82	68,19	3,62	138,32	19,29	100	49,18	18.59
B-5	Yaliciftlik well	8.00	6700	21.9	*	290,37	225,67	1455,70	40,36	3072,10	233,75	342	42,86	7.376
B-6a	Yenkuyu well	7.20	400	18.5	*	78,44	9,87	8,65	2,83	9,47	6,22	302	0,00	7.476
B-6b	Yenkuyu well	7.23	427	15.05	1.8	70,69	8,40	8,74	2,62	7,17	3,32	245	0,00	1.943
B-7	Osman Cavus drilling well	6.90	700	20.10	*	130,27	23,90	13,74	1,38	33,58	6,89	435	0,00	5.162
B-8a	Karaada Spring	6.20	61500	31.70	*	851,00	1174,43	11347,24	421,05	20282,28	2794,76	493	0,00	15.01
B-8b	Karaada Spring	6.42	57400	30.60	1.2	923,92	1284,72	11584,44	390,85	19226,41	2448,93	466	0,00	4.106
B-9a	Sea water	8.20	58600	23.30	*	556,01	1405,16	10871,88	403,00	18842,93	2661,16	69	40,00	0.032
B-9b	Sea water	8.31	58800	17.60	6.8	552,50	1459,23	11753,97	425,01	19587,06	2631,25	123	29,51	0.00
B-10	Tavsanburnu Spring ** (Dry)	7.90	10000	22.00	*	265,23	327,32	2835,50	130,09	5124,09	769,39	398	*	*
B-11	Yaliciftlik Koca well	7.50	670	15.73	6.2	100,11	14,82	18,12	4,89	22,45	13,10	330	0,00	2.094
B-12	Yaliciftlik Meydan well	7.15	3000	21.30	2	86,24	15,00	30,00	22,03	32,41	24,43	297	0,00	3.603
B-13	Yaliciftlik Yakabahce well	7.03	686	18.40	2.8	82,64	18,51	23,20	6,14	42,99	16,36	238	0,00	2.497

*Analysis could not be performed, ** Geothermal Inventory of Turkey (MTA, 2005), a= September 2004, b= April 2005.



Photo 1. Some of sample points in the study area

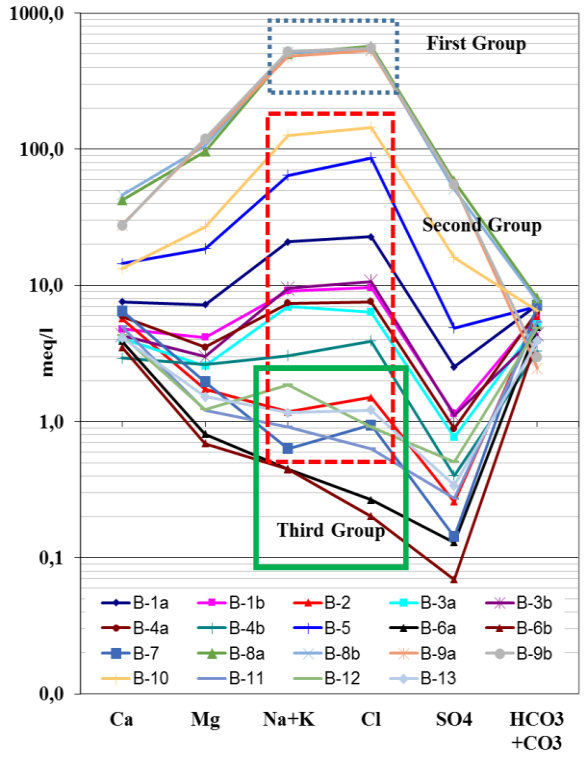

Figure 6: Schoeller diagram of the waters in the study area

4.1. Mixing of seawater

The seawater-groundwater mixing ratio in the study area was determined by the analyses of Cl concentration in the waters and the extent of seawater mixing can be seen in EC-Cl diagram (Figure 7). The diagram shows that Karaada hot and mineral spring is recharged mainly by sea water (98%) with limited groundwater (2%) contribution. Water samples from the study area are in the mixture line of the EC-Cl graph (Table 2; Figure 7).

Table 2: The contribution of sea water in each water point of the study area

No	pH	EC (µS/cm)	T (°C)	Cl (meq/l)	Amount sea water (%)
B-1a	7.15	3000	21.3	9.65	1.77
B-1b	7.20	1890	20.3	9.65	1.71
B-2	7.30	800	24.8	1.51	0.23
B-3a	8.10	1700	19.5	6.37	1.15
B-3b	7.38	1860	16.53	10.72	1.90
B-4a	7.10	1500	20.1	7.60	1.38
B-4b	9.75	817	18.1	3.90	0.65
B-5	8.00	6700	21.9	86.66	16.26
B-6a	7.20	400	18.5	0.27	0.00
B-6b	7.23	427	15.05	0.20	0.00
B-7	6.90	700	20.10	0.95	0.13
B-8a	6.42	58800	30.60	542.35	98.16
B-8b	8.20	58600	23.30	531.54	100.00
B-9a	8.31	58800	17.60	552.53	100.00
B-9b	7.90	10000	22.00	144.54	27.16
B-11	7.50	670	15.73	0.63	0.08
B-12	7.15	3000	21.30	0.91	0.13
B-13	7.03	686	18.40	1.21	0.18

4.2. Saturation of Mineral Waters

Karaada hot and mineral waters are generally saturated with respect to aragonite, calcite and dolomite as it is shown in the Saturation Index (SI) diagram (Figure 8; Phreeqc Interactive 2.8; Parkhurst and Appelo, 1999). This shows that main reservoir of the geothermal spring is the Pazardagi formation (Kt) and Kisladagi formation

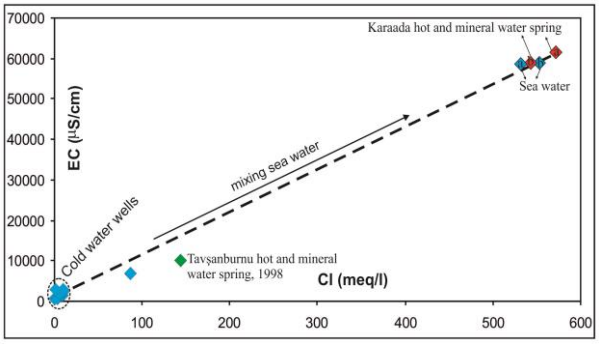

Figure 7: The EC-Cl graph of the waters in the study area

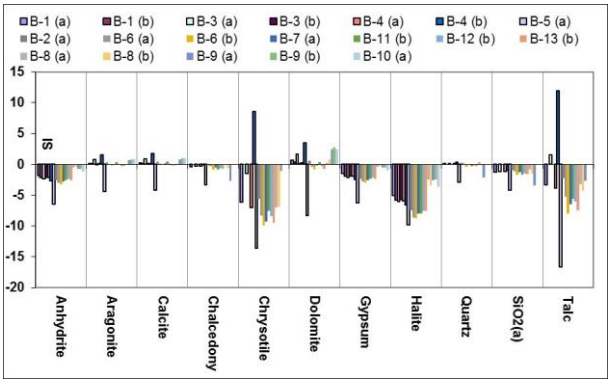

Figure 8: The Saturation Index diagram in the study area

4.3. Application of Geothermometers

The temperatures of the reservoir for the hot springs were estimated according to silica and cation geothermometers equilibrium. Temperature estimates by Silica geothermometers equations (Table 3) for the Karaada and Tavsanburnu (dry) hot water springs are given in Table 4. Silica concentration of the hot and mineral water spring in the study area was 15.01 ppm in September 2004, while in April 2005, it was reported as 4.11 ppm The estimated reservoir temperatures (according to Silica Geothermometers equilibrium) of Karaada hot spring range from 32-78°C. Cation geothermometers temperature estimates for the Karaada and Tavsanburnu hot water springs are given in Table 4. The estimated reservoir temperatures according to Cation Geothermometers equilibrium are much higher than the ones calculated using silica geothermometers. Reservoir of the hot springs is recharged mainly from seawater. Accordingly, the high cation concentration due to seawater mixing causes the estimated reservoir temperatures with cation geothermometers to be found higher than expected.

The hot waters of the study area were plotted on Na-K-Mg diagrams (Giggenbach, 1988). Tavsanburnu hot water is located in “immature” zone and Karaada hot water is located in partial equilibrium zone (Figure 9).

Thus, estimated temperatures by silica geothermometers are expected to be relatively more accurate.

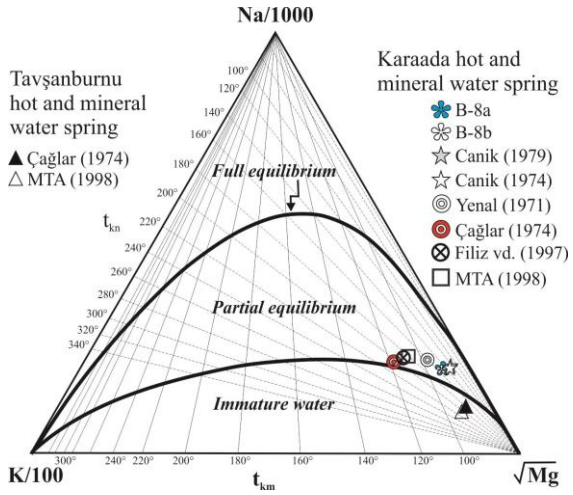

Figure 9: The Na-K-Mg diagram of Karaada and Tavsanburnu hot and mineral water

Table 3: Silica and cation Geothermometers equilibrium

	No	Geother-mometers	Geothermometers Equilibrium	Applica tion (°C)	Reference
Silica Geothermometers	1	Quartz	$t^{\circ}C = -42.2+0.28831S-3.6686x10^{-4}S^2+3.1665x10^{-7}S^3+77.034\log S$	25-900	Fournier and Potter (1982)
	2	Quartz (no steam loss)	$t^{\circ}C = (1309/(5.19 - \log S)) - 273.15$	25-250	Fournier (1977)
	3	Quartz (100 ° C max. steam loss)	$t^{\circ}C = (1522/(5.75 - \log S))-273.15$	25-250	Fournier (1977)
	4	Quartz	$t^{\circ}C = -55.3+0.36559S - 5.3954x10^{-4} S^2 + 5.5132x1\ 0^{-7} S^3+74.360\log S$	0-350	D'Amore and Arnorsson (2000)
Cation Geothermometers	1	N a - K	$t^{\circ}C =(856/(0.857+\log(Na/K)))-273.\ 15$	100-275	Truesdell(1976)
	2	N a - K	$t^{\circ}C =(833/(0.780+\log(Na/K)))-273.15$		Tonani (1980)
	3	N a - K	$t^{\circ}C =(933/(0.993+\log(Na/K)))-273.\ 15$	25 -250	Arnorsson et al. (1983)
	4	N a - K	$t^{\circ}C =(1319/(1.699+\log(Na/K)))-273.15$	250-350	Arnorsson et al. (1983)
	5	N a - K	$t^{\circ}C =(1217/(1.483+\log(Na/K)))-273.15$		Fournier(1979)
	6	N a - K	$t^{\circ}C =(1178/(1.470+\log(Na/K)))-273.15$		Nieva and Nieva (1987)
	7	N a - K	$t^{\circ}C =(1390/(1.750+\log(Na/K)))-273.\ 15$		Giggenbach (1988)
	8	Na-K[a]	$t^{\circ}C =733.6-770.551Y+378.189Y^2-95.753Y^3+9.544Y^4$	0-350	D'Amore and Arnorsson (2000)
	9	K - M g	$t^{\circ}C =(4410/(14-\log(K^2/Mg)))-273.15$		Giggenbach (1988)

Table 4: Estimated temperature of reservoir by Geothermometers

	Estimated temperature of reservoir by Silica Geothermometers (°C)								
	1	2	3	4					
Karaada spring	53	53	60	38					
Canik (1974)	48	49	56	32					
Caglar (1947)	75	74	78	60					
Tavsanburnu spring (MTA, 2005)	*	24	33	*					
	Estimated temperature of reservoir by Cation Geothermometers (°C)								
Reference	1	2	3	4	5	6	7	8	9
Karaada spring (a)	101	104	112	148	145	133	164	131	100
Karaada spring (b)	94	97	105	143	139	127	158	126	97
Canik (1979)	92	94	103	141	136	125	156	124	95
Canik (1974)	94	96	105	143	138	127	158	125	96
Yenal et al. (1971)	70	72	82	122	117	106	137	106	89
Caglar (1947)	103	106	114	150	146	135	165	132	102
Filiz et al. (1997)	114	118	125	159	156	144	175	142	106
MTA (2005)	147	151	156	185	184	171	201	168	116
Tavsanburnu spring (Caglar, 1947)	116	120	127	161	158	146	177	143	86
Tavsanburnu spring (MTA, 2005)	141	145	150	180	178	166	196	163	88

5. ENVIRONMENTAL ISOTOPE HYDROGEOLOGY

Isotope analyses as $\delta\ ^{18}O$, $\delta\ ^{2}H$ and ^{3}H were carried out on 9 samples which include seven samples from groundwater of Karaada geothermal field, one sample from Karaada hot spring and one sample from seawater. (Table 5; Figure 10-12). The uncertainty of the analysis for $\delta\ ^{2}H$ is ±‰ 1 and ±‰ 0.2 for $\delta\ ^{18}O$.

As it can be seen from the $\delta\ ^{18}O$-$\delta\ ^{2}H$ graph (Figure 10), all of the waters are located either in Eastern Mediterranean Water Line (Payne and Dincer, 1965) or on the Global Meteoric Water Line (Craig, 1961).

5.1. The relationship between $\delta\ ^{18}O$-Cl

The most of the waters in the study area are affected by seawater, based on $\delta\ ^{18}O$ value and Cl (mg/l) graphic (Figure 11).

Table 5: The stable isotope and tritium content of the samples in the study area

Sample No	T (°C)	pH	EC (µS/cm)	Altitude (asl, m)	$\delta^{18}O$ (‰ SMOW)	$\delta^{2}H$ (‰SMOW)	^{3}H (TU)
B-1	21.3	7.15	3000	17	-7.51	-31.76	3.24±0.31
B-2	24.8	7.3	800	129	-6	-29.15	2.86±0.29
B-3	19.5	8.1	1700	35	-6.37	-27.6	4.57±0.32
B-4	20.1	7.1	1500	110	-6.75	-29.06	2.63±0.29
B-5	21.9	8	6700	10	-1.69	-5.05	4.79±0.32
B-6	18.5	7.2	400	128	-7.94	-46.02	3.36±0.31
B-7	20.1	6.9	700	108	-7.09	-31.98	4.39±0.32
B-8 a	31.7	6.2	61500	0	0.17	8.54	0.61±0.25
B-8 b	30.6	6.42	57400	0	-	-	*0.14±0.20
B-9	23.3	8.2	58800	0	-0.74	8.09	1.27±0.25

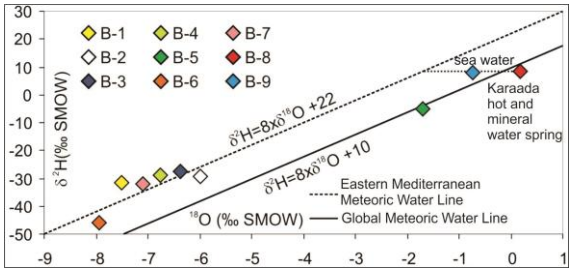

Figure 10: The graph of $\delta\ ^{18}O$-2H in the study area.

Water samples are located on the graph in three distinct groups (Figure 11). EC values less than 3,000 µS/cm were categorized as the first group. Sample B-5, which is significantly affected by seawater, is categorized as a second group. Karaada hot spring with EC values higher than 50,000 µS/cm forms the third group.

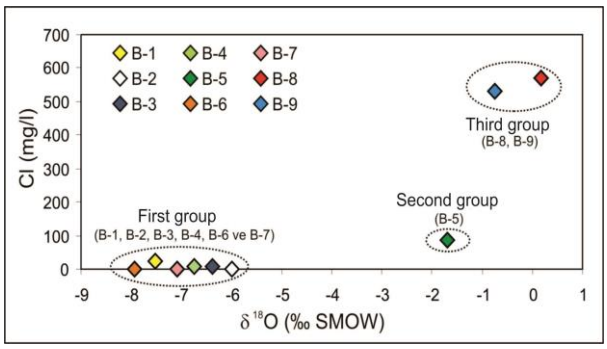

Figure 11: The δ ^{18}O-Cl graph of the waters in the study area

5.2. The relationship between δ ^{2}H-^{3}H

The most of the waters of the study area indicate a transition from fresh water to saline water as shown in the δ ^{2}H-^{3}H graph (Figure 12). As it can be seen from the graph, Yenkuyu well (B-6) is not affected from salinity in the study area. On the other hand, the Karaada hot and mineral spring water represents the most saline, hot and mineral spring water.

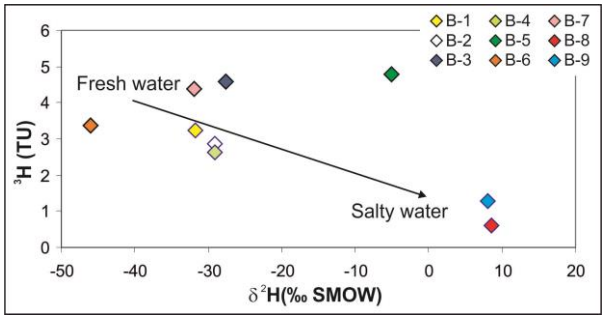

Figure 12: The δ ^{2}H-^{3}H graph of the waters

6. CONCEPTUAL HYDROTHERMAL MODEL

The conceptual hydrothermal model for the Karaada geothermal field were established, based on the results of this study (Figure 13). According to the hydrogeochemical and isotopic evaluations, it can be suggested that the aquifer in the region is comprised of limestone and dolomitic limestone. Since the Karaada hot spring is plotted on the meteoric water line near the seawater sample with an ^{18}O shift, it can be stated that the Karaada geothermal system is recharged by seawater and meteoric waters. The low ^{3}H and high δ^{18}O values in the Karaada hot and mineral spring suggest a deep groundwater flow system in the geothermal field. Based on these evaluations, the recharge-discharge mechanism of the hot spring is described. The hot spring is recharged mainly from seawater and from infiltration of precipitation on the permeable geological units in the area. The water becomes heated during its interaction with still hot magmatic rocks, which are the product of violent volcanic activity that took place after Miocene and in Quaternary additional regional geothermal gradient. Subsequently, the hot water rises along Karaada fault and emerges to the surface (fault controlled spring).

7. RESULTS AND DISCUSSION

According to the hydrogeochemical evaluations of the Karaada hot and mineral spring, the reservoir of the hot waters is determined as the rocks with high carbonate minerals content. Therefore, the possible hot water aquifers in the Karaada geothermal area are the Kisladagi and the Pazardagi Formations which are comprised of limestone and dolomitic limestones respectively. These karstic rocks, which have intense fractures and open conduits due to active tectonics, are regarded as highly permeable reservoir rocks. Possible caprocks of the hydrothermal system are the clayey and silty levels of the Bodrum Formation, which consists of interbedded sandstone, claystone and siltstone, and the Karadag formation, comprised of silty and marly limestone. Due to Kisladagi Formation being an open hydrothermal system, the temperature of the groundwater is expected in the range of 40-45°C as suggested by this study. On the other hand, higher temperatures (up to 60°C) can be expected in deeper parts below Pazardagi Formation. Therefore, to develop the reservoir and to investigate the possibility of pumping hot and mineral waters with higher temperature and flowrate, exploration wells should be drilled to these areas. According to the results of this study, it is safe to utilize Karaada hot and mineral waters in touristic facilities.

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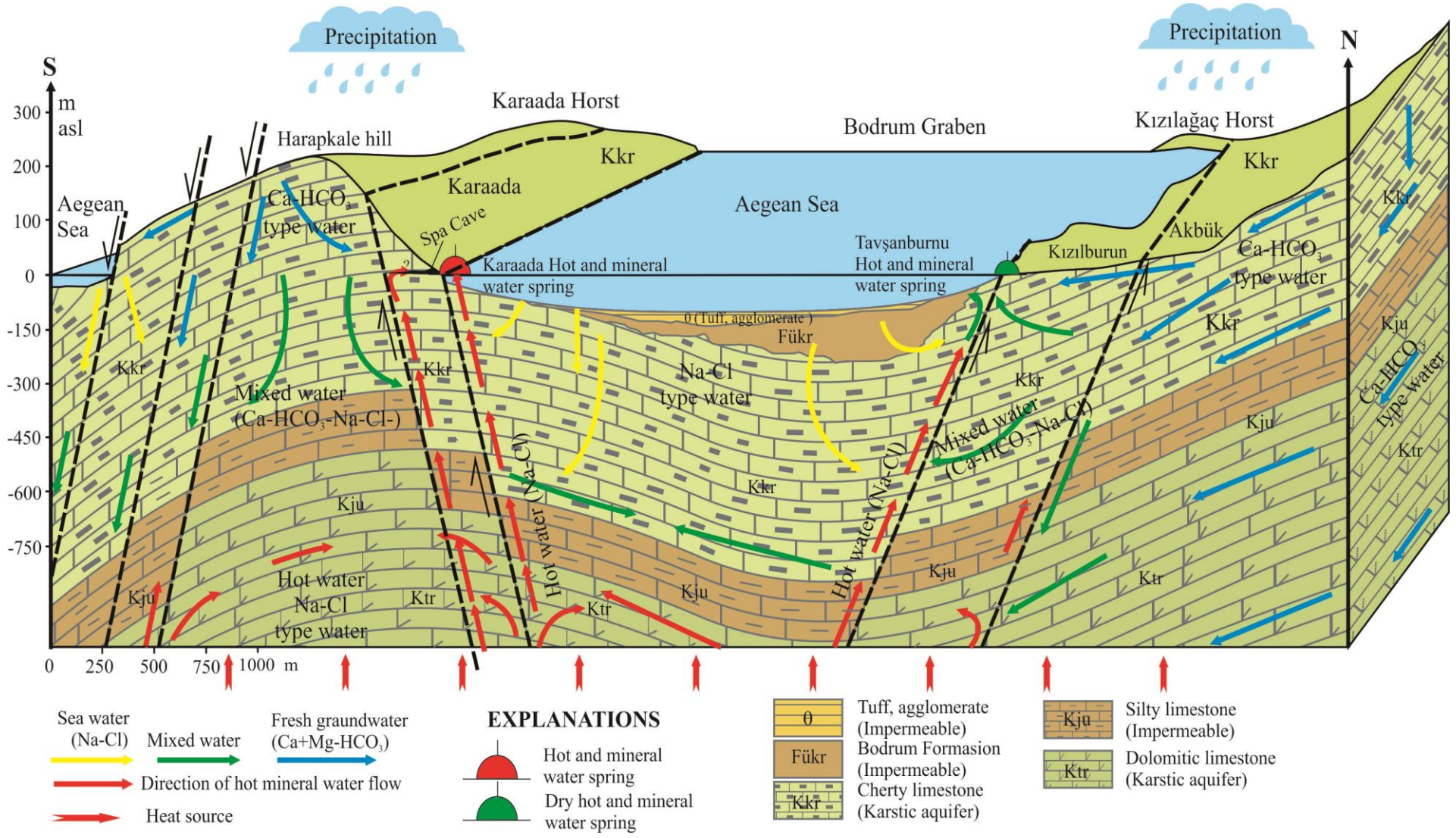

Figure 13: The conceptual hydrothermal model of the study area