Research Article

Geofluids Assessment of the Ayub and Shafa Hot Springs in Kopet-Dagh Zone (NE Iran): An Isotopic Geochemistry Approach

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Geothermal energy has a wide range of uses in our life. It is very important to characterize the temperature and the depth of geothermal reservoirs. The aim of this paper is the determination of type, origin source of water temperature, and depth of water circulation in the Ayub-Peighambar and Shafa (AP and SH) hot springs, located in NE Iran, using hydrogeochemistry and environmental isotopes (^2H and ^{18}O). AP hot spring has elevated temperature ($36\text{--}40^\circ\text{C}$) and as such is very important for balneotherapy and geotourism industry purposes. The average values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for this hot spring (-10‰ and -73‰ , resp.) are analogous to that of geothermal and meteoric waters. This indicates that the heat source cannot be related to volcanic activities (with average $\delta^{18}\text{O}$ value of about 5‰) and it is most probably associated with geothermal gradient with deep circulation of groundwater through faults. Based on Na-K geothermometers coupled with isotopic (^{18}O and ^2H) geochemistry the temperature of the AP geothermal reservoir was estimated to be in the range of $100\text{--}150^\circ\text{C}$ with 3–5 and 4.2 kilometres' depth, respectively. Chemically, the AP samples are CaSO_4 facies with a chemically homogeneous source and steam heated waters type.

1. Introduction

Characteristics of springs (especially hot springs) in orogenic regions are due to the interaction between water, the lithosphere, and environmental conditions like lithology, pathways, residence time underground, and many other factors. The origin of elevated temperatures in hydrothermal reservoirs (hot/warm springs) can be due to the geothermal gradient with deep circulation of groundwater through faults, chemical reactions (e.g., in evaporates and oil field brines), heat produced through radioactive decay of long-lived radioactive material (isotopes), and mixing of meteoric water with magmatic water or volcanic vapour in volcanic area [1–11]. The hydrothermal phenomenon most often occurs where the released water and vapour are related to regional volcanic activities. The geothermal heat transfer to the ground surface occurs through aqueous and magmatic/volcanic systems. In an aqueous system, cold surface

water can penetrate to depth through deep faults/fractures, where convective currents cause the boiling of water. Subsequently the high temperature groundwater flows upward creating a hydrothermal system on or near the ground surface as hot springs or thermal groundwater discharge within an aquifer [12]. In a geothermal field, an aqueous system can be seen as hot spring, geyser, and mudpot subsystems. Understanding the origin of hydrothermal fluids and the reason for the elevation of temperature is a very important step in revealing the temperature and pressure conditions of the underground reservoirs [13]. To determine the reason and origin of the temperature/heat in a geothermal field, several methods such as remote sensing, geological investigation, geophysical survey, thermal anomalies measurements, and hydrochemical and isotopic method can be applied [14]. Today oxygen and hydrogen isotopes are widely used in geothermal studies to determine the origin and history of geothermal fluids and often serve as natural tracers for the

FIGURE 1: The study area and the locations of the Ayub-Peighambar and Shafa (AP and SH) hot springs.

provenance of geothermal water. Most geothermal systems are recharged by meteoric waters and if recharging from shallower groundwater these systems have isotope compositions consistent with local meteoric precipitation [15]. The main objective of this paper is to determine the geothermal reservoir characteristics (type, origin, temperature, and depth of circulation) of Ayub-Peighambar and Shafa (AP and SH) hot springs, in the NE of Iran, using geothermometers and environmental ^2H and ^{18}O isotopes along with geological and thermal anomalies data of the study area.

2. Sampling Locations and Geology of the Study Area

The AP and SH hot springs, with a temperature range of 36 to 40°C, are located in the NE of Iran (Figure 1). Field parameter measurement locations and sampling points are illustrated in Figure 2(a). The geological map of the study area was generated using field observations, satellite images, and remote sensing techniques (Figure 2(a)). As illustrated on the geological map, various sedimentary lithological units including massive limestone (Tirgan Formation), marl as pencil marl (Sarcheshmeh Formation), marl-shale (Sanganeh Formation), and sandstone-shale with glauconite (Aitamir Formation) have outcropped in the study area. These formations make the Asiazow anticline with a 15-degree plunge to the west, thrusting and faulting (Figure 2(b)). By oxidation of pyrite, as clearly indicated in thin sections of both Sarcheshmeh and Aitamir Formations, dissolved sulfate was produced [17], which in turn can be reduced through microbial and thermal reduction process (Hill, 1987; [18]), which finally results in H_2SO_4 production in the groundwater [18, 19].

Travertine around AP hot spring is evidence of a long discharge history at this spring (Figure 3). This indicates that the water of AP hot spring has previously moved upward through faults where the surface temperature and pressure

conditions led to oversaturation of the water with respect to carbonate minerals (CaCO_3) which in turn caused travertine precipitation. This is confirmed by the presence of calcite and aragonite (usually aragonite forming in deep conditions rather than calcite) structures in thin sections and in Scanning Electron Microscope (SEM) images (Figure 3). The X-Ray Fluorescence (XRF) analysis of travertine indicates that CaO contains 55% of travertine and Atomic Absorption Spectrophotometry (AAS) and Energy Dispersive Spectrometer (EDX) results show that calcium (with 27%) is the major cation in AP travertine (Figure 3). The existence of a large amount of voids in the travertine can be seen clearly in both hand specimens and thin sections (Figure 3), indicating that CO_2 was escaping during formation of this thermogenic travertine. There is no evidence for volcanic activities or existence of intrusive igneous rocks, as confirmed by the field observations and reported by previously report [20].

3. Material and Methods

Water samples were collected in polyethylene 25 mL bottles, from AP and SH hot springs during 2013-2014. All samples were filtered using 0.45 μm membrane and the cation samples were acidified using concentrated HNO_3 acid. Field parameters, T , pH, Eh, EC, and TDS, were measured during sampling. The geochemical analyses of main cations and anions and the isotopic analyses of ^{18}O and ^2H in water were performed at the geochemistry and G. G. Hatch Stable Isotope laboratories at the University of Ottawa. Geological formations of the study area were investigated using available maps, remote sensing with satellite images, and field observation. The sediment samples were collected from the AP hot spring frontal pool and their mineral contents were determined from thin sections and binocular microscope. All AAS, XRF, SEM, and EDX analyses on travertine samples were done at the Ferdowsi University

(a)

(A)

(B)

(b)

FIGURE 2: (a) Sampling locations and the geological map of the study area and (b) the simulated photographs of (A) Kuh-e-Asiazow anticline; the fold axis with E-W trend has $\sim 15^\circ$ plunge to the west. The thrust plane is shown as pink sheets; the view is to the southeast, and (B) a fold-thrust fault in Sanganeh shale and marl, view is to the east [16].

FIGURE 3: Travertines hand samples, thin sections, SEM images, and EDX result.

of Mashhad. The geothermometry of water samples was determined using Aq.QA hydrochemical software [21] and cation geothermometers (Na-K) coupled with isotopic (^{18}O and ^2H) geochemistry.

4. Results and Discussion

The measured field parameters and major ion concentrations of groundwater samples are listed in Table 1. The origin and type of water and geothermal reservoir characteristics (temperature and depth) of AP and SH hot spring were investigated using geochemistry and geological studies, geothermometers, and environmental ^2H and ^{18}O isotopes.

4.1. The Origin and Type of Water in the AP and SH Hot Spring. Based on piper diagram AP and SH hot springs fall into the CaSO_4 facies (Figure 4) and according to $\text{Cl-HCO}_3\text{-SO}_4$ diagram (Figure 5) we have distinguished mature waters (high content of Cl and is saline), peripheral and shallow waters (HCO_3 is more than 50%), steam heated waters (SO_4 is more than 50% and $\text{HCO}_3 > \text{Cl}$), and magmatic and volcanic waters ($\text{HCO}_3 \approx 0$, high SO_4 and sulfate and chloride type) [22]. Chemically, the AP and SH hot springs samples have the same chemical composition as a chemically homogeneous source and are of the steam heated water type. These samples have considerable concentrations of HCO_3 , Ca, and Mg with Ca- SO_4 type, indicating deep circulation of meteoric water

through the carbonate formation and available deep faults in study area. The increasing of water temperature is probably due to deep circulation and exothermic chemical reactions (probably within the Shourijeh Formation with anhydrite and gypsum). However, a partial melting zone, which emerged through convection currents and faults in the axis of Asiazow anticline, cannot be ruled out.

4.2. Deep Water Circulation Evidence in Quartz of AP Sediment, Thermal Anomalies, and CO_2 Gas. Since there is no volcanic activity in the area [20], the possibility of a volcanic source for the AP spring's hydrothermal reservoir has been rejected. The existence of travertine around AP spring provides insight into the circulation of water through faults in the past and present. Cold meteoric waters penetrated and dissolved deep Tigran limestone formations and then became highly enriched in bicarbonate (HCO_3) and sulfate (SO_4) (due to reduction of mineral sulfates by bacteria with carbonate mineral dissolution at depth) and precipitated/or not precipitated CaCO_3 on the ground surface, depending on the pH and Eh of the spring water. This porous thermogenic travertine has had very high amount of CO_2 which resulted from deep circulation, exothermic chemical reactions, and dissolution of limestone by sulfuric acid. The thermal anomaly map of the study area, prepared based on temperature of local springs' water (Table 1), indicates that the AP and SH hot springs in the study area have the most thermal anomalies (Figure 6). These thermal anomalies are

TABLE 1: Field parameters, major anion and cation compositions of AP and SH hot spring and adjacent springs.

Sample ID	TDS (mgL ⁻¹)	Field parameter			DO (% sat)	Eh (mv)	Ca ⁺²	Cations (mgL ⁻¹)			K ⁺	CO ₃ ⁻²	Anions (mgL ⁻¹)		Cl ⁻	Isotope (‰ VSMOW)	
		EC (ms/cm)	pH	T (°C)				Mg ⁺	Na ⁺	HCO ₃ ⁻			SO ₄ ⁻²	δ ² H		δ ¹⁸ O	
Sp. 1	247	499	8.0	25.0	—	82	104	33	67	3.1	16.0	184	130	8	-62.6	-9.0	
Sp. 2	443	953	8.1	18.0	—	112	147	49	109	3.7	0.0	284	336	35	-61.8	-8.5	
Sp. 3	307	626	7.6	16.9	146	141	110	28	84	3.6	24.0	150	234	46	-58.8	-8.3	
Sp. 4	372	782	7.1	14.0	—	173	70	250	3	0.0	28.0	176	36	6	-66.2	-9.4	
Sp. 5	146	334	7.7	16.9	—	195	89	41	94	3.4	64.0	110	343	49	-70.5	-9.9	
Sp. 6	218	444	7.7	12.1	204	184	60	48	34	1.8	80.0	160	85	9	-65.6	-9.3	
Sp. 7	296	604	7.5	17.2	137	173	71	52	59	3.4	60.0	170	172	21	-66.4	-9.1	
Sp. 8	550	1120	7.5	38.0	65	-22	87	42	96	3.2	16.0	184	349	43	-73.0	-9.9	
Sp. 9	770	1559	7.1	21.0	55	104	188	84	170	29.6	8.0	286	707	166	-71.8	-9.9	
Sp. 10	469	957	7.3	36.0	19	-72	67	40	75	2.1	4.0	190	263	37	-73.1	-10.2	
Sp. 11	454	930	8.3	16.0	—	58	280	346	9	17.4	56.0	256	423	52	—	—	
Sp. 12	404	825	8.1	25.0	—	131	81	52	99	2.7	24.0	196	392	38	-65.3	-8.8	
Sp. 13	780	1591	7.6	22.3	89	196	312	552	228	4.0	21.7	10	695	127	—	—	
Sp. 14	615	1256	7.3	16.4	45	112	230	440	224	0.0	21.7	10	366	32	—	—	
R. 1	285	581	8.4	22.7	134	150	53	43	52	1.4	72.0	110	142	31	-72.1	-10.1	
R. 2	251	511	8.3	26.4	129	134	172	130	128	64.0	26.1	5	145	42	—	—	
R. 3	966	1971	8.1	27.0	97	166	318	542	164	16.0	4.3	11	880	75	—	—	
R. 4	1280	2612	8.0	29.9	107	135	30	750	202	26.1	26.1	13	980	131	—	—	
R. 5	840	1714	8.3	25.5	159	129	360	360	184	21.7	4.3	11	640	99	—	—	
W. 1	349	713	7.4	16.4	—	101	190	330	244	8.7	26.1	6	280	44	—	—	
W. 2	462	978	7.1	18.6	92	101	200	190	240	13.0	21.7	8	445	48	—	—

FIGURE 4: Situation of water samples in the study area on a piper diagram (red circles detect AP and SH hot spring).

caused by tectonically tensional conditions, which can be confirmed by the presence of travertine as well as joints and faults in the area (e.g., [23]; Liu et al., 2003). The sedimentary petrography of AP hot spring indicates quartz and rim-burned biotite has been altered to chlorite, via chloritization, which is characteristic of igneous biotite. Although assembled minerals of green chlorite, opaque mineral (pyrite), amphibole, and glauconite can be seen in thin sections (Figure 7), igneous biotite is reported for the first time in this research and needs further investigation. Large amounts of quartz in pool sediments and also in thin section of this sediment confirmed deep circulation of water. The amount of CO_2 that dissolved in AP hot spring is 9.25 mg/L with a little H_2S , exempt of bubbles that escaped [24], indicating deep

circulation of water through the deep faults [25] that were generated by sulfuric acid in phreatic zone.

4.3. Temperature and Depth Measurements of the Hydrothermal Reservoirs Using Geothermometers. The temperature of hydrothermal reservoirs can be determined using geothermometry [26]. Since geothermometers equilibrate with their surrounding environments under certain temperature and pressure, their equilibrium concentrations in water (from hot springs, soil, and rock) are applied to determine the thermodynamic equilibrium temperature and pressure conditions [26, 27]. This method is very useful in areas without drilled boreholes/wells and it is applicable for initial studies in exploration geothermal fields. To estimate the ranges

FIGURE 5: Triangular $\text{Cl-HCO}_3\text{-SO}_4$ diagram that detects source waters of AP and SH hot springs (a) and other water resources (b) in study area.

FIGURE 6: The thermal anomalies map of the study area.

of temperature in a geothermal reservoir, a large suite of geothermometry tools (minerals, elements, and chemical composition such as silica (SiO_2), cations (Na, K, and Li), and gases (H_2S , CO_2 , H_2 , CO_2/H_2 , and $\text{H}_2\text{S}/\text{H}_2$)) can be used [15, 26, 28]. The equilibrium concentrations of Na and K in aqueous and solid feldspar phases (1) strongly depend on temperature. Therefore, the Na-K geothermometer can be applied for both [29–31] hot water ($250 < T < 300^\circ\text{C}$) and very hot water ($T > 300^\circ\text{C}$) [15, 29].

Based on chemical composition of the water, the temperature of AP hot springs reservoirs were estimated using the Na-K geothermometer and (2). Also the temperatures were

estimated using Aq.QA software by defining Na-K and SiO_2 as geothermometers. The depth of geothermal reservoir of these springs was calculated using (3) [32] and all estimated temperature and depth are listed in Table 2.

$$\text{K}^+ + \text{Na-feldspar} = \text{K-feldspar} + \text{Na}^+ \quad (1)$$

$$T^\circ\text{C (Na-K)} = \left[\frac{933}{0.933 + \log(\text{Na/K})} \right] - 273.15 \quad (2)$$

$$D = \frac{(Tg - Ts)}{\Delta G}. \quad (3)$$

TABLE 2: Temperatures and depths of hydrothermal reservoirs for AP and SH hot springs, calculated based on Na-K geothermometers [28, 31], Aq.QA hydrochemical software [21], and isotopic method.

	Ayub Peighambar hot spring					Shafa hot spring	
	Sp8.1	Sp8.2	Sp8.3	Sp8.4	Sp8.5	Sp10.1	Sp10.2
Using Aq.QA hydrogeochemistry software							
Temperature (Na-K)	<150	<150	<150	<150	<150	<150	<150
Depth (km)*	<5	<5	<5	<5	<5	<5	<5
Depth (km)**	4.65	4.65	4.65	4.65	4.65	4.65	4.65
Using Mohammadi's [31] method							
Temperature (Na-K)	113	114	114	110	111	101	101
Depth (km)*	3.76	3.80	3.82	3.66	3.70	3.36	3.36
Depth (km)**	3.42	3.45	3.47	3.31	3.35	3.02	3.02
Isotopic method (all isotope data in ‰ VSMOW)							
	In cold spring	In hot spring	Difference (Δ)	Max depth (km) of water circulation			
$\delta^{18}\text{O}$	-9.29	-9.97	-0.68				
$\delta^2\text{H}$	-66.47	-73.0	-6.53				

*Based on general law of geothermal gradient (30°C/km).

**Using Marques et al. [32] approach.

FIGURE 7: Biotite in matrix of quartz in AP spring's sediment.

Here, D is the depth of reservoir (km), T_g is the calculated temperature by geothermometers, and T_s refer to the average annual temperature (10.4°C which is calculated by Domarton and Amberege methods [34]). Also ΔG is the geothermal gradient (0.03°C per 1 meter).

4.4. Heat Source Determination Using ^{18}O and ^2H Isotopes. Based on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of a geothermal water, the heat source of the water may be determined [14]. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of AP and SH hot springs are plotted within the range of geothermal and meteoric waters (Figure 8). The average $\delta^{18}\text{O}$ values of the AP and SH hot springs

(-10‰, Figure 8) indicate that the heat source cannot be related to volcanic activities (with $\delta^{18}\text{O}$ value of about 5‰) and therefore the geothermal gradient is the primary heat source. Meteoric water, by penetrating to depth through faults/fractures, is heated and altered to a geothermal water, subsequently rising and discharge at the land surface. The deuterium content of these springs (average of -73‰, $n = 21$) is within the range of granitic and metamorphic rocks (-40‰ to -90‰, Figure 8(b)), which is probably due to partial melting and alteration in Kopet-Dagh bedrock that resulted in increasing temperature in spring water (reference for partial melting and alteration). Although this can be

FIGURE 8: The range of $\delta^{18}\text{O}$ (a) and $\delta^2\text{H}$ (b) compositions in various crustal rock and water types [33] and the range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the AP hot spring and cold water springs in the study area.

confirmed with the existence of biotite in AP hot spring sediment, it needs more investigation.

4.5. Calculating the Depth of Water Circulation Using ^{18}O and ^2H Isotopes. The depth of water circulation in the AP hot spring reservoir was determined using $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic compositions and (4) [35]. The maximum depth of water circulation in AP spring is approximately 5 kilometres (Table 2).

$$\begin{aligned}
 d(\text{H}) &= -0.397\Delta^2\text{H} + 1.064 \\
 \Delta^2\text{H} &= \delta^2\text{H}_{\text{hotspring}} - \delta^2\text{H}_{\text{coldspring}} \\
 d(\text{O}) &= -1.470\Delta^{18}\text{O} + 3.162 \\
 \Delta^{18}\text{O} &= \delta^{18}\text{O}_{\text{hotspring}} - \delta^{18}\text{O}_{\text{coldspring}},
 \end{aligned}
 \tag{4}$$

where d is the depth of water circulation (in km) and Δ is $\delta^{18}\text{O}$ or $\delta^2\text{H}$ isotopes difference (in ‰) between hot water and cold water spring in the study area.

The DIC and DOC concentrations in AP hot spring are 91 and 3 mgL^{-1} , respectively. The high amount of DIC and its enriched $\delta^{13}\text{C}$ value (-1.3‰ VDPB) indicate carbonate dissolution in the geothermally heated water flow path. As illustrated in Figure 9, the ^{13}C -DIC isotope in AP spring is analogous to the range of ^{13}C derived from carbonate dissolution [36]. Therefore, the Tirgan marine carbonate formation (with $\delta^{13}\text{C}$ content about 0‰) is probably the main recharge source of the AP spring. Meteoric waters percolated through the Tirgan limestone via faults and discharged from the AP spring after passing through underground karst

FIGURE 9: The $\delta^{13}\text{C}$ -DIC and $\delta^{13}\text{C}$ -DOC in AP hot spring.

systems. The very low amount of DOC in the AP spring (3 mgL^{-1}) with $\delta^{13}\text{C}$ -DOC value of -21.4‰ VDPB probably originated from organics in the Sanganeh Formation.

5. Conclusions

According to geological, hydrogeochemical, and stable isotope studies the AP spring can be classified as a steam heated waters type. The main heat source for the high water temperature (38°C) in this spring is the geothermal gradient. Using ^{18}O and ^2H the origin of the water is meteoric which has penetrated via deep faults/dissolution conduits in the study area. Meteoric waters percolated through the Tirgan marine carbonate formation (with $\delta^{13}\text{C}$ content about 0‰) via faults and discharged from the AP spring after passing through underground karst systems. This can be confirmed by high amount of DIC and its enriched $\delta^{13}\text{C}$ value (-1.3‰ VDPB). The deep circulation of water in this area can be inferred via high concentration of HCO_3^- , Ca, Mg; CaSO_4 water type; thermogenic travertine and high amount of CO_2 gas; and thermal anomaly as well. The region is tectonized and has many folds, such as Asiazow anticline which is the main recharge zone of the AP springs. According to Na-K geothermometry, modelling, and stable isotope analyses, the depth of the AP hot spring geothermal reservoir is estimated to be 4-5 kilometres with a temperature of about 150°C . This great depth combined with the water type suggests a hypogenic karst system signature that needs more investigation.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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