

Evaluation of hydrogeochemical and isotopic properties of the geothermal waters in the east of Mount Sabalan, NW Iran

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Abstract: The Mount Sabalan district is regarded as the best place to investigate geothermal activities in northwest Iran. Since the last episode of volcanic activity in the Plio-Quaternary time, hot springs and surficial steams as conspicuous manifestation of geothermal activities have appeared around the slopes of Mount Sabalan. The hot fluids circulating in this geothermal field contains anions chiefly of HCO_3^- and Cl^- ; however, SO_4^{2-} content in some water samples is relatively high, imparting sulfate characteristics to such fluids. Geothermometric studies provided compelling evidence for estimation of the reservoir temperature ($\sim 150^\circ\text{C}$) in the study areas. Thus, in this respect, the geothermal systems in the east of Mount Sabalan were categorized as high-temperature. The composition of stable isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) indicated that the waters involved in this geothermal field have mainly meteoric origin. On the basis of ^3H isotopes, only a few water samples exhibited a residence time of ~ 63 years, which can be grouped as old waters.

Key words: Mount Sabalan, geothermal field, geothermometry, stable isotopes, residence time

1. Introduction

Geothermal research is used to identify the origin of geothermal fluids and to quantify the processes that govern their compositions and the associated chemical and mineralogical transformations of the rocks with which the fluids interact. The variation in the chemistry of geothermal fluids provides information regarding the origins, mixing, and flow regimes of the systems (Smith et al., 2011). The subject has a strong applied component. Geothermal chemistry constitutes an important tool for the exploration of geothermal resources and in assessing the production characteristics of drilled geothermal reservoirs and their response to production. Geothermal fluids are also of interest as analogues to ore-forming fluids. Understanding chemical processes within active geothermal systems has been advanced by thermodynamic and kinetic experiments and numerical modeling of fluid flow (Arnossov et al., 2007).

The Mount Sabalan district in the northwest of Iran is a part of the Azarbaijan block. From the geotectonic point of view, this block is situated between the Arabian and Eurasian plates (McKenzie, 1972; Dewey et al., 1973). In fact, the Sabalan volcano is a part of a volcanic belt stretching from the Caspian Sea in the east to the Black Sea in the west (Neprochnov et al., 1970). The volcanic

activities along this belt are observed in various parts of Armenia, Anatolia, and western Alborz.

The geothermal gradient in the young volcanic regions is normally higher and shows thermal anomalies. This was noted by various researchers in the early twentieth century and many countries having such anomalously high geothermal gradients in potential areas took measures to harness such endless thermal energies accumulated beneath the surface.

The areas around the Mount Sabalan volcano in northwest Iran were geothermally active during the Plio-Quaternary period (Alberti et al., 1976) and have higher surficial thermal anomalies relative to the other parts of the country. Thus these areas were recognized to be very important and hence were regarded as the first priority for exploiting the geothermal energy. The primary appearance of geothermal systems including hot springs and surficial steams in many areas around the Mount Sabalan is indicative of widespread young subsurface magmatic activities in this region.

The main objective of this study involves consideration of hydrogeologic characteristics, chemical composition, and isotopic aspects of the hot springs in the east of Mount Sabalan with emphasis on lithologic units hosting the geothermal fluids in this district. Since the geothermal

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fields in this district were not investigated comprehensively, the authors hope the results of this research will further contribute to the recognition and assessment of these fields.

2. Materials and methods

After implementing the primary geologic works like identification of the lithologic units and determination of tectonic occurrences in various areas, an accurate geologic map of the district was prepared. Among the numerous hot springs to the east of Mount Sabalan, those with higher flow rate and temperature were chosen for sampling. The temperature and electrical conductivity (EC) of the water samples were directly measured in the field and their HCO_3^- content was determined by titration. All water samples were collected and kept in polypropylene bottles and were used for laboratory experiments such as quantitative analysis of cations, anions, rare elements, and stable isotopes. The prepared samples were first passed through 0.45- μm filters and treated with 1% of concentrated HNO_3 to prevent precipitation of cations and rare elements.

In the present study, the chemical and stable isotope ($\delta^{18}\text{O}$ and δD) analyses were carried out in G.G. Hatch stable isotope laboratory (Gasbench + DeltaPlus XP isotope ratio mass spectrometer, ThermoFinnigan, Germany) at Ottawa University, Canada. The chemical analyses were done using ICP-MS in ACME Analytical Laboratories Ltd, Canada. Still some more samples were analyzed for $\delta^{18}\text{O}$ and δD in the hydrogeologic labs at Berman University, Germany. The precision of the measurements for $\delta^{18}\text{O}$ was $\pm 0.2\%$ and for δD $\pm 1\%$. The main cations including Mg, Ca, K, Na, and Si were analyzed by ICP-OES (PerkinElmer) and the main anions such as Cl^- , F^- , and SO_4^{2-} were measured by ion chromatography using an IC-Plus Chromatograph (Metrohm).

The ^3H values were measured in terms of tritium unit (TU), where $1 \text{ TU} = ([\text{T}]/[\text{H}]) \times 10^{18}$ (IAEA, 1979).

3. Results and discussion

The study district encompasses the eastern part of the Mount Sabalan strato-volcano and its geology was influenced by the Sabalan volcanic activities with calc-alkaline nature. The volcanic rocks in this district vary in composition from andesite through dacite to scarcely rhyolite (Dostal and Zerbi, 1978). The volcano-sedimentary rocks (agglomerate, lahar, and tuff) are the major lithologic units in this district covering the older sediments. Glacial moraines are also present in some localities. The agglomerate and lahar were likely deposited synchronously with explosive volcanic activities during the glacial period. In the Sarein and Viladara areas, there are many hot springs within these rocks. In the north of

the district, the dominant lithologic units are trachy-andesitic, dacitic, and basaltic lavas with porphyry texture manifested by plagioclase and occasionally pyroxene and amphibole phenocrysts (Figure 1) (Haddadan and Abbasi Damani, 1997). The hot springs in the Sardabeh area are discharging through these lithologic units. Around the hot springs in the Sardabeh area massive silica (principally of chalcedony and opal) accumulations (silica sinters) were formed with thicknesses up to about 300 m. The south of the district was covered by 15-m-thick porous limestone, which was likely deposited in a freshwater lacustrine environment. In addition, Quaternary alluvial sediments were also observed in this part.

Tectonically, numerous faults and fractured zones developed in this district. The major faults passed through the Sarein and Sardabeh areas (with NW–SE trend) and played a crucial role in the development of surficial hot springs. In the southern part of the district, there are some folded zones with an overall NE–SW trending. It appears that these tectonic occurrences were influenced by the last volcanic activities of Mount Sabalan and to some extent control the geothermal systems in this district.

3.1. Hydrogeochemistry

Hydrogeochemistry is an indispensable unit of hydrogeological studies because it aids in the determination of chemical properties as well as the overall qualities of groundwater, including their genesis and relationship with surface and rain waters. Therefore, it is an important part of geothermal research programs (Tarcan, 2002).

So far, little work on geothermal fluids has been carried out to the east of Mount Sabalan, and most of the previous studies were done on geothermal activities in other areas around Mount Sabalan (Masoumi et al., 2016, 2017a, 2017b, 2017c). Despite the lack of deep diamond drilling data, the important subjects such as hydrogeochemical characteristics of the fluids, isotopic issues, geologic conditions governing the geothermal reservoirs, lithologic compositions, and fluid-feeding localities in the study area merit more detailed investigations.

Hydrogeochemical studies were reckoned to be the most suitable method to consider the potential geothermal characteristics of the district with the aim of approaching to applicable geothermal energy. The data obtained from chemical (major cations and anions, rare and heavy elements), stable ($\delta^{18}\text{O}$ and δD), and radioactive isotope (^3H) analyses, and physico-chemical characteristics (temperature, pH, TDS, EC, and hot springs flow rate) are listed in Tables 1 and 2.

From the physico-chemical point of view, the hot springs in the Sabalan region demonstrate characteristics of surficial geothermal fluids (acid-sulfate waters), and the physico-chemical parameters of these hot waters vary in a wide range. Thermally, the maximum temperatures at the

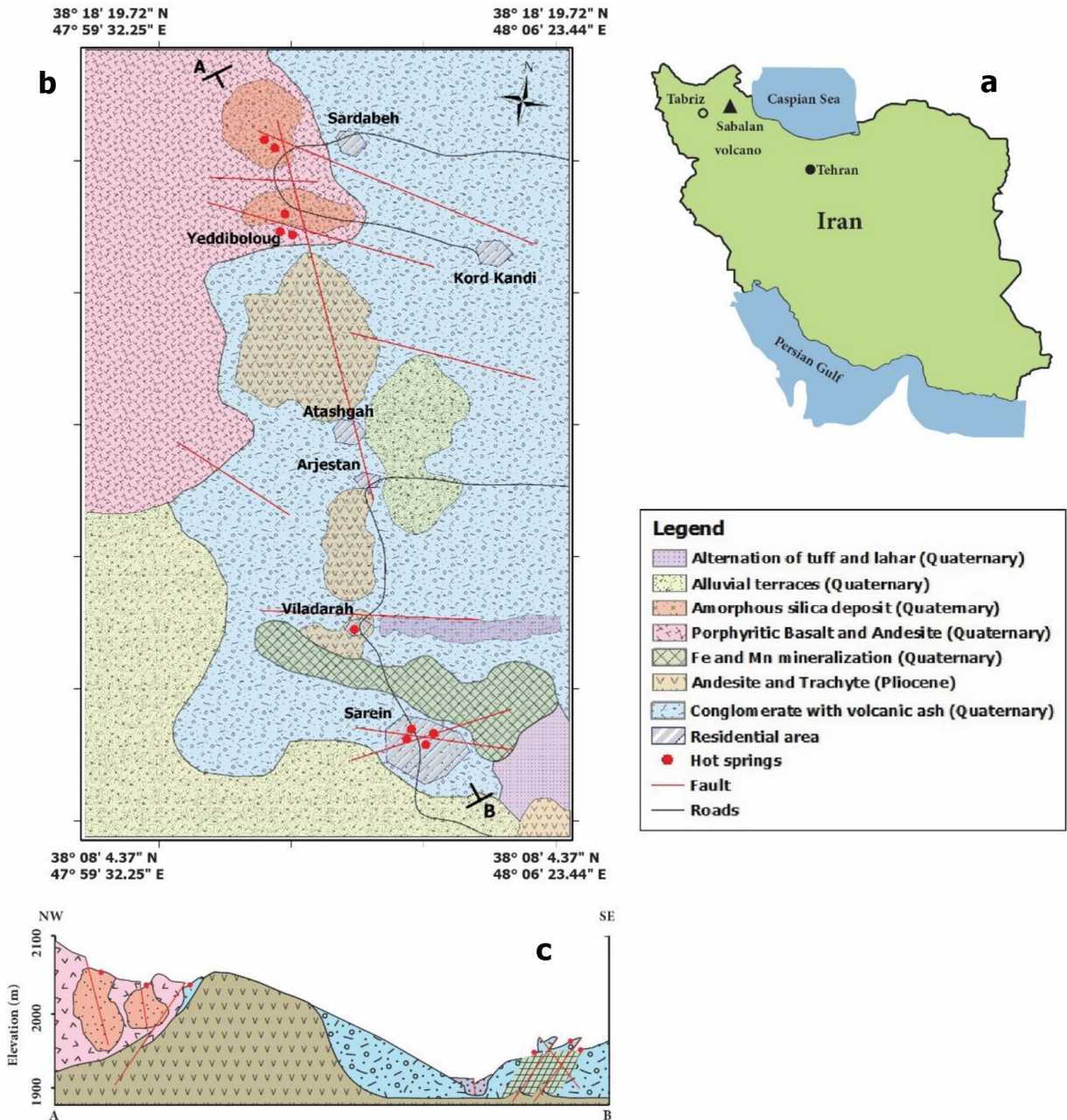


Figure 1. (a) An index map showing the position of the study district in the northwest of Iran. (b) Geologic map of the geothermal field to the east of Mount Sabalan. (c) Geological cross section in NW-SE direction (A-B).

point of discharge belong to hot springs in the Sarein area (~53 °C) and the minimum to those in the Villadara area (~20 °C).

These waters in light of acidity (pH) display notable changes, so that the minimum pH values belong to those in the Sardabeh area (4.5–8.8, mean of 5.2) and the maximum values to those in the Sarein area (5.3–6.6, mean of 5.9).

These values compared to the waters derived from melted snow in the region (pH = 7.2) or even to waters

in small lake in the Sabalan caldera (pH = 8.2) show a remarkable decrease in pH. The release of proton (H⁺) during the reaction of

$H_2S_{(g)} + 2O_{2(aq)} = 2H^+_{(aq)} + SO_4^{2-}_{(aq)}$ accounts for the low pH and hence the acidic nature of these waters (Nicholson, 1993).

The measured total dissolved solutes (TDS) in geothermal waters in this region exhibit a direct relationship with the temperature of these hot springs, so

Table 1. Physico-chemical parameters, chemical analyses, and isotopic composition data for the selected hot spring water samples from geothermal field to the east of Mount Sabalan. The sign (-) stands for lack of analytical data.

Sample ID	Sampling stations	TDS mg/L	EC μ S/cm	Elev (m)	Flow rate (L/min)	T (°C)	pH	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Fe 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 ‰	δ D ‰
ES1	Sarein	1016	1516	1670	600	50	5.3	179	39.1	70.0	19.4	2.42	199.0	0.4	96.0	439	98.0	1.3	-13.4	-75.8
ES2	Sarein	936	1397	1670	80	53	6.0	191	36.0	72.0	18.2	3.16	209.0	0.3	96.0	415	105.0	1.5	-11.2	-74.3
ES3	Sarein	396	591	1620	30	25	5.4	19	3.8	46.0	10.9	0.05	11.0	0.4	58.0	140	73.0	13.5	-13.4	-74.7
ES4	Sarein	277	413	1620	4	26	5.6	13	2.5	42.0	9.8	1.10	5.0	0.4	48.0	134	78.0	19.5	-12.4	-74.8
ES5	Sarein	910	1358	1620	50	52	6.6	172	34.8	72.0	20.7	1.86	209.0	-	96.0	329	103.0	8.5	-11.2	-
ES6	Sarein	910	1358	1650	45	52	6.3	240	40.0	75.0	-	-	194.0	-	170.0	-	60.0	12.1	-11.2	-
ES7	Sarein	-	-	1676	60	53	5.9	202	36.7	73.0	17.5	0.10	214.0	-	-	-	44.9	5.7	-11.1	-76.1
ES8	Sarein	-	-	1685	25	44	6.2	202	34.6	68.6	17.5	0.00	3.0	-	3.4	-	46.7	-	-	-
ES9	Sarein	-	-	1685	30	45	6.1	198	34.6	68.9	17.2	0.00	-	-	-	-	46.6	-	-	-
ES10	Sarein	-	-	1690	45	45	6.0	200	34.9	69.0	17.3	0.01	-	-	-	-	47.5	9.8	-10.1	-75.8
ES11	Sarein	-	-	1670	60	46	6.1	200	35.0	69.2	17.4	0.03	-	-	-	-	47.9	13.4	-11.1	-78.6
ES12	Sardabeh	830	1239	1900	-	36	4.5	21	6.6	184.0	9.5	-	6.0	-	480.0	33	85.0	0.5	-11.4	-
ES13	Sardabeh	876	1307	1910	60	36	4.6	23	6.3	174.0	8.6	0.02	2.0	0.5	480.0	16	84.0	1.2	-12.5	-74.9
ES14	Sardabeh	891	1330	1930	150	37	4.8	22	7.0	180.0	9.2	0.05	2.0	0.4	528.0	35	81.0	1.9	-11.9	-74.9
ES15	Sardabeh	510	761	1945	3	22	6.5	15	2.5	92.0	9.6	1.10	-	0.6	231.0	79	56.0	14.7	-12.0	-
ES16	Sardabeh	777	1160	1900	3	22	4.5	20	6.3	170.0	8.7	0.15	4.0	0.4	442.0	28	68.0	7.4	-11.6	-
ES17	Sardabeh	-	-	1890	10	34	4.7	23	6.8	172.3	8.6	0.02	-	-	-	-	37.7	-	-	-
ES18	Sardabeh	-	-	1907	20	33	4.6	24	7.0	178.0	8.6	0.01	-	-	-	-	38.3	0.7	-10.7	-74.8
ES19	Sardabeh	-	-	1966	25	27	8.8	0.03	0.0	0.1	0.6	0.05	0.0	-	-	-	27.7	0.9	-10.2	-68.9
ES20	Sardabeh	-	-	1934	60	35	4.7	25	6.8	198.8	9.3	0.01	6.0	-	-	-	36.0	1.8	-11.6	-75.0
ES21	Sardabeh	-	-	1915	15	28	5.0	22	6.7	177.1	9.7	0.00	-	-	-	-	38.4	-	-	-
ES22	Yeddiboloug	-	-	1970	60	35	4.9	26	6.6	170.5	8.2	0.01	-	-	6.5	-	35.8	-	-	-
ES23	Yeddiboloug	-	-	1930	45	34	5.1	23	7.0	185.0	8.1	0.07	-	-	-	-	36.5	-	-	-
ES24	Yeddiboloug	-	-	1950	30	36	4.7	23	6.8	181.1	8.1	0.01	-	-	6.5	-	38.1	4.5	-10.0	-68.4
ES25	Yeddiboloug	-	-	1940	25	32	4.6	23	6.8	183.2	8.3	0.10	-	-	-	-	37.5	8.6	-12.1	-80.2
ES26	Viladara	275	410	1850	400	21	5.8	14	3.1	48.0	12.0	0.01	3.0	0.5	37.0	183	79.0	2.4	-11.8	-
ES27	Viladara	369	551	1840	600	22	5.5	23	7.0	54.0	14.6	0.54	5.0	0.5	44.0	250	98.0	1.0	-11.5	-74.4
ES28	Viladara	288	430	1830	15	22	6.3	12	2.0	46.0	12.0	1.10	4.0	0.4	12.0	195	84.0	5.0	-10.8	-
ES29	Viladara	390	582	1850	6	20	5.9	25	6.6	54.0	13.4	1.10	4.0	0.1	35.0	256	106.0	1.9	-12.8	-74.6
ES30	Viladara	430	642	1795	30	23	6.2	32	8.6	56.0	13.4	-	6.0	-	37.0	299	118.0	3.7	-11.5	-

Table 2. Concentration values of trace elements for the selected hot spring water samples from geothermal field to the east of Mount Sabalan. The sign (-) stands for lack of analytical data.

Sample ID	Sampling stations	Li mg/L	Ba mg/L	Rb mg/L	Sr mg/L	Cs mg/L	B mg/L	As mg/L	Se mg/L	Hg mg/L	Al mg/L
ES1	Sarein	0.97	0.12	0.41	0.21	0.31	2.10	-	-	0.0081	-
ES2	Sarein	0.47	1.50	0.35	0.24	1.05	1.90	-	-	0.0005	-
ES3	Sarein	0.03	1.50	0.02	0.10	0.01	0.20	-	-	0.0015	-
ES4	Sarein	0.01	1.50	0.02	0.07	0.05	-	-	-	0.0005	-
ES5	Sarein	0.97	-	0.25	0.30	-	7.00	-	-	-	-
ES6	Sarein	-	-	-	0.30	-	-	-	-	-	-
ES7	Sarein	0.87	1.60	0.27	0.07	1.29	2.30	0.15	2.3	0.1000	0.01
ES8	Sarein	0.97	0.06	0.24	0.57	-	2.05	0.12	76.2	-	0.01
ES9	Sarein	0.93	0.06	0.23	0.56	-	2.45	0.1	65.7	-	0.01
ES10	Sarein	0.97	0.06	0.22	0.58	-	2.33	0.12	170.2	-	0.01
ES11	Sarein	0.97	0.06	0.24	0.58	-	2.24	0.14	102.2	-	0.01
ES12	Sardabeh	-	-	-	0.27	-	0.10	-	-	-	-
ES13	Sardabeh	0.01	1.50	0.04	0.20	0.06	2.80	-	-	0.0050	-
ES14	Sardabeh	0.02	1.50	0.02	0.39	-	-	-	-	0.0006	-
ES15	Sardabeh	-	0.18	0.01	0.26	0.06	2.80	-	-	0.0050	-
ES16	Sardabeh	0.02	1.50	0.02	0.33	-	0.40	-	-	0.0006	-
ES17	Sardabeh	0.02	0.02	0.03	0.32	-	0.77	0.06	0.05	-	0.15
ES18	Sardabeh	0.02	0.02	0.04	0.32	-	0.78	0.06	6.05	-	0.13
ES19	Sardabeh	0.01	0.05	5.37	2.90	2.30	0.99	0.05	0.50	0.0100	0.15
ES20	Sardabeh	0.05	0.17	0.06	0.33	1.42	0.59	0.17	0.50	0.1000	0.14
ES21	Sardabeh	0.02	0.02	0.05	0.31	-	0.10	0.08	0.05	-	0.05
ES22	Yeddiboloug	0.02	0.01	0.03	0.35	-	0.52	0.05	0.05	-	0.12
ES23	Yeddiboloug	0.02	0.01	0.05	0.37	-	0.73	0.06	0.05	-	0.13
ES24	Yeddiboloug	0.02	0.01	0.04	0.37	-	0.28	0.07	5.32	-	0.16
ES25	Yeddiboloug	0.02	0.01	0.04	0.33	-	0.23	0.04	0.05	-	0.12
ES26	Viladara	0.01	1.50	0.01	0.36	0.02	0.10	-	-	0.0015	-
ES27	Viladara	0.03	1.50	0.04	0.57	0.01	0.10	-	-	0.0004	-
ES28	Viladara	-	1.50	0.01	0.10	0.04	0.10	-	-	0.0015	-
ES29	Viladara	0.02	1.50	0.06	0.14	0.07	-	-	-	0.0005	-
ES30	Viladara	-	-	-	0.20	-	-	-	-	-	-
ES31	Snow water	-	0.02	0.03	0.13	-	0.33	0.04	0.05	-	0.62

that the maximum measured TDS belongs to samples from the Sarein area (TDS = 1016 mg/L) and the minimum to those from the Viladara area (TDS = 275 mg/L).

The origin and chemical history of hydrothermal fluids can be explored in a Cl, SO₄, and HCO₃ ternary diagram (Chang, 1984; Giggenbach, 1991; Nicholson, 1993; Giggenbach, 1997). Based on their position in the diagram, hydrothermal waters can be divided into neutral chloride, acid sulfate, and bicarbonate waters, but mixtures of the individual groups are common.

According to Figure 2, samples belonging to hot springs in this region demonstrate relatively different composition. Compositionally, the samples from the Sardabeh, Viladara, and Sarein areas chiefly contain sulfate, bicarbonate, and bicarbonate-chloride anions, respectively. In fact, their compositions are related to peripheral waters, HCO₃⁻, SO₄²⁻, and diluted Cl⁻.

The comparison of the concentration values of cations and anions in geothermal waters to the east of Mount Sabalan is shown in the diagram presented by

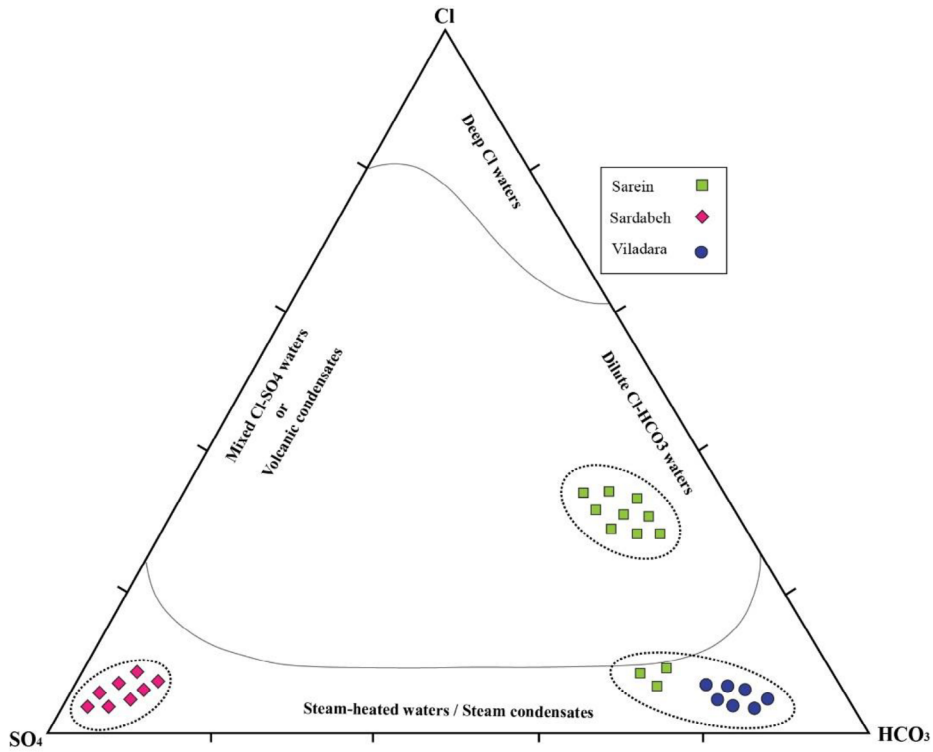


Figure 2. Ternary plot of $\text{HCO}_3\text{-SO}_4\text{-Cl}$ for the geothermal fluids to the east of Mount Sabalan.

Schoeller (1962) (Figure 3). According to this diagram the concentration values of cations and anions in the hot springs representing the three above-mentioned areas are not similar and show different distribution patterns. However, an overall trend for cations like $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ and for anions like $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ can be observed (Figure 3)

Among the cations, Na^+ (240 mg/L) and Ca^{2+} (198 mg/L) have the highest concentration values. The hot springs in the Sarein area contain the highest Na^+ content. The highest Ca^{2+} content belongs to the hot springs in the Sardabeh and Yeddiboloug areas. The maximum concentration values for K and Mg are 40 mg/L and 20 mg/L, respectively.

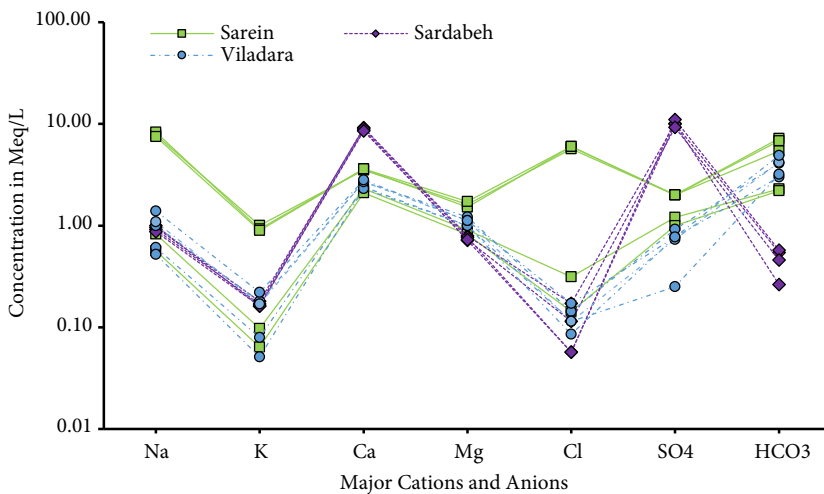


Figure 3. Concentration variations of major cations and anions for the geothermal water samples to the east of Mount Sabalan.

Among the major anions, the maximum concentration values of the sulfate ($\text{SO}_4^{2-} = 528 \text{ mg/L}$) and bicarbonate ($\text{HCO}_3^- = 439 \text{ mg/L}$) belong to samples from the Sardabeh and Sarein areas, respectively. Chloride ion (Cl^-), relative to the other two, has a lower concentration, with a maximum value of 214 mg/L in the Sarein area.

The silica content of the geothermal fluids to the east of Mount Sabalan displays a wide range ($27\text{--}118 \text{ mg/L}$) and the maximum values belong to the springs in the Viladara (118 mg/L) and Sarein (105 mg/L) areas.

Among the trace elements, the highest values belong to selenium, ranging from 0.05 mg/L to 170 mg/L . The water samples from the Sarein area possess the highest Se concentration (170 mg/L), which is very high in comparison with crustal rocks ($0.05\text{--}0.09 \text{ mg/L}$) and normal fresh waters (0.2 mg/L) (Wetang'ula, 2004). This high Se content in the geothermal fluids can be justifiable as its main source in nature, analogous to sulfur (having similar geochemical behavior), is the volcanic rocks (ATSDR, 2001).

Although Se, due to its similar behavior to sulfur, can concentrate in hydrothermal fluids, the anomalously high Se content in certain samples seems to be rather abnormal. Despite careful sampling, the occurrence of errors during the sampling and laboratory stages cannot be ruled out.

Boron in various geothermal systems shows different concentration values, which are influenced by enclosing lithologic units. Einarsson et al. (1975) reported the boron content of geothermal fluids in Ahuachapán area (El Salvador) $\sim 150 \text{ mg/L}$, but its concentration is very low (within the range of $0.1\text{--}6.6 \text{ mg/L}$) in high-temperature geothermal systems within basalts of the volcanic belt in Iceland (Arnórsson and Andrésdóttir, 1995). The high boron values in most geothermal systems have been attributed to the existing B-rich sedimentary and/or metamorphic units in the reservoirs (Smith, 2001). Nevertheless, the geothermal waters hosted by basaltic rocks have low boron content. In the study district, the maximum boron concentration value belongs to the hot springs in the Sarein area (7 mg/L). Furthermore, water samples from the Sardabeh and Viladara areas have boron contents of 2.8 mg/L and 0.1 mg/L , respectively. Therefore, the concentration values of this element in the geothermal systems of the east of Mount Sabalan range from 0.1 mg/L to 7 mg/L , which are compatible with volcanic facies of corresponding systems in other parts of the world.

Arsenic enrichment in geothermal systems occurs predominantly near the surface, along with other epithermal elements such as Sb, Au, and Hg (White, 1981).

The arsenic content of the geothermal waters in the east of Mount Sabalan varies from 0.04 mg/L to 0.17 mg/L . The average concentration of As in worldwide geothermal systems has a range of $0.1\text{--}10 \text{ mg/L}$, while its permissive

standard limit in drinkable waters is $\sim 0.01 \text{ mg/L}$. Therefore, the range of concentration variation of As to the east of Mount Sabalan ($0.04\text{--}0.17 \text{ mg/L}$) is comparable with the world's important geothermal systems. Ellis and Mahon (1964) perceived that the principal source of arsenic in geothermal systems could be the host rocks from which this element was derived by leaching processes. They also asserted that from unmineralized andesitic host rocks about 1.3 mg/L arsenic can be released into geothermal systems.

3.2. Geothermometry

Geothermometers enable the temperature of the reservoir fluid to be estimated. They are therefore valuable tools in the evaluation of new fields and in monitoring the hydrology of systems on production (Nicholson, 1993).

The basic assumptions underlying most geothermometers are that ascent of deeper, hotter waters (and the accompanying cooling) is fast enough such that kinetic factors will inhibit re-equilibration of the water, and minimal mixing with alternate water sources occurs during ascent; it should be noted that compliance with these assumptions is often "exceedingly difficult to prove" (Ferguson et al., 2009; Smith et al., 2009).

Only 13 of all analyzed samples were recognized to be suitable for geothermometric calculations and a great number of samples for various reasons were not qualified for geothermometric purposes. The analyzed samples (ES12-21) having sulfate ion (SO_4^{2-}) derived from near surface water-rock reactions because of mixing with surface waters cannot represent deep fluids and are inapplicable for geothermometric purposes (Nicholson, 1993). Similarly, some other analyzed samples (ES26-30), despite having bicarbonate (HCO_3^-) content, because of having low temperature (as the result of mixing with surficial waters) were omitted from the list of samples chosen for thermometry.

To determine the reservoir temperature of the geothermal field to the east of Mount Sabalan, the geothermometry was done on the basis of certain cations and the results are presented in Table 3.

The calculations were done according to methods presented by Fournier (1977, 1979), Fournier and Truesdell (1973), and Kharaka et al. (1982). The geothermometry of cations (Na-K, Na-Li, and Na-K-Ca) is on the basis of exchange reactions. The estimated reservoir temperatures using the above-mentioned methods (Table 3) are different. In general, the temperatures obtained from silica and Na-K-Ca methods are lower than those acquired by Na-Li and Na-K methods. The estimated temperatures obtained on the basis of the silica method (Fournier, 1977) range from $118 \text{ }^\circ\text{C}$ to $170 \text{ }^\circ\text{C}$.

As mentioned above, the silica geothermometry is based upon solubility of quartz and chalcedony and is

Table 3. Results of the solute-based geothermometries for the fluids from the geothermal field to the east of Mount Sabalan.

Sample ID	Station ID	Silica (Fournier, 1977)	Na–K–Ca (Fournier and Truesdell, 1973)	Na/K (Fournier, 1979)	Na/Li (Kharaka et al., 1982)
ES1	Sarein	170	189	242	249
ES2	Sarein	163	181	229	225
ES5	Sarein	161	184	235	252
ES6	Sarein	142	174	218	-
ES7	Sarein	130	179	225	247
ES8	Sarein	125	175	220	240
ES9	Sarein	124	177	222	238
ES10	Sarein	137	177	222	240
ES11	Sarein	140	177	222	240
ES22	Yeddiboloug	120	182	255	134
ES23	Yeddiboloug	118	188	271	139
ES24	Yeddiboloug	121	188	272	140
ES25	Yeddiboloug	122	188	270	140

widely used for estimation of subsurface temperatures. The solubility of quartz and chalcedony varies with temperature and pressure changes. At temperatures <300 °C the effect of pressure on the solubility of quartz and other silica polymorphs decreases. In fact, at temperatures >120–180 °C the silica solubility is controlled by quartz. Therefore, this method provides better results within the temperature range of 150–250 °C (Gendenjants, 2003). At lower temperatures the other silica phases (i.e. chalcedony) control the concentration of silica in the solution (Fournier, 1977). In contrast, the results obtained from Na–K geothermometry unveiled a temperature range of 218–272 °C, which are similar to those acquired by the Na–Li method (samples Es1–10). In high-temperature geothermal systems (>150 °C) the Na–K geothermometry is influenced by other minerals such as clay minerals (Nicholson, 1993).

Considering the ternary plot of $\text{HCO}_3\text{-SO}_4\text{-Cl}$ (see Figure 2) and other evidence concerning the geochemical parameters, there is much possibility of mixing surface waters with the ascending hydrothermal fluids in this geothermal field. Since the silica geothermometer is so sensitive to the mixing, the results obtained from this geothermometer in the studied samples are not very reliable and the temperatures estimated on the basis of this geothermometer show lower values in comparison with the other geothermometers (Table 3).

Although Khosrawi (1996) classified geothermal waters in the study district as immature waters by using the diagram of Na–K–Mg (Giggenbach, 1988) and this clearly points to the fact that the geothermometry of

these waters is not suitable for this purpose, it is suitable for estimation of the temperature of the reservoir, which categorized Mount Sabalan's geothermal systems as high-temperature (>150 °C).

3.3. Isotopic characteristics

It has long been recognized that chemical and isotopic compositions are important tools for studying the origin and history of geothermal waters (Young and Lewis, 1982). Hydrogen, oxygen, and carbon isotopes play particularly important roles in determining the genesis of thermal waters and when studying the hydrodynamics of geothermal systems. These parameters are also important in identifying mixing processes between cold and thermal water, tracing groundwater movement, and also in estimating the relative ages of thermal waters (Sveinbjörnsdóttir et al., 2000; Wang and Sun, 2001; Chen, 2008). Craig (1961) observed that $\delta^{18}\text{O}$ and δD values of precipitation that has not been evaporated are linearly related by $\delta\text{D} = 8\delta^{18}\text{O} + 10$. However, the equation of mean local precipitation slightly differs from that of the world's precipitation as determined to be $\delta\text{D} = 6.89\delta^{18}\text{O} + 6.57$ by Shamsi and Kazemi (2014) (Figure 4). The measured $\delta^{18}\text{O}$, δD , and ^3H values for hot springs to the east of Mount Sabalan are listed in Table 1. As can be observed in this table, the $\delta^{18}\text{O}$ and δD values vary from -9.96‰ to -13.4‰ and from 68.37‰ to 80.19‰ , respectively. According to Figure 4, most of the data points lie between GMWL and NMWL (National Meteoric Water Line) lines. In fact, the maximum oxygen shift, which resulted from fluid–reservoir rock interactions (Truesdell and Hulston, 1980), is about 5‰ . This indicates that the

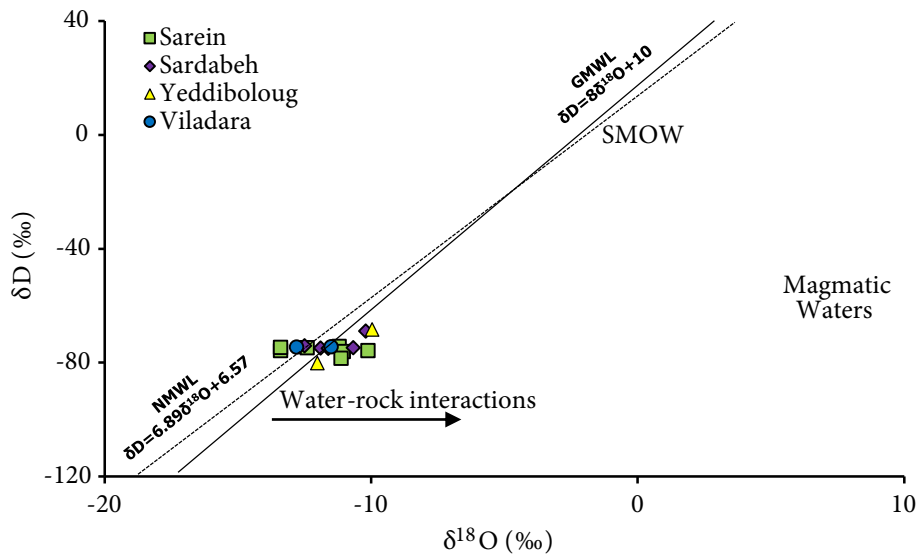


Figure 4. Bivariate plot of $\delta^{18}\text{O}$ versus δD values for the selected cold and hot spring water samples in the east of Mount Sabalan. Shown on this figure are also the national meteoric water line (NMWL) (Shamsi and Kazemi, 2014) and global meteoric water line (GMWL) (Craig, 1961).

enrichment of these waters in $\delta^{18}\text{O}$ is low. In fact, the $\delta^{18}\text{O}$ of meteoric waters can be increased by water–rock exchange reactions, mixing with magmatic waters, or a combination of the two (Craig, 1966; Gokgoz, 1998; Ohbaetal., 2000; Varekamp and Kreulen, 2000; Purnomo and Pichler, 2014). Therefore, the low $\delta^{18}\text{O}$ values of these waters can be attributed to the surficial meteoric waters but it should be noted that factors such as altitude, geographic latitude, and distance from sea can affect the $\delta^{18}\text{O}$ values. Under such conditions and because of the high precipitation rate relative to evaporation in this district, dilution of $\delta^{18}\text{O}$ is justifiably conceivable. On the other hand, since the sampling was carried out in the wet season and because of the likelihood of mixing with meteoric waters, this may be another logical reason for the low $\delta^{18}\text{O}$ values. The overall $\delta^{18}\text{O}$ data illustrated that the magmatic isotopic signature for these hot springs to the east of Mount Sabalan is negligible, and as can be seen in Figure 4 the data points have a great distance from the magmatic fluid box.

As is observed in Table 1, the δD values in most samples are about -74‰ , but in certain samples like ES11, Es13, and Es14 the values are -68‰ , -68‰ , and -80‰ , respectively, which can be regarded as slight deuterium shift. Ellis and Mahon (1977) stated that since most of rocks contain small amounts of hydrogen, relative to water, the direct water–rock interaction cannot be considered an agent for deuterium shift, and only in cases in which there exist considerable clays and micas (hydrogen-bearing minerals) in the environment can hydrogen exchange take place to some extent.

Since ^3H (half-life = 12.4 years) is an excellent tracer for estimation of temporal range of water flow and potential mixing and is also regarded as geochemically relatively conservative, it is normally used for studies of residence time <100 years (Kendall and Doctor, 2005). Gat (1980) proved that after nuclear bomb testing in 1953 the ^3H values remarkably increased in the atmosphere. The $^3\text{H} < 1\text{ TU}$ in waters indicates that they entered their present environment of residence before 1953 (Mazor, 1991; Güleç and Mutlu, 2002). The ^3H values of the geothermal waters to the east of Mount Sabalan are listed in Table 1 and vary from 0.5 TU to 14.7 TU.

Tritium–chloride relationship is a method used for separating shallowly and deeply circulating waters (Çelmen and Çelik, 2009; Bozdağ, 2016).

According to Figure 5, only two samples show values <1 TU and six others have values of approximately 1 TU. Therefore, it may suggest that the samples having ^3H values around 1 TU represent deep circulation while those being <1 TU have indication of surficial waters.

The bivariate plot of $\delta^{18}\text{O}$ versus ^3H can be used for estimation of residence time of waters in geothermal systems (Figure 6). Waters having $^3\text{H} < 1$ TU have residence time older than 1953 (Clark et al., 1997) while values >1 TU are regarded as submodern and modern waters. Ravikumar and Somashekar (2011) and Alçiçek et al. (2016) stated that tritium values varying from 1 to 8 TU are interpreted as an admixture of recent water with old groundwater and groundwater having been subjected to radioactive decay. According to Figure 6 most of the water samples from the east of Mount Sabalan lie in the “submodern waters” field.

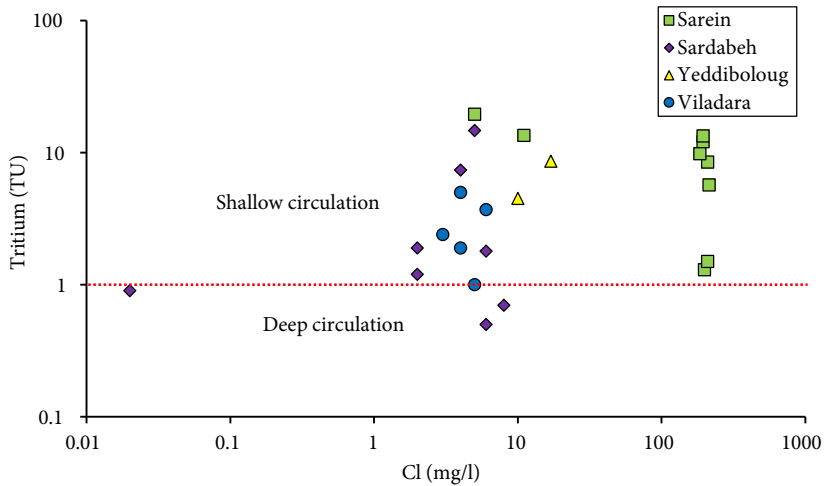


Figure 5. Bivariate plot of Cl⁻ versus ³H for the selected hot spring water samples to the east of Mount Sabalan.

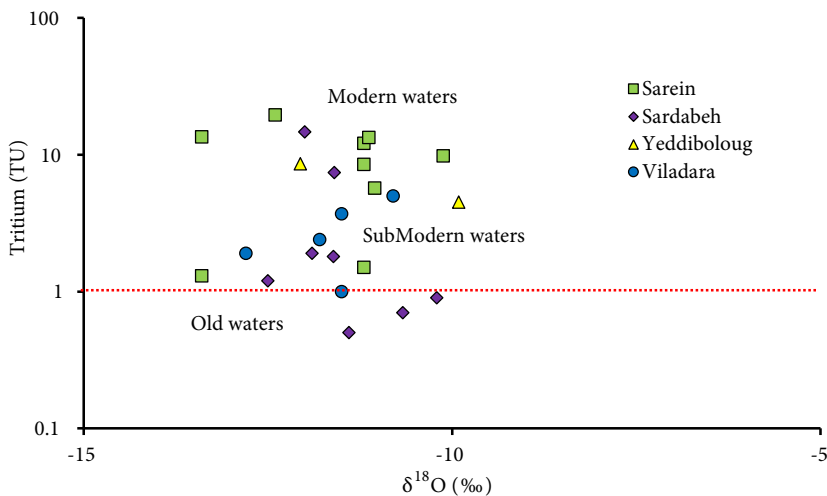


Figure 6. Bivariate plot of δ¹⁸O versus ³H for the selected hot spring water samples to the east of Mount Sabalan.

4. Conceptual model

The reservoir rocks of the geothermal system to the east of Sabalan consist generally of volcanic units that suffered intense fracturing imposed by tectonic stresses. The fracturing provided suitable secondary permeability and facilitated the upward migration of high-temperature geothermal fluids (Figure 7). The high-temperature chloride-bearing ascending fluids reach the surface as geothermal springs in the Sarein area. There are also hot spring waters of carbonate composition generated from condensation of the ascending CO₂-rich vapors by low-*f*O₂ underground waters in this area (Nicholson, 1993).

In the northern parts of the studied areas (the Sardabeh and the Yadibolagh), the compositions of the spring waters are different, and have chiefly acid-sulfate composition (Figure 7) resulting from oxidation of sulfides by high-*f*O₂ underground waters (Nicholson, 1993). Based upon geothermometric calculations, the geothermal reservoirs in these areas have a temperature range of 150–250 °C. Field observations along with examination of satellite images revealed that the principal feeding areas are located around the Sabalan caldera, which is covered constantly by glaciers and snow throughout the year. The melted waters in these areas percolate deep into the ground through the existing numerous fault zones around the caldera.

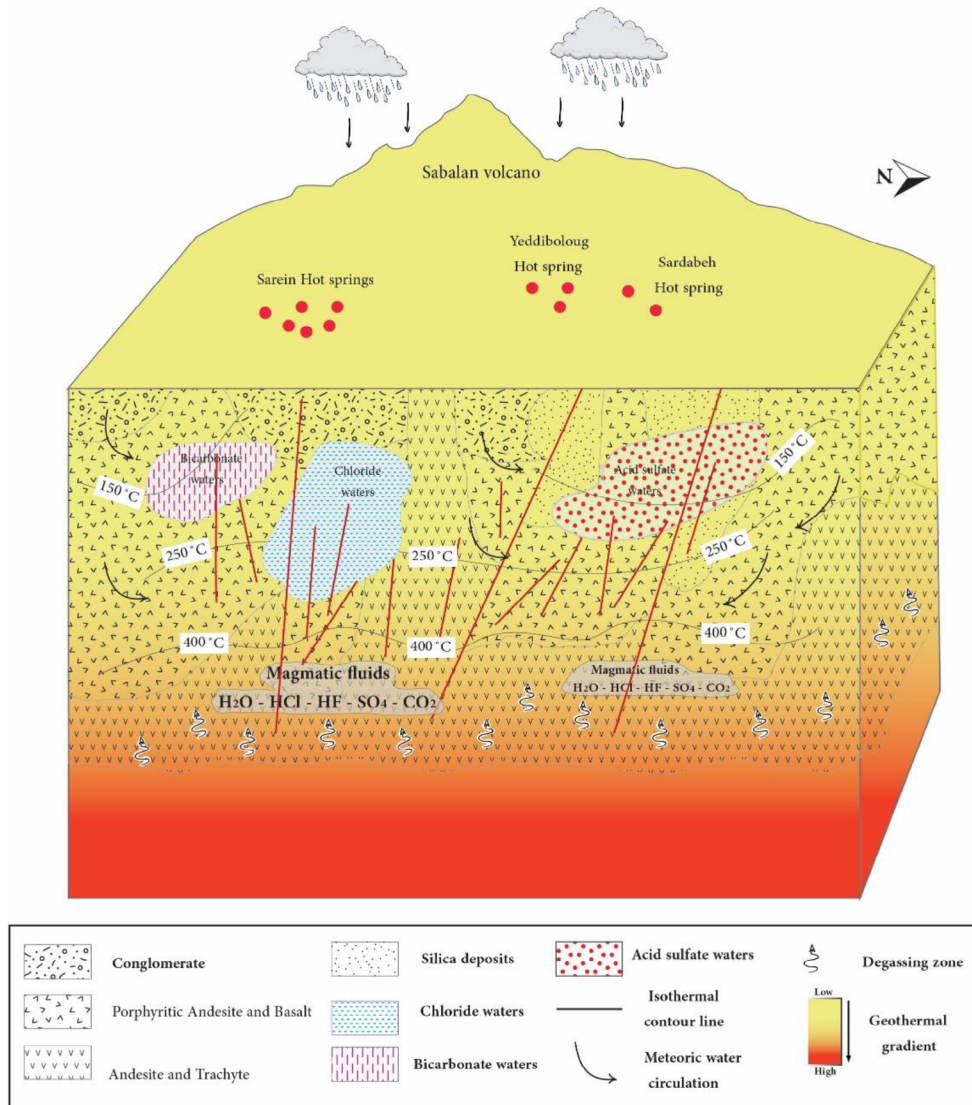


Figure 7. Conceptual model of Eastern Sabalan geothermal field showing the lithological composition of the reservoir, geothermal water types, and the reservoir thermal condition.

5. Conclusions

The most important results obtained from this study are as follows:

1- Geological considerations east of Mount Sabalan indicate that the calc-alkaline volcanic-sedimentary units constitute the great volume of the geothermal reservoir in the study district. The rocks that suffered argillic alteration acted as cap rocks for this reservoir. In some localities in the study district siliceous (chalcedony and opal) sinters developed around the orifice of the hot springs. Tectonically, the NW-SE trending faults played an important role in the development of these hot springs.

2- The geothermal fluids in the study district, in terms of physico-chemical parameters, have characteristics that

differ from those of other geothermal fields around Mount Sabalan, particularly in the southern and northwestern districts. These differences are: (a) the measured pH values of the geothermal fluids range from approximately 4.5 to 8.8, signifying a variation from acidity to alkalinity; (b) the measured TDS values of these waters, in comparison with the average TDS values for most types of geothermal systems, are low and the minimum values were recorded in the Viladara area; (c) estimations of concentration values of anions and cations in the selected spring water samples indicate that they have chiefly chloride and bicarbonate anions; however, samples from the Sardabeh area contain relatively high sulfate (SO₄²⁻) content.

3- The concentration values of trace elements in these waters are notable. Selenium has the highest concentration value (170 mg/L) among the rare elements, and considering its similarities in geochemical behavior with sulfur and besides volcanic activities are the principal source of selenium, the high selenium content in these waters can be justifiable. The maximum concentration values of boron and arsenic were measured to be 7 mg/L and 10 mg/L, respectively. The rest of the rare elements have relatively low concentration values in the studied samples.

4- The calculation of solute-based geothermometry was done on the basis of Na–Li, Na–K, Na–K, Ca, and silica for the water samples. The results of all these procedures for estimation of temperature of the geothermal reservoir to the east of Mount Sabalan were very close to one another. Nevertheless, the temperatures determined by the Na–Li and Na–K geothermometric methods are 225 °C and 239 °C, respectively, while by Na–K–Ca and silica methods they are 181 °C and 136 °C, respectively, for the geothermal reservoir.

5- Consideration of hydrogen and oxygen stable isotopes ($\delta^{18}\text{O}$ and δD) of the geothermal fluids to the east of Mount

Sabalan revealed that their δD and $\delta^{18}\text{O}$ values vary from -63.37‰ to -80.19‰ and from -9.96‰ to -13.4‰ , respectively. The bivariate plot of $\delta^{18}\text{O}$ versus δD shows that the data points mainly lie between lines GMWL and NMWL, indicating that the great portion of these waters have meteoric origin and the role of magmatic waters is almost negligible.

6- Consideration of radioactive isotope of ^3H delineated that the average ^3H content of these waters is 5.1 TU. Illustration of diagrams of tritium– $\delta^{18}\text{O}$ and tritium– Cl^- showed that most of these waters are categorized as “submodern” waters and in respect of depth have shallow circulation.

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References

- Alberti A, Chiamonti P, Batistini G, Nicoletti M, Petrucciani C, Sinigoi S (1976). Geochronology of Eastern Azerbaijan volcanic plateau (North-West Iran). *Ital Min Petr* 32: 579-589.
- Alçiçek H, Bülbül A, Alçiçek MC (2016). Hydrogeochemistry of the thermal waters from the Yenice geothermal field (Denizli Basin, Southwestern Anatolia, Turkey). *J Volcanol Geoth Res* 309: 118-138.
- Arnórsson S, Andrésdóttir A (1995). Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim Cosmochim Acta* 59: 4125-4146.
- Arnórsson S, Stefansson A, Bjarnason J (2007). Fluid-fluid interactions in geothermal systems. Institute of Earth Sciences, University of Iceland. *Rev Mineral Geochem* 65: 259-312.
- ATSDR (2001). Draft toxicological profile for selenium. U.S. Department of Health and Human Services. Agency for Toxic Substances and Disease Registry.
- Bozdağ A (2016). Hydrogeochemical and isotopic characteristics of Kavak (Seydişehir-Konya) geothermal field, Turkey. *J Afr Earth Sci* 121: 72-83.
- Çelmen O, Çelik M (2009). Hydrochemistry and environmental isotope study of the geothermal water around Beypazarı granitoids, Ankara, Turkey. *Environ Geol* 58: 1689-1701.
- Chang CL (1984). Triangular diagrams for predication of aquifer chemistry. *Geoth Res T* 8: 373-376.
- Chen G (2008). The isotopic and chemical characteristics of geothermal fluids from the western Fjords, Iceland and two selected hot spring area in Jiangxi province, SE China. Geothermal training program, Report, The United Nations University.
- Clark WB, Jenkins WJ, Top Z (1976). Determination of tritium by mass spectrometric measurements. *Int J Appl Radiat Is* 27: 515-522.
- Craig H (1966). Isotopic variations in meteoric waters. *Science* 133: 1702-1703.
- Craig H (1966). Isotopic composition and origin of the Red Sea and Salton Sea geothermal brines. *Science* 154: 1544-1548.
- Dewey JF, Pitman WC, Ryan WBF, Bonnin J (1973). Plate tectonics and the evolution of the Alpine system. *Geol Soc Am Bull* 84: 3137-3180.
- Dostal J, Zerbi M (1978). Geochemistry of the Savalan volcano (Northwestern Iran). *Chem Geol* 22: 31-42.
- Einarsson SS, Vides RA, Cuéllar G (1975). Disposal of geothermal waste water by reinjection Proceedings. 2nd United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco: 1349-1363.
- Ellis AJ, Mahon WAJ (1977). Chemistry and Geothermal Systems. New York, NY, USA: Academic Press.
- Ferguson G, Grasby SE, Hindle SR (2009). What do aqueous geothermometers really tell us? *Geofluids* 9: 39-48.
- Fournier RO (1977). Chemical geothermometers and mixing models for geothermal systems. *Geothermics* 5: 41-50.
- Fournier RO, Truesdell AH (1973). An empirical Na-K-Ca geothermometer for natural waters. *Geochim Cosmochim Acta* 37: 1255-1275.
- Fournier RO (1979). A revised equation for the Na/K geothermometer. *Geoth Res T* 3: 221-224.

- Gat JR (1980). The isotopes of hydrogen and oxygen in precipitation. In: Fritz P, editor. *Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment*. Amsterdam, Netherlands: Elsevier, pp. 21-48.
- Gendenjams OE (2003). Interpretation of chemical composition of geothermal fluids from Arskogsstrond, Dalvik and Hrisey, N-Iceland and in the Khangai area, Mongolia. Geothermal training program report, The United Nations University, Iceland.
- Giggenbach WF (1988). Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim Cosmochim Acta* 52: 2749-2765.
- Giggenbach WF (1991). Chemical techniques in geothermal exploration. In: D'Amore F, Editors. *Application of Geochemistry in Geothermal Reservoir Development*. Rome, Italy: UNITAR/UNDP, pp. 252-270.
- Giggenbach WF (1997). The origin and evolution of fluids in magmatic-hydrothermal systems. In: Barnes HL, editor. *Geochemistry of Hydrothermal Ore Deposits*. New York, NY, USA: Wiley, pp. 737-796.
- Gokgoz A (1998). Geochemistry of the Kizildere-Tekkehamambuldan-Pamukkale geothermal fields, Turkey. Geothermal training program report, United Nations University, Iceland.
- Güleç N, Mutlu H (2002). Isotope geochemistry in geothermal field. Application of earth science in geothermal, Summer School, Dokuz Eylül University: 74-103.
- Haddadan M, Abbasi Damani A (1997). 1:100000 geologic map of Ardabil. Geologic survey of Iran.
- IAEA (1979). Behaviour of Tritium in the Environment. Vienna, Austria.
- Kendall C, Doctor DH (2005). Stable isotope applications in hydrologic studies. In: Drever JL, editor. *Surface and Ground Water, Weathering and Soils*. New York, NY, USA: Elsevier.
- Kharaka YK, Lico MS, Law LM (1982). Chemical geothermometers applied to formation waters, Gulf of Mexico and California basins. *Am Assoc Petr Geol B* 66: 588.
- Khosrawi K (1996). Geochemistry of geothermal springs in the Sabalan area, Azarbayjan-Iran. Geothermal training program, Report, The United Nations University.
- Masoumi R, Calagari AA, Siahcheshm K, Porkhial S (2016). Hydrogeochemistry and origin of hydrothermal fluids on the basis of isotopic data in Sabalan geothermal system. *Quaternary Journal of Iran* 2: 183-195.
- Masoumi R, Calagari AA, Siahcheshm K, Porkhial S, Pichler T (2017a). Consideration of geological aspects and geochemical parameters of fluids in Bushdi geothermal field, south of mount Sabalan, NW Iran. *J Afr Earth Sci* 129: 692-700.
- Masoumi R, Calagari AA, Siahcheshm K, Porkhial S (2017b). Investigation of concentration values of heavy and rare elements within active hydrothermal fluids in Geothermal field, south of mount Sabalan, Ardebil province, NW Iran. *J Geosci* in press.
- Masoumi R, Calagari AA, Siahcheshm K (2017c). Using geochemical and isotopic techniques for exploration of geothermal energy in Southern Sabalan geothermal field, NW Iran. *EGU General Assembly*, Vol. 19, EGU2017-761.
- Mazor E (1991). *Applied Chemical and Isotopic Groundwater Hydrology*. 1st ed. Buckingham, UK: Open University Press.
- Mckenzie D (1972). Active tectonics of the Mediterranean region. *Geophys J Roy Astr S* 30: 109-185.
- Nicholson K (1993). *Geothermal Fluids: Chemistry and Exploration Techniques*. New York, NY, USA: Springer.
- Ohba T, Hirabayashi J, Nogami K (2000). D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of water in the crater lake at Kusatsu-Shirane volcano, Japan. *J Volcanol Geoth Res* 97: 329-346.
- Purnomo BJ, Pichler T (2014). Geothermal systems on the island of Java, Indonesia. *J Volcanol Geoth Res* 285: 47-59.
- Schoeller H (1962). *Les eausouterriens* Masson et. Cie. Paris, France.
- Smith M, Bisari T, Putra T, Blackwood V (2011). Geochemistry of geothermal fluids Rico, Colorado. Final report: 22p.
- Sveinbjörnsdóttir ÁE, Arnórsson S, Heinemeier J, Boaretto E (2000). ^{14}C ages of groundwater in Iceland. *Proceedings of the World Geothermal Congress 2000, Kyushu-Tohoku, Japan*: 1797-1802.
- Tarcan G (2002). Geothermal water chemistry. Research and Application Center for Geothermal Energy (Jenarum) Summer School, Dokuz Eylül University, İzmir: 230-272.
- Truesdell AH, Hulston JR (1980). Isotopic evidence of environments of geothermal systems. In: Fritz P, Fontes JC, editors. *Handbook of Environmental Isotope Chemistry*. New York, NY, USA: Elsevier, pp. 179-226.
- Varekamp JC, Kreulen R (2000). The stable isotope geochemistry of volcanic lakes, with examples from Indonesia. *J Volcanol Geoth Res* 97: 309-327.
- Wang J, Sun Z (2001). Brief review on the development of isotope hydrology in China. *Sci China Ser E* 44: 1-5.
- Wetang'ula GN (2004). Assessment of geothermal wastewater disposal effects, Case studies: Nesjavellir (Iceland) and Olkaria (Kenia) fields. Master thesis, University of Iceland.
- White DE (1981). Active geothermal systems and hydrothermal ore deposits. *Econ Geol* 75th Anniversary: 392-423.
- Young HW, Lewis RE (1982). Hydrology and geochemistry of thermal ground water in Southwestern Idaho and North-Central Nevada. Geological survey of United States, Professional paper: 26p.