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Chemical thermometry and origin of the Dalaki mineral springs, Bushehr Province, Iran

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Abstract

Combined geological, hydrological and hydrochemical studies and geothermometry of the Dalaki thermal springs on the margin of the Zagros Mountains, Iran, indicate that the source of the spring water is meteoric water, contaminated by oilfield brine and evaporites. The high water temperature is due mainly to circulation of the water in deep faults in a pull-apart basin northwest of the Gisakan anticline, and also to exothermic reactions. Contamination of the water also occurs in the pull-apart basin. Drilling wells in the karstic up-flow side of the Rahdar fault may help to avoid the contaminated water and have a major effect on water resource management in the area. A conceptual model for water circulation is presented.

Introduction

The Dalaki thermal springs, with water temperatures in the range of 30 to 38°C and an average total yield of 200 l/s, are located on the margin of the Zagros Mountains, east of the town of Dalaki (29°24' N and 51°17' E). The elevation of the springs is 130 meters above sea level. These perennial springs are part of a chain of thermal springs and seepages emerging along the Qatar-Kazerun fault. Thermal water in this area emerges mainly through three close springs (Fig. 1a): the Main, Zirepole and Damaneh springs, which discharge 100, 75 and 20 l/s respectively, occur at the contact between the carbonatic Asmari-Jahrom Formation and alluvium. The Dalaki springs have several distinctive characteristics, including a rotten-egg odour (probably from H_2S), channel floors lined with colourful precipitates, and oil droplets floating on the surface of the water.

Chemically the water is rich in chloride, sodium, sulfide and sulphate ions and is thus not suitable for even agricultural use. The spring waters

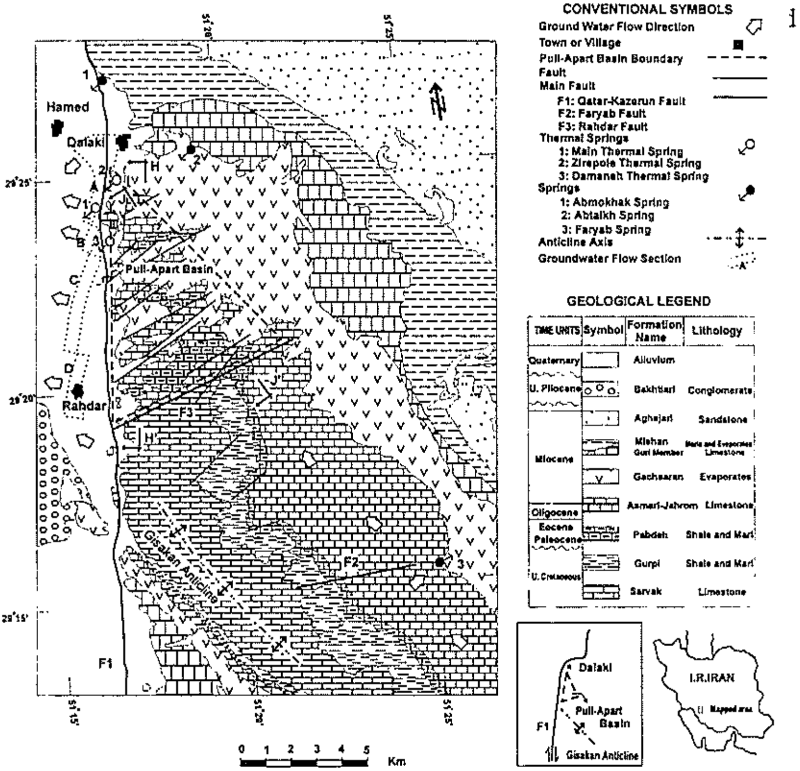
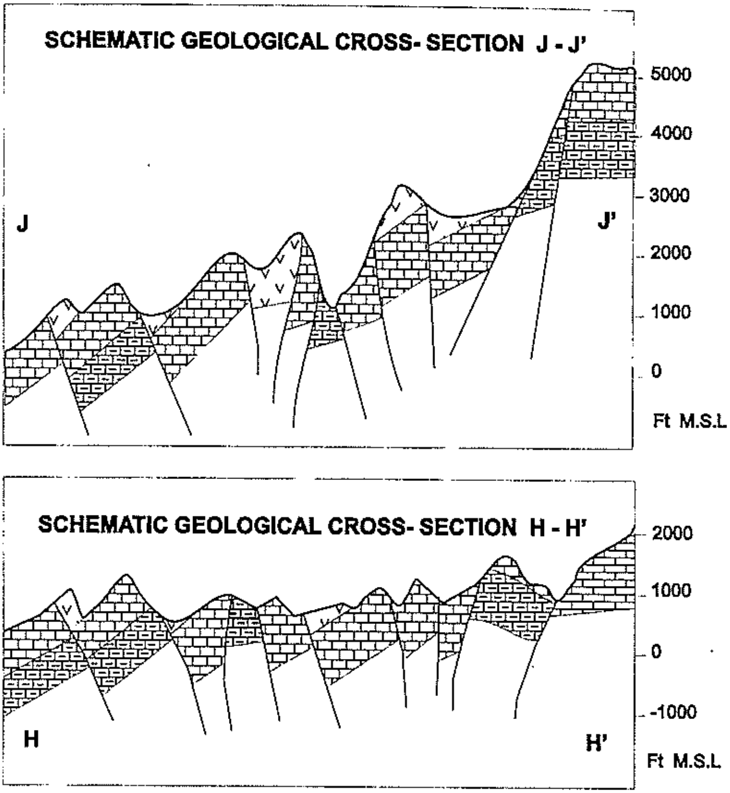


Figure 1a – Hydrogeological map of the Dalaki area and cross-sections (opposite) (compiled from Yekom Consultants with some modification).

contaminate farmlands and groundwater resources, and also damage downstream date-palm plantations. However, the springs are famous in the region for the remediation of skin diseases.

Previous studies of these springs failed to indicate their ultimate origin. Many attempts were made by governmental agencies and private companies to find water and to improve the water resources of this arid and warm region (Ministry of Energy, 1973; Yekom Consultants, 1980; Fars Regional Water Organization, 1984, 1988, 1993, 1994, 1997, 1999; Tavanab Consulting Engineers, 1996).



Figures 1b and 1c – cross-sections

The purpose of this study is to determine the physico-chemical characteristics of the Dalaki thermal springs, and also to identify their origin and source of contamination, which is considered to be the most important problem of water resource management in the area.

Geology

The geology of the Dalaki area has been described and mapped by the National Iranian Oil Operating Company (1973). The area lies southwest of the so-called simple folded belt of the Zagros mountain range (Falcon, 1974) (Fig. 1).

In the mountainous reaches, Bakhtiari Pleistocene conglomerate and Quaternary alluvium unconformably overlie upper Cretaceous to Pliocene sedimentary rocks. Pre-Cretaceous formations crop out east of the area, while the western part is covered by alluvium.

The carbonatic Turonian Sarvak and Oligocene-Miocene undifferentiated Asmari-Jahrom formations, and the calcareous Guri member of the marly Miocene Mishan formation, are all well developed karstic aquifers. They are separated by the impermeable shaly Maestrichtian Gurpi and evaporatic Miocene Gachsaran or Mishan formations (James and Wynd, 1965).

Structurally the north-south trending Qatar-Kazerun strike-slip regional fault divides the Dalaki area into two different parts: a western planar and an eastern mountainous region.

The eastern region is characterized by northwest-trending folded and faulted marine sedimentary rocks. The extension of these eastern structures is cut sharply at the boundary between the two regions. The Dalaki thermal springs emerge at the contact of the Gisakan anticline and this structural boundary (Fig. 1a).

The dextral Qatar-Kazerun fault bends to the right north of the town of Dalaki (Fig. 1a). This curvature, along with the eastward-trending extensional strike slip duplex and tulipe structure, result in the formation of a pull-apart basin near the curvature (Twiss and Moore, 1992), north of the Gisakan anticline.

The characteristics of this pull-apart basin, i.e. its topographic depression, extensional behaviour, and deeply penetrating conjugate faults, create an ideal site for the collection and deep circulation of groundwater. Drillings by Yekom Consultants(1980) confirm the existence of an appreciable amount of groundwater in this basin.

Thrust faulting on the southern flank of the Gisakan anticline has tilted the layers vertically, producing an asymmetric structure that catches most of the water and conducts it through the northern flank.

Hydrology

The main aquifers in the study area occur in the karstic Asmari-Jahrom and Sarvak formations, in the carbonatic Guri member of the Mishan formation, and also in the alluvium. Karstic aquifers cropping out on the Gisakan anticline direct their waters to the northwest and some of the aquifers discharge to the pull-apart basin. All the springs emerge where the Gisakan anticline and the pull-apart basin are cut by the Qatar-Kazerun fault. The water emerges mainly in the form of cold springs (Abmokhak and Abtalkh springs) and as thermal springs.

A good correlation exists between the rainfall and the average annual discharge of non-thermal springs in the area (Yekom Consultants, 1980). However, the average six-month precipitation of Sarqanat station (Fars Reginal Water Organization, 1978), and the average six-month discharge of the main thermal spring over a thirty-year period show a maximum correlation ($r = 0.93$) with a six-month lag time (Fig. 2). The reason for this delay time is probably the role of the pull-apart basin as a reservoir.

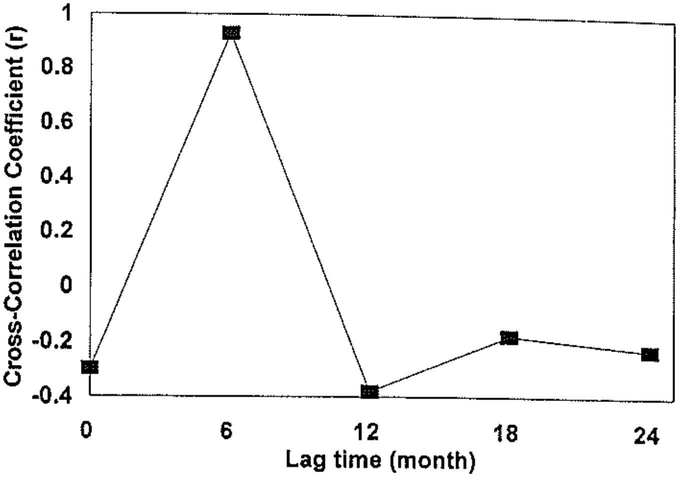


Figure 2 – Cross-correlation coefficient vs lag time between average six-month precipitation and average six-month discharge of the Main thermal spring.

The water balance for these springs is calculated for the year 1977-78. For this purpose the average surface and subsurface outflows from the pull-apart basin to the alluvium are calculated using isopotential maps and the discharge rate of the springs (Yekom Consultants, 1980). Subsurface outflow is calculated using the average three-month transmissivity and hydraulic gradient in four sections (A,B,C,D) along the contact of the pull-apart basin and the alluvium (Fig. 1a). The average surface and subsurface outflows are 165.3 and 287.8 l/s respectively. The springs' catchment area is calculated to have a surface area of 89 km^2. In measuring the catchment area, outcrops of Sarvak formation were disregarded because of their low elevation (Fig. 1c), their lack of groundwater to a depth of 270 m (Yekom Consultants, 1980) and their lack of direct contact with the alluvium. Using the recorded annual precipitation at Sarqanat station (Fars Reginal Water Organization, 1978), an isohyetal map (Tavanab Consulting Engineers, 1996), and also assuming an average infiltration coefficient of 36% for Bushehr province (Tavanab Consulting Engineers, 1996), the calculated infiltrated precipitation in the catchment area is 180 mm (equivalent to an average annual recharge of 507.9 l/s). The 36% infiltration coefficient of Bushehr province is calculated on the basis of the water balance in carbonatic formations. This rate of infiltration is in good agreement with the average total discharge of 453.1 l/s for the year 1977-78 and indicates the probable meteoric origin of all the area springs.

Hydrochemistry

Water resources were characterized for this study by sampling more than 40 thermal and one non-thermal water samples from the springs. Shapoor River, near the town of Dalaki, was also sampled. Two raw (unfiltered) samples were collected from each spring. The chemical analyses were carried out by Ghafoori (1988), Yekom Consultants (1980), and Fars Regional Water Organization (1984, 1988, 1993, 1994, 1997, 1999). The discharge rates of the springs, water temperature, electrical conductivity, pH, dissolved hydrogen sulfide and carbon dioxide were measured in the field, while calcium, potassium, magnesium, sodium, bicarbonate, sulphate and chloride ions were measured using standard titration methods. Silica was determined using a HACH DR/2000 spectrophotometer. The results are presented in Table 1.

The anion concentrations of the thermal springs in 1999 and the average anion concentrations of the Main thermal spring in different periods (Table 2) indicate a neutral chloride-type water for all the thermal springs (Fig. 3). The chemical composition of the thermal springs plots between that of seawater (W) and Shapoor River water (H), indicating mixing with connate water and anhydrite-bearing formations (Minissale, 1991). The similarity of the chemical compositions of the thermal springs suggests a single and chemically homogeneous source.

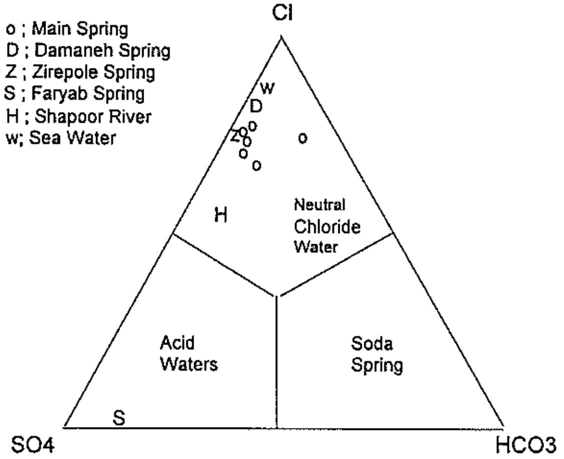


Figure 3 – Relative Cl, SO_4 and HCO_3 contents(mg/ kg) of spring waters.

Table 1 – Chemical composition of waters in the Dalaki area

Date		Month	epm				Sum of	epm			Sum of	
Month/Year	Ref	No.	Ca++	Mg++	Na+	K+	Cations	HCo3-	Cl-	So4--	Anions	Sio2 mg/
Main Spring												
12/1966	1	1	29	16	88	0	132	7	101	24	132	
5/1972	2	66	25	16	91	2	134	7	111	20	138	
5/1972	2	66	30	22	134	4	190	5	23		191	
Ave. 1972			28	19	113	3	162	6	67	20	164	
7/1977	3	128	25	17	93	3	137	4	111	22	137	
9/1977	3	130	25	17	94	2	138	5	113	19	137	
11/1977	3	132	28	20	113	2	162	25	111	26	161	
12/1977	3	133	26	16	104	2	148	4	116	28	148	
1/1978	3	134	22	23	96	1	142	3	111	25	139	
2/1978	3	135	22	21	100	2	145	5	115	23	143	
3/1978	3	136	29	15	92	1	137	5	111	29	145	
4/1978	3	137	28	16	93	1	137	6	116	23	145	
5/1978	3	138	26	20	111	1	158	4	121	25	150	
6/1978	3	139	30	17	104	1	151	2	126	26	154	
7/1978	3	140	30	13	98	1	142	3	108	30	141	
Ave. 77-78			26	18	100	1	145	6	114	25	145	
12/1990		289	33	13	71	3	120	9	90	23	122	
1/1993		314	30	15	132	1	177	8	152	24	183	
3/1993	4	316	26	21	88	1	135	3	122	25	150	
4/1993		317	28	20	83	3	133	7	123	22	151	
6/1993	4	319	24	23	106	2	155	6	132	20	157	
9/1993	4	322	29	20	93	1	142	5	123	20	148	
12/1993	4	325	29	14	95	3	140	2	123	25	150	
3/1994	4	328	30	19	93	3	144	6	124	20	149	
6/1994	4	331	30	18	80	1	128	5	119	15	139	
10/1994	4	335	26	21	106	2	155	6	121	20	147	
Ave. 93-94			28	19	97	2	145	5	126	21	153	
5/1997	4	366	35	25	90	2	152	6	123	20	149	
8/1997	4	369	30	19	98	2	149	4	125	23	152	
1/1998	4	374	29	24	90	0	143	4	124	21	149	
5/1998	4	378	28	21	72	2	123	3	119	30	152	
11/1998	4	384	30	22	109	2	163	6	127	23	156	
5/1999	4	390	34	34	104	3	174	3	136	25	164	
8/1999	4	393	32	19	101	1	152	4	126	28	158	
11/1999		396	34	20	105	2	161	8	130	29	168	12
11/1999	4	396	21	30	104	3	157	3	128	28	158	
Ave. 97-99			30	24	97	2	153	5	126	25	156	12
Zirepole Spring												
9/1977	3	130	25	18	94	2	138	4	114	21	139	
11/1977	3	132	31	18	103	2	154	4	112	22	138	
12/1977	3	133	29	14	107	2	152	4	120	28	152	
1/1978	3	134	25	20	96	1	142	3	111	24	138	
2/1978	3	135	22	22	105	1	150	3	118	27	148	
3/1978	3	136	30	15	98	1	144	3	115	36	154	
4/1978	3	137	27	18	98	2	145	3	119	27	150	
5/198	3	138	30	17	104	1	152	3	124	26	153	
6/1978	3	139	32	16	109	1	158	2	131	26	159	
7/1978	3	140	30	10	108	2	150	3	115	30	148	
Ave. 77-78			28	17	102	1	148	3	118	27	148	
Damaneh Spring												
11/1999		396	45	25	211	5	286	2	209	33	244	13
Sea Water	5		20	106	468	10	605	2	546	56	604	
Shapoor River												
11/1999		396	10	9	25	0	44	3	34	16	53	10
Faryab Spring												
8/1999	4	393	11	8	1	0	20	2	1	17	19	

1. Ghafoori (1988) 2. Ministry of Water and Electricity (1973) 3. Yekom Consultants (1980)
4. Fars Regional Water Organization (1984, 1988, 1993, 1994, 1997, 1999) 5. Fournier & Potter II (1979)

Table 2 – Chemical and physical data of Dalaki area waters

Month/Year	Ref	H_2s mg/l	CO_2 mg/l	Water Temp. T °C	Air Temp. T °C	pH	T.D.S.	Error %	EC micro s	Dis-charge l/s
Main Spring										
12/1966	1	142		37	27	6	8098	0	11600	100
5/1972	2		55	35	33	7	8549	3	11260	180
5/1972	2		55	33	31	7	12001	1	14710	98
Ave. 1972			55	34	32	7	10275	2	12985	139
7/1997	3					7	8090	0	11090	70
9/1977	3					7	8490	1	12520	56
11/1977	3					7	10020	1	10830	41
12/1977	3					7	9020	0	10170	29
1/1978	3					7	6688	2	10290	47
2/1978	3					7	8610	1	10260	41
3/1978	3					7	8750	6	10350	57
4/1978	3					7	9788	6	12170	83
5/1978	3					7	8895	5	13500	70
6/1978	3					7	9935	2	13140	59
7/1978	3					7	9595	1	13550	62
Ave. 77-78						7	8898	2	11625	56
12/1990		189	125	35	28	7	9269	2	13610	78
1/1993		198	8	36	20	7	6097	4	9960	55
3/1993	4					7	8256	11	14027	
4/1993		310	7	38	21	7	8218	13	13695	142
6/1993	4					7	9042	2	14457	
9/1993	4					7	8300	4	13469	74
12/1993	4					7	8350	7	13695	60
3/1994	4					7	8673	4	13695	82
6/1994	4					7	7900	9	13320	67
10/1994	4					7	8700	5	14028	66
Ave. 93-94		254	8	37	21	7	8171	6	13372	78
5/1997	4					7	8720	3	14440	108
8/1997	4					7	8729	2	13825	101
1/1998	4					7	8457	4	13274	101
5/1998	4					7	7967	21	13044	137
11/1998	4					7	9245	4	14130	67
5/1999	4					7	9815	6	14130	
8/1999	4					7	8950	4	13748	
11/1999		288	3	35		7	8013	4	12500	127
11/1999	4					7	9143	1	14130	142
Ave. 97-99		288	3	35		7	8782	5	13691	112
Zirepole Spring										
9/1977	3					7	8510	0	12360	68
11/1977	3					7	10230	11	11360	65
12/1977	3					7	9200	0	10360	57
1/1978	3					8	8400	3	10780	92
2/1978	3					7	8800	2	10260	67
3/1978	3					7	8616	7	13030	64
4/1978	3					7	9948	3	12630	96
5/1978	3					7	9150	1	13940	86
6/1978	3					7	10300	1	13370	74
7/1978	3					8	9815	2	13410	71
Ave. 77-78						7	9305	3	12150	74
Damaneh Spring										
11/1999				35		8	12756	16	19900	18
Sea Water	5					7	9143	0	14130	142
Shapoor River										
11/1999				20		7	2859	18	4460	
Faryab Spring										
8/1999	4					7	8950	3	13748	

1. Ghafoori (1988) 2. Ministry of Water and Electricity (1973) 3. Yekom Consultants (1980)
4. Fars Regional Water Organization (1984, 1988, 1993, 1994, 1997, 1999) 5. Fournier & Potter (1979)

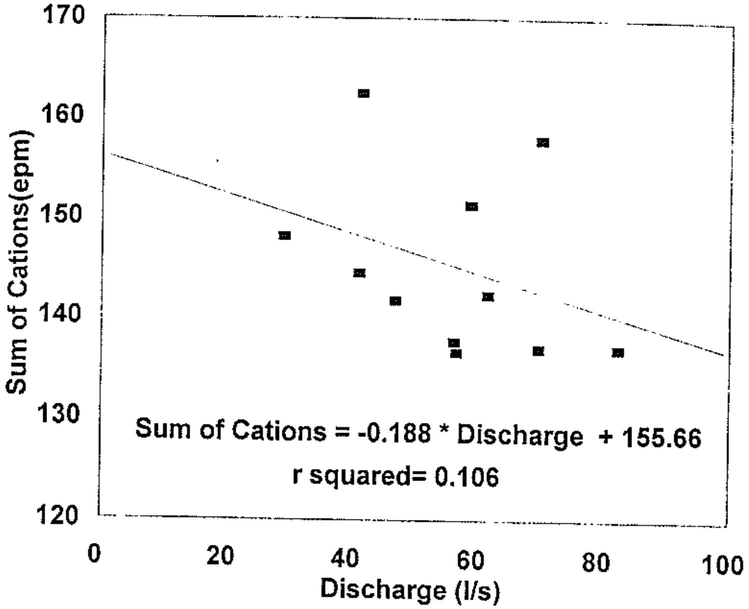


Figure 4 – Sum of cations vs discharge of the Main spring in the period 1977-1978.

The variation in constituent concentrations with time and with the springs' discharge shows that the water temperature and the amount of dissolved CO_2 do not change significantly with increasing discharge rate, while the sum of cations and the amount of dissolved H_2S shows a weak decrease and increase with discharge respectively (Figs. 4 and 5). These variations probably indicate the diluting effect of increasing meteoric recharge. The low concentration of dissolved CO_2 suggests a probable absence of deep ascending fluids (Minissale, 1991). A lack of variation in relative constituent concentrations with time (Fig. 6) is also noticeable.

Floating oil droplets on the surface of the thermal springs, especially in high discharge seasons, and high concentration of Mg^{2+} (>0.082 epm) indicate that the thermal springs are contaminated with brine connate waters from near-by oil fields (Fournier and Potter, 1979).

The chemical composition of the sampled wells and the electric conductivity map (Yekom Consultants, 1980) show that alluvial water constituent concentrations decrease with increasing distance from the pull-apart basin.

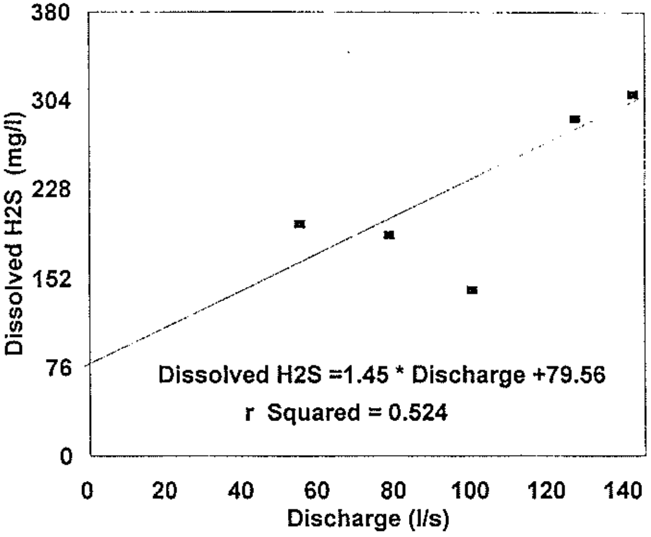


Figure 5 – Dissolved H_2S vs discharge of the Main thermal spring.

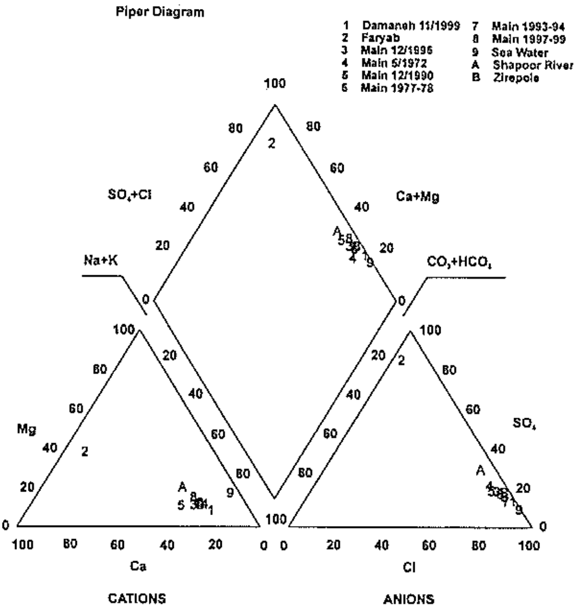


Figure 6 – Piper diagram of different water resources listed in Table 1.

Geothermometry

The chemical composition of the springs' water is used to estimate the reservoir temperature. For this reason the solubilities and exchange reactions of various solid phases must be taken into account. This hydrochemical method is commonly used to identify thermal anomalies on both local and regional scales. Chemical equilibria variables include temperature, pressure and, to a lesser extent, solubility. Of these, temperature is the dominant factor in controlling reservoir fluid composition.

The calculated subsurface reservoir temperatures within the study area, using various chemical geothermometers, are presented in Table 3.

Table 3 – Chemical geothermometry of springs' water in different intervals.

Date Month/Year Ref.	T kc (1)	T NKC (4)	Corr. Mg. (5)	T SiO$_2$ (3)	 (2)	 (1)	MI (1)	CO$_2$ mg/l (1)	P(CO$_2$) Atm (1)
Main Spring									
12/1966								4.1	0.001
Ave. 1972	127.8	184.6	35.7				1.9	10.7	0.026
Ave. 1977-78	85.7	146.4	36.7				2.0	3.4	0.007
12/1990	116.7	192.1	65.2				1.8	6.7	0.002
Ave. 1993-94	90.6	155.6	38.3				2.0	5.6	0.013
Ave. 1997-99	91.9	158.2	33.0	46.7	18.2	16.2	1.9	5.4	0.012
Zirepole Spring									
Ave. 1977-78	86.7	147.7	41.8				2.0	3.0	0.005
Damaneh Spring									
11/1999	146.9	190.3	47.5	48.5	20.0	18.2	2.0	19.3	0.049
Sea Water	199.4	203.4	2.9				2.1	158.0	0.371
Shapoor River									
11/199	-18.8	88.3	32.8	39.2	10.9	8.2	1.9	0.7	0.000
Faryab Spring									
8/1999	-28.0	179.2	28.4				0.5	0.8	0.000

1. Giggenbach (1980) 2. Amorsson (1993) 3. Fournier (1977) 4. Forcella (1982)
5. Fournier and Potter (1979)

Using Ca-Mg-K as a geothermometer (Giggenbach, 1980) gives an average reservoir temperature of 120°C (T kc in Table 3). In calcium geothermometers the calculated temperature depends on the partial pressure of CO_2 and the method is more accurate where calcite and non-acidic waters are involved. The dissolved CO_2 was therefore calculated using cation concentrations (Table 3). This shows a good agreement between the calculated and the observed concentrations of dissolved CO_2 especially in the intervals 1993-94 and 1997-99. On the other hand, in the Ca-Mg-K diagram (Fig. 7) the thermal waters plot in the field of calcite formation.

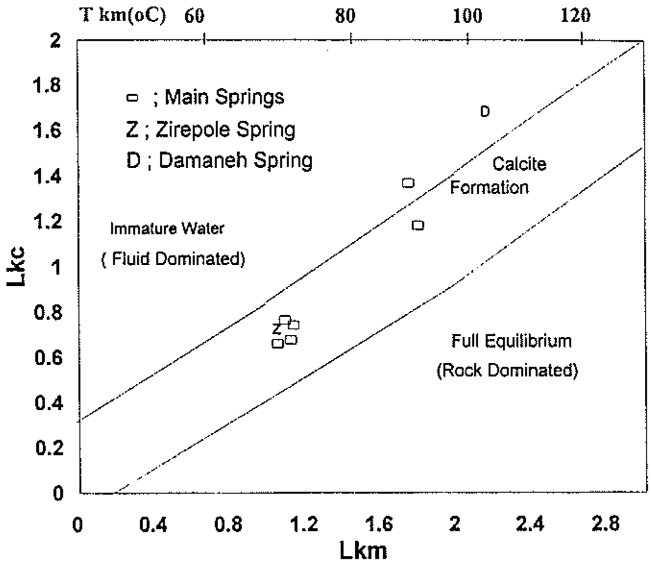


Figure 7 – Plots of the Ca-Mg-K geothermometer for the thermal springs listed in Table 3. Note that most waters are in equilibrium with calcite formations [Lkc = log(c^2_{K+} / c_{Ca2+}), Lkm = log (c^2_{K+}/ c_{Mg2+}); Giggenbach, 1980].

According to Fournier and Potter (1979), the Na-K-Ca estimated reservoir temperature (T NKC in Table 3) of thermal waters rich in Mg^{2+} (>0.082 epm) must be corrected for magnesium. Magnesium-corrected temperatures of spring samples are listed in Table 3. The average magnesium-corrected reservoir temperature is 42.6°C. This temperature is considerably lower than the temperature obtained by the Na-K-Ca geothermometer (168°C), and probably is the result of mixing of Dalaki's thermal water with oilfield brines.

Using an SiO_2 geothermometer (Fournier, 1973; Arnorsson, 1983; Forcella, 1982), an average reservoir temperature of 25°C is obtained. The silica geothermometer is highly useful in hydrothermal systems of neutral to slightly acidic pH. Quartz solubility is only slightly affected by the presence of other dissolved solids (Ellis and Mahon, 1977).

Discussion

A conceptual model for the Dalaki geothermal system can be constructed using combined hydrologic, lithologic and geochemical studies (Fig. 8). In

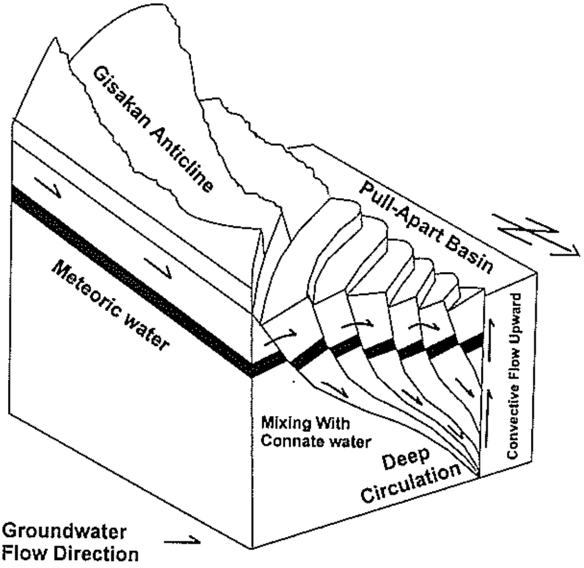


Figure 8 – Conceptual model of the Dalaki geothermal system.

such a model the circulation path of the thermal water can be summarized as follows:

1) The thermal waters originate from dominantly carbonatic meteoric water, mixed effectively with connate oilfield brines.
2) Deep circulation and exothermic chemical reactions increase the water temperature within the deeply faulted pull-apart basin.
3) The outflow of the thermal springs is convective up the main fault and then gravitational; the springs emerge in the topographically lowest part of the pull-apart basin.

The geology and hydrology of the Gisakan anticline confirm the meteoric origin of the thermal springs and their contamination by connate oil field brines. The major evidences includes:

a) equilibrium between the thermal water and calcite formation in the Ca-Mg-K geothermometer, indicating a karstic origin for the thermal springs;
b) low concentration of dissolved $CO_{2,}$ indicating the absence of deep ascending fluids;

c) low reservoir temperature calculated using an SiO_2 and magnesium-corrected geothermometer (i.e. near ambient temperature);
d) the pull-apart basin water balance in the interval 1977- 1978;
e) good correlation between average six-month precipitation and average six-month springs yield, with a six-month lag time.

The increase in water temperature is probably due to exothermic chemical reactions and the deep circulation of the water. The occurrence of floating oil droplets, high concentration of magnesium ions, and alternating outcrops of Gachsaran and Asmari-Jahrom formation all confirm the existence of local oil traps in the pull-apart basin. Where petroleum fluids come into contact with sulphatic strata, the following exothermic reaction can take place (Hill, 1987):

$$SO_{4\,(S)} + C_nH_{m\,(L)} \longrightarrow CO_{2\,(G)} + H_2O_{\,(L)} + H_2S_{\,(G)}$$

According to Kempe and Thode (1968), bacteria can play an important role in this reaction.

The extensional pull-apart basin and deep faults cause the collection and deep circulation of water, especially near the Qatar-Kazerun fault. The circulation of mixed meteoric and connate water occurs to the depths where normal gradient temperatures reach 30-38°C.

The outflow of the thermal springs is convective up the main fault and then gravitational. The springs emerge in the topographically lowest part of the pull-apart basin along the main fault.

An isopotential and isoelectrical conductivity map (Yekom Consultants, 1980) shows that the pull-apart basin is the single most important source of contamination of alluvial water in the Dalaki region and the adjacent Borazjan plain.

Conclusion

Geological, hydrological, chemical and geothermal studies indicate the mixed meteoric/karstic/connate origin of the Dalaki thermal springs. The data also indicate that the increase in water temperature is mainly due to circulation of water in deep faults and to exothermic chemical reactions. The outflow of the thermal springs is convective and gravitational.

Chemically, Dalaki thermal springs are of neutral chloride type with high concentration of sulfides and sulphates. The high concentration of chloride, sulfide and sulphate is due to mixing of meteoric karstic water with connate brines, and also reaction with evaporitic host rocks. The chemical composition of upstream springs (e.g. Faryab spring) illustrate that the karstic water of the Gisakan anticline is of better quality before it enters the pull-apart basin. High quality karstic waters of the Gisakan anticline can be intercepted by drilling karstic wells in the Asmari-Jahrom formation before the water reaches the Rahdar fault and the pull-apart basin.

By drilling wells two goals can be achieved: access to a high-quality water supply with an approximate yield of 200 l/s; and avoiding contaminated alluvial ground water.

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