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Fluid Geochemistry at the Nir Geothermal Field, Nw-Iran

Mohammad Reza Rahmani

Renewable Energy Organization of Iran (SUNA), Yadegar-e Emam Highway, Pounak Bakhtari Ave., P.O.Box 14665 – 1169 Tehran, Iran

mrrahmani@suna.org.ir

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ABSTRACT

The most southerly of the Mt. Sabalan thermal features is the thermal springs at the Nir area. This area hosts many thermal springs include Boshli, Ilanjigh, Doshanjigh, Saqezchi and Qarashiran. The temperatures of these springs range from 13°C to 77 °C. Thermal waters have a high chloride concentration with mixed chemistry of HCO_3 and SO_4. The values of the Mg concentrations in these waters are also high. This is suggestive that the Nir springs are the product of deep, low Mg-high Cl geothermal waters being cooled and quenched through mixing with groundwater associated with limestone and calcareous sediments. Such karst type waters contain much magnesium and sulphate through dissolution of dolomite and sulphates far beyond their normal solubility. Thermal waters plot as immature waters on the Na-K-Mg triangular diagram, except 4 samples that they plot at the boundary between immature and partially equilibrated waters. These waters occur in an area where Quaternary intrusive domes are mapped and may be more closely associated with these than Mt. Sabalan. Estimation of subsurface temperature with quartz conductive predicts temperature in the range of 115-161°C. The Nir springs have a $\delta^{18}O$ shift from meteoric trend line and define a mixing line between meteoric water precipitated and the andesitic water field. Thermal waters have a range of - 4.2 to - 3.0 ‰ which may be these values due to the CO_2 being derived from limestones. Geothermal waters have low absorption of B/Cl steam indicating that the fluid migrates from the old hydrothermal system.

1. INTRODUCTION

The Nir geothermal field is located in south of Mt. Sabalan in the northwest of Iran (Figure 1). Several geochemical surveys have been conducted at Mt.Sabalan. A reconnaissance-scale sampling program carried out by Entes Nazionale per L'Energia Elettrica of Italy (ENEL) in 1975, and a later geochemical sampling and analysis programme undertaken by Tehran Berkley Consulting Engineers (TBCE) under sub-contract to ENEL (TBCE, 1979). For the TBCE study, all known thermal and cold springs and gas vents in the greater Mt.Sabalan area were sampled. River samples were also collected to determine possible contributions from unknown thermal springs. During the period of the survey, thermal springs were sampled on two occasions. In August and September 1977 during the dry summer season and again in May 1978 during the wet season . Detailed sampling data and the results of chemical analyses are given in the Tehran Berkeley report (1979). These data were re- presented by Stefansson (1989) and Fotouhi (1995) without any new primary data. Finally, all previously documented and newly discovered thermal features in Sabalan area were re-sampled by Kingston Morrison (KM) in 1998 and samples were analyzed and results are incorporated with other historical geochemical analyses for springs from Mt. Sabalan and then they were re-interpreted and reported.

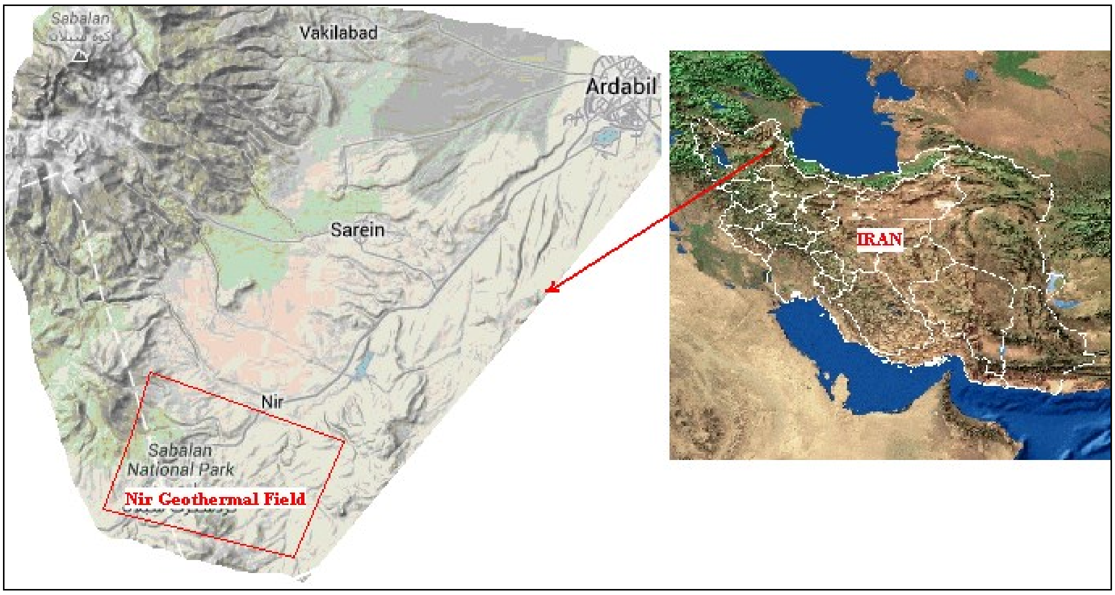

Figure 1: Location of the Nir geothermal field

2. PROPERTIES OF THERMAL AND COLD SPRINGS

The chemical composition of thermal and cold spring's waters from the Nir area is given in Table 1. Many of the springs are reported to exhibit large seasonal variations in flow rate that are low during August- September and high during May. The latter corresponding to the spring melts. However there is no significant seasonal variation in temperature or chemistry of the springs. This indicates that there has been storage in the aquifers and that aquifers must be large otherwise there would be indications of cooling and dilution. The springs that exhibit this behaviour must therefore fed by large perched groundwater aquifers that come under pressure during the spring season due to an increased rate of recharge. These springs are therefore not supplied from a deep geothermal aquifer but must be receiving heat and some proportion of their solutes from condensed volatiles. There are several cold springs in the Nir area with temperatures of less than about 12 $^{\circ}$C. All these springs have low chloride concentrations (7-64 mg/kg) but significant bicarbonate and sulphate with calcium the main cation followed by magnesium and sodium. These are considered to be typical of the regional groundwater and have no geothermal significance. Thermal springs have high Cl and Mg concentrations in the range 1985-3014 mg/kg and 24-59 mg/kg respectively. All waters occur in an area where Quaternary intrusive domes are mapped and may be more closely associated with these than Mt. Sabalan, but have a similar origin as neutralized magmatic condensates.

2.2.1 Cl- SO4- HCO3 ternary diagram

This diagram classifies geothermal waters using the major anion concentrations (chlorides, sulphates and bicarbonates) (Giggenbach, 1988) and also helps distinguish the waters as mature, peripheral and volcanic and steam-heated waters. Waters from the thermal springs have high chloride concentrations and plot in the mature water field or close to it, albeit with mixed chemistry as indicated by the significant HCO_3 and SO_4 (Figure 2). The chloride may have a source in a deep, high temperature, neutral chloride reservoir although in magmatic environments, the water may also represent a neutralised outflow of acidic condensate formed from the absorption of HCl and steam in shallow groundwater. All samples which plot in the area of HCO_3 are cold groundwater.

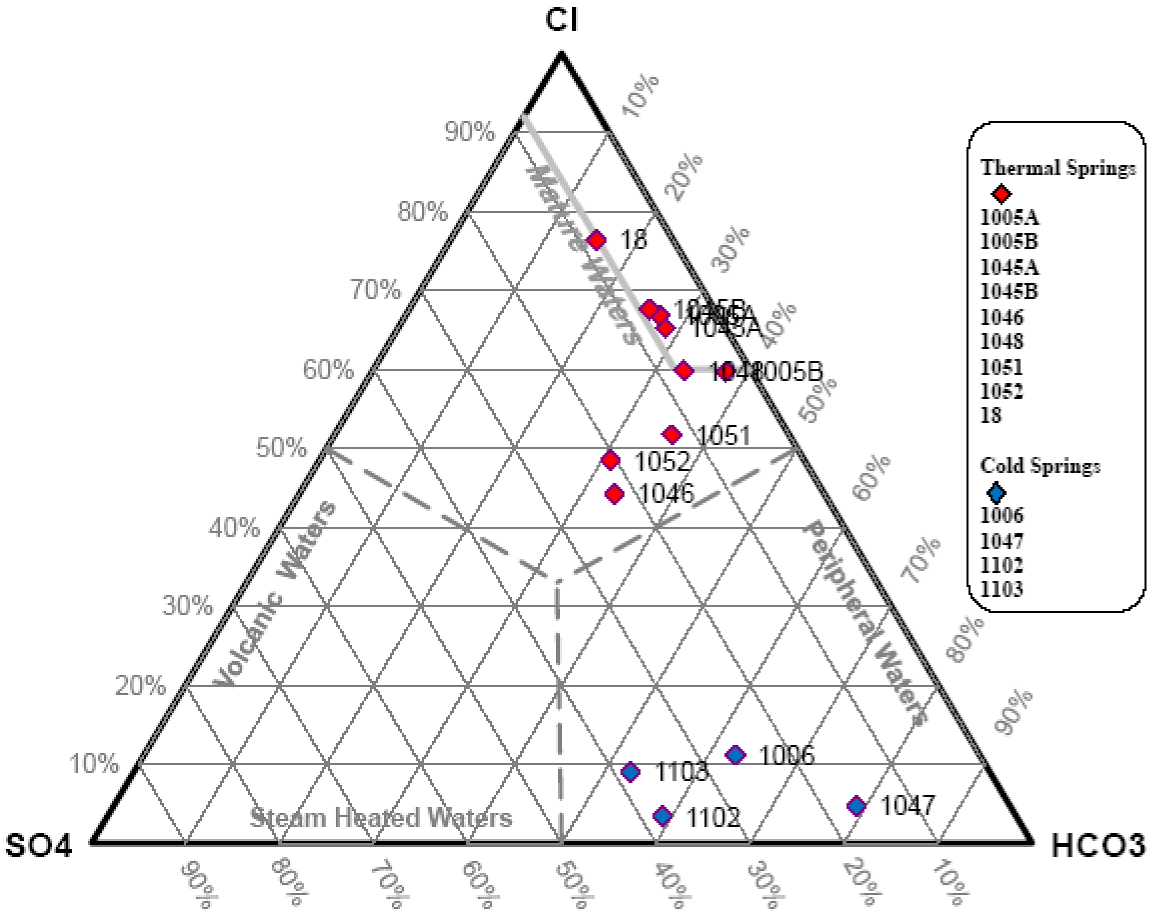

Figure 2: Cl-SO_4-HCO_3 diagram for thermal and cold springs from the Nir geothermal field

2.2.2 Na- K- Mg ternary diagram

The Na-K-Mg triangular diagram (Giggenbach, 1988) is used for evaluating equilibrium between the hot waters and rocks at depth and to estimate reservoir temperature. Figure 3 shows that all samples plot in the area of immature waters with orientation to Mg corner, natch with the exception of samples 1005B, 1045A, 1045B and 1046 which plot on the boundary between partially equilibrated and immature waters. Samples 1102, 1103, 1006 and 1047 that plot very close to Mg corner are from cold springs and have no geothermal significance. This is suggestive that the Nir springs are the product of deep, low Mg-high Cl geothermal waters being cooled and quenched through mixing with groundwater associated with limestone and calcareous sediments. Such karst type waters contain much magnesium and sulphate through dissolution of dolomite and sulphates far beyond their normal solubility.

This suggestion is supported with outcrop of carbonate rocks in vicinity of thermal springs and also a plot of Ca vs. Mg that shows Mg concentrations are proportional to Ca, in these waters (Figure 4).

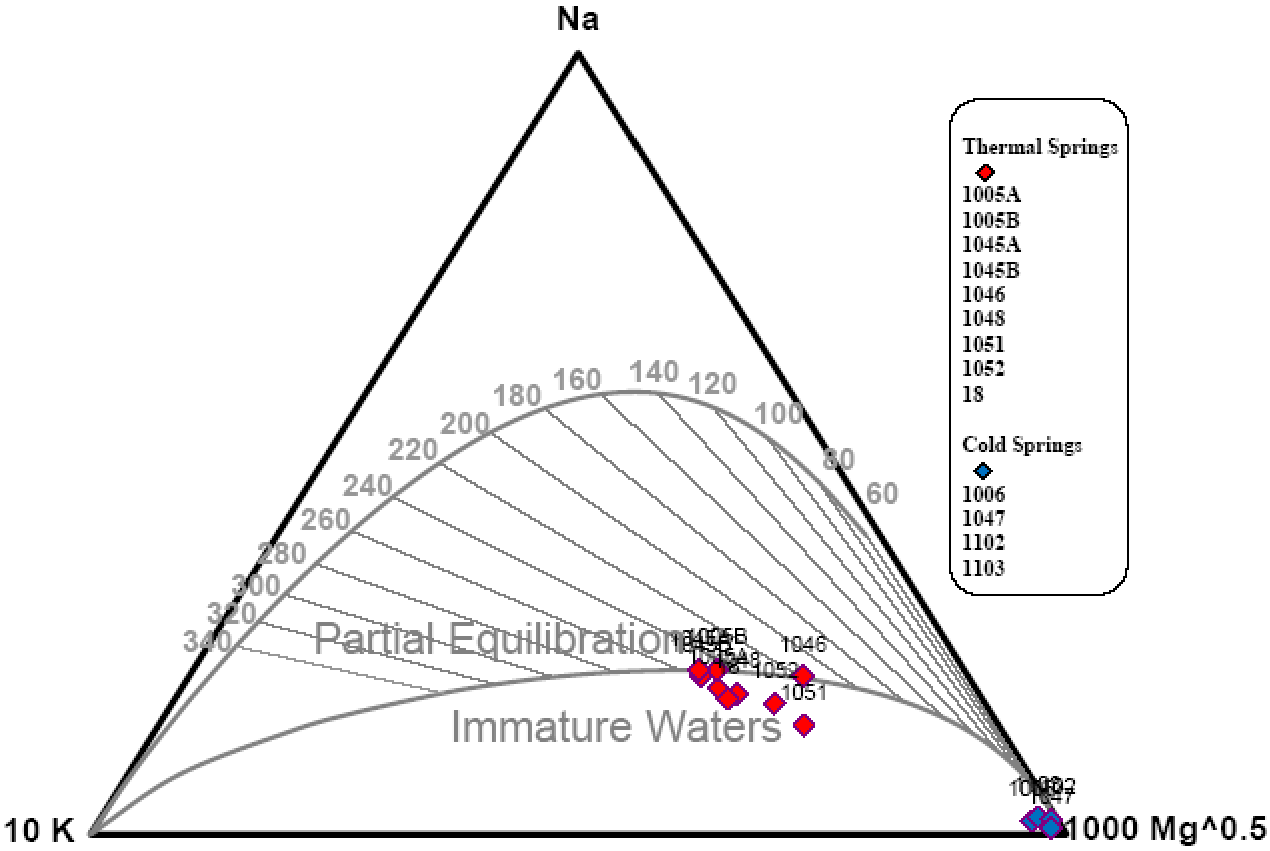

Figure 3: Na-K-Mg diagram for thermal and cold springs from the Nir area

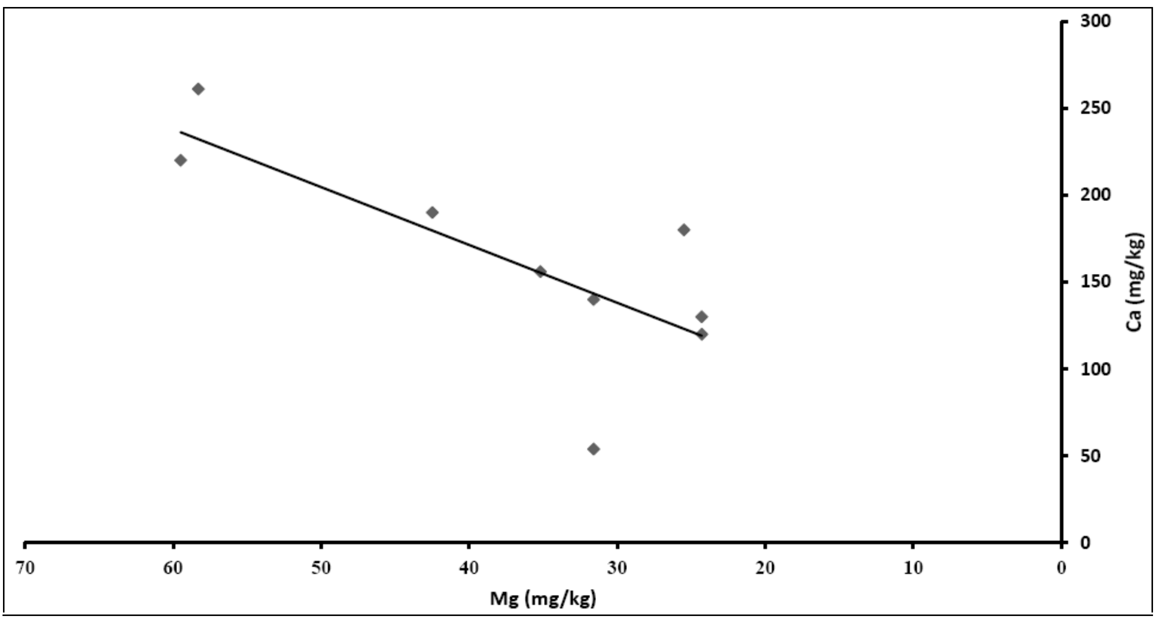

Figure 4: Plot of Ca vs. Mg for waters from thermal springs of the Nir geothermal field

2.2.3 Cl-Li-B ternary diagram

Lithium is the alkali metal affected by secondary processes. It is therefore used as a tracer for the initial deep rock dissolution process and to evaluate the possible origin of two important conservative constituents of geothermal water. The boron content of thermal fluids reflects the degree of maturity of a geothermal system. It is expelled during the early stages of heating up due to its volatility. Fluids from older hydrothermal systems therefore have less boron content but higher contents for younger hydrothermal systems. At high temperatures, chloride occurs as hydrochloric acid (HCl) and boron as boric acid (H_3BO_3) and both are volatile and able to be mobilized by high temperature steam. At lower temperatures, the acidity of HCl rapidly increase and it is changed by the rock to the less volatile NaCl but B remains in its volatile form and is carried to the surface in the vapour phase. Figure 5 shows that all water samples from thermal springs plot near the Cl corner where there is low absorption of B/Cl steam indicating that the fluid migrates from the old hydrothermal system.

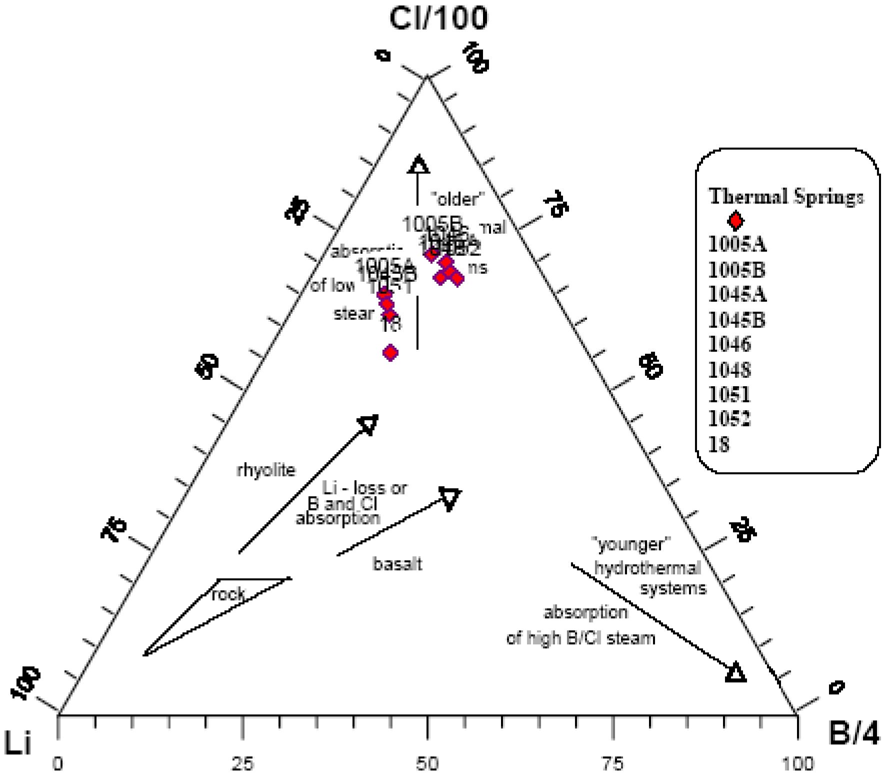

Figure 5: Cl-Li-B diagram for the thermal fluids of Nir

<u>2.2.4 Mg evaluation</u>

High- temperature, neutral- pH geothermal brine characteristically has low Mg concentrations (typically less than 1 mg/kg) because the magnesium is fixed in alteration clay minerals in the geothermal reservoir (primarily in the mineral chlorite). These low concentrations are usually preserved in chloride waters that flow to surface (particularly for high flow rate boiling springs), hence the incorporation of magnesium into geothermometer expressions. The values of the Mg concentrations in the thermal waters from the Nir area are high. These values are variable from 24 to 59 mg/kg Mg for the Ilanjigh springs (lowest Mg) to Saqezchi (highest Mg) springs. Thermal waters have high Mg values as noted, high Cl values up to 3014 mg/kg, high SO_4 values up to 1057 mg/kg, and high HCO_3 values up to 1831 mg/kg.

<u>2.2.5 Isotopic studies</u>

The stable isotope data for waters are all from springs and therefore removed from the point of precipitation, hence variation in isotopic composition with altitude or in comparison to prevailing winds cannot be established. The Nir springs have a $\delta^{18}O$ shift from meteoric trend line and define a mixing line between meteoric water precipitated and the andesitic water field (Figure 6). These waters would therefore have received the proportion of magmatic steam. Analyses of $\delta^{13}C$ were made on CO_2 collected from springs (ENEL, 1983). These are presented in Table 2. Nir springs have a range of - 4.2 to - 3.0 ‰ . ENEL (1979) attribute these values to the CO_2 being derived from limestones. Limestones have $\delta^{13}C$ values of between -3 and 3 ‰.

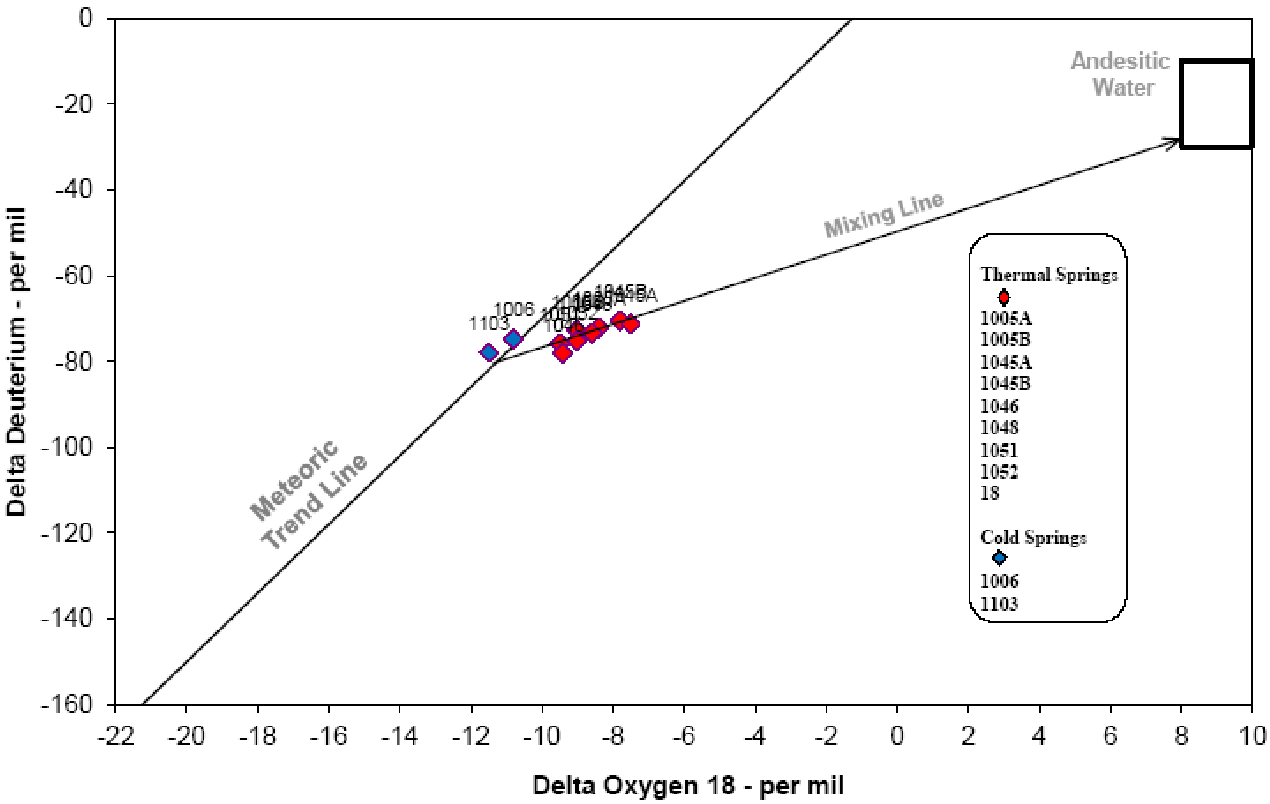

Figure 6: The $\delta^{18}O$ vs. δ^2H relationship for thermal and cold spring waters in the Nir geothermal area

3. ESTIMATION OF SUBSURFACE TEMPERATURE

Chemical data can be used to estimate the subsurface fluid temperatures. Subsurface temperatures in the study area have been estimated by chemical geothermometry. The chalcedony, quartz, Na-K and Na-K-Ca temperatures were calculated with the Geochemical Plotting Spreadsheet (Powell & Cumming, 2010). Results for solute geothermometry are reported in Table 3. The calculated chalcedony, quartz (Conductive), quartz (Adiabatic), Na-K (Fournier), Na-K (Truesdell), Na-K (Giggenbach) and Na-K-Ca geothermometer temperatures for spring waters studied indicate reservoir temperatures of 86-137°C, 115-161°C, 114-153°C, 203-255°C, 170-236°C, 219-267°C and 197-234°C respectively. The results for solute geothermometers show that temperatures estimated by the Na-K and Na-K-Ca geothermometers are much higher than those estimated by silica geothermometers); this could possibly be due to high concentration of Ca, Mg and CO_2 in the spring waters and calcium carbonate deposition during up flow. The silica quartz conductive cooling geothermometer is best used for springs at sub-boiling temperatures (giving a maximum estimate of the reservoir temperatures based on quartz solubility). As the springs are not boiling and based on explained above, the most appropriate geothermometer is the quartz conductive, which gives the reservoir temperature of 115-161°C.

4. CONCLUSION

Geothermal waters have high Cl and Mg concentrations in the range 1985-3014 mg/kg and 24-59 mg/kg respectively, while cold waters have low chloride concentrations (7-64 mg/kg) but significant bicarbonate and sulphate with calcium the main cation followed by magnesium and sodium.Thermal waters lie in the mature water field or close to it on the Cl- SO4- HCO3 ternary diagram, but with mixed chemistry of HCO_3 and SO_4.The chloride may have a source in a deep reservoir although in magmatic environments, the water may also represent a neutralised outflow of acidic condensate formed from the absorption of HCl and steam in shallow groundwater. The Na-K-Mg triangular diagram shows that all samples plot in the area of immature waters, natch with the exception of samples 1005B, 1045A,1045B and 1046 which plot on the boundary between partially equilibrated and immature waters. This is more suggestive that the Nir springs are the product of deep, low Mg-high Cl geothermal waters being cooled and quenched through mixing with groundwater associated with limestone and calcareous sediments. Such karst type waters contain much magnesium and sulphate through dissolution of dolomite and sulphates far beyond their normal solubility. This suggestion is supported with outcrop of carbonate rocks in vicinity of thermal springs and also a plot of Ca vs. Mg that shows Mg concentrations are proportional to Ca in these waters . The Cl-Li-B ternary diagram shows that all thermal waters plot near the Cl corner where there is low absorption of B/Cl steam indicating that the fluid migrates from the old hydrothermal system. Waters from thermal springs have a $\delta^{18}O$ shift from meteoric line and define a mixing line between meteoric water and the andesitic water area. These waters would therefore have received the proportion of magmatic steam. Waters have $\delta^{13}C$ in the range - 4.2 to - 3.0 ‰ that may be these values due to the CO_2 being derived from limestones. chalcedony, quartz (Conductive), quartz (Adiabatic), Na-K (Fournier), Na-K (Truesdell), Na-K (Giggenbach) and Na-K-Ca geothermometers give temperatures for the reservoir in ranges of 86-137°C, 115-161°C, 114-153°C, 203-255°C, 170-236°C, 219-267°C and 197-234°C respectively. As the springs are not boiling and based on some problems to apply the cation geothermometers for waters from Nir, the most appropriate geothermometer is the quartz conductive which gives the reservoir temperature of 115-161°C. As noted, cold and thermal springs have Cl concentrations with range from 7-64 mg/kg and 1985-3014 mg/kg respectively; indicating may be a deep geothermal fluid component with high Cl in the range from 1900 to more than 3000 mg/kg Cl mixes in the near surface with low Cl water (Cold groundwater). This suggestion and other results in this paper indicate that the Nir geothermal field needed to more investigations in deep levels, especially MT surveys to explore deep geophysical anomalies.

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Table 1: Chemical composition of water samples from thermal and cold springs of the Nir geothermal field (mg/kg)

Sample	Spring	Temp. (°C)	pH	Li	Na	K	Ca	Mg	Rb	Cs	Sr	Fe	Mn	Ba	Cl	F	SO_4	HCO_3	B	SiO_2	NH_3	$S^{=}$	CO_2t	Hg	TDS
1006	Bosh	11	7	0.39	85	14.1	120	23.1	0.12	0.17	1.62	0.54	0.36	1.5	64	0.9	149	360	0.8	43	0.7	3.1	85	0.00140	701
1005A	Bosh	62	7.1	9.72	1908	269.8	140	31.6	3.16	3.32	6.13	0.02	0.07	0.20	3014	3.2	279	1220	23.8	77	0.6	3.1	430	0.00020	6250
1005B	Bosh	77	7.3	5.69	2207	265.9	54	31.6	3.16	10.37	2.1	1.1	1.8	0.23	2907	2.8	130	1831	24.9	76	1.3	0.1	69	0.00050	6316
1048	Bosh	53	7	4.23	1586	219	180	25.5	1.54	2.13	3.81	0.04	0.08	0.16	1985	1.5	235	1098	20.5	87	1.1	3.1	470	0.005	4729
18*	Bosh	52	6.8	11.8	1816	273.7	156	35.2	3.42	-	4.34	0.37	0.06	-	2836	-	303	574	33.5	72	0.0	-	910	-	5900
1045A	Ilanj	41	6.7	5.41	2000	258	130	24.3	2.22	5.71	3.29	0.05	0.07	0.19	2801	1.8	274	1220	29.2	92	0.8	0.5	365	0.00050	6446
1045B	Ilanj	42	6.9	9.72	1908	258	120	24.3	2.73	2.79	5.7	0.04	0.06	0.20	2907	2.3	298	1098	24.9	88	1.0	3.1	380	0.00110	6227
1103	Saqe	12	6.5	0.12	120	10.2	120.2	26.7	0.05	0.03	1	0.54	0.36	1.5	64	0.7	269	372	0.6	34	1.3	3.2	41	0.00080	835
1052	Saqe	41	6.5	4.72	2092	269.8	220	59.5	1.54	1.59	7.89	2.05	0.18	0.09	2482	0.5	1057	1586	28.1	77	1.2	3.1	820	0.005	6474
1051	Saqe	28	6.5	7.64	1609	230.7	261	58.3	0.94	1.46	7.01	0.10	0.30	1.5	2198	1.4	528	1525	20.5	66	1.4	0.2	1040	0.00100	5866
1047	Dosh	13	7.4	0.01	16	2.7	32	4.4	0.01	0.00	0.22	0.02	0.36	1.5	7	0.4	24	116	0.1	58	0.7	3.1	10	0.00100	227
1046	Qara	42	6.7	3.89	2092	175.9	190	42.5	1.20	3.19	3.90	0.91	0.17	0.11	2092	1.9	1057	1586	20.5	150	2.5	6.9	580	0.005	7006
1102	Qara	11	6.5	0.03	99	3.2	86	26.7	0.00	0.02	1.80	0.54	1.8	1.5	22	0.4	245	384	0.4	40	11	3.1	32	0.00050	768

***ENEL; Others from TBCE; Bosh: Boshli; Ilanj: Ilanjigh; Saqe: Saqezchi; Dosh: Doshanjigh; Qara: Qarashiran**

Table 2: The Isotope composition of the Nir geothermal field

Sample	Spring	Temp. (°C)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{13}C$ (‰)
1006	Bosh	11	-10.8	-74.7	-
1005A	Bosh	62	-8.4	-72.2	-3.0
1005B	Bosh	77	-9.0	-72.8	-
1048	Bosh	53	-8.6	-73.4	-3.9
18*	Bosh	52	-8.5	-	-
1045A	Ilanj	41	-7.5	-71.2	-
1045B	Ilanj	42	-7.8	-70.6	-3.0
1103	Saq	12	-11.5	-77.9	-
1052	Saq	41	-9.0	-75.2	-3.7
1051	Saq	28	-9.5	-75.8	-4.2
1047	Dosh	13	-12.4	-	-3.5
1046	Qara	42	-9.4	-78.1	-
1102	Qara	11	-10.3	-	-

***ENEL; Others from TBCE; Bosh: Boshli; Ilanj: Ilanjigh;**

Saqe: Saqezchi; Dosh: Doshanjigh; Qara: Qarashiran

Table 3: Results of different geothermometers for water samples from thermal springs in the Nir geothermal field (°C)

Sample	$T_{Chalcedony}$	T_{Quartz} (Conductive)	T_{Quartz} (Adiabatic)	$T_{Na\text{-}K\text{-}Ca}$	$T_{Na/K}$ (Fournier)	$T_{Na/K}$ (Truesdell)	$T_{Na/K}$ (Giggenbach)
1005A	95	123	121	230	249	228	262
1005B	94	123	120	234	233	209	248
1048	102	130	126	222	246	225	259
18	91	120	118	232	255	236	267
1045A	105	133	129	226	240	217	253
1045B	103	130	127	229	244	222	258
1052	95	123	121	221	240	217	253
1051	86	115	114	221	250	230	263
1046	137	161	153	197	203	170	219