Proceedings World Geothermal Congress 2010
Bali, Indonesia, 25-29 April 2010

The Geochemistry of the Thermal Fluids of Qotur Valley Geothermal Field, Nw-Iran

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Keywords: Iran, geothermal, Qotur valley, geochemistry, hot springs

ABSTRACT

A reservoir temperature of 94-139 ºC is indicated by the silica geothermometers. Gas analysis shows that the main component of the gases sampled from bubbling springs is CO_2 at up to 99 mole percent. The waters are predominantly meteoric and of local origin, with a slight $\delta^{18}O$ shift which may be an indication that: hydrothermal alteration reactions have long ceased to take place; aquifer temperatures are not high; or good permeability exists.The Cl-SO_4-HCO_3 ternary diagram shows that the thermal waters have high HCO_3 suggesting that they are peripheral waters or having a high proportion of cold groundwater. In the Na-K-Mg triangular diagram, thermal waters are located in the immature waters area and near the Mg corner indicating that the thermal waters are immature and also, they have a high proportion of cold groundwater. There are nearly linear relationships between SiO_2, B, Na, ^2H, ^{18}O and the conservative element Cl that constitute evidence that mixing has occurred. The Log(Q/K) diagrams appear to have a similar pattern for all samples and do not show a clear convergence to the zero saturation index by any group of minerals.

1. INTRODUCTION

Geothermal exploration in north and northwest Iran was started by the Iran's Ministry of Energy in 1975. A contract was made between the Iranian Ministry of Energy and the Electric Company of Italy (ENEL). The Khoy-Maku, Mount Sabalan, Sahand and Damavand regions were proposed for detailed geothermal exploration (Figure 1). The Qotur valley geothermal field is within the Khoy-Maku geothermal region in northwest of Iran and about 35 km to the southwest of Khoy.

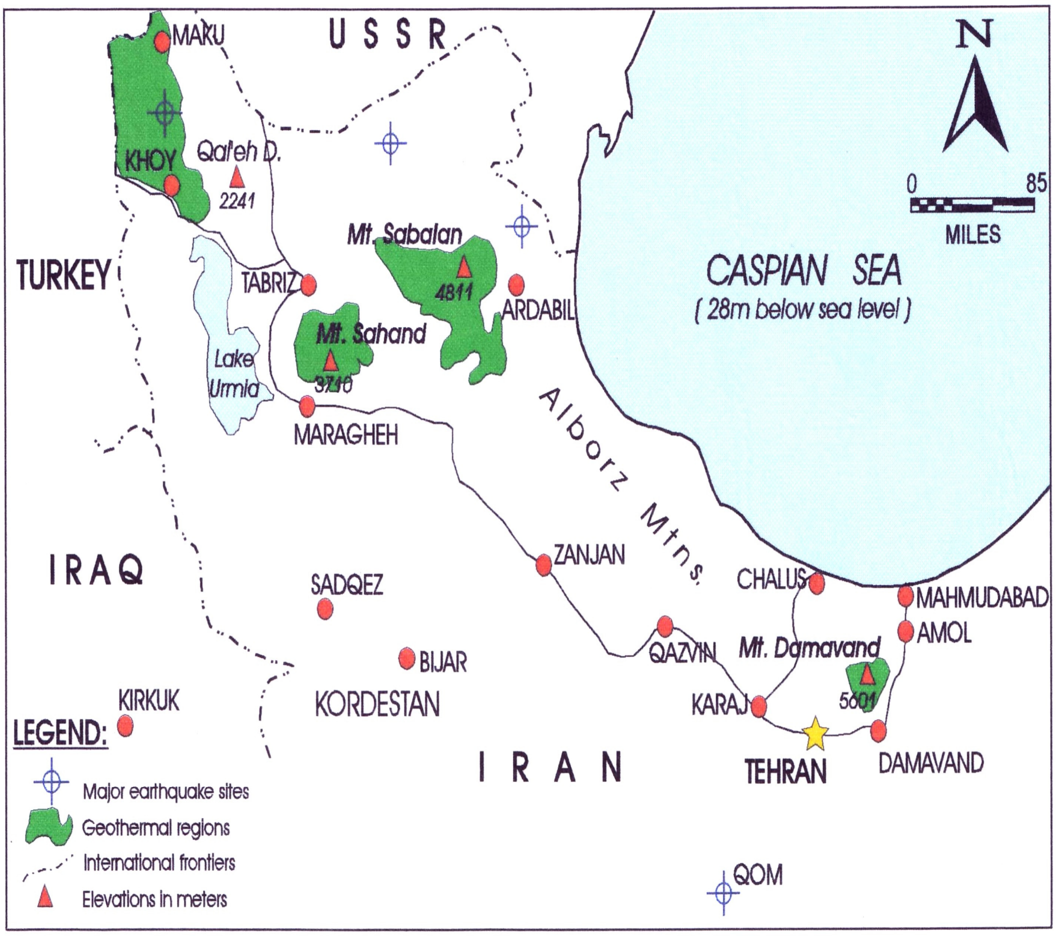

Figure 1: Geothermal prospects in north and northwestern Iran

In 1997 carried out a detailed investigation program in the Qotur valley geothermal field. The investigations were undertaken by the Centre for Renewable Energy Research and Application (CRERA) of Iran which were carried out under a contract by a Company from Philippines, PNOC-EDC. These investigations were limited to Qotur valley and were based on geological, geophysical and geochemical surveys. The study area lies in the Ophiolitic and coloured melange zone of Maku-Khoy and can be regarded as one tectonic block bounded by the Zari fault in the southwest, the Qaragol –Qotur fault in the southeast and the Gheleligh lineament in the northeast. The line of Tertiary volcanics and Cretaceous metamorphics running from Zari in the south to Mt. Averin in the north define the western limit of this block. From old to recent time four main units of the rocks and sediments namely Cretaceous metamorphics, Tertiary sediments, Tertiary volcanics and quaternary deposits have been identified in this area (Figure 2).

2. CHARACTERISTICS OF THERMAL FLUIDS

2.1 Sampling and analysis

A total of 14 acidified and 18 unacidified water samples were taken from the study area for chemical analysis for the following parameters and elements; Mg, Ca, K, Na, Cl, SO_4, HCO_3, SiO_2, Fe, B, H_2S, NH_3, CO_2 and pH. Results of the chemical analysis of water samples from Qotur valley geothermal field are listed in Table 1. A further 24 50-ml samples were taken for the determination of δD and $\delta^{18}O$ in water (Table3). Using evacuated glass flasks containing NaOH solution, 6 gas samples were successfully taken from the hot springs of Dareh khan bala and cold springs at Saray, all of Qotur valley. These were analyzed for CO_2 and H_2S using potentiometry and for CH_4, H_2, N_2, Ar, He and O_2 using gas chromatography(Table 2). At Dareh khan bala, two attempts were made to obtain a non-alkaline sample for NH_3 analysis but these were not successful as the springs do not discharge steam; only gas bubbles emanate through the water discharge. In any case, most of the NH_3 should have been absorbed in the water phase as the pH in situ (using pH paper) is either neutral or slightly acidic.

2.2 Triangular diagrams

2.2.1 Cl-SO_4-HCO_3 Triangular Diagram

The Cl-SO_4-HCO_3 triangular diagram is commonly used for classification of the thermal fluids. The diagram indicates several types of thermal fluids such as immature waters, peripheral waters, volcanic and steam-heated waters. Figure 3 shows the Cl-SO_4-HCO_3 triangular diagram for the samples from the Qotur valley area. All samples plot in the peripheral waters region, close to the HCO_3 corner, which may indicate mixing with cold groundwater. The HCO_3 rich waters are may due to presence of carbonate rocks in the area.

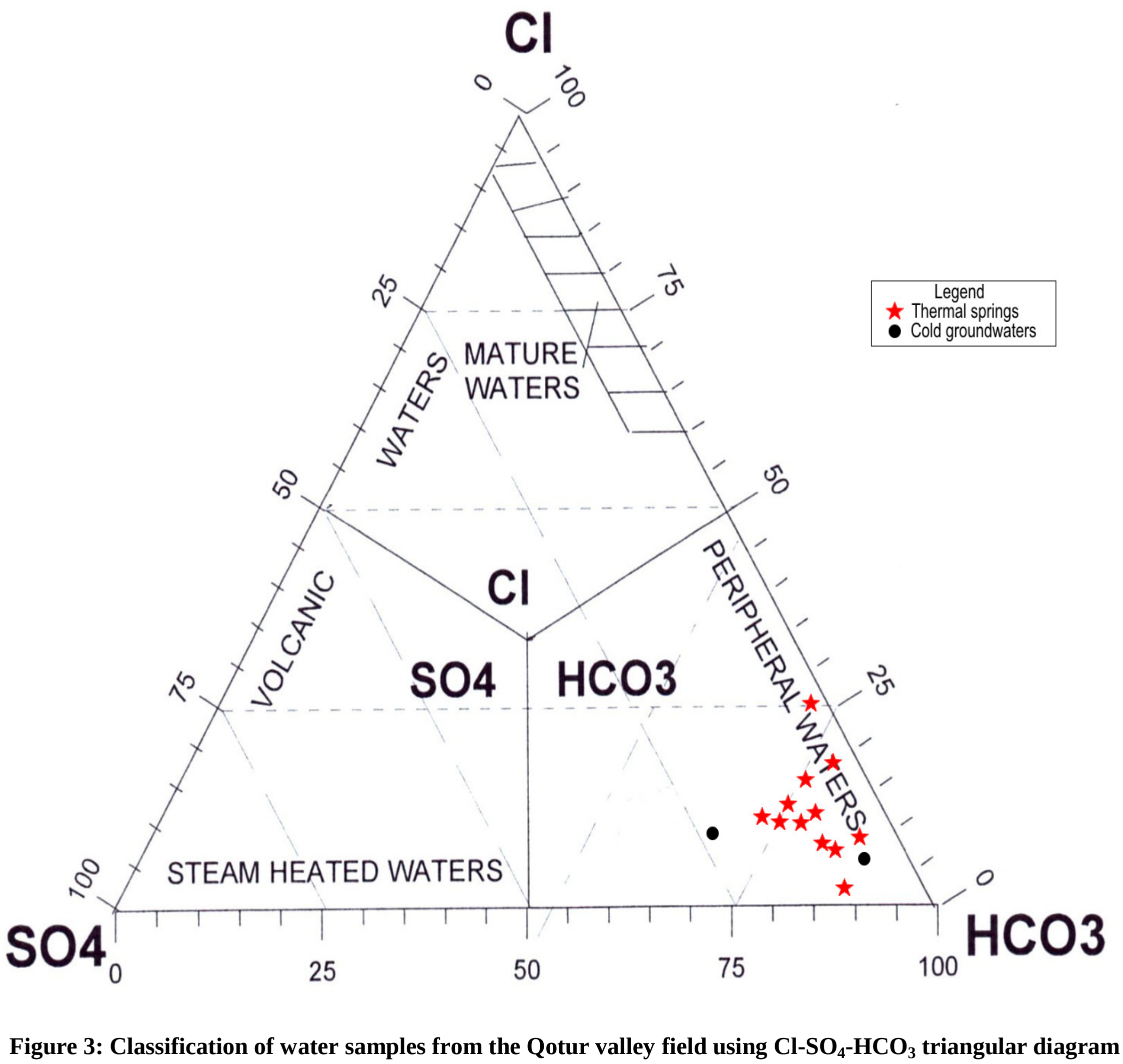

Figure 3: Classification of water samples from the Qotur valley field using Cl-SO_4-HCO_3 triangular diagram

2.2.2 Na-K-Mg triangular diagram

This diagram is used to evaluate equilibrium between the hot waters and rocks at depth and to estimate reservoir temperature. Figure 4 Shows that all the geothermal fluids plot in the area of immature waters, close to the Mg corner of the diagram, indicating that the thermal fluids are a mixture of cold groundwater. The relatively high Mg concentration is due to the bicarbonate type of the water. Therefore, it is difficult to estimate reservoir temperature.

2.3 Origin of the geothermal fluids

By using isotopic techniques, Craig (1961) proved that the meteoric origin of geothermal waters can be determined by measuring the hydrogen and oxygen isotopic compositions of steam and water from geothermal fields. Figure 5 shows the relationship between δD and $\delta^{18}O$ values of water from the study area. All the points plot close to the Local meteoric water line as shown in Figure 5 implying that the waters are meteoric, with a slight $\delta^{18}O$ shift which may be an indication that: hydrothermal alteration reactions have long ceased to take place; aquifer temperatures are not high; or good permeability exists.

2.4 Binary plots of Cl Versus Other Constituents

Mixing of geothermal water with cold groundwater in shallow zones of hydrothermal systems appears to be common. As shown in Figure 6 some of the hot spring waters in the study area may be mixed with cold groundwater. Mixing of two kinds of waters can be shown on a plot of one conservative species against another. A nearly linear relationship between Cl and SiO_2, B, and Na in Figure 6 is evidence that the ascending water might have been mixed with cold groundwaters in upflow zones.

2.5 Log (Q/K) Diagrams

The WATCH and SOLVEQ computer programs were used to make the log (Q/K) diagrams. The log (Q/K) vs. temperature diagrams for the samples Kh-3, Kh-4, and Kh-7 are shown in Figure 7. The diagrams appear to have a similar pattern for these samples and do not show a clear convergence to the zero saturation index by any group of minerals. In other words, the fluid is not in equilibrium with the mineral assemblage at a certain temperature. The saturation index (SI) can be applied for the scaling potential. The fluid is oversaturated with respect to calcite at all temperatures. The other important mineral found to be supersaturated at most temperature range is goethite, which represents the low-temperature iron oxides. In the area several springs are surrounded by travertine and iron oxides deposits which verified the above mentioned.

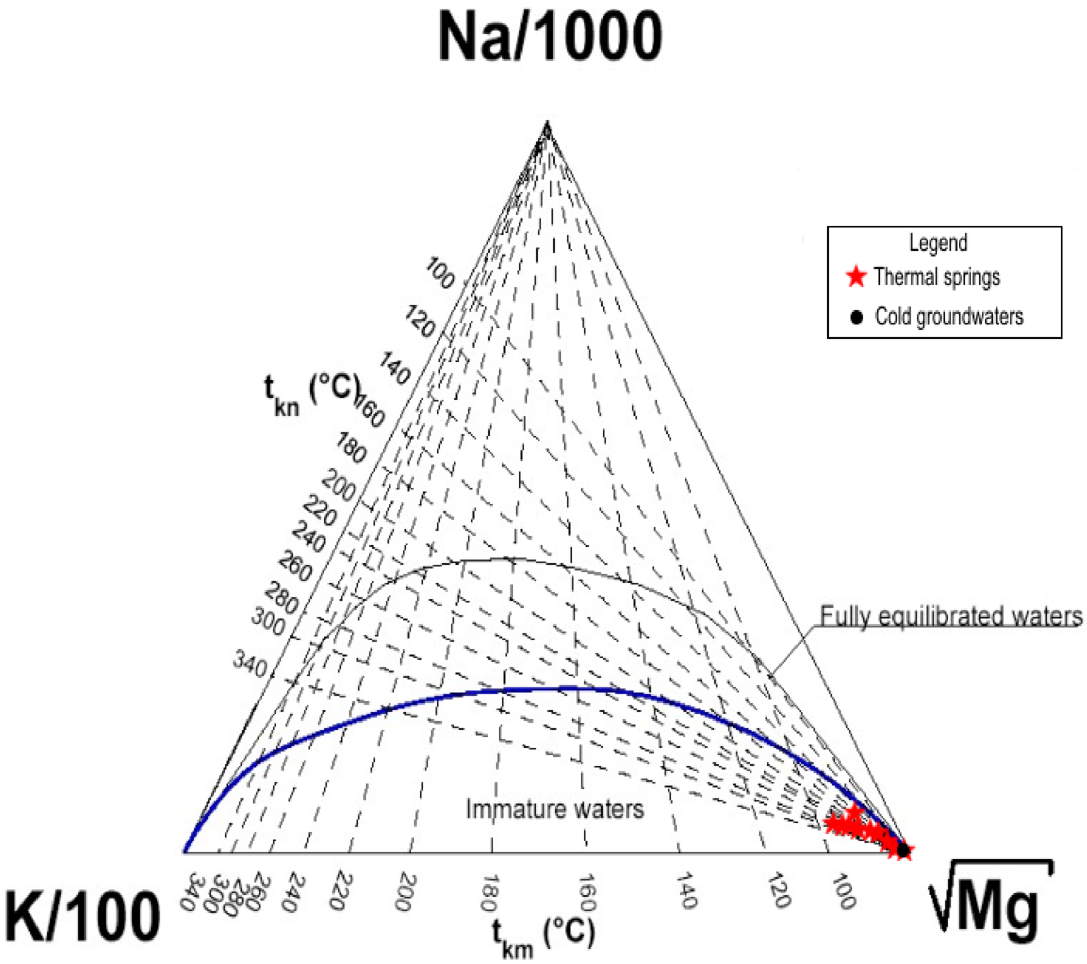

Figure 4: The Na-K-Mg triangular diagram for water samples from the Qotur valley field

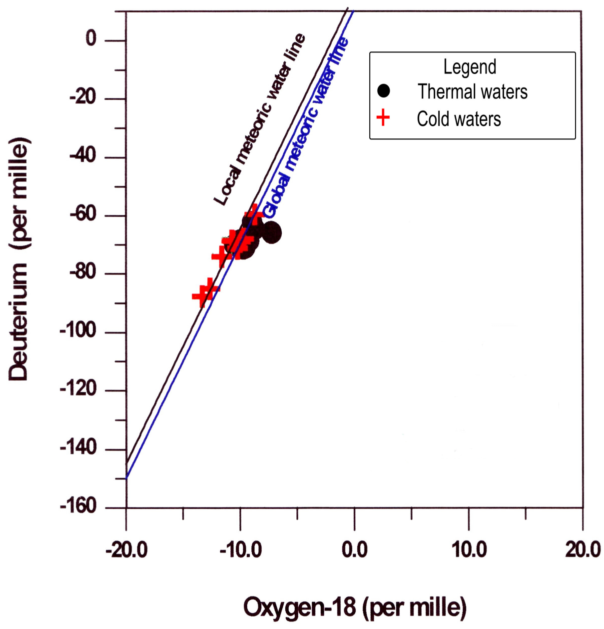

Figure 5: δ18O vs. δD for the Qotur valley waters (Ruaya, 1997)

2.6 Geothermometry

The Na-K geothermometer temperature can be regarded as unrealistic as they fall out of range for the respective geothermometers (Truesdell, 1976, Arnorsson et al., 1983). In figure 4 samples plot in an area which is not suitable for Na-K geothermometry. The results for solute geothermometers show that temperatures estimated by the Na-K-Ca geothermometer are much higher (Table 4) than those estimated by silica geothermometers; this could possibly be due to calcium carbonate deposition during upflow which prevents aqueous K and Na from interacting with the country rock (Fournier and Trusdell, 1973). High values are also expected in Mg^{2+} rich waters. Nevertheless the Na-K-Ca geothermometer is best used for waters above 200 ºC, waters that give anomalously high calculated temperatures when applying the Na-K method.

The calculated chalcedony geothermometer temperatures for the hot springs give the lowest subsurface temperature of 94ºC for sample Kh-6 and the highest temperature of 112ºC for sample Kh-4; the quartz geothermometer gives the lowest subsurface temperature of 122ºC for sample Kh-6 and the highest temperature of 139ºC for sample Kh-4; the Na-K geothermometer indicates the lowest subsurface temperature of 252ºC for sample Kh-7 and the highest temperature of 268ºC for sample Kh-3; while the Na-K-Ca geothermometer suggests 203ºC for sample Kh-7 as the lowest subsurface temperature and the highest temperature of 225ºC for sample Kh-3.

Table 4: The results of solute geothermometers; values marked with ? are thought to be unrealistic

Sample	T_{quartz} (°C)	$T_{Chalcedony}$ (°C)	T_{Na-K} (°C)	$T_{Na-K-Ca}$ (°C)
Kh- 3	132	104	268 ?	225 ?
Kh- 4	139	112	258 ?	216 ?
Kh- 6	122	94	255 ?	204 ?
Kh- 7	125	97	252 ?	203 ?

3. CONCLUSION

Considering the major anions, the geothermal waters of the Qotur valley are bicarbonate waters. Also, with reference to the major cations, the geothermal waters are classified as immature waters. The log (Q/K) vs. temperature diagrams appear to have a similar pattern for selected samples and do not show a clear convergence to the zero saturation index by any group of minerals. In other words, the fluid is not in equilibrium with the mineral assemblage at a certain temperature. The waters are meteoric, with a slight $\delta^{18}O$ shift which may be an indication that: hydrothermal alteration reactions have long ceased to take place; aquifer temperatures are not high; or good permeability exists. Estimations of subsurface temperatures with silica geothermometers predict temperatures in the range of 94-139 ºC.

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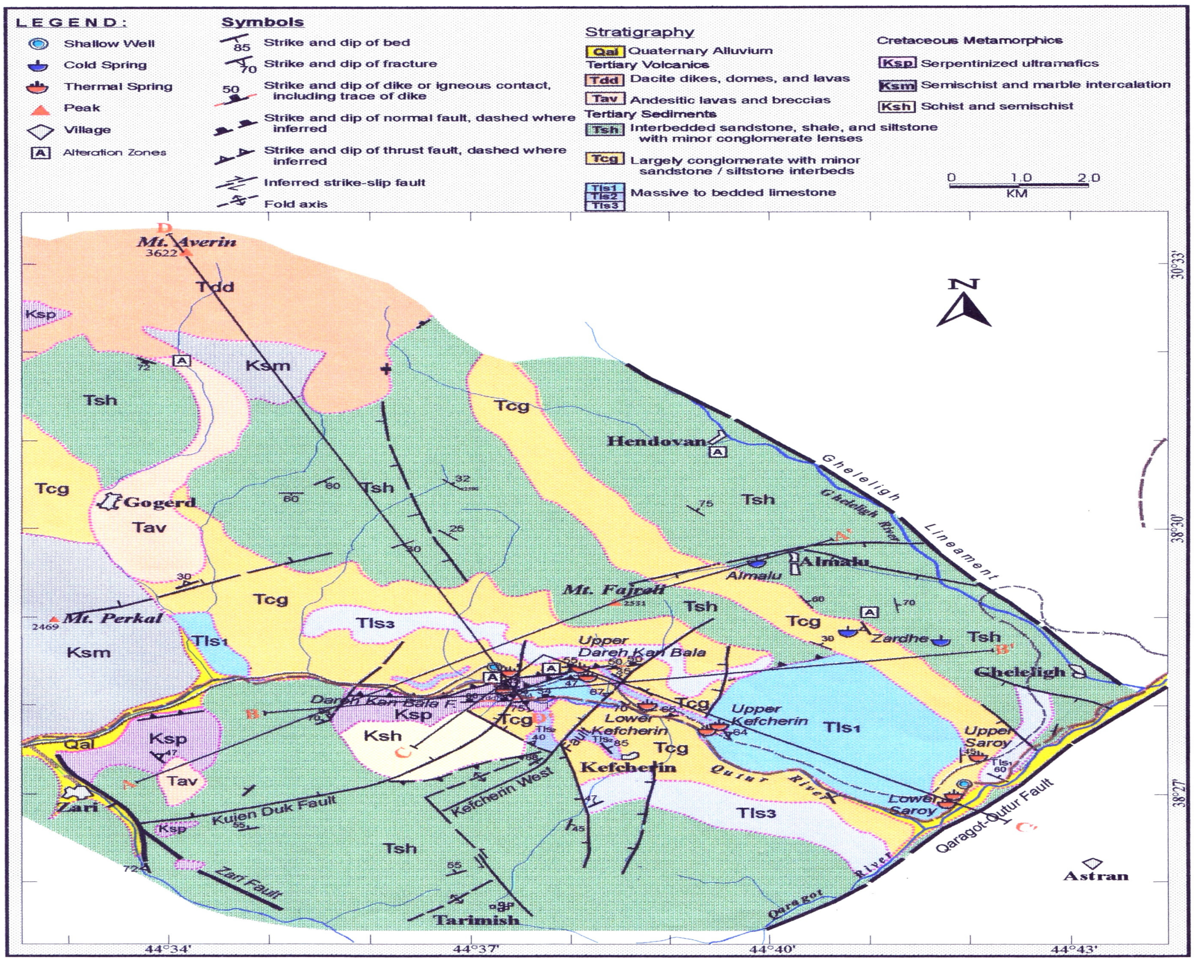

Figure 2: Geological map of the Qotur valley geothermal field (Delfin and Zaide-Delfin, 1997)

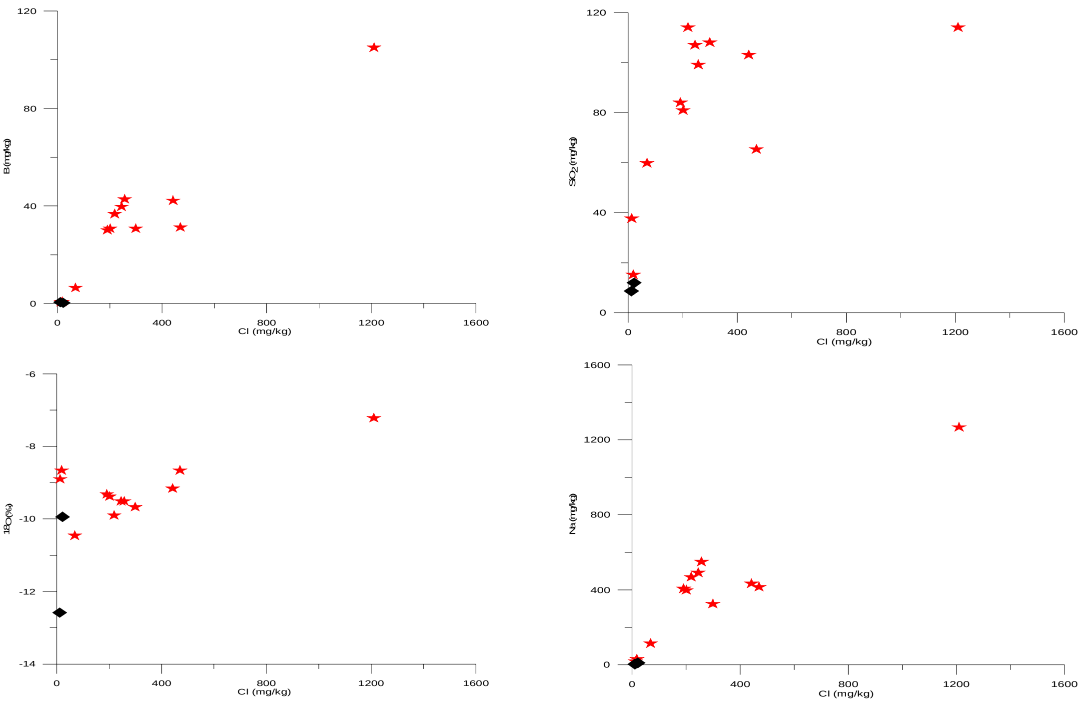

Figure 6: Binary plots of Cl vs. B, SiO_2, Na, and ^{18}O; dots are cold groundwaters and stars are thermal waters

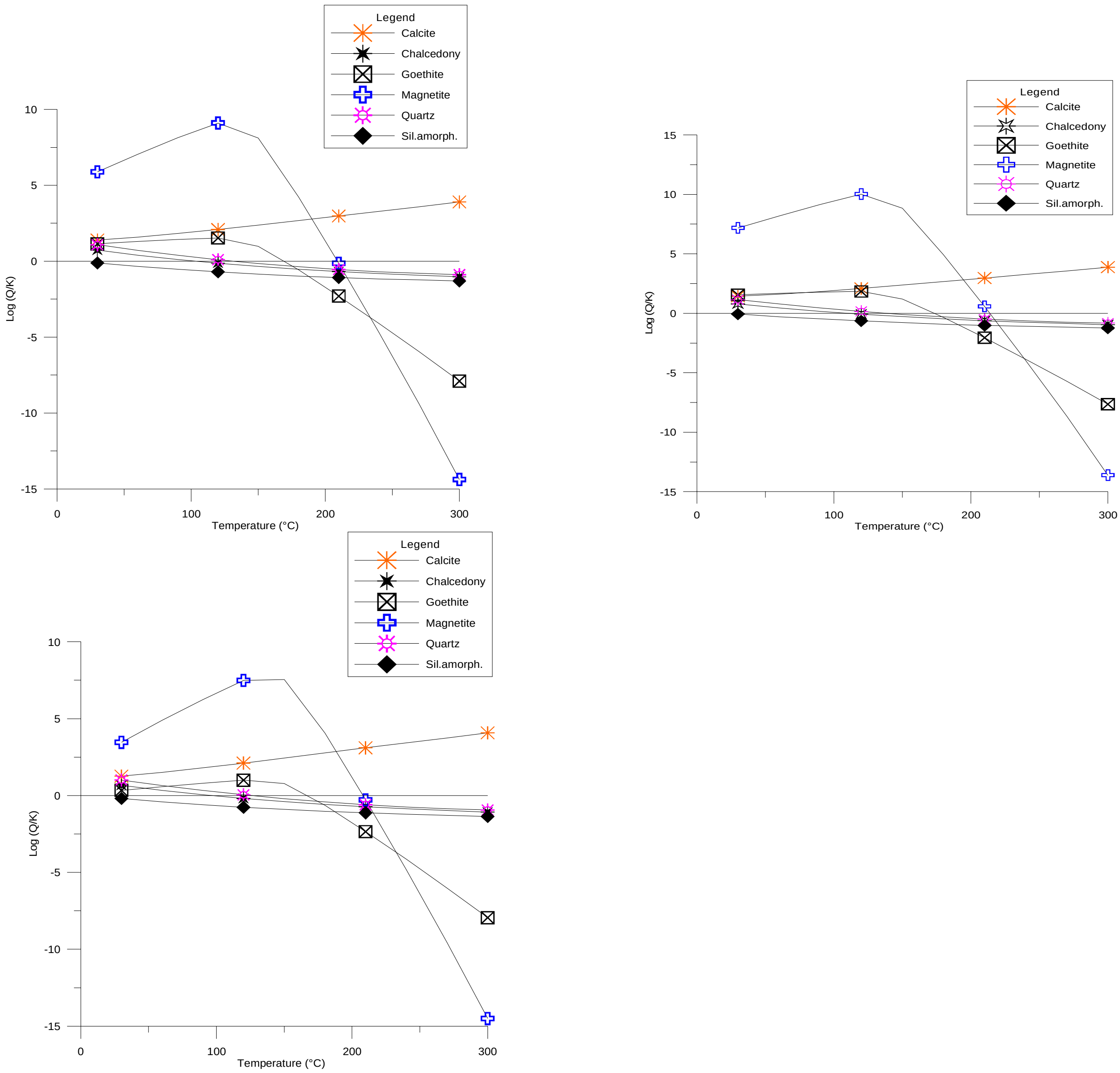

Figure 7: Log (Q/K) Diagram; The above graphs from right to left are relative to sample Kh- 3 and Kh- 4 respectively, and one down is relative to sample Kh-7

Table 1: Chemical analysis of water samples from Qotur valley geothermal field (mg/kg) ; data from Ruaya, 1997

Sample	Location	Water temp. (°C)	pH	Na	K	Ca	Mg	Fe	Cl	B	SO_4	HCO_3	CO_2t	H_2S	NH_3	SiO_2
Kh-1	Dareh khan cold sp.	13	7.70	415	37.0	417	131	2.96	470	31.2	77.8	1977	1671	10.2	1.90	65.3
Kh-2	Well No.1	19	7.95	433	46.0	326	193	0.01	442	42.2	198	2102	1623	10.1	3.32	103
Kh-3	Dareh khan bala sp.-1	50	7.94	549	102	100	83.2	0.39	257	42.8	260	1541	1134	10.8	5.59	99.1
Kh-4	Dareh khan bala sp.-2	54	8.04	468	79.8	99.1	76.6	0.67	219	36.7	268	1326	972	10.4	5.23	114
Kh-5	Dareh khan bala sp.-3	51	7.94	491	96.0	112	94.0	0.86	245	39.7	256	1457	1068	10.1	3.12	107
Kh-6	Upper dareh khan sp.	51	7.95	398	65.3	185	72.8	0.65	201	30.7	147	1330	981	10.4	4.70	80.9
Kh-7	Dareh khan pool	38	7.58	406	65.0	180	67.3	0.27	191	30.1	147	1268	957	10.1	3.83	84.0
Kh-9	Zardeh cold spring	10	7.92	3.43	0.73	45.0	13.1	0.00	11.1	0.48	12.4	183	132	10.1	0.03	8.66
Kh-10	Almalu cold spring	11	7.64	10.7	0.79	48.7	17.4	0.02	21.6	0.29	54.8	165	122	10.1	0.04	12.0
Kh-12	Kefcherin spring -1	14	7.70	114	15.0	67.6	96.0	0.00	68.8	6.39	86.2	812	614	9.96	0.05	59.8
Kh-13	Kefcherin spring -2	18	7.88	18.6	3.01	76.5	51.2	0.00	12.6	0.48	55.6	452	334	10.0	0.03	37.7
Kh-16	Lake Averin	11	7.82	12.4	1.26	56.4	31.0	0.34	30.1	0.26	16.7	292	215	10.0	0.11	18.0
Kh-17	Saray spring-1	18	7.10	325	31.4	494	194	----	299	30.7	214	1956	1574	9.28	2.82	108
Kh-18	Saray spring-2	17	7.55	1267	106	46.4	324	----	1210	105	83.0	3237	2466	9.00	0.05	114
Kh-20	Railway bridge sp.	18	8.14	30.3	0.79	28.7	19.7	----	18.2	0.71	25.8	195	141	8.96	0.02	15.2

Table 2: Chemical composition of gas samples from Qotur valley geothermal field (mole % gas) ; data from Ruaya, 1997

Sample	Location	Water temp. (°C)	CO_2	H_2S	Cl	He	H_2	Ar	O_2	N_2	CH_4	CO_2/H_2S
KH-1	Upper dareh khan bala sp	51	97.16	0.021	0.00	0.000	0.000	0.020	0.59	2.21	0.000	4560
KH-2	Upper dareh khan bala sp	51	99.62	0.032	0.00	0.000	0.000	0.004	0.11	0.24	0.000	3070
KH-4	Dareh khan bala sp.	51	99.51	0.038	0.00	0.000	0.000	0.007	0.08	0.36	0.000	2640
KH-5	Dareh khan bala sp.	51	99.45	0.026	0.00	0.000	0.000	0.009	0.09	0.43	0.000	3890
KH-6	Lower saray sp.	17	99.50	0.031	0.00	0.000	0.000	0.005	0.15	0.31	0.000	3177
KH-7	Lower saray sp.	17	99.79	0.020	0.00	0.000	0.000	0.002	0.06	0.11	0.000	4870

Table 3: ^{18}O and D contents of the waters from Qotur valley geothermal field (‰); data from Ruaya, 1997

Sample	Location	Elevation (m)	δD	$\delta^{18}O$
Kh-1	Dareh khan cold sp.	1470	-64.5	-8.66
Kh-2	Well No.1	1470	-68.6	-9.16
Kh-3	Dareh khan bala sp. -1	1660	-71.1	-9.51
Kh-4	Dareh khan bala sp. -2	1660	-68.3	-9.90
Kh-5	Dareh khan bala sp. -3	1690	-70.4	-9.51
Kh-6	Upper dareh khan sp.	1700	-69.1	-9.38
Kh-7	Dareh khan pool	1700	-67.4	-9.32
Kh-9	Zardeh cold spring	2000	-85.0	-12.58
Kh-10	Almalu cold spring	1970	-69.0	-9.94
Kh-11	Kefcherin cold spring	1680	-68.0	-9.64
Kh-13	Kefcherin spring -2	1580	-62.1	-8.90
Kh-14	Averin snow	3220	-87.6	-13.26
Kh-15	Averin creek	3100	-74.1	-11.54
Kh-16	Lake Averin	3100	-68.7	-10.55
Kh-17	Saray spring-1	1470	-71.3	-9.67
Kh-18	Saray spring-2	1470	-65.5	-7.22
Kh-20	Railway bridge spring	1400	-59.5	-8.66