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Consideration of geological aspects and geochemical parameters of fluids in Bushdi geothermal field, south of mount Sabalan, NW Iran

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1. Introduction

Surface manifestations such as thermal springs, steaming grounds, fumaroles, mud pools, and geysers together with their locality, geologic control, physical environment, temperature, chemistry, and the rate of fluid discharge are the most important features for geothermal exploration (Gupta and Roy, 2007). Spring waters varying in temperature from cold atmospheric (ambient) to boiling can be found in many localities throughout the world. Geological and geochemical studies of these spring waters are the preliminary measures for exploring geothermal systems (Pentecost, 2005). Following this trend, geological studies of the area, tectonic characteristics of the fault system, petrological characteristics of the reservoir and cap rocks, and the chemical composition of the circulating waters in the geothermal system

should be comprehensively assessed. Since all stages including exploration, estimation, and exploitation of a geothermal field are directly related to the fluid phase, a profound perception of the chemistry of the fluid phase is necessary. The chemical characteristics of these fluids provide valuable information on the hydrology of both the reservoir and the whole system (Nicholson, 1993). Preliminary activities in the context of the geothermal systems of Iran go back to 1975 when an Italian company (ENEL) carried out comprehensive investigations of the nation's geothermal fields. Since then, numerous studies concerning geothermal explorations were done in Iran and many potential prospect areas were identified.

A geothermal prospect area that is considered to be of prime importance is located around the Sabalan volcano in Azarbaijan Block, northwest of Iran. The Azarbaijan Block is a tectonically active region and its geotectonic characteristics are influenced by late Mesozoic geologic events. The Azarbaijan Block is located at the collision point of the Arabic-Eurasian plates along the Alp-Himalayan orogenic belt, and has Cenozoic plutonic and volcanic

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sequences (e.g., Berberian and Berberian, 1981; Alavi, 1994; Mohajjel et al., 2003; Jahangiri, 2007; Dilek et al., 2010). Masson et al. (2006) concluded that besides the collision of the Arabic-Eurasian plates, the southward movement of the oceanic crust of the southern Caspian Sea had a lateral influence on the geotectonic conditions of the Azarbaijan Block (Fig. 1). Considering the distribution of several Quaternary volcanoes of similar geothermal characteristics in the region spreading from the Black Sea through the Caspian Sea to the Anatolian Block, many researchers regarded the Azarbaijan Block as the northern part of the Urmia-Dokhtar structural zone of Iran. The most westerly and one of the most distinctive volcano in this zone is the Sabalan stratovolcano covering a vast area (with a radius of ~10 km) with lavas, pyroclastics, and alteration zones (Dostal and Zerbi, 1978). The Sabalan volcano was formed during extensional activities during the upper Eocene-early Oligocene period (Alberti et al., 1976). The volcanic rocks are of andesitic, dacitic, and rhyolitic composition with a calc-alkaline character containing high K, Sr, and Ba (Dostal and Zerbi, 1978). In fact, the high-K calc-alkaline to shoshonitic characteristics of these rocks testify to a tectonic setting of post-collision island arcs (Riou et al., 1981; Shahbazi Shiran and Shafai Moghadam, 2014). Around the Sabalan stratovolcano, there are several surface manifestations of a potentially widespread geothermal systems at depth. In the northwest of the Sabalan caldera in the Moil valley, there are several localities where thermal springs, gases and steams are currently emanating from the ground. In the east of Sabalan (Sarein and Sardabeh district), there are numerous cold and hot springs with gas and steam vents pointing to the geothermal activities beneath the surface. In the present study, the authors assess the geological characteristics of the geothermal field in the south of Sabalan volcano with special emphasis on the chemical composition of geothermal fluids.

At present, measures have been taken for exploration and exploitation of geothermal energy only in northwestern part of the mount Sabelan. In most localities, these hot springs are used merely for bathing and curing (dermatosis) aspects. Detailed studies on the

geothermal fluids in the area have not been carried out so far. Therefore, the authorities in the Ministry of Energy have proposed a series of exploratory investigations which may lead to utilization of the geothermal energy in this region. To achieve this goal, the authors have endeavored to consider some geological and geochemical aspects particularly assessment of isotopic characteristics of the active hot springs in the region. The residence time in the reservoir rocks, origin, and mixing of these fluids with near-surface waters will be considered in detail in order to have a proper conception of the physico-chemical conditions prevailing in the geothermal environment in this region. These measures are the preliminary steps in direction of implementing drilling operation and detailed exploration for geothermal energy in near future.

2. Method of investigation

The study area was mapped at a scale of 1:60,000 (Fig. 2) and 27 samples from high fluid flow springs were collected. In sampling the hot springs priority was given to those with high discharge rates and temperatures. The water samples were collected from six springs in the following areas: Bushdi (#7), Sagizchi (#6), Gaynarja (#5), Garashiran (#4), Ilanjig (#3), and Doshanjig (#2). In this study, 27 water samples (19 from hot springs and 8 from cold springs) from these areas were chemically analyzed.

All water samples were kept in polypropylene bottles. The chemical analyses of these samples for determination of major and trace elements as well as for stable isotopes were carried out in the hydrogeochemistry lab at Bremen University (Germany). The samples were passed through a 0.45 μm filter and treated with concentrated HNO_3 in order to stabilize the sample for chemical analyses. Temperature and pH were measured directly in the field and HCO_3^- was determined by titration. The stable isotope analyses (δD and $\delta^{18}\text{O}$) were carried out using a LGR DLT-100 Laser Spectrometer (Los Gatos Research). The analytical precision of $\delta^{18}\text{O}$ and δD were $\pm 0.2\text{‰}$ and $\pm 1\text{‰}$, respectively. The ^3H values were measured in terms of tritium unit (TU) where $1 \text{ TU} = ([\text{T}]/[\text{H}]) \times 10^{18}$ (IAEA, 1979). Magnesium, Ca, K, Na, and Si were analyzed by ICP-OES (Perkin-Elmer) and Cl, F and SO_4 were determined by ion chromatography using IC-Plus Chromatograph (Metrohm).

3. Geology of the study area

Geologically, the geothermal field in south of the mount Sabelan is situated in a volcanic terrain. The volcanic rocks are the dominant lithologic units in the study area. However, some volcanic-sedimentary and sedimentary rock units are also cropping out in the area.

The Bushdi and Gaynarja hot springs pass through dacitic-andesitic rocks cropping out in the middle of the study area (Fig. 2). The dacitic lavas (varying in color from grey to violet) consist of phenocrysts of plagioclase, hornblende, biotite, augite, and rarely altered olivine set in a fine microlitic cryptocrystalline matrix showing typically porphyritic texture.

Basaltic and andesitic-basaltic rock units (with overall thickness of ~800 m) cover the northwestern part of the study area, and include lava flows and brecciated lavas accompanied occasionally by scoria. These rocks are often porous, and contain phenocrysts of plagioclase, hornblende, and augite showing typically porphyritic to aphanitic texture. These lavas, in most places, show alteration as a result of the infiltrating hydrothermal fluids almost obliterating their original mineralogy and texture (Amini, 1994). Apparently, the andesitic-basaltic rock units along with the associated pyroclastic units acted as reservoir rocks for the geothermal fluids in south of mount Sabelan. The pyroclastic unit contains lahar and

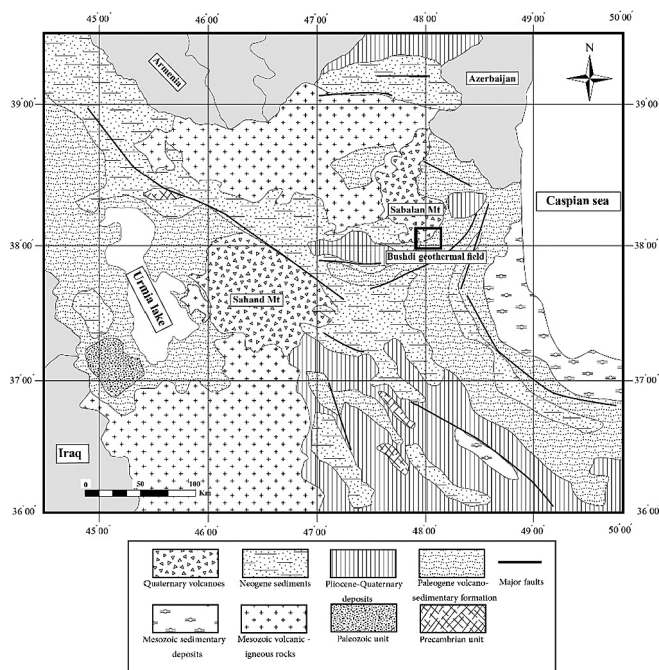


Fig. 1. Simplified geologic map (modified after Solaymani Azad et al., 2011) of the northwest of Iran on which the location of study area is shown.

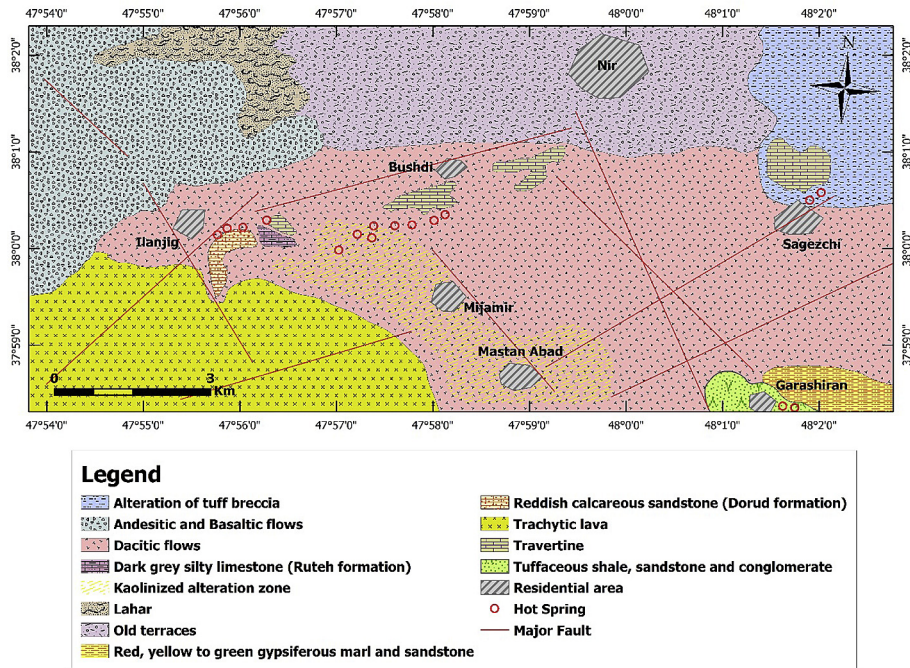


Fig. 2. Geologic map of the Bushdi geothermal field in the south of mount Sabalan.

unconsolidated detrital sediments. The lahars (10–50 m thick) consist of angular to rounded fragments (of varying sizes) of volcanic rocks (earlier lavas) set in a matrix of fine volcanic ashes (Fig. 2).

In the western part of the study area, outcrops of calcareous sandstone of Lower Permian age (Dorud Formation) are conformably overlain by the Upper Permian limestone (Ruteh Formation). These sedimentary formations are covered by the Neogene andesitic-basaltic lavas (Amini, 1994). Amini (1994) believes that a Paleozoic metamorphic unit (amphibole schist and layered crystalline limestone) constitutes the basement rocks in the area.

The major hot springs (e.g., Bushdi and Sagezchi) are present around the Quaternary lenticular cone of travertine deposits in central and eastern parts of the study area (Fig. 2). The travertine deposits in the area are lenticular-shaped, have massive spongy textures and range in color from milky to brick red. Their thickness reaches up to about 20 m in some places. The travertine deposition rate is a function of various factors such as discharge temperature, temperature decrease rate, flow path morphology, biologic activities, evaporation rate, and CO₂ degassing (Friedman, 1970; Minissale, 2004).

In northern part of the study area, there are Quaternary stream sediments which contain volcanic rock fragments (vary in composition from trachy-andesite, andesite, to trachyte) varying from sand to boulder sizes.

Tectonically, the area contains numerous shear and fault zones. The major fault zone in the area has an E-W trend and extend up to 50 km. Apparently, this fault provides pathways for most major hot springs in the study area. Many minor faults with overall trends of NW-SE and NE-SW have also played crucial role in geothermal activities in the study area (Fig. 2).

4. Results and discussion

4.1. Physico-chemical characteristics of the fluids

The physico-chemical parameters as temperature, pH, total

dissolved solids (TDS), and chemical composition of 27 hot spring water samples taken from south of the mount Sabalan are listed in Table 1. In the study area, the hot water samples depict temperature and pH ranges of 22–77 °C and 6.4–7.3, respectively. The total dissolved solids (TDS) vary from 456 mg/L to 7006 mg/L. On the other hand, the cold spring waters in the area have temperature, pH, and TDS ranges of 11–15.5 °C, 6.5–7.4, and 227–885 mg/L, respectively. Among the major cations Na⁺ has the highest concentration value varying from 16.09 mg/L to 2207 mg/L. The Na⁺ content of these waters varies with temperature so that the low-temperature and high-temperature waters have the least and the most Na⁺ concentrations, respectively. The relatively high concentration values of K⁺ and Ca²⁺ are the other conspicuous characteristics of these geothermal fluids in the Bushdi area which range from 2.69 mg/l to 273 mg/l and from 27.33 mg/l to 260.5 mg/l, respectively. The silica concentrations of these waters range from 30 mg/l to 140 mg/l. Among the anions, Cl⁻ is dominant in some samples and it reaches up to 3013 mg/l. The total alkalinity (HCO₃⁻) value is relatively high and varies from 115 mg/l to 1830 mg/l. SO₄²⁻ shows a wide fluctuation and ranges from 4.6 mg/l to 1296 mg/l. Comparing the results obtained from the earlier studies in the area, and in this study; Ca²⁺, Mg²⁺, and F⁻ exhibit relatively lower concentration values. This might be explained by climate changes in the area which resulted in considerable reduction in the annual meteoric precipitations rate. Therefore, the climate variations might have influenced the ionic content of the geothermal fluids. The concentration of rare metallic and non-metallic elements such as Li, Rb, B, Ba, Sr, CS, Se, Al, As, Hg in cold and hot spring waters in the Bushdi area were also analyzed (see Table 2).

5. Hydrogeochemistry

The chemical composition of spring waters was assessed by using the computer program AquaChem 2011.1 (Calmbach, 1997), and the hydrogeochemical characteristics of the samples were determined. Plotting the concentration values of the analyzed samples on the Piper diagram (Piper, 1944) illustrated that on the

Table 1

Chemical and isotopic analyses of some selected cold and hot spring water samples from the Bushdi geothermal field in the south of mount Sabalan.

Sample ID	Sampling Stations	TDS mg/L	Elev (m)	FR (l/min)	T (°C)	pH	Na ⁺ mg/L	K ⁺ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Fe ²⁺ mg/L	Mn ²⁺ mg/L	Cl ⁻ mg/L	F ⁻ mg/L	SO ₄ ²⁻ mg/L	HCO ₃ mg/L	SiO ₂ mg/L	³ H TU	δ ¹⁸ O ‰	δD ‰	CBE
SS1	Bushdi	701	1800	15	11	7	85.06	14	120	23.08	0.54	0.36	63.8	0.85	148	360	43	96.8	-10.8	-74.7	5.24
SS2	Bushdi	692	1800	1	15.5	7.1	85.06	14	110	23.08	1.1	1.8	70.9	1.19	134	390	54	105	-11.7	-74.4	1.61
SS3	Bushdi	6250	1790	300	62	7.1	1908	269	140	31.59	0.02	0.06	3013	3.22	278	1220	77	5.6	-8.4	-72.2	-5.35
SS4	Bushdi	6316	1804	5	77	7.3	2207	265	54.1	31.59	1.1	1.8	2907	2.84	129	1830	76	0.8	-9	-72.7	-2.89
SS5	Bushdi	4715	1801	60	59	7	1402	199	200	26.73	0.54	0.06	2091	1.89	278	915	71	28	-9.2	-73.7	-0.09
SS6	Bushdi	4729	1820	12	52.5	7	1586	218	180	25.52	0.039	0.07	1985	1.53	235	1098	87	30.9	-8.6	-73.3	4.14
SS7	Bushdi	5900	1799	-	51.52	6.8	1816	273	156.3	35.24	0.37	0.05	2836	-	302	573	72	-	-8.5	-	0.56
SS8	Doshanjigh	227	2000	80	13	7.4	16.09	2.69	32.06	4.374	0.02	0.36	7.09	0.36	24.5	115	58	15	-12.4	-	2.74
SS9	Doshanjigh	245	2000	8	12	7.2	17.01	3.01	28.05	4.131	0.02	1.8	8.863	5.3	13.4	128	60	14.9	-12	-	-0.09
SS10	Ilanjigh	456	1801	50	40	6.5	85.06	9.38	62.12	7.899	0.02	0.02	120.5	0.28	24.97	231	66	-	-12.2	-	-0.08
SS11	Ilanjigh	6227	1800	50	42	6.9	1908	258	120.2	24.30	0.03	0.06	2907	2.27	297	1098	88	-	-7.8	-70.6	-4.18
SS12	Ilanjigh	6446	1805	3	40.5	6.7	2000	258	130.2	24.30	0.05	0.06	2800	1.84	273	1220	92	5.07	-7.5	-71.1	-1.21
SS13	Garashiran	761	1650	150	11	7.2	101	3.28	120.2	29.16	0.54	0.009	25.88	0.45	288	292	30	36.8	-10.7	-	5.64
SS14	Garashiran	768	1650	5	11	6.5	98.85	3.20	86.17	26.73	0.54	1.8	21.98	0.41	244	384	40	41.4	-10.3	-	-4.5
SS15	Garashiran	6857	1650	50	44	7.1	2000	179.8	190.3	43.74	0.72	0.15	2304	2.46	1296	1708	140	2.1	-9.8	-77.3	-6.78
SS16	Garashiran	7006	1650	3	41.5	6.7	2092	175.9	190.3	42.53	0.91	0.17	2091	1.89	1056	1586	140	0.65	-9.4	-78.0	0.74
SS17	Gaynarja	-	1710	-	69	6.8	1920	240	138.3	19.49	0.002	0.02	-	-	-	-	-	-	-10.6	-73.2	-
SS18	Gaynarja	-	1705	-	55	7.1	1929	242	105.3	19.71	0.002	-	28.11	0.17	4.6	-	-	-	-	-	-
SS19	Gaynarja	-	1705	-	49	6.8	1912	243	37.52	19.71	0.002	0.001	28.03	0.17	4.6	-	-	-	-	-	-
SS20	Gaynarja	-	1697	-	65	7	1921	243	149.4	19.84	0.002	0.03	-	-	-	-	-	-	-	-	-
SS21	Gaynarja	-	1694	-	53	7.1	1934	242	27.33	19.09	0.002	0.001	-	-	-	-	-	-	-	-	-
SS22	Sagizchi	835	1600	70	12	6.5	119	10.16	120.2	26.73	0.54	0.36	63.81	0.72	268	372	34	32.1	-11.5	-77.9	0.68
SS23	Sagizchi	885	1600	26	13.5	6.8	124	12.12	124.2	27.95	0.08	1.8	77.99	0.41	259	433	58	34.6	-11.1	-78.6	-1.47
SS24	Sagizchi	6394	1600	50	40	6.4	1908	230	240.4	61.97	0.67	0.14	2588	2.08	528	1281	64	1.9	-8.9	-74.7	0.5
SS25	Sagizchi	6474	1600	10	40.5	6.5	2092	269	220.44	59.54	2.047	0.181	2481	0.51	1056	1586	77	0.7	-9	-75.1	-1.76
SS26	Sagizchi	5866	1600	300	28	6.5	1609	230	260.5	58.33	0.1	0.3	2198	1.4	528	1525	66	1.7	-9.5	-75.8	-2.23
SS27	Sagizchi	5605	1600	10	22	6.6	181	218	220.4	52.25	0.08	0.26	2198	1.1	461	1342	86	2.7	-9	-76.2	-

basis of hydrogeochemical characteristics, the cold and hot spring waters in the Bushdi area can be divided into two compositional groups, (1) Na-Cl and (2) Ca-Na-HCO₃ (Fig. 3). The hot-water springs have Na-Cl and Ca-Na-HCO₃ compositions, whereas the cold-water springs show mainly Ca-Na-HCO₃ composition.

The major cation and anion content of the analyzed geothermal waters were plotted on diagram of Schoeller (1962) (Fig. 4).

This diagram is semi-logarithmic and the solute content of the

waters is plotted in terms of milli-equivalent per liter. The patterns of concentration values of cations follow the trend of Na⁺ >> Ca²⁺ > K⁺ > Mg²⁺, but anions illustrate two relatively different trends, (1) Cl⁻ >> HCO₃⁻ > SO₄²⁻ and (2) HCO₃⁻ > Cl⁻ > SO₄²⁻ (Fig. 4).

The relationship between Cl⁻ and components such as Na⁺, Mg²⁺, B³⁺, Li⁺, SO₄²⁻, and HCO₃⁻ are illustrated in Fig. 5. The halides Cl⁻, Br⁻ and I⁻ are relatively conservative anions that migrate with surface and underground waters with a minimum of water-rock

Table 2

Concentration values of minor and trace elements for some selected cold and hot spring water samples from the Bushdi geothermal field in the south of mount Sabalan.

Sample ID	Sampling Stations	Li ppb	Ba ppb	Rb ppb	Sr ppb	Cs ppb	B ppb	As ppb	Se ppb	Hg ppb	Al ppb
SS1	Bushdi	388	1500	119	1620	172	778	-	-	1.4	-
SS2	Bushdi	194	1500	179	1314	770	1081	-	-	5	-
SS3	Bushdi	9717	199	3162	6133	3322	23,782	-	-	0.2	-
SS4	Bushdi	5691	226	3162	2102	10,366	24,863	-	-	0.5	-
SS5	Bushdi	7635	199	2393	4819	2259	19,458	-	-	2.8	-
SS6	Bushdi	4234	157	1538	3811	2126	20,539	-	-	5	-
SS7	Bushdi	11,799	-	3418	4337	-	33,511	-	-	-	-
SS8	Doshanjigh	5.96	1500	9.4	219	1.99	60.53	-	-	1	-
SS9	Doshanjigh	580	1500	5.98	78.85	39.87	799	-	-	5	-
SS10	Ilanjigh	312	102	47.86	525	26.58	832	-	-	0.6	-
SS11	Ilanjigh	9717	199	2734	5695	2791	24,863	-	-	1.1	-
SS12	Ilanjigh	5413	192	2222	3285	5714	29,187	-	-	0.5	-
SS13	Garashiran	65.24	102	4.01	1796	15	497	-	-	1	-
SS14	Garashiran	29.15	1500	4.95	1796	19.93	389	-	-	0.5	-
SS15	Garashiran	6941	1500	1794	9200	1594	19,458	-	-	1	-
SS16	Garashiran	3886	109	1196	3899	3189	20,539	-	-	5	-
SS17	Gaynarja	14,066	159	3217	5062	-	26,316	4146	243,352	-	10
SS18	Gaynarja	14,265	129	3316	4629	-	26,470	3993	273,770	-	10
SS19	Gaynarja	14,203	76.49	3346	3559	-	26,884	4159	162,172	-	10
SS20	Gaynarja	13,970	163	3299	5119	-	26,604	3820	135,118	-	10
SS21	Gaynarja	14,223	101	3324	3903	-	26,693	4033	226,643	-	10
SS22	Sagizchi	117	1500	47.86	1314	34.55	605	-	-	0.8	-
SS23	Sagizchi	63.16	1500	4.95	1401	59.8	399	-	-	0.5	-
SS24	Sagizchi	8329	1500	2307	7447	1727	23,782	-	-	1.1	-
SS25	Sagizchi	4719	89.26	1538	7885	1594	28106	-	-	5	-
SS26	Sagizchi	7635	1500	940	7009	1461	20,539	-	-	1	-
SS27	Sagizchi	4095	1500	1282	5257	1329	23,782	-	-	5	-

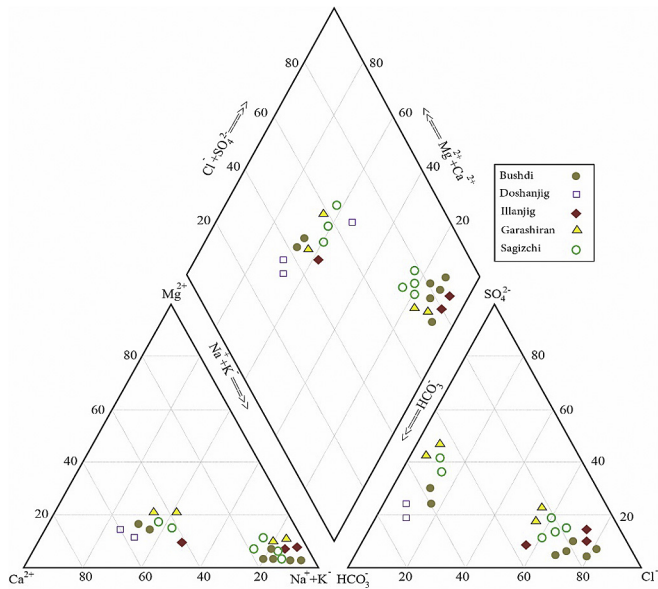


Fig. 3. The position of the data points belonging to the selected water samples from the Bushdi geothermal field on Piper diagram (Piper, 1944).

interaction. Thus these elements were selected as potential tracers for water source (Hem, 1985; Panno et al., 2006).

The Na^+ versus Cl^- diagram (Fig. 5a) shows that $R^2 = 0.95$. Considering the high concentration values of both ions in the water samples and the tectonic setting of the reservoir host rocks, the interaction between the geothermal fluids and the reservoir rocks resulted in leaching of Na from volcanic rocks (lavas and pyroclastics) (Sbrana et al., 2010). The high R^2 value (0.95) testifies to the

same source for these two elements (Taran and Peiffer, 2009). The R^2 value in the Mg-Cl diagram (Fig. 5b) is 0.45. The Mg^{2+} value in the geothermal water samples shows a relatively low concentration which may be due to the existence of considerable amounts of this element in the spring waters and its incorporation in the structure of the secondary clay minerals. This phenomenon is quite common in geothermal fluids (Giggenbach, 1988).

The weak positive correlation of Mg with chloride (Fig. 5b) may support this reasoning. This correlation is even more positive in water samples from the cold springs than in those of the hot springs. The relatively high Mg concentration in some water samples (SS1, SS2, SS13, SS14, SS23) may be due either to leaching of this element from the local near-surface rocks by geothermal fluids or to mixing of the geothermal fluids with the underground waters of high Mg content (Nicholson, 1993).

B^{3+} and Li^+ are index ions which can be used for recognition of mixing processes in geothermal fluids (Giggenbach and Corrales, 1992). The B^{3+} versus Cl^- plot (Fig. 5c) shows a relatively high concentration of B in these waters and seemingly the water-rock interaction played an important role for this enrichment.

The Cl/B ratio is a parameter that can be used for interpretation of geothermal environment. This ratio in sea waters is greater than in the common igneous and metamorphic rocks because of absorption of boron by marine sediments. On the other hand, the concentration of boron in the divergent plate boundaries (MORB) rocks is much lower than that of volcanic rocks in the convergent plate boundaries (Arnorsson, 2002, 2003). The concentration of boron in hydrothermal fluids of the geothermal systems in volcanic rocks of convergent environment may reach up to 100 ppm (Ellis and Mahon, 1967). Boron is commonly partitioned into andesitic magma generated by partial melting of the hydrous rocks of the upper mantle. Therefore, rocks derived from this magma and hence the relevant geothermal systems become enriched with this element. The Cl/B ratio of the analyzed water samples ranges from

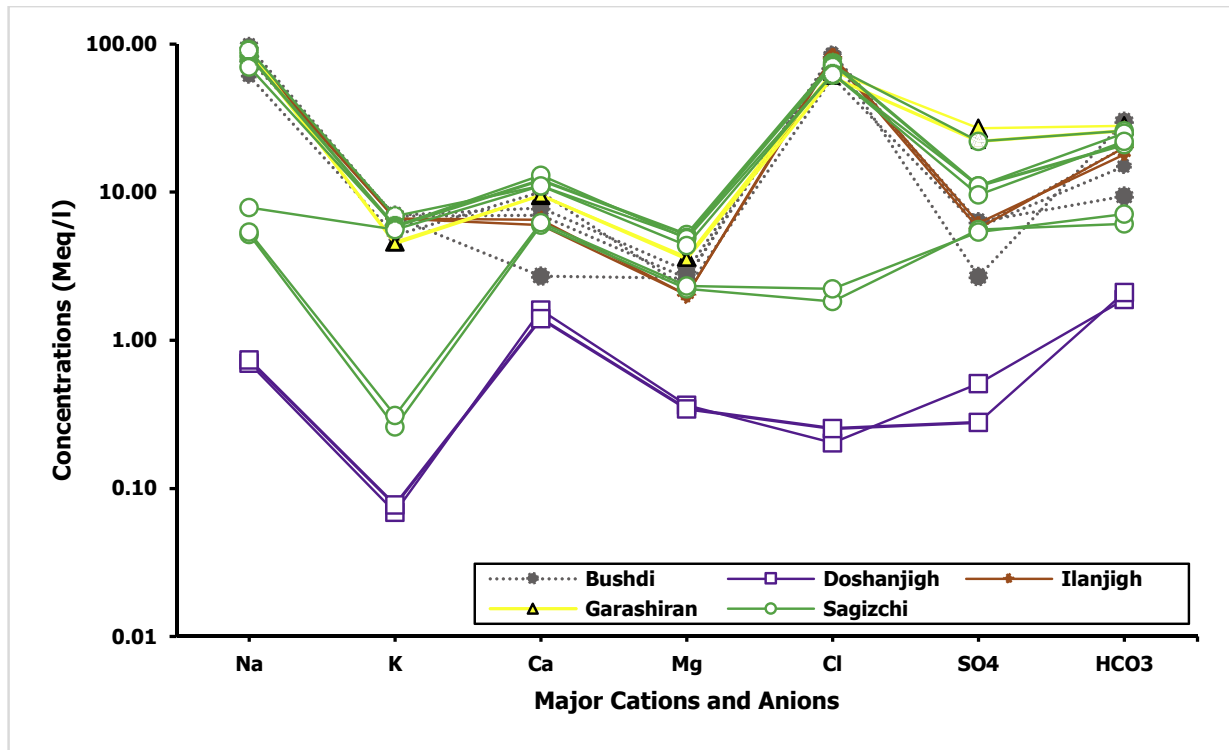


Fig. 4. Concentration variations of major cations and anions for the Bushdi geothermal water samples from the south of mount Sabalan.

0.01 to ~610 (maximum concentration of boron is ~33 mg/l) which is likely due to the water-rock interaction and degassing of intruding andesitic magma.

Li^+ displays a good positive correlation with Cl^- (Fig. 5d). Li^+ is an alkaline mobile element in aqueous systems and has relatively high concentrations in the high-temperature hot waters and low concentrations in cold waters. It commonly tends to concentrate in secondary minerals such as clays (kaolinite, illite, and smectite) (Starkey, 1982).

Considering the similarity of geothermal behavior of Li^+ with ions like B^{3+} and Cl^- in geothermal environments, the concentration of Li^+ can be used for the assessment of the source of the geothermal fluid. The relatively high concentration of Li^+ in the

geothermal fluids of the study area and its good correlation with Cl^- may testify to the involvement of magmatic waters in the geothermal system. The low partition coefficient of Li^+ in the structure of secondary alteration minerals as well as the relatively high concentration of this element in rhyolitic and andesitic rocks may account for the high lithium value in the studied water samples.

HCO_3^- marks relatively high concentrations in the collected water samples (Table 1). The HCO_3^- versus Cl^- diagram (Fig. 5e) demonstrates that HCO_3^- may have different sources. It may stem from solution of CO_2 (due to condensation of CO_2 -bearing steams) in the fluids of the geothermal system at moderate depth. HCO_3^- -rich geothermal waters are commonly observed in peripheral zones

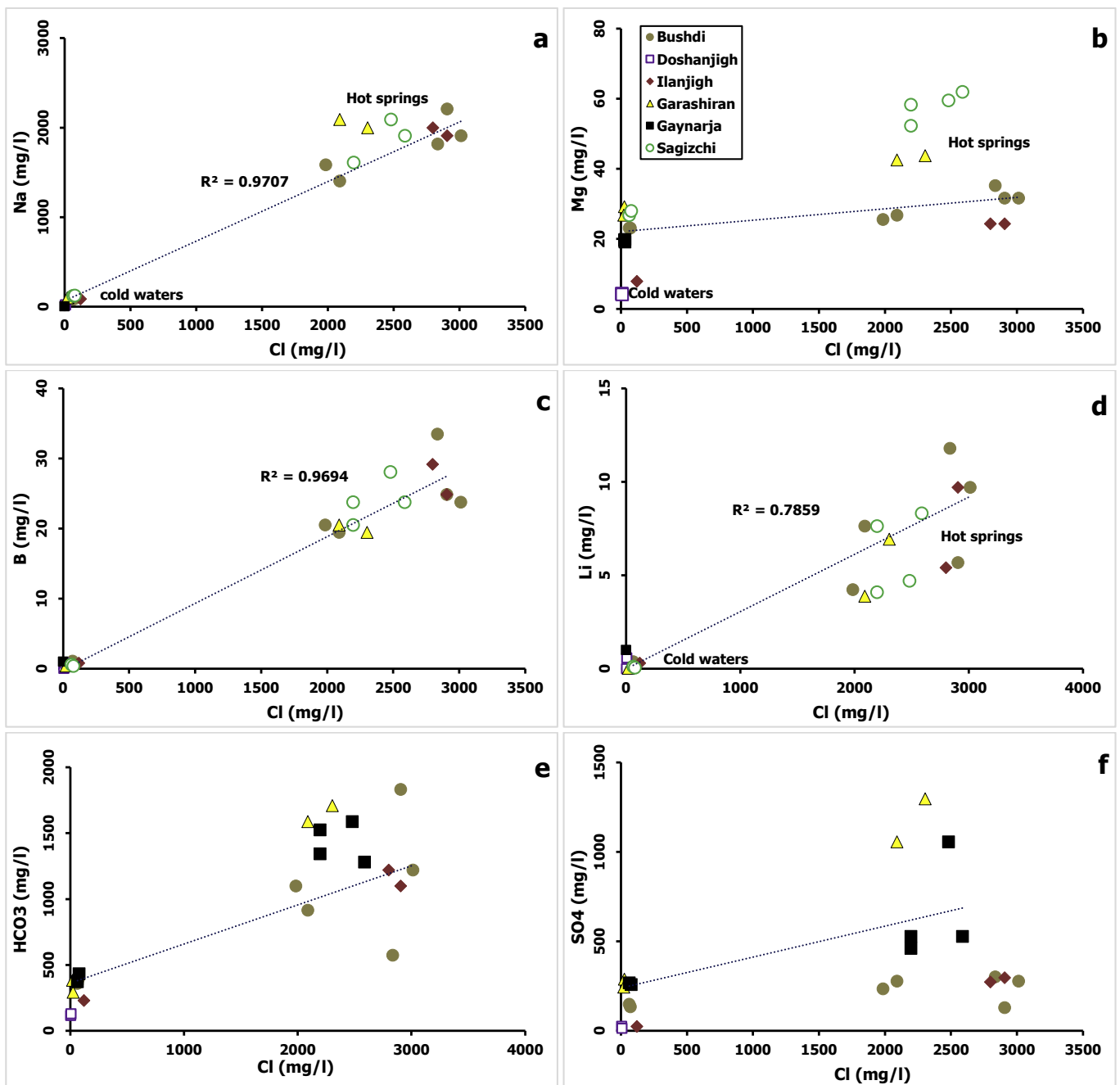


Fig. 5. Diagrams showing the correlations of Cl^- with some major and minor cations and anions in the selected water samples from the Bushdi geothermal field in the south of mount Sabalan.

of either vapor-rich or liquid-rich geothermal systems (Marini, 2000). It seems that the basement crystalline limestone in the study area had considerable effect on the high HCO_3^- concentration of the geothermal waters.

SO_4^{2-} shows a weak correlation with Cl^- (Fig. 5f). The diagram in Fig. 5f displays two discrete relatively decreasing and increasing trends for SO_4^{2-} . The first trend may be due to the deposition of sulfate minerals, and the second to the addition of sulfide species to the geothermal fluids (Sbrana et al., 2010). The acid-sulfate composition is the characteristic of near-surface low-temperature geothermal fluids (Nicholson, 1993). Deep geothermal fluids have relatively low SO_4^{2-} concentration (<50 mg/l). In fact, the SO_4^{2-} and Chloride-rich fluids are regarded as two end members in hydrothermal fluids. Therefore, the weak correlation between these two in the hydrothermal fluids of the studied area is not unexpected.

6. Isotope geochemistry

6.1. Oxygen-18 and deuterium

The obtained values for ^3H , $\delta^{18}\text{O}$ and δD of 18 cold and hot spring water samples from the Bushdi area are presented in Table 1. The $\delta^{18}\text{O}$ values of these samples vary from -12.4‰ to -7.5‰ . The δD values range from -78.6‰ to -70.6‰ . ^3H values vary from 0.65 TU to 105 TU. The linear relation between δD and $\delta^{18}\text{O}$ can be used to determine of the origin of spring waters (Wang, 1991; Clark and Fritz, 1997; Pichler, 2005; Zhou et al., 2008). Plotting $\delta^{18}\text{O}$ versus δD (Fig. 6) demonstrates that the data points are clustered close to both, the global meteoric water line (GMWL) with the equation $\delta\text{D} = 8 \delta^{18}\text{O} + 10$ (Craig, 1961), and the national meteoric water line (NMWL) with the equation $\delta\text{D} = 6.89 \delta^{18}\text{O} + 6.57$ (Shamsi and Kazemi, 2014). The continental hot waters commonly have a meteoric origin (Pasvanoglu, 2011). The meteoric waters percolate downward along the fractured and brecciated fault zones and are

heated because of the anomalous geothermal gradient and then ascend upward toward the ground surface through appropriate channel ways.

According to Fig. 6, most of the data points plot between GMWL and NMWL. In fact the oxygen shift is almost low ($\sim 5\text{‰}$) which is supposed to be as a result of interaction of geothermal fluids with reservoir rocks (Truesdell and Hulston, 1980). Consideration of $\delta^{18}\text{O}$ values of the analyzed water samples indicates relatively low enrichment in ^{18}O . Since the $\delta^{18}\text{O}$ content of meteoric waters is not in equilibrium with the reservoir rocks, the water-rock isotopic exchange reactions, evaporation, mixing with magmatic waters, and combination of these processes can lead to enrichment of ^{18}O in geothermal fluids (Craig, 1966; Gokgoz, 1998; Ohba et al., 2000; Varekamp and Kreulen, 2000; Purnomo and Pichler, 2014). Therefore, the relatively low $\delta^{18}\text{O}$ value of the analyzed water samples can be attributed to mixing of near-surface waters with the geothermal fluids. However, with regards to parameters such as elevation, geographic latitude, and distance from the sea which can influence the $\delta^{18}\text{O}$ content of the hydrothermal fluids, the high meteoric precipitation (relative to evaporation) in the area may account for the $\delta^{18}\text{O}$ dilution. On the other hand, collection of the water samples in wet season (due to likely mixing with meteoric waters) may be another reason for the low $\delta^{18}\text{O}$ values. In general, consideration of $\delta^{18}\text{O}$ values has demonstrated that the magmatic share of $\delta^{18}\text{O}$ in these hot waters in south of the mount Sabalan is almost trivial as is evident from the position of the data points in Fig. 6 which lies far from the magmatic fluid box (see Fig. 6).

As can be observed in Fig. 6, the geothermal fluids in the Bushdi area show relatively slight increase in $\delta^{18}\text{O}$ values that may be caused by interaction of hot fluids with host volcanic rocks. In fact, this relatively slight increment in $\delta^{18}\text{O}$ values may indicate the low to moderate temperature of the geothermal system (Clark and Fritz, 1997). The δD values, in general, do not show notable variation because of very low hydrogen content of the host rocks. The slight

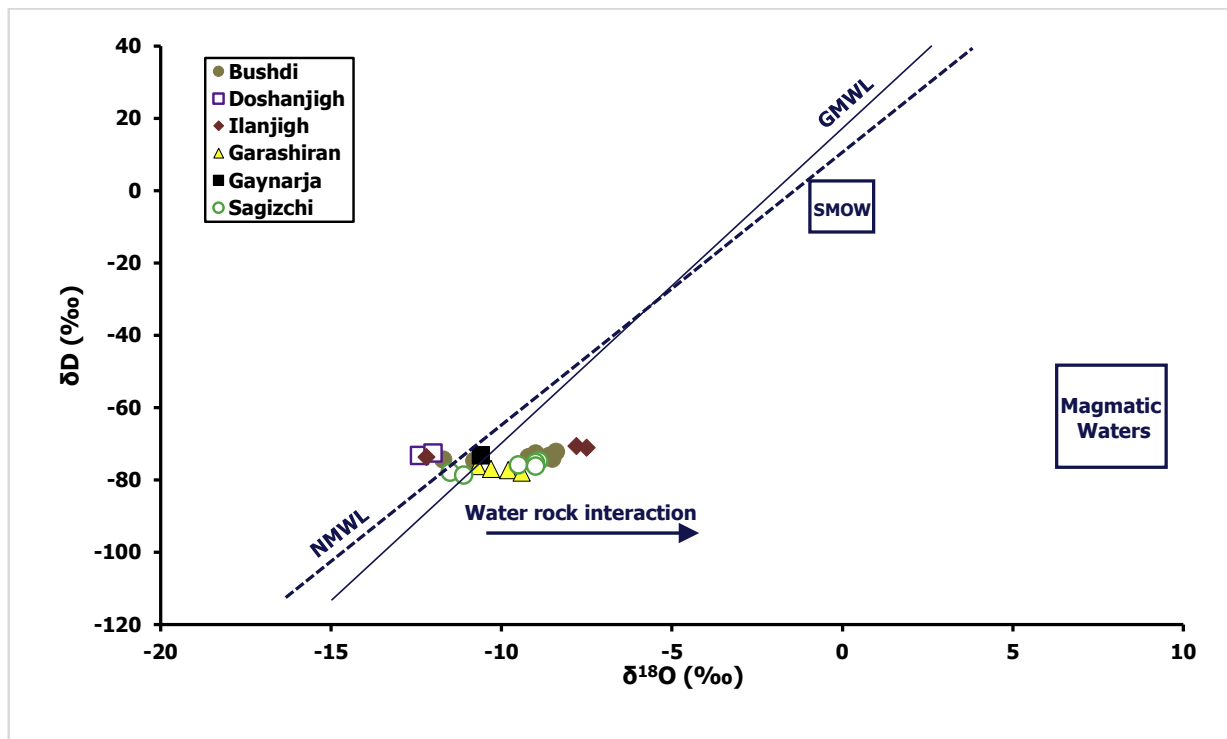


Fig. 6. Plot of $\delta^{18}\text{O}$ versus δD values for some selected cold and hot spring water samples from the Bushdi geothermal field in the south of mount Sabalan. Shown on this figure are also the national meteoric water line, NMWL (Shamsi and Kazemi, 2014) and the global meteoric water line, GMWL (Craig, 1961).

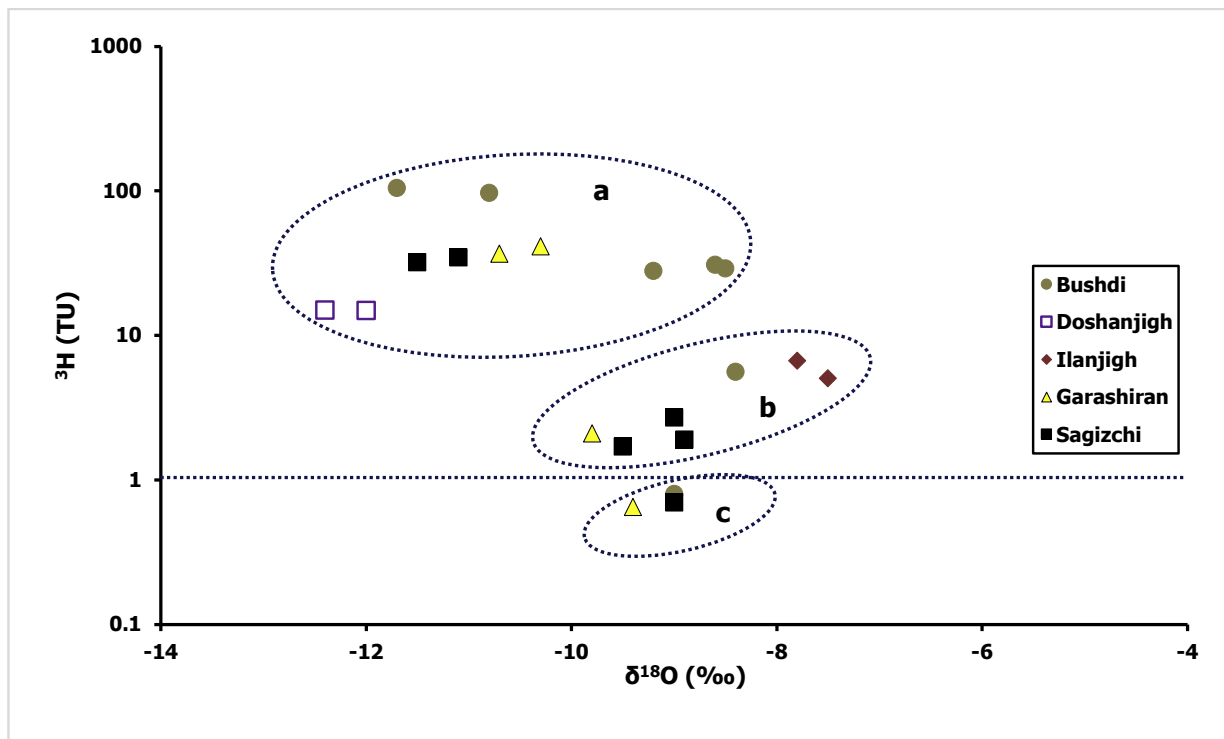


Fig. 7. Plot of $\delta^{18}\text{O}$ versus ^3H for some selected cold and hot spring water samples from the Bushdi geothermal field in the south of mount Sabalan.

increase in δD , however, may be in conjunction with vaporization and isotopic interaction with the host rocks.

6.2. Tritium

There are several methods for estimating the residence time of geothermal waters in host rocks. One of the most common methods is utilizing the unstable isotope of hydrogen, tritium (^3H). Tritium which has the lowest abundance among the hydrogen isotopes (Gerardo-Abaya et al., 2000) has a short half-life and will decay (by β^- disintegration) to form ^3He . The tritium content of geothermal fluids is a function of the amount of ^3H at the place of intake, the residence time, and the flow nature of the system (Young and Lewis, 1982). Although the ^3H concentration varies in different seasons and geographic positions, by calculating the residence time and subsequently the time span of ^3H circulation in an aquifer, the feeding area and the fluid flow rate in a geothermal system can be determined. The ^3H content of the cold and hot waters in the Bushdi area is relatively high and varies from 0.65 TU to 41.4 TU (see Table 1). This may be caused either by mixing with meteoric sources or rapid fluid flow within the system in a shorter time than the β^- disintegration of the isotope ^3H (Imbach, 1997). The $\delta^{18}\text{O}$ versus ^3H diagram demonstrates that the data are plotted in three distinct domains, *a*, *b*, and *c* (Fig. 7). In the domain *a*, the ^3H content is > 10 TU indicating modern waters. The domain *b* belongs to samples whose ^3H values are within the range of 1 TU to 10 TU being temporally categorized as sub-modern waters. The water samples lying in the domain *c* possess ^3H values < 1 TU indicating the oldest waters within the geothermal system in the study area. Mazor (1991) and Pasvanoglu (2011) stated that the $^3\text{H} > 1$ TU belongs to hot waters whose residence time is < 54 years. Considering the ^3H content of the cold and hot waters in the Bushdi geothermal field and the position of the data points on the ^3H versus $\delta^{18}\text{O}$ diagram (Fig. 7), the circulating fluids in this system

were relatively young. According to δD and $\delta^{18}\text{O}$ data, it can be stated that the Bushdi geothermal field is proximal to the feeding source of the system that is actually the mount Sabalan (the northern part of the study area) containing an extensive fault system.

7. Conclusions

According to the data and discussion presented above, the following results have been obtained from this investigation:

- 1 The volcanic lavas and pyroclastics (andesite, trachy-andesite, and basalt) in the Bushdi area are reservoir rocks for the geothermal field in the south of mount Sabalan. The basement limestone is crucial for the generation of Ca^{2+} and HCO_3^- and the deposition of travertine around the mouth and conduit of hot springs. The clays formed by alteration of the reservoir rocks likely acted as impermeable materials in the overlying cap rocks for the geothermal system.
- 2 In view of the considerable abundance of Cl^- , Na^+ , Ca^{2+} , and HCO_3^- , the geothermal fluids in the study area are chemically categorized as both Na-Cl and Ca-Na- HCO_3 systems. The high concentration values of Cl^- , Na^+ , and Ca^{2+} stem from water-rock chemical interactions, and the high HCO_3^- values may be due either to solution of ascending CO_2 gas in underground waters or to dissolution of basement crystalline limestone.
- 3 Geochemically, concentration values of mercury and arsenic in the geothermal water samples are negligible. However, the values for Se are notable and for B and Li higher than normal.
- 4 Consideration of isotopic compositions of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) show that the analyzed samples are slightly enriched in $\delta^{18}\text{O}$ which may be related to the water-rock isotopic exchange reactions. The water-rock interactions caused a slight increase in δD as well.

5 The measurement of ^3H in the Bushdi geothermal fluids indicates that the circulating geothermal fluids can temporally be divided in three groups. The first group has ^3H values > 10 TU and belongs to modern waters. The second group, so-called sub-modern waters, has ^3H values within the range of 1 TU to 10 TU. The third group which has ^3H values < 1 TU is regarded as old waters.

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