Geochemical controls on the distribution of radio-trace elements in groundwater resources of Shir-Kuh granitoid aquifer, central Iran
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ABSTRACT
Granitic groundwaters are important resources in arid regions. However, they are not always pure due to having appreciable amounts of trace elements. The present study was conducted to investigate chemical compositions for finding controls on distribution of heavy metals and natural radioelements (U and Th) in groundwater resources of Shir-Kuh granitoid aquifer (SGA), central Iran. Thirty water samples were collected and analyzed for major and trace elements. The average values of electrical conductivity (EC) and pH are 624 μs/cm and 7.5, respectively. The dominant groundwater type is Ca-HCO₃, as a result of the calcite dissolution and biotite weathering. Principal component analysis in support of mass balance studies recognizes dissolution of fracture-filling sediments and rock mineral weathering as the main factors enhancing major ions in SGA. These processes also release trace elements in decreasing order of Sr > Ba > Sn > W > Cu > U > Zn > Th. Weathering of biotite enclosing accessory minerals of monazite and zircon is introduced as the main source of radio-trace elements in SGA. Health concerns are currently related to U in drinking groundwater, as the maximum concentration (13.6 μg/L) approaches the Iranian drinking standard of 15 μg/L, in response to the oxidizing nature of the groundwater, calcite dissolution-related mobilization, and the degree of the water–rock interactions.

Key words | heavy metal, silicate weathering, thorium, uranium, Yazd

INTRODUCTION
Granitoid is a preliminary term used for plutonic rocks which essentially contain quartz and feldspars, tentatively identified as granite, granodiorite, or tonalite (Le Maitre et al. 2005). These rocks have appreciable amounts of quartz, alkali feldspar, and/or plagioclase and other aluminosilicate minerals such as micas. Quartz has very low solubility under existing pH and temperature; however, incongruent dissolution of aluminosilicates releases common cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) into groundwater (Singhal & Gupta 2010). Very low weatherability of silicate minerals in addition to the low residence time of groundwater mainly through the fissures and fractures result in the total dissolved solids (TDS) of granitic groundwater to be usually less than 300 mg/L. As a result of the silicates weathering, the general groundwater type from granitoids is Ca-HCO₃ and the silica content ranges from 10 to 30 mg/L. High concentrations of trace elements such as Pb, Cr, Fe, and Mn are also possible to detect (Singhal & Gupta 2010). For example, high values of Pb (about 0.19 mg/L) and Cr (around 2.6 mg/L) were reported in acidic granitic groundwater in Ghana (Pelig-Ba et al. 1991). Analysis results of the water samples collected around granitic rocks in Turkey (Yuce et al. 2009) revealed high concentrations of trace elements, including Al, Ba, Fe, and Cr, over the drinking water norms.
High natural values of major and trace elements were observed in water samples collected from boreholes in granitic bedrock aquifer in Norway (Banks et al. 1995a), with some of them, including F, Na, Fe, U, Rn, and Al, exceeding drinking water norms. Banks et al. (1998) compared the hydrochemistry of the granitic island aquifers of Scilly (UK) and Hvaler (Norway) with similar bulk lithologies of peraluminous S-type, U/Th-enriched granites. The results showed dissimilarities in health-related trace elements of Rn, U, and F due to differences in trace elements’ composition of granite and fracture fillings, weathering histories and hydrodynamic factors. Assessing the geochemistry of groundwater in structurally deformed granitic terrain in India (Satyanarayan et al. 2007) revealed significant variations of some trace elements (Fe, Mn, Al, Be, Co, Pb, U, and Zn) in dug and bore wells in relation to differential mineral weathering and dissolution/precipitation reactions along the fractures.

In terms of natural radioactivity, granitic rocks are strongly enriched in U (on average 5 ppm) and Th (on average 15 ppm) (Tzortzis & Tsertos 2004), compared to the Earth’s continental crust (average 1.8 and 7.2 ppm for U and Th, respectively) (Mason & Moore 1982). U and Th increase mainly in accessory minerals like orthite or alunite, monazite, zircon, apatite, and sphene which usually concentrate in granites (Mason & Moore 1982). As a result of mineral weathering, the most commonly found radioelements in granitic groundwater belong to the U and Th family (Örgün et al. 2005). Their concentrations in groundwater depend on the type of mineral sources in the aquifer, chemical composition of water, and residence time of water in contact with the rocks (Freeze & Cherry 1979). The mobility of U in groundwater is strongly redox- and pH-sensitive. Solubility is high over a wide range of pH in oxidizing groundwater systems, where U occurs in its hexavalent (U(VI)) state (Frengstad & Banks 2014). The concerns regarding U in drinking water are linked to its chemotoxicity rather than radiotoxicity (Milvy & Cothern 1990). The guideline values (maximum admissible concentrations) for U in drinking water have now been set at 30 μg/L by both the World Health Organization (WHO 2011) and US Environmental Protection Agency (EPA 2002). In contrast to uranium, Th is highly insoluble under all conditions, existing almost exclusively in an oxidation state of 4+ (Banks et al. 1995b).

In general, groundwaters coming from granitic rocks are not highly pure. It is widely recognized from several studies (e.g., Bonotto 1989; Gascoyne 1989; Banks et al. 1995a, 1995b; Hagedorn & Hasholt 2004; Örgün et al. 2005; Skeppström & Olofsson 2007; Raju et al. 2012; Ramaiah et al. 2012; Singh et al. 2013; Thivy et al. 2014, 2016; Desbarats et al. 2016) that they may contain minor and trace elements, such as heavy metals (Pb, Zn, Cu, Sb, Hg) and radioelements (U, Th, Rn, Ra) at levels over the allowable standards for drinking water.

The Shir-Kuh granitoid batholith contains important groundwater resources in Yazd province, a semi-arid region in central Iran, where groundwater is mainly utilized by local residents for domestic and agricultural uses. In addition, it is the major recharge zone of the surrounding alluvial plain aquifers. This research aimed to investigate the chemistry of groundwater resources in this important granitic aquifer with the emphasis on heavy metals and natural radioelements.

**HYDROGEOLOGICAL SETTING OF THE STUDY AREA**

The elongated northeast–southwest trending batholith of Shir-Kuh granitoid in central Iran (31°23’–31°45’N, 53°50’–54°30’E) covers an area of about 550 km² (Figure 1). To the east, the batholith is covered with lower Cretaceous conglomerate and sandstones of the Sangestan formation which are overlain by the thick-beded limestone of the Taft formation. This non-conformity indicates a Middle Jurassic age for the emplacement of the Shir-Kuh pluton (Sheibi et al. 2010). The Shir-Kuh granitoid outcrop consists of three units: granodiorite, mozogranite, and leucogranite (Figure 1). The mozogranites, which range from relatively mafic (cordierite-bearing) to felsic (muscovite-bearing) rocks, are the main ones spread throughout the region. They are composed mainly of plagioclase, quartz, K-feldspar, biotite, muscovite, garnet, cordierite, zircon, and monazite minerals (Sheibi et al. 2010).

From a hydrogeological point of view, the occurrence and the movement of groundwater in the Shir-Kuh granitoid aquifer (SGA) with a hard rock double-porosity characteristic are mainly controlled by fractures and the weathered layer (Jafari 2003). Fractures and other discontinuities...
mainly control groundwater flow and occurrences in the highland massive (unweathered) granitic rocks, where they form potential passages of groundwater movements. The weathered layer (regolith) is developed on the granitic basement in the valleys intersecting the Shir-Kuh batholith. This is an important source of groundwater for rural water supply and the groundwater is now being used by local villagers via the qanats (horizontal dug wells that drain the aquifer gravitationally) and wells. The recharge into the SGA takes place in topographic highs (average elevation of more than 4,000 m above the mean sea level) by the rain and snow falls. It is discharged by 64 springs and 101 qanats located along the valleys intersecting the granitic mass. Most of them have a discharge flow rate between 1 and 10 L/s (Taheri 2017). There are also 68 private dug wells at rural houses that discharge the weathered layer accumulated in the valley bottom. No piezometers have been installed in this hard rock aquifer. Regarding the surface topography, general groundwater flow direction is from the highlands toward the valleys (Figure 2), where the flow paths are concentrated and finally discharged by the springs and qanats or drained underground into the surrounding alluvial plains (Jafari 2003). The mean annual temperature and precipitation are about 12 °C and 250 mm, respectively. About half of the precipitation is snow, falling entirely during the wet season (November to April). Subsequent melting of the snow and its infiltration through the fractures provides suitable conditions for aquifer recharge in this arid region (Taheri 2017).

**MATERIALS AND METHODS**

Thirty water samples were collected from springs and qanats in March 2016. Electrical conductivity (EC) and pH values were measured in the field using a portable HANA Multi-range EC Meter-HI8733 and an AZ pH Meter-8601, respectively. Two clean polyethylene bottles
for measuring the major ions and trace elements were filled at each sampling location. The samples for measuring trace elements were filtered and acidified by commercially available high-purity nitric acid (65%) to a pH of less than 2. Standard methods (Rice & Bridgewater 2012) were applied to determine the values of major ions (Table 1). Ca\(^{2+}\) and Mg\(^{2+}\) were measured by titration with EDTA, and Murexide and Eriochrome Black T as indicators. Concentrations of Na\(^{+}\) and K\(^{+}\) were determined by flame photometry. Cl\(^{-}\) and SO\(_4^{2-}\) were measured by the Mohr and turbidity methods, respectively. HCO\(_3^-\) was determined by titration with HCl and methyl orange as indicator. The charge balance errors (Equation (1)) for the samples (Table 1) were less than the reasonable range of 5–10% (Freeze & Cherry 1979).

\[
\text{Charge balance error} \, (\%) = \frac{\sum \text{Anions (epm)} - \sum \text{Cations (epm)}}{\sum \text{Anions (epm)} + \sum \text{Cations (epm)}} \times 100
\]

A set of more than 50 trace elements including Si, heavy metals, and radioelements (U, Th) was determined using HP Agilent 4500 ICP-MS (USA) at Iranian Zar-Azma Mineral Studies Company. The quality assurance/quality control (QA/QC) was carried out by qualified experts of the laboratory, including the analysis of reagent blanks, analytical duplicates, and certified reference materials.

**RESULTS AND DISCUSSION**

**Major ions chemistry**

The average values of EC and pH in the studied groundwater of the SGA are 624 μS/cm and 7.5, respectively. The silica contents vary in a range of 5.2 to 10.6 with an average value of 8.7 mg/L. The steep hydraulic gradient of groundwater which is expected to occur in this hard rock aquifer results in fast movement, thus, lower residence time of the groundwater in contact with granitic rocks. In addition, very low solubility of the quartz and other silicate minerals limit releasing elements from weathering of the granitic rocks into the groundwater.

The results of the major ions analysis in groundwater samples from the SGA are plotted on a Piper diagram (Figure 3), indicating the dominant water type as Ca-HCO\(_3^-\),
basically due to dissolution of the calcite from the rock matrix or as fracture mineralization and also weathering of the silicate minerals (Edmunds & Shand 1980) such as plagioclase feldspar (Na0.8Ca0.2Al1.4Si2.6O8) found in granitic rocks of Shir-Kuh (Khalili 1997). The results of mass balance studies (Jafari 2003) confirm the role of both the calcite dissolution and silicate weathering in chemical evolution of the groundwaters from SGA (Table 2). Calcite presents in minor amounts (1–5%) in Shir-Kuh granitic rocks (Khalili 1997). However, the dissolution rate of calcite is typically six orders of magnitude more than the aluminosilicate minerals under neutral pH conditions (Mast et al. 1990). It highlights the importance of calcite dissolution compared with silicate weathering in supplying calcium and bicarbonate ions into the groundwater resources of SGA (Table 2). In addition, dissolution of halite and gypsum as secondary minerals filling fractures of the granitic rocks, was also introduced as the origin of Cl and SO4 (Table 2) as they are not significant constituents in silicate rocks (Freeze & Cherry 1979). The process is likely the main cause of a little

| Sample ID | EC (μS/cm) | pH  | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | Na⁺ (mg/L) | K⁺ (mg/L) | HCO₃⁻ (mg/L) | Cl⁻ (mg/L) | SO₄²⁻ (mg/L) | Charge balance error |
|-----------|------------|-----|-------------|-------------|------------|-----------|--------------|-----------|-------------|---------------------|
| S1        | 649        | 7.89| 64          | 25.2        | 47.9       | 1.9       | 176.9        | 99.4      | 66          | 2.5                 |
| S2        | 725        | 7.73| 84          | 20.4        | 41.2       | 1.9       | 170.8        | 106.5     | 71          | 3.1                 |
| S3        | 446        | 7.65| 78          | 7.2         | 28.7       | 1.8       | 152.5        | 63.9      | 49          | 4.3                 |
| S4        | 725        | 7.7 | 90          | 6.0         | 35.5       | 1.3       | 170.8        | 85.2      | 55          | 1.8                 |
| S5        | 649        | 7.67| 132         | 1.2         | 39.8       | 2.0       | 164.7        | 117.1     | 78          | 5.3                 |
| S6        | 640        | 7.55| 60          | 6.0         | 17.5       | 0.5       | 122          | 53.2      | 38          | 0.2                 |
| S7        | 815        | 7.59| 94          | 8.4         | 40.3       | 1.6       | 201.3        | 113.6     | 74          | 5.6                 |
| S8        | 592        | 7.50| 90          | 19.2        | 25.8       | 0.8       | 164.7        | 95.8      | 51          | 5.7                 |
| S9        | 592        | 7.21| 72          | 2.4         | 16.4       | 0.2       | 115.9        | 60.3      | 42          | 0.5                 |
| S10       | 709        | 7.39| 92          | 19.2        | 21.1       | 0.9       | 201.3        | 71.0      | 43          | 7.1                 |
| S11       | 715        | 7.43| 96          | 25.2        | 33         | 1.0       | 183.0        | 113.6     | 68          | 4.7                 |
| S12       | 590        | 7.54| 96          | 4.8         | 24.8       | 1.6       | 134.2        | 78.1      | 56          | 6.3                 |
| S13       | 665        | 7.48| 88          | 13.2        | 19.8       | 1.4       | 152.5        | 67.4      | 47          | 8.7                 |
| S14       | 540        | 7.63| 78          | 16.8        | 32.8       | 1.2       | 134.2        | 78.1      | 59          | 9.1                 |
| S15       | 620        | 7.50| 70          | 16.8        | 14.7       | 0.5       | 170.8        | 53.2      | 27          | 6.6                 |
| S16       | 665        | 7.55| 62          | 25.2        | 17.4       | 0.9       | 189.1        | 56.8      | 38          | 4.3                 |
| S17       | 540        | 7.61| 76          | 1.2         | 38.9       | 1.5       | 128.1        | 71.0      | 52          | 4.1                 |
| S18       | 865        | 7.72| 116         | 26.4        | 42.3       | 3.2       | 231.8        | 124.2     | 92          | 3.7                 |
| S19       | 640        | 7.52| 98          | 15.6        | 28.4       | 2.0       | 189.1        | 99.4      | 61          | 2.2                 |
| S20       | 485        | 7.32| 76          | 14.4        | 17.7       | 1.3       | 176.9        | 63.9      | 41          | 2.2                 |
| S21       | 522        | 7.12| 70          | 10.8        | 16.1       | 1.2       | 128.1        | 67.4      | 36          | 3.9                 |
| S22       | 402        | 7.40| 44          | 20.4        | 13.8       | 0.5       | 128.1        | 49.7      | 29          | 4.7                 |
| S23       | 525        | 7.71| 92          | 13.2        | 17.9       | 1.4       | 176.9        | 60.3      | 43          | 8.5                 |
| S24       | 520        | 7.51| 90          | 7.2         | 11.6       | 0.8       | 170.8        | 53.2      | 50          | 2.6                 |
| S25       | 590        | 7.60| 106         | 3.6         | 24.3       | 1.9       | 201.3        | 92.3      | 55          | 2.5                 |
| S26       | 758        | 7.53| 102         | 14.4        | 25.7       | 1.2       | 262.3        | 99.4      | 60          | 5.7                 |
| S27       | 590        | 7.49| 94          | 21.6        | 12.7       | 0.9       | 244.0        | 67.4      | 34          | 3.4                 |
| S28       | 786        | 7.66| 110         | 19.2        | 25.9       | 1.4       | 298.9        | 74.5      | 54          | 0.8                 |
| S29       | 665        | 7.69| 110         | 3.6         | 27.5       | 2.3       | 213.5        | 78.1      | 50          | 2.3                 |
| S30       | 486        | 7.45| 70          | 10.8        | 17.2       | 1.2       | 195.2        | 53.2      | 37          | 2.7                 |
shift of the water samples towards the Cl and SO₄ corners in the Piper diagram (Figure 3). It must be mentioned that the higher solubility and availability of halite in comparison with gypsum explains Cl concentrations more than SO₄ in groundwater from the SGA. The observed changes in cation concentrations along the groundwater flow path (Ca reduction with increase in Mg and Na) are also attributed to the cation exchange process, as proved in previous studies (Jafari 2003).

A multivariate statistical technique of principal component analysis (PCA), performed by IBM SPSS Statistics software (Version 21), was applied to recognize the principal processes affecting the distribution of major ions in the groundwaters of the SGA. The chemical data were first examined using the Kolmogorov–Smirnov test for normal distribution, choosing a significance level of 0.05 ($P < 0.05$). All the considered data sets follow a normal distribution around the mean value, confirming their suitability for PCA test in the raw form. The PCA method which is

![Figure 3](image-url) A plot of groundwater samples collected from the SGA on a Piper diagram.

| Table 2 | Summary of the groundwater mass balance results in the SGA (Jafari 2003) |
|---|---|
| Reaction (coefficients × 10⁴) | Altered mineral and product (moles/L × 10⁴) |
| Halite dissolution | 20.25NaCl = 20.25Na⁺ + 20.25Cl⁻ |
| Gypsum dissolution | 6.85CaSO₄ = 6.85Ca²⁺ + 6.85SO₄²⁻ |
| Weathering of biotite to kaolinite | 2.61K₂Mg₃Al₂Si₅O₁₀(OH)₂ + 18.27CO₂ + 9.135H₂O = 1.31Al₂Si₂O₅(OH)₄ + 7.85 Mg²⁺ + 2.61 K⁺ + 5.22SiO₂ + 18.27HCO₃⁻ |
| Weathering of plagioclase to kaolinite | 0.1Na₀.₃Co₀.₂Al₁.₄Si₂.₆O₈ + 0.12CO₂ + 0.2H₂O = 0.07Al₂Si₂O₅(OH)₄ + 0.08Na⁺ + 0.02Ca²⁺ + 0.12SiO₂ + 0.12HCO₃⁻ |
| Calcite dissolution | 12.55CaCO₃ + 12.55CO₂ + 12.55H₂O = 12.55 Calcite |
| 12.55Ca²⁺ + 25.1HCO₃⁻ | 12.55 Calcite |

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commonly used to form uncorrelated linear combinations of the observed variables (Wang et al. 2013) was applied for extracting information by transforming original, interrelated variables into fewer, uncorrelated ones named principal components. The first component has maximum variance and the successive components explain smaller portions of the variance. In order to simplify the interpretation of the components, the orthogonal rotation method of varimax that minimizes the number of variables that have high loadings on each component was used. The PCA reduced the major ions to three hidden (unknown) factors explaining 93.6% of the sampling variance responsible for the data structure. The rotated factor loadings for each element are presented in Table 3. Loading values that represent the importance of the variables for the components are marked in boldface type. The first component (PC1) comprises Na (0.95), Cl (0.91), and SO4 (0.94) and accounts for about 47.3% of the total variance in the data set. It can be named as fracture-fillings (halite and gypsum) dissolution factor. The higher solubility of the fracture-fillings as compared with the other minerals in the rock matrix explains the higher variance of this component, and confirms its greater effect on the major ions chemistry of the groundwater from the SGA. The third component (PC3), named as the biotite weathering factor, is described by the highest loading in Mg (0.98) which is also related to HCO3 with the loading value of 0.35. Biotite weathering enhances Mg and HCO3 along the groundwater flow paths. It also supplies SiO2 in groundwater resources of the SGA based on the following:

\[ \text{KMg}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{K}^+ + \text{Mg}^{2+} + \text{HCO}_3^- + \text{SiO}_2 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \downarrow \] (3)

In conclusion, PCA in supporting the mass balance studies (Table 2) confirms the dissolution of fracture-filling sediments and weathering of the calcite and biotite as the main processes enhancing major ions in the SGA.

The mean values of the major ions in groundwater resources of the SGA are presented in a Schoeller diagram (Figure 4) in comparison with other granitic waters around the world. As is observed, SO4 ion varies a great deal in granitic waters. The overall increases of the ions concentration and resulting higher salinity values of the groundwaters in the SGA highlights the impact of climatic conditions on the groundwater quality. The mean rate of annual evaporation (E) in the study area is about 1,370 mm, which is at least five times above the average precipitation (250 mm/year), resulting in more salinity of the groundwater resources.

### Spatial distribution of the trace elements

Igneous rock weathering is a possible natural (geogenic) source of the trace elements, especially heavy metals in groundwater (Singhal & Gupta 2010). The occurrence of these elements may limit the groundwater for drinking uses due to the possible effects on health.

More than 50 trace elements in groundwater samples were investigated. However, the elements U, Th, Ba, Sr, Sn, W, Cu, and Zn with concentrations above the detection limit of the instrument were determined (Table 4). The box-and-whisker plots for these elements are presented in Figure 5. They reveal normal distribution of the elements, as approximately 95% of the data lie between the inner fences (whisker). The mean (or median) values arranged in descending order are as follows: Sr > Ba > Sn > W > Cu > U > Zn > Th.
Figure 4 | The mean values of the major ions in groundwater samples from the SGA in comparison with other granitic waters in the world. The numbers in the Schoeller diagram indicate:
1: Shir-Kuh, Iran (this study); 2: Shir-Kuh, Iran (Jafari 2003); 3: Maryland, USA (Hamill & Bell 2013); 4: Baltimore, USA (Hem 1985); 5: Czech Republic (Jezerský 2007); 6: Ephemeral springs of Sierra Nevada, USA (Garrels & Mackenzie 1967); 7: Perennial springs of Sierra Nevada, USA (Garrels & Mackenzie 1967).

Table 4 | Concentration of the trace elements in groundwater samples from the SGA

| Sample ID | Ba (ppb) | Cu (ppb) | Sn (ppb) | Sr (ppm) | W (ppb) | Zn (ppb) | U (ppb) | Th (ppb) |
|-----------|----------|----------|----------|----------|---------|----------|---------|---------|
| S2        | 214      | 8.2      | 30.9     | 1.11     | 34.5    | 13.5     | 11.9    | 5.2     |
| S3        | 48       | 9.6      | 11.4     | 0.74     | 14.5    | 10.2     | 11.2    | 4.8     |
| S7        | 77       | 10.1     | 3.4      | 1.15     | 10.6    | 6.6      | 13.6    | 4.7     |
| S8        | 40       | 9.5      | 2.2      | 0.86     | 9.9     | 3.6      | 6.8     | 4.6     |
| S12       | 56       | 11.2     | 7.4      | 0.9      | 9.6     | 8.2      | 9.9     | 4.4     |
| S13       | 35       | 10.8     | 2.5      | 0.82     | 7.7     | 6.8      | 6.8     | 5       |
| S14       | 16       | 7.1      | 13.7     | 0.94     | 12.5    | 0.5      | 10.3    | 4.4     |
| S15       | 30       | 8.4      | 128.9    | 0.75     | 18.2    | 3.3      | 1.1     | 4.1     |
| S17       | 138      | 7        | 31.1     | 1.06     | 18.1    | 0.5      | 1.9     | 4       |
| S19       | 34       | 8.5      | 2.2      | 0.91     | 8.3     | 11.3     | 8.8     | 4       |
| S22       | 19       | 8.8      | 5.3      | 0.56     | 13.1    | 10.7     | 2.9     | 4.1     |
| S24       | 22       | 8.7      | 8.5      | 0.68     | 17.6    | 7.4      | 2.8     | 4.1     |
| S25       | 31       | 7.4      | 12.9     | 0.84     | 20.1    | 2.6      | 4.6     | 3.9     |
| S28       | 32       | 8.3      | 12.9     | 0.99     | 8.9     | 5        | 9.5     | 3.9     |
| S30       | 26       | 8.9      | 9.6      | 0.8      | 8.7     | 8.1      | 2       | 4       |
| Detection limit | 1.0 | 1.00 | 0.10 | 0.01 | 1 | 1.00 | 1 | 0.10 |
Figure 5 | Box-and-whisker plots showing descriptive statistics of the trace elements detected by ICP-MS in groundwater resources of the SGA. Boxes show interquartile range of data with the line at the median value. Whiskers display the range of non-outlying data. The asterisks or circles are extreme outliers.
The Shir-Kuh granitoid with the S-type nature of magma was derived from the local anatexis of a metasedimentary source which is characterized by enrichment in large ions lithophile elements such as Rb, U, Th, and K (Sheibi et al. 2010). No distinctive minerals were identified in the granitic rocks as the primary source of the above-mentioned elements having high concentrations in the groundwater samples. Nevertheless, the similarity in chemistry causes entry of the trace elements into the crystal lattices of the primary minerals. For example, Sr is a fairly common element replacing Ca and K in granitic igneous rocks (Hem 1985). Therefore, the occurrence of trace elements in groundwater resources is expected as the primary minerals are weathered. Regarding the mass balance studies, weathering of the primary silicate mineral of biotite is introduced as the possible source of the heavy metals in groundwater resources of the SGA.

The spatial distribution of the trace elements in the SGA is shown in Figures 6 and 7. In general, higher concentrations, especially for U and Th (Figure 7), are observed in the northwest, where the felsic granitic rocks with expected higher enrichment in heavy metals are more relatively dominant. From a hydrogeological viewpoint, the longest groundwater flow path from highland recharge areas to the discharge points at the valley bottom (Sanij valley) occurs in this area. Consequently, higher weathering rate of the granitic rocks in relation to the longer residence time of the groundwater in contact with the aquifer materials could be the other reason for the enhanced trace elements in groundwater samples located downstream of the flow path or discharge zones (Figure 2). The Zn concentration is clearly increased in the samples adjacent to the limestone units on the Shir-Kuh granitoid in the east. The existence of the typical carbonate-hosted Zn deposit of Darreh-Zanjir (Maghfouri et al. 2017) in cretaceous sediments of the Taft formation in the east of the study area, suggests the carbonate dissolution as the main possible source of Zn in the groundwater samples.

U and Th geochemistry

The minimum, maximum, and average values of U in groundwater samples are 1.1, 13.6, and 6.9 µg/L, respectively. The accessory minerals of zircon and monazite enclosed in biotite minerals of the Shir-Kuh granitoid (Sheibi et al. 2010) are potentially considered as the main source of U ion in the groundwater from the SGA. These heavy minerals accumulate U and other incompatible elements from magma in the later stages of crystallization (Porcelli & Swarzenski 2003). The direct relationship between U and SiO2 (Figure 8(a)) confirms the major role of silicate mineral weathering in enhancement of U in groundwater resources. The U concentration also increases with the rise in EC (Figure 8(b)), which may be attributed to the increase in the residence time of water in contact with the rock minerals.

The geochemical behavior and distribution of U in groundwater which is controlled by redox processes, pH, and partial pressure of CO2 (Langmuir 1997) is more complex. In summary, uranium is rather soluble in oxidizing and particularly acidic conditions (Banks et al. 1995b). Complexation with hydroxide, carbonate, and phosphate results in elevated solubility as well (Drever 1988). Estimation of redox potential of groundwater in the SGA has been made from iron (Fe) values. Total Fe concentrations in groundwater from the SGA are less than 0.01 ppm (below detection limit of the ICP-MS) and the groundwaters lie in the narrow pH range of 7.1 to 7.9. At these pH values, Fe2+ (soluble form of Fe) becomes stable at low Eh (<0) values (Fetter & Fetter 1999). Consequently, the low Fe concentrations suggest that the SGA groundwaters are more oxidizing than this value. Oxidizing conditions are generally the direct result of dissolved oxygen in the SGA groundwaters. In addition, abundance of the bicarbonate ions resulting from calcite dissolution and biotite weathering are extremely important in mobilization of U in the SGA, as they greatly increase the solubility of U-bearing minerals, facilitate the oxidation of U(IV), and also limit the adsorption of uranium in oxidized waters (Langmuir 1997). The concurrent increase of U and pH (Figure 8(c)) confirms the major impacts of calcite dissolution on complexation of U with carbonate and resulting solubility enhancement in groundwater from the SGA. In pH ranges of the SGA groundwaters (7.1–7.9) the most prevalent stable species of U are expected to be UO2(CO3)2+ and UO2(CO3)3+ complexes (Fetter & Fetter 1999). Carbonate ions are mostly supplied from calcite dissolution (Table 2), which consumes carbon dioxide and then enhances groundwater pH. The processes explain the direct relationship of U and pH.
Figure 6 | The spatial distribution of trace elements in the SGA.
observed in Figure 8(c). This relation also may reflect kinetic factors (Frengstad & Banks 2014), for example, lowest uranium concentrations occur in low pH groundwaters with a low degree of water–rock interaction and low residence time, and vice versa.

The concentration of Th in the groundwaters from SGA varied in a range of 3.9–5.2 μg/L, averaging as 4.3 μg/L. The lower mobility of thorium as compared with uranium (Langmuir 1997) explains its lower concentration in the groundwater resources. The direct relationship between Th
and U concentrations (Figure 8(d)) suggests their occurrence from the same origin of rock weathering process. However, the lower solubility of Th in oxidized conditions (tetravalent state) tends to retain thorium in restitute mineral (Hem 1985), decreasing its concentration in the groundwater resources.

In terms of correlations, U is highly correlated with Ba (R = 0.66), Th (R = 0.61), and Sr (R = 0.58) at a significance level of 0.05. This suggests the same origin for these elements, likely from weathering of silicate minerals such as biotite. The idea was further examined by hierarchical agglomerative cluster analysis (HACA) of the trace elements, excluding the extreme outlier values observed in box-and-whisker plots (Figure 5). HACA is the most common method to classify variables into clusters, by starting with the most similar pair of objects and forming higher clusters step by step. The results of HACA are illustrated by a dendrogram that provides a visual summary of the clustering process (Wang et al. 2013). In this study, HACA was performed using IBM SPSS Statistics software (Version 21) for classification of trace elements into different groups, and the achievement of HACA was through the between-group linkage method using squared Euclidean distances. Based on the resulting dendrogram (Figure 9), the elements are differentiated in three clusters. U and Th are grouped with Sr, Ba, and Cu in cluster 1. The elements Sr and Ba in this group, with chemical similarities to Mg (released from biotite weathering as previously mentioned), are considered as the key for introduction of the biotite as the main source of these elements in groundwater resources. It must be stated that all these elements generally migrate in carbonate forms (Fetter & Fetter 1999) and the carbonate ions in the SGA groundwaters also mainly come from carbonate dissolution. The element Zn is individually situated in cluster 2, probably due to the different origin from dissolution of carbonates. The Sn–W pair in cluster 3 may be linked to continental collision-related Sn–W mineralizations observed in peraluminous S-type granitoids of the middle Jurassic period like Shir-Kuh (Jazi et al. 2013). The idea merits more research to confirm the details.

**Drinking water health-related concerns**

The maximum admissible concentrations of Ba, Cu, Zn, and U in drinking water have been set at 700, 1,000, 3,000...
and 15 μg/L, respectively, by the Institute of Standards and Industrial Research of Iran (ISIRI 2010). There are no legislated maximum permissible values for Sr, Sn, W, and Th in Iran. Regarding the measured values of the trace elements in the SGA (Table 4), the maximum concentrations of most elements are too far below the ISIRI permissible limits in drinking water. The only health concerns may relate to U, as the maximum observed values are closer to the ISIRI maximum permissible standards. There is a general agreement that the chemotoxicity rather than the radiotoxicity related to U in drinking water becomes a concern in the range of 10–30 μg/L, as the prolonged consumption of U-rich waters may lead to renal injuries (Frengstad & Banks 2014). Current drinking-water standards for U in different countries display a range of 2–30 (Frengstad & Banks 2014). The strictest limits were established by Germany, where the maximum values are defined as 2 μg/L for the preparation of baby food and 10 μg/L for others. Regarding these limits, 80% of the water resources are unusable for baby food and about 33%, including those located in the Sanij valley at the northwest of the Shir-Kuh granitoid mass, are not suitable for drinking. Based on the maximum standard limit of 30 μg/L, recommended by both the WHO (2011) and EPA (2002), there are no drinking water health concerns over U in groundwater resources from the SGA at the present time. However, an increase in groundwater’s EC from a mean value of 516 μS/cm in 2003 (Jafari 2003) to 624 μS/cm in 2016 demands a continuous quality monitoring program, especially on the U values in drinking groundwater resources.

**CONCLUSION**

Geochemistry of groundwater in the SGA has evolved to Ca-HCO₃ type, mainly as a result of the calcite dissolution and biotite weathering. The processes, in combination with dissolution of fracture fillings increase water salinity, releasing the trace elements of Sr, Ba, Sn, W, Cu, U, Zn, and Th (arranged in decreasing order of abundance) in the groundwater resources as well. Except for Zn, the trace elements are spatially enhanced in the northwest of the study area, where the felsic rocks with expected higher enrichment in heavy metals are more relatively dominant and the longest groundwater flow path with a resulting increase in water–rock interactions also occurs. Elevated values of Zn are observed in the east, where limestone units overlaid on the granitic rocks with typical carbonate-hosted Zn deposits are found. Weathering of the biotite with the enclosed accessory minerals of zircon and monazite are considered as the potential source of radionuclides (U and Th) in the groundwater resources of the SGA. The oxidizing nature of the groundwater, inferred from the absence of Fe in water samples, the major impact of calcite dissolution on mobilization of U, and the degree of water–rock interactions are the main factors controlling U in the groundwater resources from the SGA. The maximum concentrations are currently less than the Iranian drinking guidelines. However, concentration enhancement is expected in the future, as the salinity of the groundwater resources are being temporally increased. The lower solubility of Th in oxidized conditions explains its low concentration in the SGA groundwater.

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REFERENCES

Appelo, C. A. J. & Postma, D. 2004 Geochemistry, Groundwater and Pollution. CRC Press, Boca Raton, FL, USA.

Banks, D., Reimann, C., Rosset, O., Skarphagen, H. & Sæther, O. M. 1995a Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. Applied Geochemistry 10 (1), 1–16.

Banks, D., Rosset, O., Strand, T. & Skarphagen, H. 1995b Radioelement (U, Th, Rn) concentrations in Norwegian bedrock groundwaters. Environmental Geology 25 (3), 165–180.

Banks, D., Reimann, C. & Skarphagen, H. 1998 The comparative hydrochemistry of two granitic island aquifers: the Isles of Scilly, UK and the Hvaler Islands, Norway. Science of the Total Environment 209 (2–3), 169–183.

Bonotto, D. M. 1989 The behavior of dissolved uranium in groundwaters of the Morro do Ferro thorium deposit, Brazil. Journal of Hydrology 107 (1–4), 155–168.

Desbarats, A. J., Percival, J. B. & Venance, K. E. 2016 Trace element mobility in mine waters from granitic pegmatite U–Th–REE deposits, Bancroft area, Ontario. Applied Geochemistry 67, 153–167.

Drever, J. I. 1988 The Geochemistry of Natural Waters, Vol. 437. Prentice Hall, Englewood Cliffs, NJ, USA.

Edmunds, W. M. & Shand, P. 2008 Natural Groundwater Quality. Wiley–Blackwell, Oxford, UK.

EPA 2002 Technical Fact Sheet: Final Rule for (non-Radon) Radionuclides in Drinking Water 815-F-00-013. USEPA, Washington, DC, USA.

Fetter, C. W. & Fetter, C. W. 1999 Contaminant Hydrogeology. Prentice Hall, Englewood Cliffs, NJ, USA.

Freeze, R. A. & Cherry, J. A. 1979 Groundwater. Prentice-Hall, Englewood Cliffs, NJ, USA.

Frengstad, B. S. & Banks, D. 2014 Uranium distribution in groundwater from fractured crystalline aquifers in Norway. Fractured Rock Hydrogeology, International Association of Hydrogeologists Selected Papers 20, 257–276.

Garrels, R. M. & Mackenzie, F. T. 1967 Origin of the chemical compositions of some springs and lakes. In: Equilibrium Concepts in Natural Water Systems (W. Stumm, ed.). ACS Publications, Washington, DC, USA, pp. 222–243.

Gascoyne, M. 1989 High levels of uranium and radium in groundwaters at Canada’s underground research laboratory, Lac du Bonnet, Manitoba, Canada. Applied Geochemistry 4 (6), 577–591.

Hagedorn, B. & Hasholt, B. 2004 Hydrology, geochemistry and Sr isotopes in solids and solutes of the meltwater from Mittivakkat Gletscher, SE Greenland. Hydrology Research 35 (4–5), 369–380.

Hamill, L. & Bell, F. G. 2013 Groundwater Resource Development. Butterworth, London, UK.

Hem, J. D. 1985 Study and Interpretation of the Chemical Characteristics of Natural Water. Water Supply Paper 2254.

Department of the Interior, US Geological Survey, Reston, VA, USA.

ISIRI 2010 Drinking Water – Physical and Chemical Specifications, 5th revision. Institute of Standards and Industrial Research of Iran, Tehran, Iran.

Jafari, H. 2003 Hydrochemical Evolution of Groundwater in Shir-Kuh Hard Rock Aquifer, Yazd. MSc thesis, Shiraz University, Iran.

Jazi, M. A., Mohammad Hassan, K. & Azadeh, M. S. 2013 A new insight on tectono-magmatism and mineralization of middle Jurassic period granitoid intrusions in Iran. In: The 5th Iranian Society of Economic Geology Symposium. Ferdowsi University of Mashhad, Iran.

Jezersky, Z. 2007 Hydrogeochmistry of a deep gas-storage cavern, Czech Republic. Hydrogeology Journal 15 (3), 599–614.

Khalili, M. 1997 Petrography, Mineral Chemistry and Geochemistry of Shir-Kuh Granite Southwest of Yazd Central Iran. PhD thesis, University Hamburg, Germany.

Langmuir, D. 1997 Aqueous Environmental Geochemistry. Prentice-Hall, Upper Saddle River, NJ, USA.

Le Maitre, R. W., Streckeisen, A., Zanettin, B., Le Bas, M. J., Bonin, B. & Bateman, P. 2005 Igneous Rocks: A Classification and Glossary of Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks. Cambridge University Press, Cambridge, UK.

Maghfouri, S., Hosseinzadeh, M. R., Rajabi, A. & Azimzadeh, A. M. 2017 Darreh-Zanjir deposit: a typical carbonate hosted Zn-Pb deposit (MVT) in early cretaceous sedimentary sequence, southern Yazd basin. Geosciences 26 (103), 13–28.

Mason, B. & Moore, C. B. 1982 Principle of Geochemistry. John Wiley, Hoboken, NJ, USA.

Mast, M. A., Drever, J. I. & Baron, J. 1990 Chemical weathering in the Loch Vale watershed, Rocky Mountain National Park, Colorado. Water Resources Research 26 (12), 2971–2978.

Milvy, P. & Cothern, R. 1990 Scientific background for the development of regulations for radionuclides in drinking water. In: Radon, Radium and Uranium in Drinking Water (C. R. Cothern, ed.). Taylor and Francis, Boca Raton, FL, USA, pp. 1–17.

Örgün, Y., Altunsoy, N., Gültekin, A. H., Karahan, G. & Celebi, N. 2005 Natural radioactivity levels in granitic plutons and groundwaters in Southeast part of Eskisehir, Turkey. Applied Radiation and Isotopes 63 (2), 267–275.

Pelig-Ba, K. B., Biney, C. A. & Antwi, L. A. 1991 Trace metal concentrations in borehole waters from the upper regions and the Accra plains of Ghana. Water, Air, & Soil Pollution 59 (3), 333–345.

Porcelli, D. & Swarzenski, P. W. 2005 The behavior of U-and Th-series nuclides in groundwater. Reviews in Mineralogy and Geochemistry 52 (1), 317–361.

Raju, N. J., Dey, S., Glossel, W. & Wycisk, P. 2012 Fluoride hazard and assessment of groundwater quality in the semi-arid Upper Panda River basin, Sonbhadra district, Uttar Pradesh, India. Hydrological Sciences Journal 57 (7), 1433–1452.
Ramaiah, S. N., Gopalakrishna, G. S., Vittala, S. S. & Najeeb, K. M. 2012 Geomorphological mapping for identification of ground water potential zones in hard rock areas using geo-spatial information – a case study in Malur Taluk, Kolar District, Karnataka, India. *Nature, Environment and Pollution Technology* **11** (3), 369–376.

Rice, E. W. & Bridgewater, L. 2012 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Satyanarayanan, M., Balaram, V., Al Hussin, M. S., Al Jemaili, M. A. R., Rao, T. G., Mathur, R., Dasaram, B. & Ramesh, S. L. 2007 Assessment of groundwater quality in a structurally deformed granitic terrain in Hyderabad, India. *Environmental Monitoring and Assessment* **131** (1–3), 117–127.

Sheibi, M., Esmaily, D., Nédélec, A., Bouchez, J. L. & Kananian, A. 2010 Geochemistry and petrology of garnet-bearing S-type Shir-Kuh Granite, southwest Yazd, Central Iran. *Island Arc* **19** (2), 292–312.

Singh, C. K., Kumari, R., Singh, N., Mallick, J. & Mukherjee, S. 2013 Fluoride enrichment in aquifers of the Thar Desert: controlling factors and its geochemical modelling. *Hydrological Processes* **27** (17), 2462–2474.

Singhal, B. B. S. & Gupta, R. P. 2010 *Applied Hydrogeology of Fractured Rocks*. Springer Science & Business Media, The Netherlands.

Skeppström, K. & Olofsson, B. 2007 Uranium and radon in groundwater. *European Water* **17** (18), 51–62.

Taheri, F. 2017 *Identification of Groundwater Potential Zones in Granitic Mass of Shir-Kuh, Yazd*. MSc thesis, Shahrood University of Technology, Iran.

Thivya, C., Chidambaram, S., Tirumalesh, K., Prasanna, M. V., Thilagavathi, R. & Nepolian, M. 2014 Occurrence of the radionuclides in groundwater of crystalline hard rock regions of central Tamil Nadu, India. *Journal of Radioanalytical and Nuclear Chemistry* **302** (3), 1349–1355.

Thivya, C., Chidambaram, S., Keesari, T., Prasanna, M. V., Thilagavathi, R., Adithya, V. S. & Singaraja, C. 2016 Lithological and hydrochemical controls on distribution and speciation of uranium in groundwaters of hard-rock granitic aquifers of Madurai District, Tamil Nadu (India). *Environmental Geochemistry and Health* **38** (2), 497–509.

Tzortzis, M. & Tsertos, H. 2004 Determination of thorium, uranium and potassium elemental concentrations in surface soils in Cyprus. *Journal of Environmental Radioactivity* **77** (3), 325–338.

Wang, Y., Wang, P., Bai, Y., Tian, Z., Li, J. & Shao, X. 2013 Assessment of surface water quality via multivariate statistical techniques: a case study of the Songhua River Harbin region, China. *Journal of Hydro-Environment Research* **7** (1), 30–40.

WHO 2011 *Guidelines for Drinking-Water Quality*, Vol. 38, 4th edn. WHO Chronicle, IWA Publishing, London, pp. 104–108.

Yuce, G., Ugurluoglu, D., Dilaver, A. T., Eser, T., Sayin, M., Donmez, M., Ozcelik, S. & Aydin, F. 2009 The effects of lithology on water pollution: natural radioactivity and trace elements in water resources of Eskisehir Region (Turkey). *Water, Air, and Soil Pollution* **202** (1–4), 69.

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