Hydrogeochemical Analysis of Bidkhan Stream of Bardsir (Southeast Iran) Using Principal Component and Cluster Analyses

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Introduction

Thermodynamically, the surface waters in mountain environments are unstable and their chemical composition is a reflection of water-rock interactions. Few studies have also been undertaken on the geochemistry of the surface waters in mountain environments. Hence, this paper deals with the source of elements as well as the chemistry of the stream which drains from the caldera of Bidkhan volcano.

The Bidkhan is an inactive stratovolcano having a caldera located at southeast Iran at a distance of 115 Km from Kerman (40 Km southeast of Bardsir town). Its geographical coordinates include 56°, 25′ to 56°, 30′ eastern longitude and 29°, 35′ to 29°, 40′ northern latitude. This volcano lies at the southeastern part of the volcanic belt of central Iran (Orumieh-Dokhtar belt). The Bidkhan volcano occupies an area of 400 km^2 and its highest summit lies at about 3800 m above mean sea level. The Bidkhan stream drains its caldera. The caldera lies in almost 12 kilometers of the course of the Bidkhan stream and supplies several villages in its course. There is no hydrometric station along this stream, but based on field observations, the highest flow is about 600 L/s in April. This stream usually dries out in the August-December period. Its average flow is about 610 L/s. According to the undertaken measurements, the water temperature varies from 15 to 20 C° along its course in summer times. The pH values range from 6.9 to 7.4.

Geology

Surge deposits which cover unconformably Eocene rocks are considered as the first products of the eruption of this volcano. According to geochronological studies undertaken by Khalili et al (2008),Its activity has initiated about 13 million years ago. This volcanic structure consists of alternatives of andesitic-dacitic and rhyolitic lavas as well as pyroclastic and epiclastic deposits as the products of several cycles of its activity. After ceasing volcanic activity, a period of plug and dyke intrusion has taken place. This volcano has entered an erosion phase since about 10 million years ago.

Materials and methods

In this study, 12 water samples were collected from the Bidkhan stream as shown in Fig 1. Polyethylene bottles were used at each sampling point, and three separate samples, for major anions, major cation, and metals, were taken. In order to prohibit ion precipitation and bioticactivities, the cation and metal ones were acidified using nitric acid. The temperature and pH were measured in the field and geographical locations were determined by a GPS device. Major ions were measured in the laboratory of Regional Water Organization of Kerman and heavy metals were measured in the central laboratory of Shahid Bahonar University. Ca^{2+}, Mg^{2+}, HCO_3^-, and Cl^- were analysed by titration method and sodium by flame photometry.

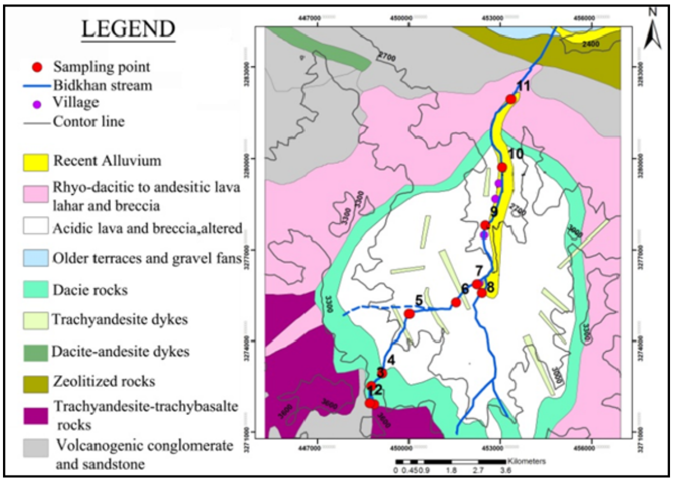

Figure 1. Location of sampling points in Bidkhan river on the geological map of the area

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Sulfate concentration was determined using gravimetric assay. Finally, the metals were analysed using ICP-OES technique. In order to determine the source of analytes, statistical methods of PCA and CA as well as correlation matrix were employed.

Results and discussion

In PCA test, four factors were identified. Factor 1 includes Li^{+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, Na^{+}, Mg^{2+} cations and HCO_3^{-}, SO_4^{2-} and Cl^{-} anions. Fe, Mn and Al comprise factor 2. Factor 3 includes V and pH. And, lastly, Cd is located lonely in factor 4 (Table 1).

Fig. 2 shows the cluster analysis of the components. In the cluster analysis, Li^{+}, Sr^{2+}, Na^{+}, SO_4^{2-}, Mg^{2+}, Cl^{-}, Ba^{2+}, HCO_3^{-} and Ca^{2+} form a major cluster. The other important cluster includes Fe, Mn and Al. Vanadium and pH make up another cluster and Cd is almost isolated from the other components (Fig. 2).

Overally, comparison of the results of PCA and CA tests supports each other and both are matched with correlation coefficients. The elements and compounds in the factor 1 indicate the influence of the major processes such as rain water chemistry, silicate hydrolysis, and possibly pyrite oxidation. Those located in the factor 2 (Fe, Mn and Al) represent release from silicate hydrolysis and pyrite decomposition (Fe), but all these elements are very insoluble and precipitate as oxides and hydroxides.

Those comprising the factor 3 (vanadium and pH) exhibit a strong dependence on V with pH changes. Cd lonely lies in the factor 4 highlighting major differences in its chemical behavior in comparison with the other analytes.

Detection limit for Zn, Cu, and Ni elements is 10 µg/l. Also, detection limits for Mo and Cr are 2 and 1 µg/l, respectively. Concentration of these elements in all samples is not only below the detection limits but also lower than the EPA and WHO standards. The detection limits for Arsenic and Pb are 5 and 10 µg/l, respectively. There is only one sample higher than the detection limits in both of these elements. Arsenic concentration just in this sample reaches to 8.64 µg/l that is lower than the EPA and WHO standards. The Pb concentration in this sample is 14.19 µg/l that is lower than the EPA standard and higher than the WHO standard. The concentration of V, Ba, Li, Sr, and Cd elements was described in the following.

The vanadium concentration ranges from less than 20 to 59.22 µg/l with a median of 24.03 µg/l, which is 4.48 times higher than its average content in the rivers across the world. According to the studies undertaken by Khalili (2012) and Atapour (2008), the average concentration of this element in the rocks of this area is about 3.75 times higher than the average content in the intermediate rocks. High-V rocks in the studied area have led to the enrichment of waters with respect to this element. There are not any standards for the V concentration in waters. So, we compared the concentration of this element with drinking water in other countries. The result is that the concentration of this element in the Bidkhan stream is higher than that of drinking water in other countries.

The barium and lithium concentrations range from 0.28 to 23.56 with a median of 13.01 µg/l and 1.08 to 20.85 with a median of 5.86 µg/l, respectively. These medians are, respectively, 13.01 and 1.7 times higher than the average content in the rivers across the word. The highest concentration of these elements is lower than the EPA and WHO standards.

Strontium concentration ranges from 25.47 to 394.14 µg/l with a median of 145.767 µg/l, which is 2.9 times higher than the average content in the rivers across the world. According to the studies undertaken by Khalili (2012) and Atapour (2008), the average concentration of this element in the rocks of the studied area is about 2.2 times higher than the average content in the intermediate rocks. Hence, the strontium concentration in the Bidkhan river reflects the concentration of this element in the rocks. There is not any standard for the Sr as well. Hence, we compared the concentration of this element in the Bidkhan stream with the one in drinking water in other countries which indicates similar situations.

The cadmium concentration ranges from less than 0.5 to 4.54 µg/l with a median of 0.38 µg/l. Samples 2 and 9 are slightly higher than the maximum level of cadmium in natural waters (3 µg/l). The highest Cd concentration is lower than the EPA standard and higher than the WHO standard.

Table 1. PCA of elements in the Bidkhan river

Parameter	Rotated Component Matrix[a]			
	Component			
	1	2	3	4
Ba	0.59			
Li	0.96			
Sr	0.96			
Ca^{2+}	0.65			
Mg^{2+}	0.78			
Na^{+}	0.93			
HCO_3^{-}	0.81			
SO_4^{2-}	0.83			
Cl^{-}	0.77			
Al		- 0.89		
Fe		- 0.92		
Mn		- 0.93		
V			0.86	
PH			0.83	
Cd				0.82

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 6 iterations.

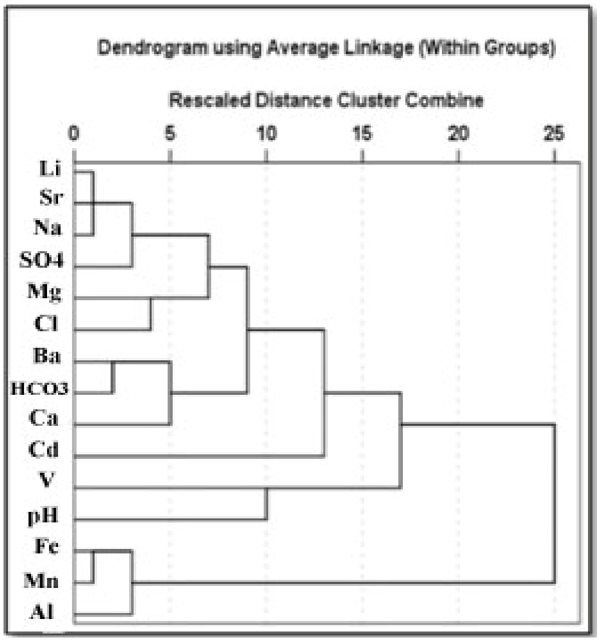

Figure 2. Cluster analysis of elements in the Bidkhan river

Conclusion

In all, although the source of some elements is rain water, the main source of major cations as well as heavy metals is the hydrolysis of silicates. Since igneous rocks are poor in chlorine, the main source of this element is the rain water. The sulfate cation may originate from the Pyrite oxidation and/or rain water.

Separation of the analytes in four factors revealed that they follow the basic rules governinig their concentration in waters. Also, the concentration of some elements such as Ba, Li, Sr, and V is higher than their average concentrations in river waters. As an example, V is 5 times higher in concentration than the average. Some elements such as Cu and Cr have not been solved due to Eh and pH conditions. The presence of Al, Mn, and Fe hydroxides in bottom sediments leads to adsorption of some elements. So, it is proposed that the concentration of elements be determined in bottom sediments to get a better idea on some processes such as adsorption and desorption.

Keywords: Bidkhan stream, cluster analysis, hydrogeochemistry, principal component analysis, volcanic rocks.