

Geochemical and hydrogeochemical evolution of groundwater in Ferdows area, northeast of Iran

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Abstract The chemical analysis of 19 water wells in Ferdows area, Northeastern Iran, has been evaluated to determine the hydrogeochemical processes and ion concentration background in the region. In the study area, the order of cation and anion abundance is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$, respectively, and the dominating hydrochemical types are Na–Cl. Most metal concentrations in water depend on the mineral solubility, and pH, Eh, and salinity of the solution. Their ΣREE concentrations showed excellent correlations with parameters such as TDS and pH. North American Shale Composite (NASC)-normalized REE patterns are enriched in the HREEs relative to the LREEs for all groundwaters. They all have positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.752\text{--}3.934$) and slightly negative Ce anomalies ($\text{Ce}/\text{Ce}^* = 0.019\text{--}1.057$). Reduction–oxidation, complexation, desorption, and re-adsorption alter groundwater REE concentrations and fractionation patterns. The positive Eu anomalies in groundwaters are probably due to preferential mobilization of Eu^{2+} relative to the trivalent REEs in the reducing condition.

Keywords Hydrogeochemical · Groundwaters · Iran

Introduction

Water shortage has become an increasingly serious problem in Iran, especially in the arid and semi-arid regions of

western Iran (Jalali 2006). Iran is located in a semi-arid area with an average annual precipitation of less than one-third of that of the world (Baghvand et al. 2010). Therefore, water is a rare and precious resource.

Intense agricultural and urban development has placed a high demand on groundwater resources, especially in the Ferdows region, and these resources are now at greater risk of contamination. Variation in groundwater chemistry is mainly a function through the interaction between the groundwater and the mineral composition of the aquifer materials through which it moves and is controlled by various factors, like evaporation, dissolution–precipitation, weathering of silicates, oxidation–reduction, sorption and exchange reactions, transformation of organic matter, and mixing processes (Carrilo-Rivera et al. 2007; Sharif et al. 2008). The interaction of all factors leads to various water types (Azaza et al. 2010). The importance of water quality to human health has recently attracted a great deal of interest (Pazand et al. 2011). The evaluation and management of groundwater resources require an understanding of hydrogeological and hydrochemical properties of the aquifer. Rare earth elements (REEs) are believed to be potential tracers for studying groundwater–aquifer rock interactions because of their generally coherent and predictable behavior (Tang and Johannesson 2006). This coherent behavior of the REEs, combined with their sensitivity to changes in pH, redox conditions and adsorption/desorption reactions, makes the REEs particularly useful in hydrogeochemical studies (Wood 1990). Because the REEs typically behave coherently, perturbations from the expected patterns can yield critical information about the types of processes occurring within a water–rock system. Increased knowledge of geochemical evolution of groundwater quality could lead to improved understanding of hydrochemical systems in such areas, leading to

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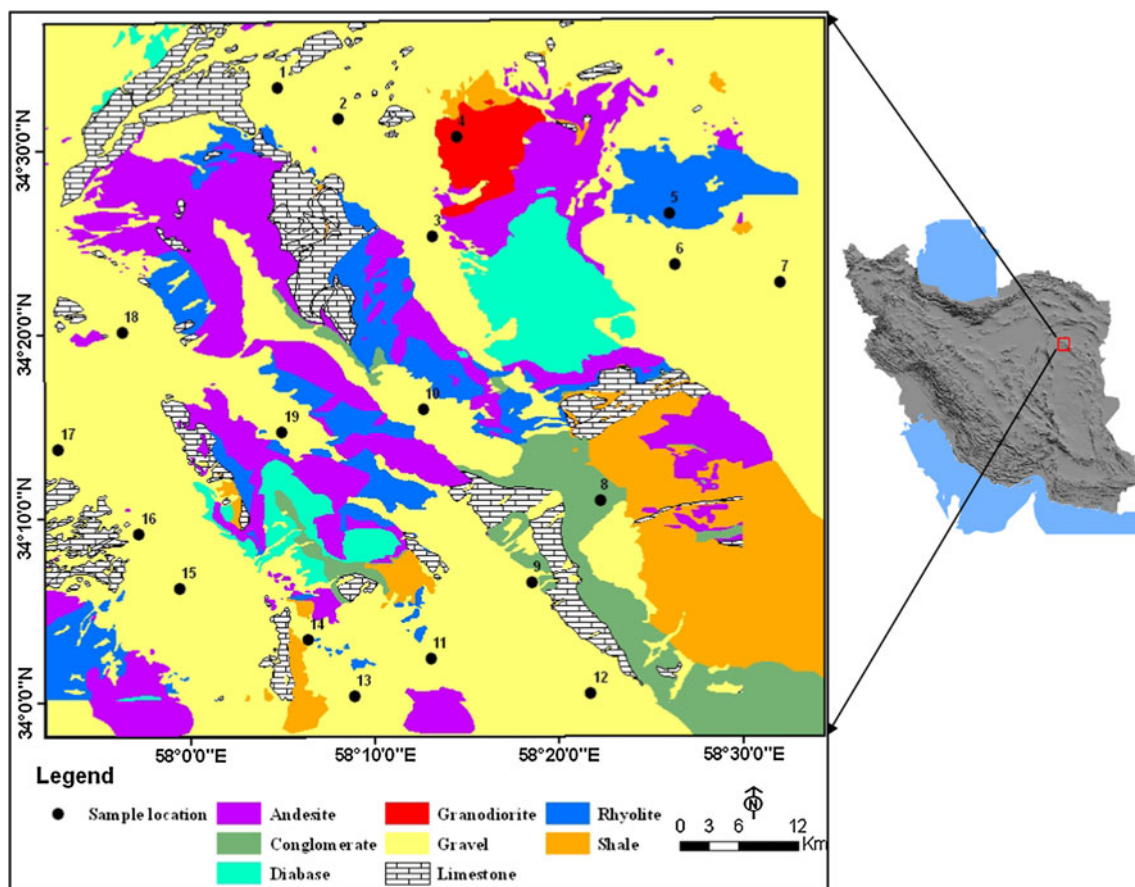


Fig. 1 Geologic map of study area (after Pourlatifi 1995)

sustainable development of water resources and effective management of the groundwater resource (Azaza et al. 2010). Therefore, the objective of this study was to identify the processes controlling the geochemical evolution of groundwater quality and to characterize water–rock interaction and its effects on the chemistry of the water. Finally, to aid the management and future development of groundwater resources in the region, the hydrochemical approach and statistical methods were also applied to divide the territory into areas with distinct groundwater quality. This may help in the long run to support new and more efficient remedial measures to combat the deterioration of water quality.

Geology and hydrogeological setting

The study area lies in the northeastern Iran. The topography of the study area is the mixture of rugged mountains with flat plains (Fig. 1). The average elevation (altitude) for the study area is 2,000 m a.s.l. The area has a hot

temperate climate, with mean maximum summer temperatures (July) of about 40 °C and minimum winter temperatures (January) of 15 °C. The climate of the study area is considered to be arid, the annual precipitation being approximately 100 mm (Pourlatifi 1995).

The Mountain region is part of the Alpine-Himalayan organizations that their shaping as a result of the convergence zone of Eurasia, Arabia and India continental. Most of the study area is formed by recent alluvium that consists of gravel. Volcanic Rocks consist of andesite and rhyolite in the Cenozoic period that was affected by granodiorite intrusions placed above sediment with Carboniferous and Jurassic age (Eftekhari Nezhad and Valeh 1977; Pourlatifi 1995).

Materials and methods

Field sampling and field parameter measurement

A total of 19 groundwater samples were collected from existing wells in the study areas in October 2010 (Fig. 2).

Fig. 2 Location of some sampling site (Well 10, 12, 15)



The geographical locations of the wells were determined with a GARMIN handheld global positioning system (GPS). The selected wells are used for agricultural and domestic purposes. Groundwater samples were collected following the standard procedures (Halim et al. 2009) which included (1) filtered using 0.45 μm filters and acidified with supra pure 0.7 N HNO_3 to $\text{pH} \sim 2$ for the analysis of heavy and trace elements and (2) filtered, but not acidified, for the analysis of major ions. The samples were collected in 100 mL polyethylene bottles, after pumping continuously 15–30 min until the temperature, electrical conductivity (EC) and pH reading had stabilized. Immediately, after sampling, pH, temperature and electrical conductivity (EC) were measured in the field using a portable pH meter (Metrohum) (Table 1).

Analytical techniques

Samples were analyzed at the laboratory for the major ions employing standard methods. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) was determined titrimetrically using standard EDTA. Chloride (Cl^-) was determined by standard AgNO_3 titration method. Carbonate CO_3^{2-} and bicarbonates (HCO_3^-) were determined by titration with HCl. Sodium (Na^+) and potassium (K^+) were measured by flame photometry, sulfate SO_4^{2-} by spectrophotometric turbidimetry, and NO_3^- by colorimetry with an UV–visible spectrophotometer. Total dissolved solids (TDS) were determined gravimetrically at 105–110 $^\circ\text{C}$ (Table 1). Major and trace elements were measured with inductively coupled plasma and mass spectrometry (ICP–MS) in the filtered and acidified water samples within 2 weeks after sampling (Table 2).

Results and discussion

Geochemistry of major ions

The pH of the groundwater in the study area ranged from 7.30 to 8.69 with an average value of 7.82, indicating an alkaline nature of the samples. Eh varies between -70 and 6.30 mV. The relationship between Eh and pH show that Eh is decreased with increasing pH; this relationship probably indicates the progressive reduction of Fe^{2+} with deeper circulation associated with pH increase. The relative content of a cation or an anion is defined as the percentage of the comparative amount of that ion to the total cations or anions, respectively (Pazand et al. 2012). The concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ represent on average 14.39, 5.18, 79.95, and 0.48 % of all the cations, respectively. Among the anions, the concentrations of HCO_3^- , Cl^- , NO_3^- , and SO_4^{2-} represent on average 9.60, 51.37, 1.93, and 37.10 %, respectively. Thus, the order of cation and anion abundance is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$, respectively. If halite dissolution is responsible for sodium, the Na^+/Cl^- ratio should be approximately equal to 1, whereas the ratio greater than 1 is typically interpreted as Na released from silicate weathering reactions (Meyback 1987). Samples having Na^+/Cl^- ratio greater and less than 1 in the study area are nearly equal and hence sodium might have come from irrigation return flow, anthropogenic activity, and silicate weathering (Fig. 3). The chloro-alkaline index, $\text{CAI} = [\text{Cl} - (\text{Na} + \text{K})]/\text{Cl}$, is suggested by Schoeller (1977), which indicates the ion exchange between the groundwater and its host environment. If there is ion

Table 1 Physicochemical parameters of groundwater samples

Sample	pH	Eh (mv)	T °C	TDS	Cl	NO ₃	SO ₄	HCO ₃ (mg/l)	Ca	K	Mg	Na
1	7.30	6.30	27.20	881	424.00	33.00	294.00	130.00	159.70	3.33	35.61	381.40
2	7.83	-25	26.70	2,336	905.00	110.00	1,171.00	150.00	211.20	5.15	90.38	1,040.00
3	8.08	-35	25.70	668	172.00	31.00	290.00	175.00	44.98	1.77	7.53	335.10
4	8.10	-40.30	30.10	459	59.00	3.00	62.00	335.00	27.48	1.53	4.08	238.90
5	8.69	-70	21.80	1,209	306.00	42.00	511.00	350.00	18.42	3.73	4.53	674.70
6	7.62	-11 to 70	26.40	1,606	995.00	27.00	459.00	125.00	167.40	3.97	25.92	893.40
7	7.61	-10.30	25.20	3,325	2,139.00	75.00	1,026.00	85.00	365.00	5.68	91.86	1,601.00
8	7.60	-10	21.60	305	35.00	13.00	57.00	200.00	51.33	1.87	17.06	95.19
9	7.73	-16	22.70	559	169.00	9.00	151.00	230.00	60.48	3.02	35.84	234.20
10	8.03	-33.70	25.70	961	561.00	22.00	168.00	210.00	74.14	1.24	15.70	576.40
11	7.34	5.30	23.57	2,288	987.00	55.00	1,056.00	190.00	335.80	5.84	141.80	755.70
12	7.75	-17	26.00	919	301.00	10.00	288.00	320.00	55.51	3.85	52.11	424.70
13	7.71	-15	21.20	4,271	2,176.00	124.00	1,761.00	210.00	469.30	27.31	118.20	1,931.00
14	7.59	-7.20	23.80	3,506	3,194.00	74.00	43.00	195.00	527.70	11.40	278.20	2,444.00
15	7.57	-6.70	23.80	4,355	2,206.00	43.00	1,891.00	215.00	280.40	13.81	134.80	2,122.00
16	7.69	-14	24.00	4,246	2,169.00	21.00	1,926.00	130.00	342.90	10.38	104.00	2,130.00
17	7.56	-7	24.80	4,767	2,574.00	22.00	2,006.00	165.00	330.40	11.58	124.90	2,404.00
18	8.53	-63	26.20	1,850	648.00	14.00	963.00	225.00	64.88	3.39	20.15	1,033.00
19	8.22	-45	23.50	1,648	628.00	48.00	788.00	220.00	66.19	2.32	13.97	990.30

Table 2 Concentrations of major elements of groundwater samples (µg/l)

Row	Ag	As	Cd	Co	Cu	Fe	Mo	Mn	Ni	Pb	Pt	Sb	Se	Si	Sr	V	Zn
1	0.04	1.10	0.04	0.09	8.50	20.00	1.60	6.31	2.50	2.20	0.01	1.11	1.10	6,109	3.25	16.00	12.70
2	0.07	1.80	0.04	0.16	7.60	40.00	7.00	5.29	2.30	2.70	0.01	1.43	14.40	5,841	5.38	34.10	15.90
3	0.04	7.00	0.04	0.08	6.90	60.00	3.20	2.77	1.70	1.30	0.02	1.59	5.10	6,019	0.89	10.00	69.90
4	0.04	22.30	0.04	0.12	13.30	90.00	9.30	5.65	1.10	2.50	0.01	1.56	1.20	6,080	0.40	6.00	11.30
5	0.04	9.40	0.04	0.18	3.60	40.00	19.80	7.26	0.60	0.10	0.01	1.41	10.20	8,054	0.43	43.10	0.38
6	0.09	20.60	0.10	0.11	6.70	30.00	6.00	4.33	1.60	3.30	0.01	1.57	4.40	9,689	3.16	23.00	23.80
7	0.12	6.70	0.04	0.28	9.20	40.00	5.60	3.11	3.40	4.30	0.01	1.29	10.20	8,056	10.05	38.10	11.50
8	0.04	0.38	0.04	0.06	5.50	10.00	0.90	2.90	0.80	0.60	0.01	1.18	1.40	6,246	1.23	7.00	9.40
9	0.04	0.38	0.04	0.02	8.70	10.00	2.70	2.38	2.60	0.60	0.02	1.18	1.20	5,946	1.73	12.00	7.20
10	0.04	26.00	0.04	0.03	8.90	20.00	16.10	5.00	0.90	1.40	0.01	1.28	4.90	10,806	1.56	33.10	5.00
11	0.04	1.90	0.04	0.27	20.20	20.00	1.90	5.76	3.70	0.70	0.02	1.22	13.40	8,065	8.37	49.10	11.20
12	0.04	1.60	0.07	0.02	2.40	7.50	3.10	3.41	0.70	0.08	0.01	1.50	6.10	6,353	1.60	20.00	2.40
13	0.06	15.40	0.04	0.45	19.90	40.00	11.00	4.97	5.90	2.70	0.02	1.49	18.10	23,932	9.16	75.20	6.20
14	0.19	4.10	0.05	0.44	20.30	10.00	3.60	3.94	6.80	1.30	0.01	1.23	24.60	13,973	17.86	84.20	5.70
15	0.06	5.10	0.04	0.23	9.60	30.00	4.40	4.68	4.50	2.00	0.01	1.31	20.30	12,699	8.81	53.10	3.40
16	0.25	4.20	0.04	0.33	14.60	50.00	11.70	4.88	4.50	2.60	0.01	1.72	15.80	10,991	8.82	43.10	6.50
17	0.14	7.20	0.04	0.33	12.20	100.00	8.60	6.09	4.10	1.80	0.02	1.37	17.80	14,539	9.79	51.10	6.90
18	0.04	3.80	0.04	0.04	2.60	7.50	17.10	1.87	0.90	0.08	0.01	1.83	16.20	7,225	1.68	18.00	0.38
19	0.04	11.50	0.12	0.11	5.90	30.00	18.30	2.95	6.10	1.70	0.01	1.49	10.60	9,073	1.62	18.00	2.60

exchange of Na⁺ and K⁺ from water with Mg²⁺ and Ca²⁺ in the rock, the exchange is known as direct when the indices are positive. If the exchange is reverse, then the exchange is indirect and the indices are found to be negative. Positive CAI values noted in 1, 6, 7, 11, 13, 14, 15,

16, and 17 well areas suggest that sodium and potassium from water are exchanged with magnesium and calcium in rock following base exchange reactions (chloro-alkaline equilibrium), whereas negative CAI values noted at 2, 3, 4, 5, 8, 9, 10, 12, 18, and 19 wells suggest that magnesium

Fig. 3 Na/Cl and CAI ratio of well samples in the study area

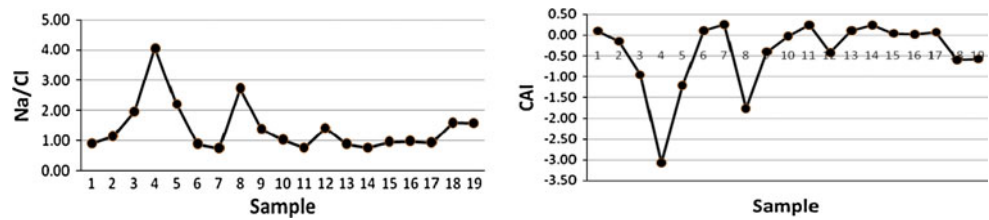
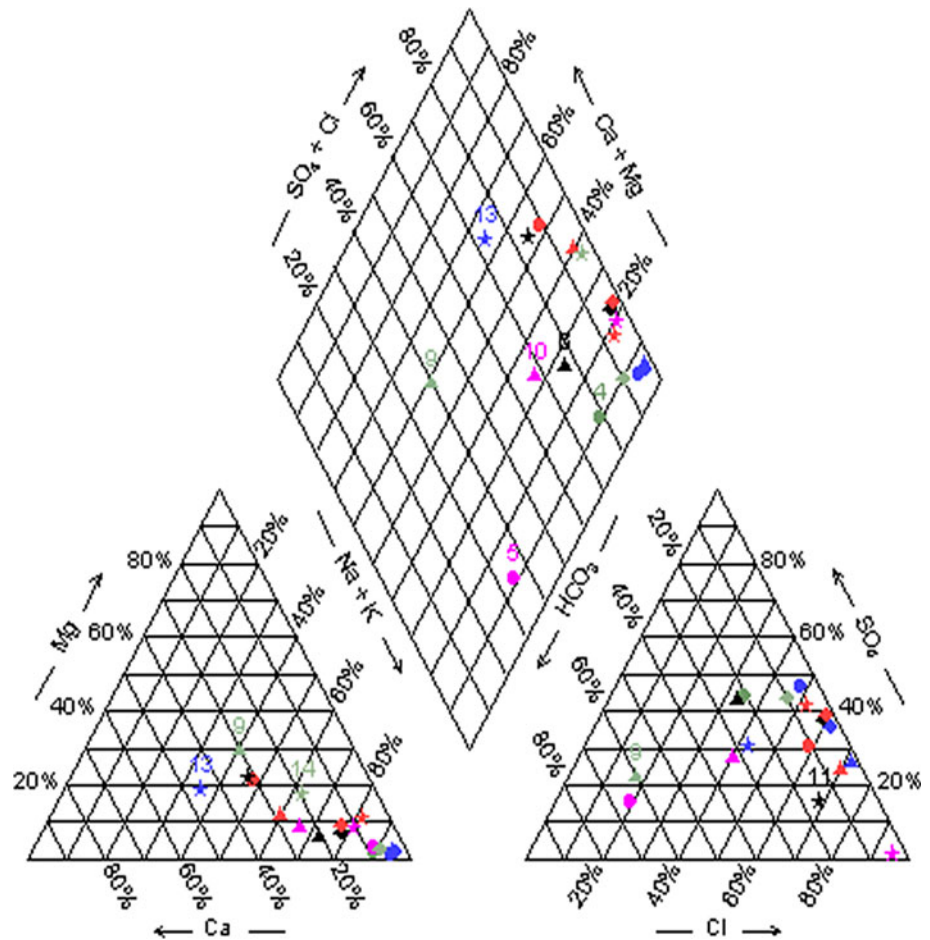


Fig. 4 The piper diagram for the groundwater samples of the study area



and calcium from water are exchanged with sodium and potassium in rock favoring cation–anion exchange reactions (chloro-alkaline disequilibrium).

Hydrochemical facies

The term hydrochemical facies is used to describe the bodies of groundwater in an aquifer that differs in chemical composition (Aghazadeh and Mogaddam 2011). The facies are a function of the lithology, solution kinetics, and flow patterns of the aquifer (Raju et al. 2009). Large tables of analytical data are usually difficult to interpret regarding the variations in water quality. Graphs are useful for this purpose and several specialized types are in use. Piper’s diagram is one of them. Based on the dominant cations and

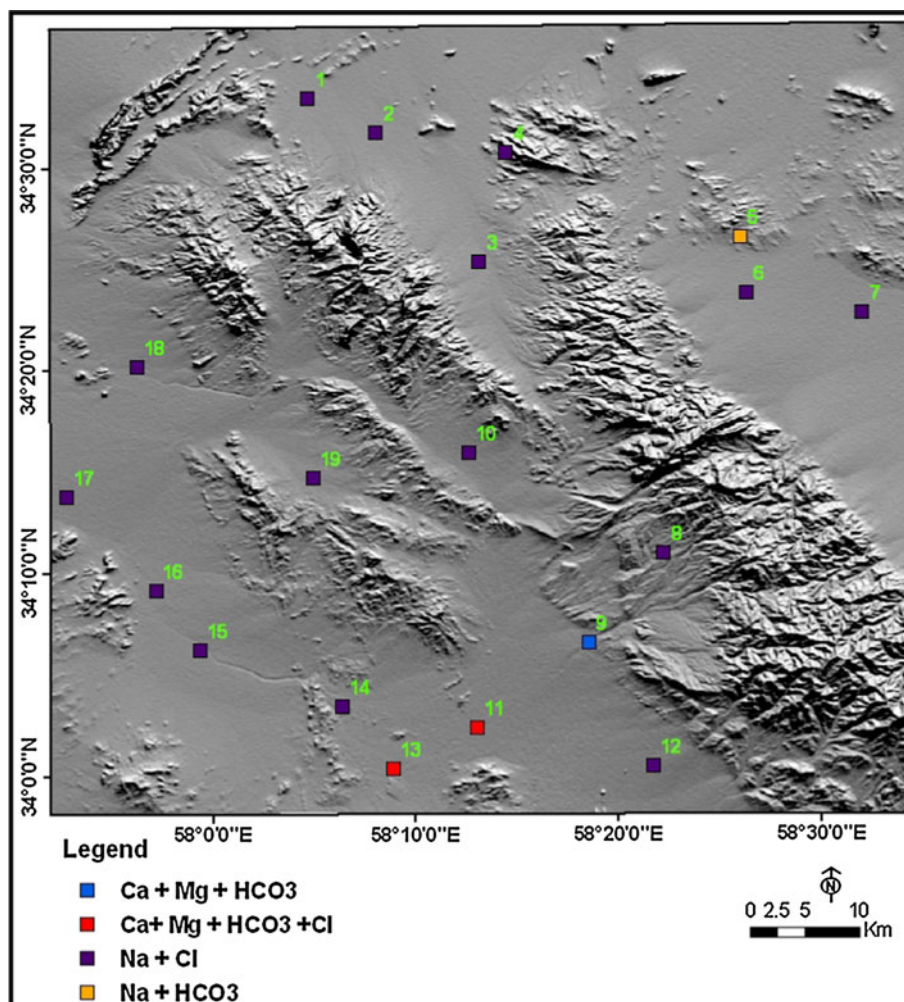
anions, four water types were found among the water samples (Fig. 4):

Na + HCO₃, Na + Cl, Ca + Mg + HCO₃ + Cl, and Ca + Mg + HCO₃ represent 5, 79, 11, and 5 % of the total number of water samples, respectively (Fig. 5).

Distribution of metal and other solutes

Concentration of metals in groundwater, including As, Cu, Se, Fe, and Mn are presented in Table 2. Most metal concentrations in water depend on the mineral solubility, and pH, Eh, and salinity of the solution (Caron et al. 2008). Concentration of Cu in groundwater is observed between 2.4 and 20.3 µg/l in the study area. Bioavailability of Cu in the water influenced by size of the initial Cu amendment,

Fig. 5 Distribution of water types in the groundwater of the study area



time-dependent changes in speciation, and soil humidity and the retention of Cu are enhanced under stable humid conditions (Halim et al. 2009). The contents of As, Fe, and Mn are 0.38–26, 7.5–100, and 1.87–7.26 $\mu\text{g/l}$, respectively. Concentrations of Fe and Mn in the studied groundwater samples show a distinct relationship to the concentration of As (Table 2). The groundwaters with high dissolved Fe relative to Mn have elevated levels of As and suggest that As is released into groundwater due to reductive dissolution of Fe-oxyhydroxide. The Mo, Se, V, and Pb concentrations range from 0.9 to 19.8, 1.1 to 24.6, 6 to 84.2, and 0.08 to 4.3 $\mu\text{g/l}$, respectively. The content of these metals is dependent on oxidation–reduction condition of groundwater. There are high positive correlations between V and Se ($R = 0.82$), Co ($R = 0.78$), between Ni and Co ($R = 0.67$), Cu ($R = 0.70$), between Se and Co ($R = 0.68$), between Cu and Co ($R = 0.72$), between Mo and As ($R = 0.69$), and positive correlations between Fe and As, Fe and Co, V and Cu, Ni and Se, Ni and V (Table 3). These robust correlations indicate strong geochemical and hydrogeochemical relationships between

these metals. Contrary to many investigations which confirm negative correlation between arsenic and sulfate (e.g. Hasan et al. 2007; Halim et al. 2009), a positive correlation exists between arsenic and this anion in the study area that is due to mixing of ground waters from different sources. The low concentrations of SO_4^{2-} in groundwater samples and negative correlation between SO_4^{2-} and Cd ($R = -0.26$) and Pb ($R = -0.07$) indicate that Pb and Cd have not been directly mobilized from sulfide minerals. The negative correlation coefficient indicates that the dissolved Cu, Co, Fe, Mn, Ni, Se, V, and Pb concentration is likely not controlled by the amount of uncomplexed carbonate ions in the groundwater.

REE concentrations

The concentrations of individual REE and ΣREE in the studied groundwaters are presented in Table 4.

Rare earth element concentrations in the study area are low. The correlations of ΣREE with TDS and pH are also

Table 3 Main anion-cations and metal correlation

Parameter	pH	Eh	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	As	Cd	Co	Cu	Mo	Fe	Mn	Ni	Se	V	Pb
pH	1																				
Eh	-1.00	1																			
Ca ²⁺	-0.61	0.61	1																		
Na ⁺	-0.27	0.26	0.81	1																	
K ⁺	-0.53	0.53	0.79	0.83	1																
Mg ²⁺	-0.73	0.73	0.86	0.69	0.87	1															
Cl ⁻	-0.46	0.46	0.89	0.96	0.87	0.79	1														
NO ₃ ⁻	-0.22	0.23	0.63	0.56	0.54	0.44	0.59	1													
SO ₄ ²⁻	-0.19	0.19	0.51	0.66	0.67	0.46	0.63	0.42	1												
HCO ₃ ⁻	0.58	-0.57	-0.60	-0.35	-0.32	-0.39	-0.45	-0.39	-0.34	1											
As	0.36	-0.37	0.02	0.21	-0.06	-0.31	0.21	0.14	0.14	0.07	1										
Cd	0.09	-0.09	0.04	0.12	0.01	-0.01	0.11	0.05	-0.26	0.05	0.14	1									
Co	-0.38	0.38	0.73	0.77	0.78	0.60	0.78	0.63	0.55	-0.36	0.28	-0.11	1								
Cu	-0.51	0.51	0.71	0.47	0.51	0.62	0.57	0.33	0.23	-0.29	0.19	-0.26	0.72	1							
Mo	0.66	-0.67	-0.04	0.38	0.00	-0.31	0.22	0.10	0.34	0.27	0.69	0.05	0.21	-0.08	1						
Fe	0.08	-0.10	0.09	0.25	0.16	-0.10	0.20	0.20	0.47	-0.28	0.56	-0.31	0.54	0.34	0.37	1					
Mn	-0.25	0.24	0.15	0.16	0.24	0.12	0.21	0.24	0.31	-0.10	0.27	-0.27	0.44	0.36	0.16	0.44	1				
Ni	-0.44	0.44	0.77	0.67	0.60	0.65	0.71	0.54	0.41	-0.33	0.07	0.14	0.67	0.70	0.01	0.22	0.00	1			
Se	-0.13	0.13	0.64	0.89	0.78	0.66	0.82	0.53	0.60	-0.06	0.10	0.04	0.68	0.39	0.34	0.11	0.04	0.58	1		
V	-0.38	0.38	0.77	0.85	0.87	0.77	0.88	0.64	0.56	-0.20	0.18	0.01	0.78	0.56	0.22	0.14	0.38	0.55	0.82	1	
Pb	-0.34	0.34	0.09	-0.25	-0.12	-0.02	-0.12	0.11	-0.07	-0.68	0.45	-0.18	0.05	0.21	0.49	0.37	0.08	0.04	0.52	0.55	1

Table 4 Concentrations of REEs in groundwater from the Ferdows district (unit: $\mu\text{g/L}$)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	Ce/Ce*	Eu/Eu*	(La/Yb) N	(Pr/Yb) N
1	0.030	0.060	0.010	0.030	0.010	0.020	0.110	0.008	0.001	0.008	0.010	0.008	0.075	0.010	0.388	0.807	1.478	0.039	0.052
2	0.050	0.090	0.020	0.110	0.020	0.010	0.040	0.010	0.020	0.008	0.010	0.010	0.075	0.008	0.480	0.652	1.504	0.066	0.103
3	0.040	0.050	0.010	0.008	0.020	0.008	0.040	0.008	0.001	0.010	0.020	0.008	0.075	0.008	0.303	0.587	1.128	0.052	0.052
4	0.060	0.110	0.020	0.130	0.010	0.008	0.008	0.010	0.001	0.008	0.010	0.008	0.020	0.008	0.408	0.739	3.934	0.295	0.387
5	0.030	0.050	0.020	0.040	0.008	0.008	0.020	0.008	0.001	0.008	0.008	0.008	0.010	0.008	0.223	0.429	2.450	0.295	0.775
6	0.040	0.050	0.008	0.040	0.020	0.010	0.020	0.008	0.001	0.008	0.010	0.008	0.075	0.008	0.303	0.671	2.283	0.052	0.039
7	0.040	0.050	0.010	0.060	0.050	0.010	0.060	0.008	0.001	0.008	0.020	0.008	0.075	0.008	0.406	0.587	0.827	0.052	0.052
8	0.040	0.030	0.010	0.010	0.040	0.010	0.080	0.008	0.001	0.008	0.008	0.008	0.075	0.008	0.333	0.352	0.752	0.052	0.052
9	0.010	0.040	0.008	0.040	0.010	0.010	0.080	0.008	0.001	0.008	0.008	0.008	0.075	0.008	0.311	0.944	0.987	0.013	0.039
10	0.020	0.040	0.010	0.020	0.008	0.010	0.070	0.010	0.020	0.008	0.010	0.008	0.075	0.008	0.315	0.628	1.145	0.026	0.052
11	0.040	0.050	0.010	0.030	0.008	0.010	0.090	0.008	0.010	0.008	0.020	0.008	0.010	0.008	0.308	0.587	0.909	0.394	0.387
12	0.008	0.001	0.008	0.020	0.010	0.010	0.030	0.008	0.001	0.008	0.030	0.008	0.020	0.008	0.167	0.019	2.243	0.037	0.145
13	0.060	0.080	0.010	0.140	0.030	0.010	0.030	0.010	0.010	0.008	0.020	0.008	0.075	0.010	0.500	0.751	1.522	0.079	0.052
14	0.040	0.040	0.010	0.070	0.020	0.010	0.008	0.008	0.010	0.008	0.008	0.008	0.010	0.008	0.255	0.470	3.376	0.394	0.387
15	0.040	0.090	0.010	0.070	0.010	0.008	0.030	0.008	0.020	0.008	0.010	0.008	0.075	0.008	0.393	1.057	1.682	0.052	0.052
16	0.060	0.110	0.020	0.070	0.020	0.010	0.080	0.008	0.010	0.008	0.020	0.008	0.010	0.008	0.440	0.739	0.894	0.590	0.775
17	0.090	0.120	0.030	0.100	0.040	0.020	0.050	0.008	0.020	0.008	0.008	0.008	0.020	0.008	0.528	0.538	2.021	0.443	0.581
18	0.008	0.001	0.008	0.008	0.010	0.010	0.030	0.008	0.001	0.008	0.010	0.008	0.075	0.008	0.189	0.019	2.243	0.010	0.039
19	0.030	0.040	0.010	0.050	0.010	0.008	0.010	0.008	0.020	0.008	0.010	0.008	0.075	0.008	0.293	0.538	3.425	0.039	0.052

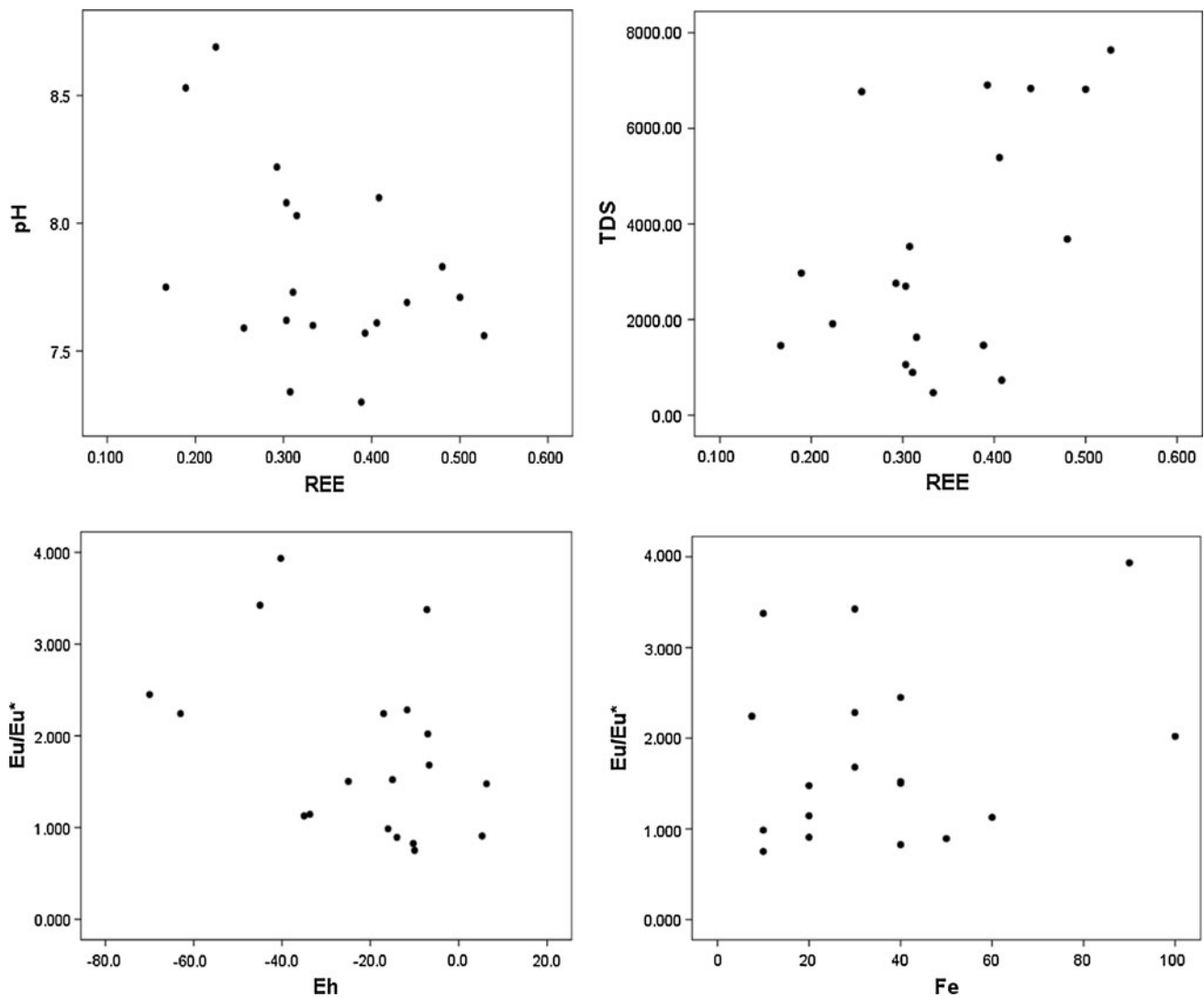
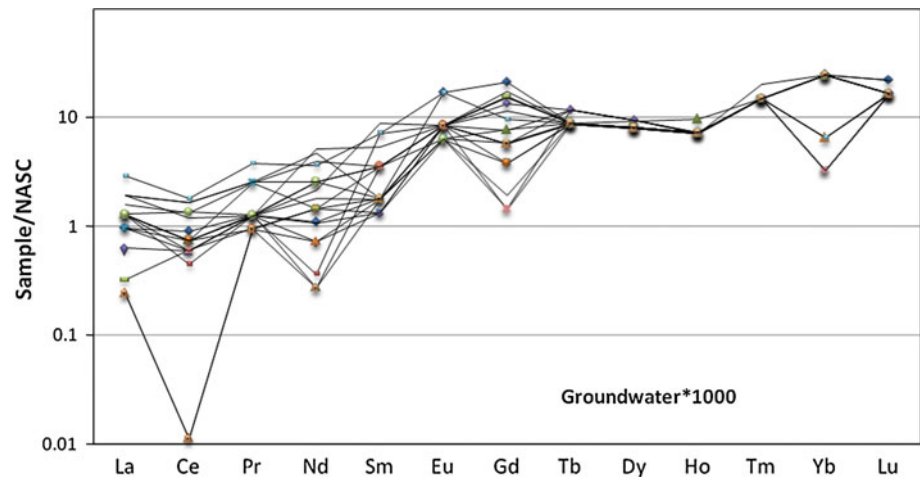


Fig. 6 Relationships between pH and REE, TDS and REE, Eu/Eu* and Eh, Eu/Eu* and Fe in study area

presented in Fig. 6. The Σ REE concentrations in groundwater exhibit a positive correlation with the TDS contents ($R = 0.55$) indicating that Σ REE concentrations are related to the salinity (TDS) of the water samples. Many studies have shown that pH can play an important role in the mobility of REEs and that higher REE concentrations are typically associated with lower pH values (Keasler and Loveland 1982; Guo et al. 2010). The pH affects carbonate complexations of the REEs, with higher pH leading to the predominance of REE decarbonate complexes. On the other hand, pH control REE read sorption onto oxide surfaces. However, our plot of REE concentrations versus pH (Fig. 6) shows no correlation between pH and Σ REE concentrations. The Ce anomaly is mostly negative with the Ce/Ce* values ranging from 0.019 to 1.057. The possible explanation for slightly negative Ce anomalies would be that more Ce has been

fixed as CeO_2 than that adsorbed on Fe oxy-hydroxides in an oxic environment. When conditions become more reducing (the actual situation), reduction of Fe oxy-hydroxides first releases the adsorbed Ce, while reduction of CeO_2 is slower and only gradually mobilizes Ce into the waters. In contrast, the Eu anomaly is more variable than the Ce anomaly and was predominantly positive with the Eu/Eu* values narrowly ranging between 0.752 and 3.934. In the results from this study, Eu/Eu* ratios have a negative correlation with Eh values (Fig. 6). The ratios are systematically higher in the lower Eh (reducing) groundwaters than in the higher Eh (oxidizing-mildly reducing) groundwaters suggesting that reducing conditions are the dominant factors contributing to the positive Eu anomalies. Europium is the only lanthanide that, under reducing conditions, can be divalent, and is thus segregated from other REEs under such conditions (Lee et al. 2003). The

Fig. 7 NASC-normalized REE patterns for groundwaters from the study area



poor correlation between dissolved Fe and Eu/Eu^* suggests that the reductive dissolution of Fe oxy-hydroxides should not be the only source for the Eu anomalies (Fig. 6). The preferential desorption of Eu(II) should also play an important role (Guo et al. 2010).

Normalized patterns with respect to the estimated average composition of the North American Shale Composite (NASC) are displayed on Fig. 7 for groundwaters from the study area. The groundwaters exhibit enrichment in the HREEs relative to the LREEs (Fig. 7). This can be explained by the differences in geochemical mobility between LREEs and HREEs during water–rock interaction at depth.

Conclusions

The hydrogeochemical characteristics of groundwater are evaluated in Ferdows area, northeastern Iran. Groundwater is mostly Na–Cl type for the study area with Cl^- as the dominant anion, although other types of water were observed. The results show that groundwater in the region with volcanic rocks are in chemical reaction and ion exchange and major cations Ca^{2+} , Mg^{2+} and Na^+ may release through the dissolution of carbonates, cation-exchange, and weathering of silicates. Concentration of the main metals, such as As, Cu, Fe, Mn, and Se, in groundwater, is low and is released into groundwaters from different sources. The TDS has an important role in the mobility of REEs in the study area. The REE concentrations and shale-normalized patterns show highly positive Eu anomalies and slightly negative Ce anomalies. There are differences in geochemical mobility between LREEs and HREEs during water–rock interaction at depth; therefore, groundwaters exhibit enrichment in the HREEs relative to the LREEs. The major contribution to positive Eu anomalies in groundwaters is expected to be preferential mobilization of Eu^{2+} relative to the trivalent REEs.

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