Geochemistry of Bazman thermal springs, southeast Iran

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\section*{A B S T R A C T}

Thermal springs of the Bazman geothermal field, 27 km south of the Holocene Bazman volcano caldera in Makran continental margin, SE Iran, were studied for the first time. New data on major components, selected trace elements (Li, Rb, Cs, Ba, Sr, Fe, Al), water isotopic composition (H, O and S), chemical and isotopic (δ\textsubscript{13}C of CO\textsubscript{2} and CH\textsubscript{4}, δ\textsubscript{3}He/δ\textsubscript{4}He and 40Ar/36Ar) composition of dissolved and bubbling gases from the hottest vents are presented. Four groups of springs with temperature range of 27–44°C discharge Na-Cl waters with total dissolved solids (TDS) of ~800 to ~7000 mg/L from different aquifers composed of diverse type of rocks including granites and limestone. Only the hottest and most saline springs of the Bazman field with low bicarbonate are close to equilibrium with surrounding rocks whereas the others discharge immature waters. Geothermometry based on SiO\textsubscript{2} concentrations, Na-K and Na-K-Ca-Mg systems shows low equilibrium temperatures of up to 130°C, consist with the temperatures estimated by alunino-silicate minerals saturation indices. The water isotopic composition (δ\textsubscript{18}O and δD) indicates meteoric origin with a small oxygen isotopic shift measured in the saline waters. The δ\textsubscript{34}S values of SO\textsubscript{4} indicate influence of gypsum and anhydrite dissolution from the host rock. Dissolved and free gases are N\textsubscript{2}-rich (>95 vol.%) with a high He content (0.5 vol.%). A biogenic origin may be suggested for CH\textsubscript{4} and CO\textsubscript{2} based on their carbon isotopic characteristics (−62‰ and −13‰ vs. V-PDB, respectively). The R/Ra value of 0.5 indicates a contribution of about 6% of He from the mantle. It is suggested that the Bazman thermal waters are heated at considerable depth (4–5 km) in a deep fault system most probably by the regional heat flow according to the local geothermal gradient.

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1. Introduction

The first steps in geothermal resource exploration is the understanding of geochemical process and estimating subsurface temperature in the reservoir by using geochemical and isotopic compositions of thermal springs (e.g. D’Amore and Arnórsson, 2000). The previously published geological investigations indicate that Iran hosts many geothermal features (Fotouhi and Noorollahi, 2000; Yousefi et al., 2007, 2010). Geothermal energy development in Iran started since 1975, with an exploration program in the northwestern part of the country. The results of these studies reveal four geothermal regions with development potential, including Sabalan, Damavand, Khoy-Maku and Sahand (ENEL, 1983). Further exploration surveys between 1996–1999 by the Renewable Energy Organization of Iran (SUNA), introduced ten important geothermal areas (Yousefi et al., 2007), in which the Bazman geothermal field was ranked as the fifth. Northeast Iran geothermal fields (Sablan and Changel) were studied by Mehdizadeh et al., 2002; Noorollahi et al., 2008; Mohammadi et al., 2010; Torbehbar and Sattari, 2015. Hot springs associated with Taftan volcano in southeast Iran were studied by Shakeri et al. (2008, 2015).

Bazman area is one of the largest geothermal fields in eastern Iran, located in the Makran flysch zone, about 95 km northwest of Iransahr city (Fig. 1). Only a few geological surveys were carried out there, with the most important being the one at the description of the Bazman field by Mehrabi et al. (2002). The area is mostly covered by peneplain and is limited by the Makran mountain to the west and the Caspian Sea to the east. The discharge of the springs is mainly related to the NW-SE trending faults that extend NW from the Makran mountain. The geochemical signature of the springs in the Bazman field suggests that the field is hosted in the basement rocks of the central Makran. The geothermal gradient in the area is very steep (5°C/m) and the temperature of the reservoir waters is estimated as 340°C. The geothermal resources of the Bazman area are located in the Makran flysch zone, which is a part of the Makran continental margin. The flysch sediments are composed of marine and continental deposits, with a thickness of several kilometers. The sediments are subjected to tectonic deformation and metamorphism, resulting in the formation of a complex geologic structure. The regional geothermal resources are distributed along NW-SE and NW-SE trending faults, which are well represented in the Bazman area. The geothermal reservoir is formed by the injection of seawater through the NW-SE trending faults, resulting in the formation of a geothermal system.
out in the Bazman area so far (Firouzkouhi et al., 2017; Ghodsi et al., 2016; Saadat and Charles, 2011). To the best of our knowledge, there were no published studies on thermal springs of the area. In this paper we report our data on chemical and isotopic composition of waters and gases sampled in 2017 from four groups of thermal springs located ~30 km to the south of the main Bazman volcano caldera at the eastern margin of a large granitoid batholite. We use water geochemistry, solute geothermometers and saturation indices of a set of possible secondary minerals for estimating water temperature at depth. We also report isotopic composition of water, He, Ar and carbon of CO₂ and CH₄ in bubbling and dissolved gases and propose a preliminary conceptual model for the Bazman geothermal field based on the collected data.

2. General settings

Bazman geothermal area is in the Makran structural zone in southeastern Iran, within 26° 36′ N - 27° 52′ N latitudes and 59° 57′-60° 11′E longitudes (Figs. 1 and 2). The study area is located in the south-eastern extremity of the Urmieh-Bazman volcano-plutonic belt, north of the Makran accretionary prisms, west of the Sistan suture zone (Flysch zone) and south of the Lut block, where the Iranian microcontinent experienced several subduction and collision events with the Arabian plate initiated from the Late Cretaceous and continued up to the Miocene arc stage and Quaternary volcanism (Burg, 2018) (Fig. 1).

Bazman, Taftan and Sultan (southwestern Pakistan) volcanoes have been regarded as a continental volcanic arc formed by the subduction of the Oman Oceanic crust beneath the Lut and Helmand blocks along the southern margin of the Makran region (Farhoudi and Karige, 1977; Berberian and King, 1981).

The Late Miocene-Pliocene Bazman stratovolcano (3490 m.a.s.l.) mainly consists of andesitic to dacitic lava flows and pyroclastic rocks with aged of ~7.5 Ma (Pang et al., 2014) to 0.7 Ma (Conrad et al., 1981). A number of peripheral basaltic cinder cones and small andesitic lava flows were also recognized in the region (Saadat and Charles, 2011; Conrad et al., 1981).

Study area is surrounded by the Palaeozoic sedimentary rocks that locally experienced contact metamorphism. These sedimentary rocks are mainly shale, sandstone, limestone and dolomite. Close to their contact with the main Cretaceous Bazman Granite Complex, the sedimentary country rocks were metamorphosed to hornfels, quartzite and marble depending on the local lithology (Vahdati Daneshmand et al., 2004; Sahandi and Padashi, 2005) (Fig. 2). The Bazman Granite Complex is divided into western and eastern parts. The western part includes a zoned pluton with 30 km diameter and gabbro to meladiorite rim characterized by an average width of 1000 m, changing inwardly to felsic rocks with a composition shifting from monzodiorite, granodiorite to porphyroid granites in the core (Ghodsi et al., 2016). The eastern part of the Bazman granitoid complex consists of various types of granites, wrapped by each other, demonstrating a complicated pattern of
emplacement. It seems that the main portion of the eastern granite is covered by the younger eruption products of the Bazman volcano (Fig. 2).

Thermal springs of the Bazman geothermal field (Figs. 1 and 2) occur at 27°–54 km distance to the south of the Holocene Bazman cone. In the Bazman granitoid complex there are four groups of springs (Fig. 2 and Table 1), as follows: group A) Sargar, Hamam Bazman 1 and 2; springs; group B) Koozeh 1, Koozeh 2 and Khaneh Gel springs and Surface water (a drainage from Koozeh 1 and Koozeh 2 springs), group C) Abargam Bazman 1 and 2 springs and group D) Espidezh, Maksan 1 and Maksan 2 springs. Main geothermal springs and lithology of discharge points are presented in Fig. 3 and Table 1 respectively. Discharge rates of the springs varied from less than 1.5 L/s (Abargam Bazman 1) to 50 L/s (Koozeh 2) and the water temperatures are in a range of 27°C–44°C. The hottest months in the study area are June to August with mean maximum temperature of ~32°C. Rainfall in the region is scant with an average annual of 112 mm.

3. Sampling and analysis

Twelve water samples were collected from the Bazman geothermal area in August 2017 (Fig. 2). Water samples were filtered using 0.45 μm membrane filters on site. Samples were stored in 350 mL polyethylene bottles which were rinsed with deionized water twice before sampling. For cation analysis, reagent-grade HNO3 with molar concentration of 14 M was added to each sample to bring the pH to <2 and then analyzed by ICP-OES/MS at Zar-Azma Lab., Tehran, Iran. Bicarbonate was measured in the lab. using standard titration method, whereas the other anions were analyzed by ion chromatography (IC) using a Metrohm 861 instrument. The uncertainties are ±5 % for ICP-MS and IC, respectively. The isotopic analysis of water samples was carried out at University of Ottawa, Canada, using Finnigan MAT Delta plus XP and Gas Bench. For sulfur isotope analysis, water samples were filtered through 0.4 μm cellulose acetate filters into a 1 L polypropylene bottles and 5 mL of 1 M BaCl2 solution and 1 mL of 1 M HCl were added to the filtered waters in order to precipitate SO4 as BaSO4. Solid BaSO4 was subsequently filtered off using a 0.4 μm filter and collected from filter paper. Conversion of BaSO4 to SO2 was completed via high-temperature combustion along with SiO2 and V2O5 at 980°C and sulfur isotope ratios were determined by a Finnigan MAT-251 mass spectrometer in the Geological Institute, Moscow. The δ34S values of sulfate in water expressed in permil (‰) and reported relative to the Canyon Diablo Troilite standard (δ34S-CDT = 0‰). Quality control on sulfur isotope measurements was carried out using NBS 127 international standard and LTB-2 lab. standard with measured δ34S values of 20.22‰ and 1.84‰ respectively. Duplicate preparations and analyses of δ34S are agreed within ±0.2‰.

Dissolved gases of the Bazman thermal springs (two samples) were collected using pre-evacuated 300 mL glass gas flasks equipped with a Teflon stopcock. The gas flasks were filled with water up to ¾ of the flasks inner volume (Caliro et al., 2008). Samples were analyzed for their chemical (CO2, N2, Ar, CH4 and O2) and isotopic composition (δ13C-CO2, δ34S-C-H2O, 3He/4He and 36Ar/38Ar) at the Laboratory of Fluid Geochemistry, Department of Earth Sciences, Florence University (Italy). Analysis of the main gas compounds was carried out using a Shimadzu 15A gas chromatograph (GC) system equipped with a 9 m long 5A molecular sieve column and thermal conductivity detector (TCD)/(Vaseli et al., 2006). Ar and O2 were analyzed using a Thermo Focus gas chromatograph equipped with a 30 m long capillary molecular sieve column on TCD. Analytical error for GC is <5 %.

The 13C/12C ratios of CO2 and CH4 (expressed as δ13C in ‰ relative to V-PDB standard) was measured with a Finnigan Delta Plus XP continuous flow IRMS with a TRACE gas chromatograph system equipped with a Porap Bond Plot capillary column with 0.2‰ accuracy.
Helium and argon isotopic ratios were determined by using a double collector mass spectrometer (VG 5400-TF) according to the methodology described in Inguaggiato and Rizzo (2004) with ±1% analytical error. He isotopic ratios are expressed as R/Ra, where R is the $^3\text{He}/^4\text{He}$ measured ratio and Ra is the $^3\text{He}/^4\text{He}$ ratio in the air ($1.39 \times 10^{-6}$; Mamyrin and Tolstikhin, 1984).

The SOLVEQ computer code with the updated SOLVThERM thermodynamic data base (Reed and Spycher, 1984) was used for calculating saturation indices (SI).

### 4. Results and discussion

#### 4.1. Gas geochemistry

Both bubbling and dissolved gas were sampled from the Abagram spring (site B5, group C) and only dissolved gas was sampled from the Makson 1 spring (site B8, group D) and their compositions are shown in Table 2. Gases are $N_2$-rich (>95 vol%), with very low $CO_2$ of ~0.15 vol% (B5) to low $CO_2$ of 3.35 vol% (B8) in the dissolved and not detectable in the free gas. $N_2$/Ar ratio in the bubbling gas is close to the dissolved air; in the bubbling gas $N_2$/Ar (90) is a bit higher than air (84; Wallace and Hobbs, 2006). A noticeable concentration of methane is detected in the dissolved gas and a significantly lower one in the free gas. Very low concentrations of $H_2$ and $CO$ were detected in free gas (0.0016 and 0.00032 vol%, respectively). The most intriguing is a high He concentration (0.5 vol%) in bubbling gas. In the bubbling gas $He$/Ne and $Ar$/Ne are ~570 and ~1000 respectively which is in-between that of Ar/Ne in air (~520) and in ASW-20°C (1550) (Colt, 2012). The $^{13}\text{C}-\text{CO}_2$ value of the B8 sample is ~13‰ (V-PDB), whereas the $^{13}\text{C}$-CH$_4$ values in the both dissolved gases (B5 and B8) are ~61.3‰ and ~62.7‰ (V-PDB). The $^{13}\text{C}$-CO$_2$ value may correspond to the mixing of biogenic CO$_2$ with air or other (maggmatic?) CO$_2$ source (e.g., Venturi et al., 2017; Stefansson et al., 2016, and references therein). The isotopic composition of CH$_4$ corresponds to a biogenic source of methane (Schoell, 1980, 1988) that is in agreement with the above suggestion on the CO$_2$ origin. The helium isotopic ratio in the free gas of B5 spring (R/Ra = 0.5) indicates a noticeable contribution of mantle He (~6%). This can be estimated considering a very low fraction of the air He (He/Ne = 570) and implying that released He is a mixture of the crustal He with $^3\text{He}/^4\text{He} = 10^{-8}$ and mantle He with $^3\text{He}/^4\text{He} = 1.2 \times 10^{-8}$ (e.g., Ozima and Podosek, 2002; Polyak et al., 2000). The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 308 ± 0.1 is noticeably higher than the air ratio of 295, indicating the presence of crustal Ar. Amount of crustal Ar can be estimated as $\text{Ar}^* = \text{Ar}_{\text{meas}} / (1 - 295/308) = 0.04 \text{vol} %$, and $^4\text{He}/^4\text{Ar}^* ~ 13$, which is higher than the average crustal ratio of 5 (Ozima and Podosek, 2002).

#### 4.2. Water chemistry

##### 4.2.1. Major ions

The physico-chemical parameters, concentrations of major components and selected trace elements (Li, Cs, Rb, B, Ba, Sr, Al and Fe) of thermal springs in the Bazman geothermal area are presented in Table 3. The Bazman thermal springs are warm with a maximum temperature of 44°C measured in the group C springs (Abgram Bazman, B5 and B6). The pH values are from almost neutral to slightly alkaline (6.8–8.4). TDS values of the thermal water samples are in a range of 778 to 6917 mg/L. The basis of the salinity for all springs is a Na⁺-Cl⁻-solution (Cl⁻-and Na⁺) concentrations up to 2532 and 1460 mg/L, respectively) with variable amounts of other anions and cations (Fig. 4a). Ca²⁺ concentrations are up to 662 mg/L. In the hottest springs (B5 and B6, group C) Ca²⁺+Na⁺ pair is almost charge balanced with chloride. Other springs show close to 1:1 charge balance for Ca²⁺+SO₄²⁻ (Fig. 4b). With the exception of group C springs (B5 and B6) all other waters are characterized by significant bicarbonate concentrations with the highest concentrations of ~450 mg/L in springs of the group B (B3, B4, B7, B11, Table 3). Based on the anion (Cl⁻-SO₄²⁻-HCO₃⁻) ternary diagram (Fig. 5) all data points are clustered in the central part of the triangle except for the group C springs with a low bicarbonate concentration. However, each group of springs forms its own cluster in the anions ternary diagram. Groups A and D show noticeable overlap in the Na-Ca-Cl diagram (Fig. 4) and similar CI/SO₄ ratios on the anion triangle (Fig. 5). Yet, points for the D group are much closer to the high-temperature C group compared to groups A and B (Fig. 2). The highest SiO₂ contents of 83–89 mg/L were measured in the group A springs (B1, B2 and B10) and the lowest, 20–22 mg/L, in the group D springs (B8, B9 and B12).
4.2.2. Trace elements

Concentrations of Sr, Ba, Li, Rb and Cs of all springs are presented in Table 3. A number of academics have tried to apply these elements concentration for investigating origin and formation condition of natural cold and thermal waters (e.g., Goguel, 1983; Giggenbach, 1991; Arsanova, 1974; Peiffer et al., 2011). The main problem is a large variability in concentrations of these elements in any type of host rocks which is difficult to interpret. For example, the Ba/Sr ratio in limestone of different types and tectonic settings can vary within 4 orders of magnitude (Zhang et al., 2017). Data points for Ca, Sr, Ba in the Bazman springs are plotted in the Ca-Sr-Ba ternary diagram (Fig. 6a), in which different groups clustered far from the average crust (Wedepohl, 1995) and typical limestone and dolomite fields (plotted data of Zhang et al., 2017; Frondini et al.,

Table 2

<table>
<thead>
<tr>
<th>Site</th>
<th>CO₂</th>
<th>CO</th>
<th>N₂</th>
<th>O₂</th>
<th>Ar</th>
<th>CH₄</th>
<th>He</th>
<th>³²He/²¹Ne Ra</th>
<th>⁴³Ar/³⁶Ar Ar</th>
<th>δ¹³C-CO₂</th>
<th>δ¹³C-CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5 bubbles</td>
<td>n.d.</td>
<td>0.0003</td>
<td>0.0016</td>
<td>97.9</td>
<td>0.46</td>
<td>1.03</td>
<td>0.09</td>
<td>0.5</td>
<td>0.5</td>
<td>570</td>
<td>308</td>
</tr>
<tr>
<td>B5 dissolved</td>
<td>0.15</td>
<td>n.a.</td>
<td>n.d.</td>
<td>97.3</td>
<td>0.31</td>
<td>2.24</td>
<td>1.11</td>
<td>n.a.</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
</tr>
<tr>
<td>B8 dissolved</td>
<td>3.35</td>
<td>n.a.</td>
<td>n.d.</td>
<td>85.3</td>
<td>3.65</td>
<td>2.11</td>
<td>5.56</td>
<td>n.a.</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a</td>
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</tbody>
</table>

Fig. 3. Field photograph of the Bazman geothermal springs (a) Hamam Bazman 1, (b) Hamam Bazman 2, (c) Koozeh 1, (d) Koozeh 2, (e) Abgarm Bazman 1, (f) Abgarm Bazman 2, (g) Maksan 1, and (h) Espidezh.
Table 3
Field measurements, chemical and isotopic composition of water samples and also Na/K and SiO$_2$ (quartz + chalcedony) geothermometry data. AD and $\delta^{18}$O are relative to V-SMOW and $^{34}$S-SO$_4$ is relative V-CDT, empty cell means no data.

<table>
<thead>
<tr>
<th>Group</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>B1</td>
<td>B2</td>
<td>B3</td>
<td>B4</td>
<td>B5</td>
<td>B6</td>
<td>B7</td>
<td>B8</td>
</tr>
<tr>
<td>T$_{\text{C}}$</td>
<td>37.1</td>
<td>35.3</td>
<td>37.7</td>
<td>34.3</td>
<td>44</td>
<td>41</td>
<td>28.1</td>
<td>35.5</td>
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<tr>
<td>pH</td>
<td>7.16</td>
<td>7.14</td>
<td>6.97</td>
<td>6.80</td>
<td>7.92</td>
<td>8.40</td>
<td>7.62</td>
<td>7.15</td>
</tr>
<tr>
<td>EC ($\mu$S)</td>
<td>1,032</td>
<td>1,070</td>
<td>2,063</td>
<td>2,639</td>
<td>10,583</td>
<td>11,024</td>
<td>3,087</td>
<td>1,455</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>813</td>
<td>778</td>
<td>1,707</td>
<td>1,304</td>
<td>6,848</td>
<td>6917</td>
<td>2,180</td>
<td>846</td>
</tr>
</tbody>
</table>

Major components (mg/L)

| HCO$_3$ | 34.3| 34.3| 34.3| 34.3| 34.3| 34.3| 34.3| 34.3|
| SO$_4$ | 120| 120| 120| 120| 120| 120| 120| 120|
| Ca    | 27 | 27 | 27 | 27 | 27 | 27 | 27 | 27 |
| Mg    | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 |
| Sr    | 110| 110| 110| 110| 110| 110| 110| 110|
| B     | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| SiO$_2$ | 83 | 83 | 83 | 83 | 83 | 83 | 83 | 83 |

Trace elements (µg/L)

| Li | 33 | 33 | 33 | 33 | 33 | 33 | 33 | 33 |
| Cs | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 |
| Rb | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Ba | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 |
| Sr | 170 | 170 | 170 | 170 | 170 | 170 | 170 | 170 |
| Al | 150 | 150 | 150 | 150 | 150 | 150 | 150 | 150 |
| Fe | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| $^{38}$O | −3.75 | −3.75 | −3.75 | −3.75 | −3.75 | −3.75 | −3.75 | −3.75 |
| $^{18}$O | −24.9 | −24.9 | −24.9 | −24.9 | −24.9 | −24.9 | −24.9 | −24.9 |
| $^{34}$S-SO$_4$ | 10.5 | 10.5 | 10.5 | 10.5 | 10.5 | 10.5 | 10.5 | 10.5 |

Na/K and SiO$_2$ estimated temperatures (Giggenbach, 1988)

| Na/K | 206 | 197 | 196 | 198 | 132 | 131 | 238 | 140 |
| SiO$_2$ | 114 | 114 | 77 | 72 | 71 | 72 | 71 | 73 |

2014; Abedini and Calagari, 2015). There are two trends for high-temperature thermal fluids, including mainly basaltic aquifers with temperatures of 250–290°C in Iceland (Arnórsson et al., 2008) and Cerro Prieto a high-temperature (>340°C) system within sedimentary aquifer in Mexico (Taran and Inguagiato, unpublished). Both high-temperature Icelandic “basaltic” trend and high-temperature “sedimentary” Cerro Prieto trend show almost constant Ca/Sr ratio while Ba concentration varies within wide ranges. In contrast, the Bazman springs data show different trends, indicating variable Ca/Sr ratios similar to Ca/Ba ratios.

In the ternary plot (Fig. 6b), rare alkali metals of the Bazman springs outline clusters with a highly variable Li/Rb ratio. The composition field of high-temperature thermal waters and the average composition of carbonates rocks (L) from Turekian and Wedepohl (1961) are also plotted as a reference. Usually, for hydrothermal fields in volcanic areas, proportion of Li-Rb-Cs varies is a narrow range. For example, rare alkalis in thermal waters of Kamchatka, except steam-heated SO$_4$ waters, show Li-Rb-Cs weight proportion of ~10:9:10 (Arsanova, 1974). Similar relations are common for high-temperature waters in New Zealand (Goguel, 1983). The variability of Rb/Li and Cs/Rb ratios in the Bazman springs are presented in log-log diagrams (Fig. 7a, b). Similar variability and clustering of the data points is depicted in CI-Li-B ternary diagram (Fig. 8). We modified the original diagram proposed by Giggenbach (1991) with replacing Li by 10Li. On the diagram, the compositions of fluids from high-temperature hydrothermal systems (wells with t >250°C) are shown as a dashed area, and average compositions for high-temperature fluids from Iceland (Arnórsson et al., 2008) and from Cerro-Prieto, Mexico (unpublished data) are also plotted as a reference.

It is difficult to interpret such compositional variability of rare alkali and alkali earth elements in the Bazman waters. It may be explained by a mixed set of the host rocks on the pathway of waters to the surface and/or by mixing of deep and shallow waters close to the surface. More detailed studies of the surrounded geology may help for resolving this problem.

5. Geothermometry
5.1. Chemical geothermometers

Deep geothermal water temperature may be directly estimated by using one of the SiO$_2$ geothermometers including those based on I) the quartz solubility ($t_{\text{SiO}_2} = 1309/(5.19-\log\text{SiO}_2)$ -273, Fournier, 1977), and II) quartz + chalcedony solubility ($t_{\text{SiO}_2} = 1000/(4.5-\log\text{SiO}_2)$ -273) (Giggenbach et al., 1983). The SiO$_2$ concentrations in the Bazman waters are low (20–90 mg/L) indicating temperatures of 40°C–120°C. By applying the Giggenbach’s expression for the SiO$_2$ geothermometer, the highest estimated temperatures (114–119°C) recorded in the northernmost group A springs, discharging from lava flows of the Bazman volcanic complex at elevation about 1000 m.a.s.l. (Table 3). The SiO$_2$ base estimated temperatures for the highest outlet temperature springs of group C (BS and B6), located at the lowest elevations (~660 m.a.s.l.) and characterized by a low outflow rate (1.5 L/s), are 71–73°C. Similar SiO$_2$ estimated temperatures (up to 85°C) are shown by the group B springs, which have the highest outflow rates (to 150L/s). The group D springs, located closest to group C at ~730 m.a.s.l elevation, are the lowest temperature and diluted ones (40–42°C). In evaluation of these results, it should be considered that silica concentration depends on dilution and may decrease also as a result of re-equilibration upon cooling and SiO$_2$ precipitation along the pathway to the surface. The Na/K geothermometer for neutral waters discharging from aquifers with a common hydrothermal alteration are less sensitive to dilution. This ratio is also more conservative because of the low water–rock reaction rates for the Na-K system (Giggenbach, 1988). Based on a modification of the original ternary diagram by Giggenbach (1988) to a log-log plot (Fig. 9), it
is possible to evaluate fluid rock equilibrium condition in terms of the “maturity” of thermal waters, in which the most “equilibrated” waters of the Bazman springs are B5 and B6 hottest springs, group C, plotted within the “partially equilibrated” field (Fig. 9a). All other springs are “immature” waters, which means that they are not equilibrated with the hydrothermally altered average crustal rocks. B5 and B6 springs are also plotted close to the equilibrium line (Fig. 9b) on the 10Mg/ (10Mg+Ca) vs. 10K/ (10K+Na) diagram proposed by Giggenbach (1988). The Na/K ratios of B5 and B6 springs correspond to temperatures close to 130°C (Fig. 9a and b) which is significantly higher than the quartz yield temperature (92°C), whereas the equilibrium temperatures in the Na-K-Ca-Mg systems are ~110°C.

5.2. Geothermometry based on saturation indices

Saturation indices are defined as SI = logQ/K where Q is the ion solubility product for a mineral in water and K is its theoretical value at a given temperature (Reed and Spycher, 1984; Pang and Reed, 1998; Spycher et al., 2014). We used SOLVEQ computer code (Reed and Spycher, 1984) with the updated thermodynamic data base (Spycher et al., 2014) for calculating saturation indices and their temperature dependence for a set of hydrothermal minerals. Aluminosilicates, carbonates and sulfates saturation indices were calculated and for B5 spring, group C and are presented in Fig. 10a. Lines for aluminosilicates cross the saturation line (Fig. 10a) over a wide range of temperature (80–140°C) though still are in agreement with the calculated quartz and Na/K (Table 3). Lines for carbonates roughly converge at lower temperatures, below 75°C. Among sulfates minerals, barite is saturated close to the sam-
plunging temperature ($\leq 44{\degree}C$), anhydrite shows saturation at $\sim 140{\degree}C$, i.e. consistent with the other geothermometers, whereas gypsum and celestine are undersaturated in the whole considered temperature range. The next set of plots (Fig. 10b) shows the same dependences for B1 spring, group A. For group A spring aluminosilicate lines do not converge at the saturation line (except illite and andalusite) probably as a result of the overestimated Al concentration (Pang and Reed, 1998). Lines of carbonates for B1 spring cross the saturation line in the range of $75−120{\degree}C$. All sulfates are unsaturated within the whole temperature range. Saturation indices for groups B and D springs (not presented here) show similar patterns with a wide range of saturation temperatures for aluminosilicates ($60−140{\degree}C$), saturation close to spring temperature for carbonates and under saturation for sulfates.

Comparison of obtained results from different chemical thermometers in the Bazman springs with other important geothermal area in Iran, such as Sabalan ($\sim 226−229{\degree}C$), Taftan (a minimum temperature of $150{\degree}C$) and Damavand ($\sim 150{\degree}C$) (Strelbitskaya and Radmehr, 2010; Shakeri et al., 2008; Nouraliee et al., 2010), indicating that the Bazman geothermal area could rank fourth/fifth in importance list. Also the worthy distribution of the Bazman springs and their low altitude ($\sim 660−1050$ m.a.s.l.) compared to other geothermal areas in Iran indicate that it is highly promising for further exploration and geothermal power generation, although so far, the first geothermal power project in Sabalan geothermal area (Meshkin-Shahr) of Iran has not been operational yet.

6. Isotope geochemistry

6.1 Water isotopes

Water isotopic composition of the Bazman springs (Table 3) is plotted on the $\delta D$ vs. $\delta^{18}O$ diagram (Fig. 11) along with isotopic compositions of the area cold waters of the nearby Taftan volcano thermal springs (Shakeri et al., 2008) and fumarolic condensates of Taftan volcano (Zelenski et al., 2019). The data of Taftan waters
and volcanic vapors are also added for comparison. In Fig. 11, the world meteoric water line presented as a reference (MWL, Craig, 1961) and field A indicating “arc magmatic water” according to Taran et al. (1989). All spring waters are close to the MWL line with small oxygen and hydrogen isotopic shifts. The ultra-acidic Taftan thermal waters that discharge on the volcano slopes with chloride of ~5000 mg/L are mostly formed as a result of mixing of meteoric water with the volcanic vapors (Shakeri et al., 2008). Therefore, the isotopic shift for Taftan waters is the result of this mixing process. For the Bazman springs, considering the arid and hot climate of the area and a significant distance from the volcanic edifice, these shifts can be caused by surface evaporation or both evaporation and water-rock isotopic exchange. However, taking into account the high chloride content in the group C springs (>3000 mg/L) and the presence of a small portion of the mantle He in the bubbling gas (spring B5), some contribution from the magmatic component in this water cannot be excluded. The interpretation is difficult because the global arc magmatic water box on the diagram (see also Taran and Zelenski, 2014) has a ΔD range similar to that of meteoric and thermal waters of the Bazman-Taftan area.

6.2. Sulfur isotopes

Sulfate sources in thermal waters are highly variable and can be related to sulfate mineral dissolution (e.g., gypsum and anhydrite), sulfide (e.g., pyrite) oxidation and biological activity (e.g., Ohmoto and Goldhaber, 1997). Sulfate from dissolution of marine evaporite deposits, such as gypsum/anhydrite, usually is characterized by δ34S values ranging from +10‰ to +30‰, while sulfate derived from the oxidation of sedimentary sulfides usually shows negative δ34S values. The δ34S values of the Bazman springs (B3, B5 and B10: Koozeh 1, Abgarm Bazman I and Sargar) vary insignificantly from +9‰ to +11‰ vs. CDT, which are common for many thermal waters in different tectonic and geological settings. Most probably these compositions are due to the dissolution of anhydrite and gypsum of different origin and are not associated with magmatic sulfur.

7. Model and concluding remarks

Discharging thermal waters in the south of Bazman volcano are similar to the so-called nitrogen-bearing waters of tectonically active regions (e.g., Barabanov and Disler, 1968). These waters are
formed through a deep penetration of meteoric waters, conductive heating at considerable depths (up to 5 km) and rising to the surface through fault systems. Temperature of waters depends on the local thermal gradient and degree of the conductive cooling on the pathway to the surface. The composition of these waters depends on the host rocks and mixing at shallow levels with ground waters. It should be noted that all groups of springs surrounding the eastern margin of the Bazman Granitoid Complex (BGC) located ~30 km to the south of Bazman edifice. The BGC consists of several plutonic bodies and covers an area of ~900 km² (Fig. 2). The BGC was emplaced during the late Cretaceous period at 83–72 Ma and cuts older (Paleozoic) sedimentary rocks (Ghodsi et al., 2016). The B5 and B6 springs (group C) discharge at the lowest altitude within a granitic terrain (biotite-hornblende granites with an age of 83–84 Ma; Ghodsi et al., 2016). Granites with such an age release helium with <0.1 (e.g., Ballentine and Burnard, 2002), and therefore, the measured R/Ra (0.5) in the bubbling gas of the B5 spring undoubtedly means the presence of a small amount of mantle He (~6 %, see above). Different chemical composition, relatively high mineralization of the C group springs and the presence of mantle He may sign the existence of a deep aquifer associated with evaporitic lenses or other Na-Ca-Cl-SO₄-bearing complexes in contact with a younger cooling plutonic body. This intrusion may belong to the magmatic system of Bazman volcano related to the modern Makran subduction. All other springs rise to the surface through a system of faults, cutting through different rock types (limestone, dolomite, sandstone, etc.), mix with ground waters and show evidences of water-rock interaction at different degrees. A simple model for such hydrothermal activity in the region is shown in Fig. 12. If there is no additional heating source(s), by considering just presence of a cooling intrusive body, the depth of the main aquifer can be estimated as 4–5 km, taking into account the equilibrium depth temperature of 130 °C and an average thermal gradient of 30 °C/100 km.

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