

## Multivariate statistical analyzing of chemical parameters of thermal and non-thermal springs of Mahalat area in Iran

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### Abstract

In this study multivariate statistical analysis are used to characterize relationships between hydrochemical properties of thermal and non-thermal springs. Four factors for thermal waters and two for non-thermal springs were extracted based on factor analysis. In thermal springs, the first factor showed high loading on Ca, Mg, Na and K and this factor was interpreted as leaching of cations in the rocks by meteoric thermal water. The second factor showed high loading on SO<sub>4</sub> and it was assumed to be extracted from gypsum dissolution. The third factor showed loading on HCO<sub>3</sub> and it was interpreted to be caused by dissolution of limestone. The fourth factor showed high loading on SiO<sub>2</sub> and it was supposed to be result of alteration of silicate minerals. The δ<sup>18</sup>O-enrichment with respect to the meteoric water line (MWL), confirms that thermal waters have been diluted by shallow waters with meteoric origin. Comparison of the chemistry of thermal and non-thermal springs and other evidences are indicative of an immature hydrothermal water system in Mahalat. Quartz and Chalcedony geothermometry show the range of 96°C to 131 °C temperature for the Mahalat reservoir.

**Keywords:** Hydrochemical data, multivariate analysis, non-thermal springs, thermal springs, Iran.

### Introduction

In recent decades, many countries have conducted research into geothermal resource exploitation. In Iran, with increasing demand for clean energy, the feasibility of using geothermal fields of low-to-medium temperature is being investigated. A large amount of the researches have been about the study of the origins of geothermal water and hydrogeochemical processes which were occurred in these waters. Hydrochemical indicators, such as major ions ratios, can be used to study recharge origin and mixing behavior of thermal waters (Karimi & Moor, 2008). Establishing a regional hydrogeological conceptual model can help to determine flow path including recharge-through flow-discharge processes, as well as mixing behavior (Karakus & Simsek, 2013; Han *et al.*, 2010).

Mahalat area is situated in the central part of volcanic zone in Iran and has abundant resources of thermal and non-thermal springs (Araghi, 2009). Tourism culture in Mahalat has been developed over two hundred years and many villas and hotels equipped with facilities of thermal water. Springs can be classified into different water types based on compositions of their major ions (Samsudin *et al.*, 1997; Minissale *et al.*, 1997; Mariner *et al.*, 2003). Major ions in spring water include HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> which mainly

originates from dissolution and mineralization of rocks (Minissale *et al.*, 1997; Davison *et al.*, 1994). Water quality of springs is highly associated with their geological conditions (Sanada *et al.*, 2006; Tarits *et al.*, 2006; Chandrajith *et al.*, 2013). Furthermore, temperature and pH of the springs exhibit variability in hydrochemical parameters. For instance, bicarbonate ions originate from the dissolution of carbonate-rich rocks and are controlled by pH. Bicarbonate ions present within the range of 4 to 10 of pH (Chan *et al.*, 2009; Zhu & Yu, 1995). High temperature in springs causes to increase dissolution of certain ions, such as K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> and SiO<sub>2</sub> (Davison *et al.*, 1994).

The multivariate analysis is a group of statistical techniques, which enables us to calculate multivariable, and allows us to consider co-variances in several properties simultaneously (Davis, 1986). However, recently, multivariate analysis has been improved for application in geochemical and hydrochemical fields (Anazawa & Yoshida, 1997; Laaksoharjo *et al.*, 1998). Factor analysis is a multivariate analysis and is a commonly tool which used to partition numerous hydrochemical parameters into few main properties called factor (Liu *et al.*, 2003).

In this work, the hydrochemical chemistry of thermal and non-thermal springs in Mahalat area was determined. The results of hydrochemical

composition were subjected to the multivariate statistical techniques and described the geochemical factors affecting over the composition of springs in Mahalat.

**Materials and methods**

*Geology of the study area*

The study area is situated in the central part of Iran in Markazi province near the Mahalat city (Fig. 1). According to the tectonic zone of Iran, the study area is located in the volcanic zone.

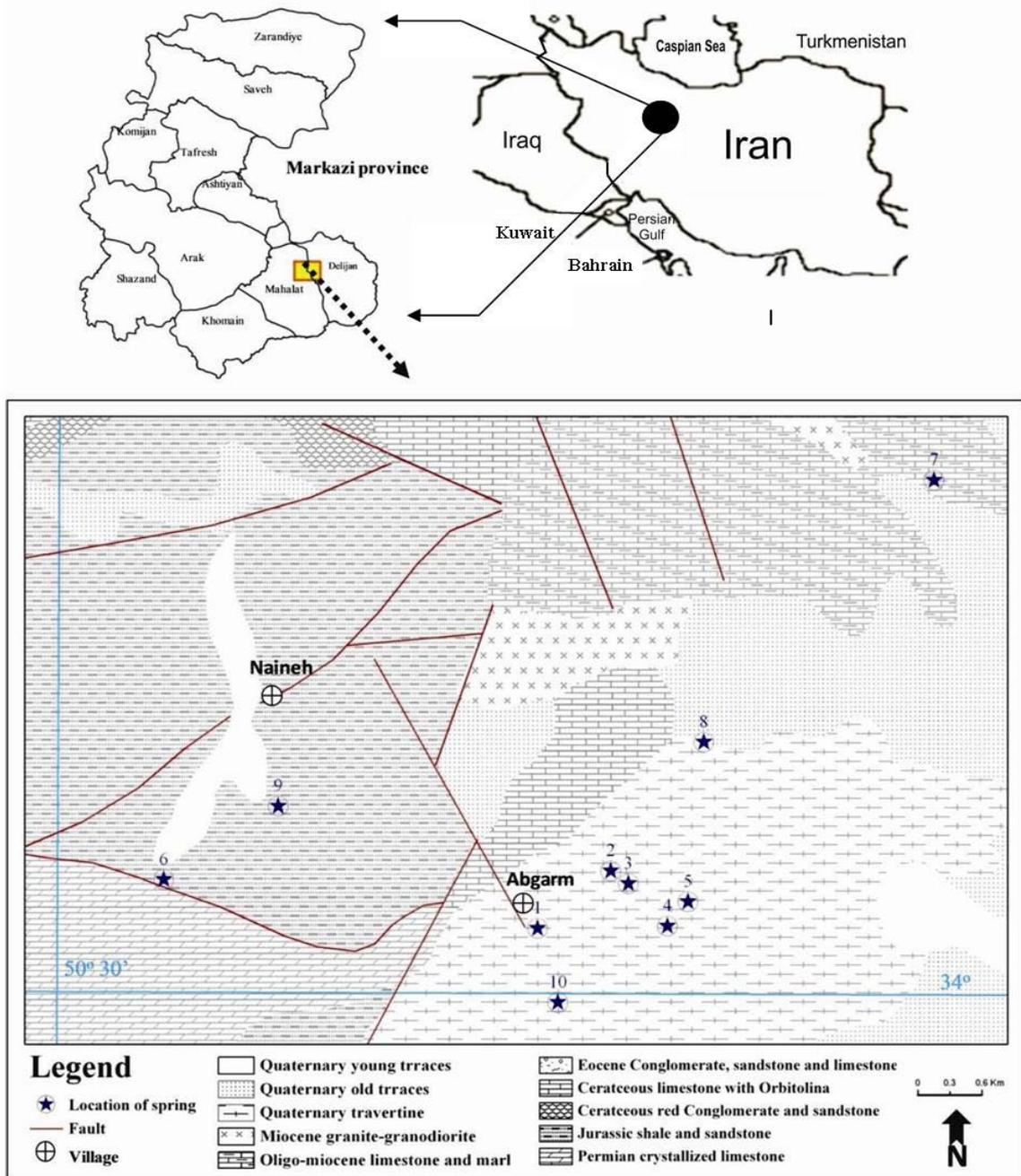


Figure 1: Geological map of Mahalat Abgarm, showing formation and sample points.

Formation of the basin is related to Paleozoic, Mesozoic and Cenozoic eras. Dolomite and limestone with Permian age can be observed abundant in the study area. The geomorphology of the region is consisted of mountain-hill land. The

sediments of Eocene in the region are consisting of marl, sandstone, shale and conglomerate units (Araghi, 2009). Mahalat region can be considered as anticline folding with north-east to south-west direction. It was determined that the performance of

tectonic activities in the past geological eras have formed some fault in the formation of the region and adjacent area. The most important fault of the region is Mahalat fault that has approximately west-east direction. The length of the fault is about 30 kilometers and the age of formation on the two sides of the fault is very different (Araghi, 2009).

Climate of the study area is semiarid. The local measured 30-year average annual precipitation is 350 mm, and the mean temperature is 16°C. The potential annual evapo-transpiration value is about 2020 mm (Ghadimi, 2006).

### Sampling and analytical methods

Fifty thermal and thirty non-thermal samples of springs were collected in four periods i.e., 1995, 2009 (Ghorbani, 2009), June 2010 and September 2010 (Water Organization, 2010). The discharge rates of these springs vary from 0.5 to 5 l/s and their fluid temperatures range between 18.2°C and

47.3°C. Hydrochemical parameters of the water such as temperature, pH and electrical conductivity (EC), were measured in the field, while calcium, potassium, magnesium, sodium, bicarbonate, sulfate and chloride ions were measured in the laboratory. The results of the hydrochemical measured data are presented in Table 1. All elements were above the detection limit. The water samples were analyzed in Water Organization of Markazi Province, Iran. Stable isotopes of water ( $d_{18}O$  and  $d_2H$ ) were determined by isotope ratio mass spectrometry using Finnigan MAT 253 after online pyrolysis with a Thermo Finnigan High Temperature Conversion Elemental Analyzer (TC/EA) and reported relative to the VSMOW standard (Vienna Standard Mean Ocean Water) in per mille (‰). Stable isotopes ( $d_{18}O$  and  $d_2H$ ) of the sampled water were analyzed at the Cornell University laboratory of Australia.

Table1: Chemical data average for thermal and non-thermal springs studied at Mahalat

NO.	Name	Dis.	Tem	pH	EC	TDS	Na	K	Ca	Mg	SO <sub>4</sub>	Cl	HCO <sub>3</sub>	SiO <sub>2</sub>	δ <sup>18</sup> O	δ <sup>2</sup> H
		Lit/Min	°C		µs/cm	mg/l										‰
1	Shafa	2400	47.3	6.7	1783	1137	131	46	257	447	735	502	222	40	-9.40	-66.5
2	Dombeh	360	46	6.7	1782	1142	131	42	253	486	904	504	198	41	-9.47	-68.4
3	Solimani	300	46	6.8	1781	1131	130	55	263	484	889	50	207	42	-9.29	-66.6
4	Soda	800	45.1	6.8	1786	1140	126	35	262	497	969	495	209	35	-9.25	-63.9
5	Abgarm	100	35.8	7.1	1782	1146	125	47	252	53	889	494	203	37	-9.11	-64.3
6	Naineh	150	19.9	8.2	652	362	47	22	112	213	170	554	171	40	-9.42	-64.4
7	Ziaratghah	8	18.4	8	332	572	10	27	64	151	47	214	140	13.1	-8.97	-56.8
8	Siagohar	6	18.2	7.3	1612	912	133	35	271	429	905	677	187	32.4	-8.80	-63.3
9	Talkkeh	0.2	25	8.1	2470	1434	184	43	350	96	1634	76	138	22.2	-7.20	-54.4
10	Biname	100	19.8	8.1	2170	1259	166	40	318	78	1318	635	215	37	-8.52	-61.3

## Results and discussion

### Chemistry of springs

Hydrochemical data of springs were mapped on piper diagram (Fig. 2). The central diamond-shaped figure displays that most springs water have high SO<sub>4</sub> and are related to gypsum dissolution. Saturation index for gypsum and anhydrite is under saturation in thermal and non-thermal springs and can explain high SO<sub>4</sub><sup>2-</sup> in springs (Table 2). All of the thermal and non-thermal springs fall into SO<sub>4</sub>-Ca regions but one spring of non-thermal springs with relatively high bicarbonate is distant from the above group. Table 3 indicated statistics regarding hydrochemical parameters in thermal and non-

thermal springs. For thermal springs, temperature and pH of discharging water range from 35.8 to 47.3 °C and from 6.7 to 7.1, respectively. The spring water is rich in SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> ions and contains the small amount Cl<sup>-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> ions except spring 7 that is rich in HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> ions.

All of the thermal springs are rich in SO<sub>4</sub><sup>2-</sup> and emerged springs from limestone rocks have abundant Ca<sup>2+</sup> ions. Spring 7 is non-thermal and far from thermal springs, therefore, has abundant HCO<sub>3</sub><sup>-</sup>. Hosted rocks of all springs are limestone and have abundant Ca<sup>2+</sup> ions.

Thermal springs have Ca<sup>2+</sup> > (Na<sup>+</sup>+K<sup>+</sup>) > Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> and have high SiO<sub>2</sub>

concentrations. SiO<sub>2</sub> contents of thermal springs range from 35 to 42 mg/l. The average of EC values for thermal springs are 1783 μs/cm. Non-thermal springs have Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and SiO<sub>2</sub>

less than thermal springs (except Mg<sup>2+</sup> and Cl<sup>-</sup>). EC values for these springs are 908 μs/cm and SiO<sub>2</sub> values change from 13.10 to 40 mg/l.

Table2: Calculated saturation index (SI) for thermal and non-thermal spring waters studied at Mahalat

	Shafa	Dombeh	Solimani	Soda	Abgarm	Naineh	Ziaratgah	Siagohar	Talkheh	Biname
Anhydrite	-0.71	-0.71	-0.71	-0.72	-0.75	-0.69	-0.92	-0.58	-1.74	-0.55
Aragonite	-0.12	-0.17	-0.13	-0.06	-0.14	0.45	0.10	0.39	0.61	0.35
Calcite	0.01	0.04	0.01	0.07	0.01	0.60	0.24	0.54	0.75	0.50
Dolomite	-0.20	-0.33	-0.31	-0.34	-0.25	0.79	0.18	0.63	1.49	0.68
Gypsum	-0.62	-0.62	-0.60	-0.62	-0.62	-0.46	-0.69	-0.34	-1.51	-0.36
Halite	-6.88	-6.85	-6.82	-6.87	-6.88	-6.73	-6.40	-6.53	-6.81	-6.23

Table 3: Statistics associated with hydrochemical parameters of thermal and non-thermal springs.

Statistical parameters		Tem.	pH	EC	TDS	Na	K	Ca	Mg	SO <sub>4</sub>	Cl	HCO <sub>3</sub>	SiO <sub>2</sub>
		°C		μs/cm		mg/l							
Thermal springs	Average	43.84	6.82	1783	1139	129	4.50	257	49	877	49.9	208	39
	Maximum	47.30	7.10	1786	1146	131	5.50	263	53	969	50.4	222	42
	Minimum	35.80	6.70	1781	1131	125	3.50	252	45	735	49.4	198	35
Non-thermal spring	Average	20.26	7.94	1367	908	108	3.40	223	51	815	56.8	170	29
	Maximum	25	8.20	2470	1434	184	4.29	350	96	1634	76	215	40
	Minimum	18.20	7.10	332	362	101	2.20	64	15	47	21.4	138	13

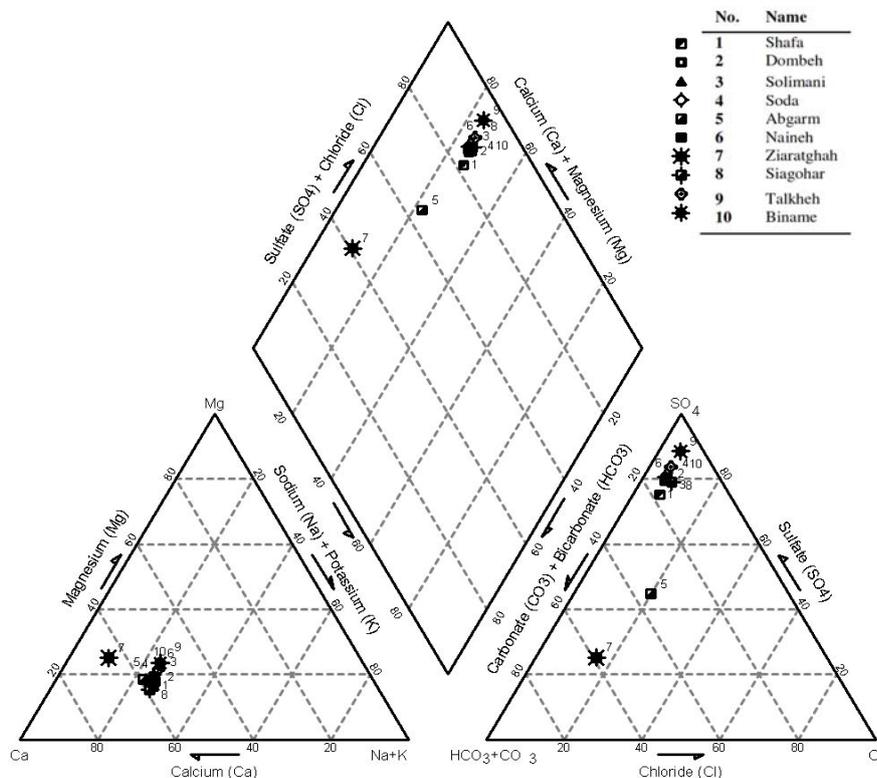


Figure2: Piper diagram of thermal and non-thermal springs in Mahalat

Major ion composition can act as a track-record of water-rock interaction during flow (Moller *et al.*, 2007). Thermal spring samples are  $\text{SO}_4\text{-Ca}$  type (Fig. 2). TDS, EC,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{SiO}_2$  concentration with mean TDS 1139 mg/l are higher than in non-thermal springs.  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  concentrations are lower in the thermal springs than non-thermal water. Higher TDS concentrations in thermal springs probably reflect longer circulation and residence times. In the thermal spring, water flows through limestone aquifers. This is likely responsible for the higher  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in this water. Non-thermal springs mainly contain  $\text{SO}_4\text{-Ca}$  and  $\text{HCO}_3\text{-Ca}$  with TDS mean of 908 mg/l, which

are close to the thermal region. This may reflect mixing with thermal springs (Han *et al.*, 2010).

The Na-K-Mg content diagram of Giggenbach (1988) can be used to determine the maturity of water samples as well as to obtain Na/K and Mg/K geothermometer. The samples were plotted near the Mg corner below the partial-equilibrium line in the field of immature waters. The high relative concentration of Mg in these springs suggests that they are immature waters and are not in equilibrium with the host rock. It indicates water-rock interactions during through flow. Therefore, mixing rock with cold groundwater have not yet reached to ionic equilibrium (Han *et al.*, 2010).

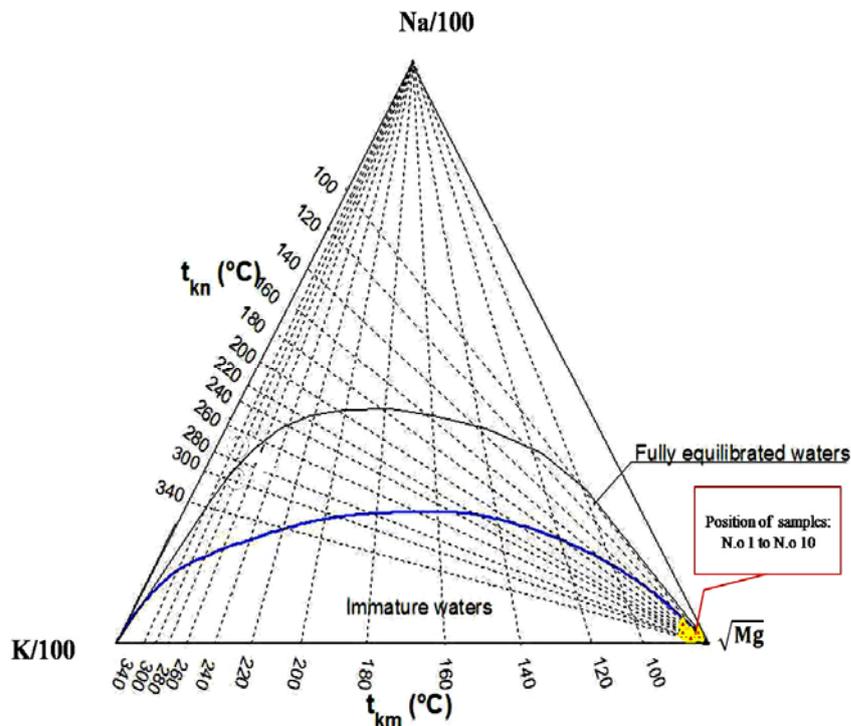


Figure 3: The triangular of Na-K-Mg diagram for all of the springs

## Multivariate statistical analysis

### Thermal springs

Table 4 is a report of the correlation coefficients among the hydrochemical parameters of the thermal springs. The parameters that are highly related to each other including: Temperature with pH; EC with TDS and  $\text{Mg}^{2+}$ ; pH with  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ;  $\text{Ca}^{2+}$  with  $\text{Na}^+$  and  $\text{K}^+$ ; ( $r > 0.6$ ) and correlation EC with pH,  $\text{Na}^+$  and  $\text{K}^+$ ; TDS with  $\text{K}^+$ ; pH with  $\text{Ca}^{2+}$ ;  $\text{Ca}^{2+}$  with  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ ;  $\text{Na}^+$  with  $\text{Cl}^-$  is moderate.

Factor analysis is a multivariate statistical analysis that calculates the common relationships between measured hydrochemical variables and

help to classify the original data. Factor analyses can effectively reduce numerous hydrochemical data into few major factors with eigenvalue exceed one (Davis, 1986; Love *et al.*, 2004). The geochemical interpretation of factors gives insight into the main processes that may govern the distribution of hydrochemical variables. The first step was to standardize the raw data on hydrochemical parameters and then, the data was transformed into factors. The contribution of each factor was

computed at each site. The distribution of factor scores and the residual variable were expressed in

units of standard deviation. In this study, varimax scheme was employed (Sharma, 1996).

Table 4: Correlation matrix of hydrochemical parameters of thermal springs. (\* Marked correlations are significant  $P < 0.05$ )

Parameters	Tem	EC	TDS	pH	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	SiO <sub>2</sub>
Tem	1											
EC	0.37	1										
TDS	0.35	0.99*	1									
pH	-0.75*	-0.59	-0.56	1								
Ca <sup>2+</sup>	0.13	0.08	0.01	-0.50	1							
Mg <sup>2+</sup>	-0.42	-0.74*	-0.71*	0.64*	-0.52	1						
Na <sup>+</sup>	-0.22	-0.54	-0.48	0.67*	-0.84*	0.73*	1					
K <sup>+</sup>	0.30	0.59	0.52	0.66*	0.67*	-0.69*	-0.85*	1				
HCO <sub>3</sub> <sup>-</sup>	0.13	-0.18	-0.18	-0.08	0.13	-0.03	0.03	-0.07	1			
Cl <sup>-</sup>	0.24	0.03	0.03	0.09	-0.58	0.26	0.50	-0.21	-0.13	1		
SO <sub>4</sub> <sup>2-</sup>	-0.26	-0.41	-0.43	0.01	0.39	0.34	-0.24	0.14	-0.23	-0.32	1	
SiO <sub>2</sub>	0.30	0.12	0.03	-0.12	-0.01	-0.10	0.04	0.10	-0.01	-0.03	-0.12	1

Eigenvalue, percentage of variance and cumulative percentage of variance were listed in table 5. The eigenvalue of the four factors explains 83.49 % of the total variance. The absolute values of factor loading over 0.7 were considered as strong correlation in table 5 and elucidate the relationships between the factors and the hydrochemical data.

Factor 1, which explains 38.65 % of the total variance, has positive loadings on K<sup>+</sup> and Ca<sup>2+</sup> and

negative loading on Na<sup>+</sup> and Mg<sup>2+</sup> and values of factor loading are high than >0.7 and the loading values on EC and Cl<sup>-</sup> are also significant. Factor 2 shows high negative loading values on SO<sub>4</sub><sup>2-</sup>, with the variance of 21.80%. Factor 3 explains 12.38 % of the total variance with spring negative loading of HCO<sub>3</sub><sup>-</sup> and factor 4 includes high positive loading on SiO<sub>2</sub> with variance of 10.65 %.

Table 5: Factor loading of hydrochemical data in thermal springs

Hydrochemical parameters	Factor1	Factor2	Factor3	Factor4
Temperature	0.29	0.47	-0.08	0.59
EC	0.61	0.67	0.26	-0.06
Ca	0.82*	-0.41	-0.20	0.03
Mg	-0.83*	-0.44	0.07	-0.05
Na	-0.98*	0.10	-0.03	0.05
K	0.89*	0.06	0.16	0.11
HCO <sub>3</sub>	-0.01	0.07	-0.95*	0.02
Cl	-0.5	0.54	0.31	0.11
SO <sub>4</sub>	0.13	-0.86*	0.27	-0.03
SiO <sub>2</sub>	0.01	-0.01	-0.01	0.92*
Eigenvalues	3.86	2.18	1.24	1.10
Percentage of variance	38.65	21.8	12.38	10.65
Cumulative percentage of variance	38.65	60.45	72.83	83.49

Factor 1 explains strong loading of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>. The cations of these solutes can be derived from rock dissolution by chemical weathering. The mineralogical compositions of rocks in this area were determined based on previous studies (Hatafi, et al., 2009). The results showed that calcite, quartz, goethite, gypsum, plagioclase, orthoclase, biotite,

illite, muscovite and clay minerals (such as montmorillonite and vermiculite) are constituents of rocks in the study area. This composition suggests that the leaching of Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> should be significant in the initial stage of water interaction process (Goldish, 1938). Experimental works demonstrate that dissolution of calcite, plagioclase

and orthoclase affects the initial water composition (Tamari *et al.*, 1988). Therefore, the first factor shows the chemical interaction between meteoric water and host rocks.

The second factor (F2) showed high loading on  $\text{SO}_4^{2-}$  with the percentage of variance 21.80%. Samples from this factor, present very high sulfate contents and suggested that water composition is controlled by dissolution process. Because of the pH ranges in the thermal springs (6.7-7.1), it is possible, gypsum dissolution related to high  $\text{SO}_4^{2-}$  (Table 2). Based on Giggenback (1997) and Hem (1989) sulfur springs usually present lower pH values and have volcanic origin. Therefore, as a factor, the study area has not influenced by volcanic activities.

The third factor (F3) showed high loading on  $\text{HCO}_3^-$  with the percentage of variance 12.38%. The high  $\text{HCO}_3^-$  of the water from thermal waters after  $\text{SO}_4^{2-}$  is typical of meteoric waters and is due to the dissolution of limestone (Giggenback, 1997). The high  $\text{HCO}_3^-$  value was produced from the dissolution of limestone in a deeper aquifer (Baitollahi, 1995) and interacting with shallow meteoric waters. Meteoric origin is clearly shown by the fact that the samples lie close to the GMWL on the  $\delta^{18}\text{O}$ -D plot (Fig. 4). The stable isotope analysis of five Mahalat thermal springs and five non-thermal springs are given in Table 1. The waters are plotted on the isotopically heavier part of SMOW line. This is because of the fractionation due to evaporation resulted from high temperature and the aridity of the region. For thermal springs, the average  $\delta\text{O}^{18}$  is  $-9.3\text{‰}$  and  $\delta\text{D}$   $-65.7\text{‰}$ . The

average values for  $\delta\text{O}^{18}$  and  $\delta\text{D}$  in the five non-thermal springs are  $-8.6\text{‰}$  and  $-60\text{‰}$ . For comparison, the meteoric water line (MWL) is also plotted based on analysis of worldwide precipitations. The parallel lines to meteoric water show the percentage of magmatic water in mixture with meteoric water. In the  $\delta\text{D}$  vs.  $\delta^{18}\text{O}$  diagram, the non-thermal and thermal samples plotted on the meteoric water line (Fig. 4). The plot suggests that non-thermal and thermal water samples are from meteoric water source. The main formation of host rock for thermal water is Permian limestone and there is also thick travertine around the thermal springs (Araghi, 2009) that confirms degassing of  $\text{CO}_2$  from the springs (Ghorbani, 2009).

The fourth factor (F4) showed positive loading on  $\text{SiO}_2$  and the percentage of variance was 10.65. Based on the study of Ghorbani (2009) the content of  $\text{SiO}_2$  was high and formed during alteration of silicate minerals such as plagioclase, orthoclase and other minerals in depths.

#### Non-thermal springs

The results of correlation coefficients for non-thermal springs are shown in Table 6. Based on Table 6 the parameters that are highly related to each other including: temperature with EC, TDS,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ ; EC with TDS,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ; TDS with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ;  $\text{Ca}^{2+}$  with  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ;  $\text{Mg}^{2+}$  with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ;  $\text{Na}^+$  with  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ;  $\text{K}^+$  with  $\text{Cl}^-$ ;  $\text{HCO}_3^-$  with  $\text{SiO}_2$  and  $\text{Cl}^-$  with  $\text{SO}_4^{2-}$ .

Table 6: Correlation matrix of hydrochemical parameters of non-thermal springs (\* Marked correlations are significant  $P < 0.05$ ).

Parameters	Tem	EC	TDS	pH	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{HCO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{SiO}_2$
Tem	1											
EC	0.63*	1										
TDS	0.63*	0.95	1									
pH	0.45	-0.07	-0.04	1								
$\text{Ca}^{2+}$	0.56	0.99*	0.93*	-0.18	1							
$\text{Mg}^{2+}$	0.75*	0.97*	0.97*	0.13	0.94*	1						
$\text{Na}^+$	0.56	0.99*	0.93*	-0.15	0.99*	0.94*	1					
$\text{K}^+$	0.51	0.94*	0.99*	-0.10	0.93*	0.93*	0.92*	1				
$\text{HCO}_3^-$	-0.43	0.22	0.05	-0.16	0.27	0.08	0.29	0.17	1			
$\text{Cl}^-$	0.56	0.85*	0.66*	-0.17	0.87*	0.76*	0.88*	0.63*	0.33	1		
$\text{SO}_4^{2-}$	0.67*	0.99*	0.97*	-0.16	0.98*	0.98*	0.98*	0.01	0.15	0.82*	1	
$\text{SiO}_2$	-0.14	0.20	-0.07	-0.01	0.24	0.08	0.27	-0.02	0.84*	0.53	0.13	1

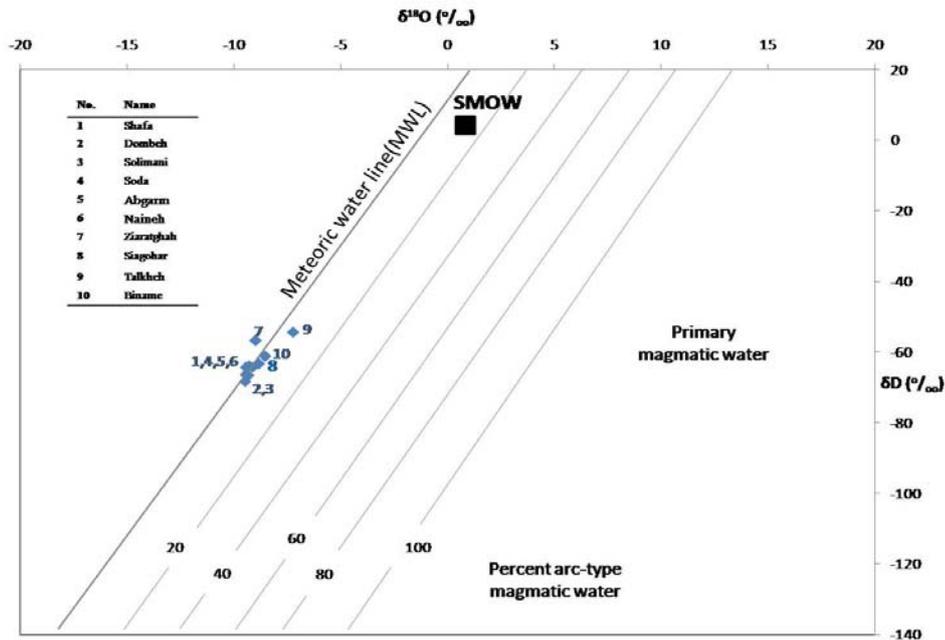


Figure 4:  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  Plot for thermal and non-thermal springs in Mahalat

Table 7 reported the loading of varimax normalized factor matrix for the two factor model. The first factor (F1) shows high loading on EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . The values of factor loading are more than  $>0.7$  and percentage of variance was calculated to be 70.05%. Major solutes in this factor were leached and discharged by dissolution from rocks such as marl, sandstone and conglomerate. The second factor shows high loading on  $\text{HCO}_3^-$

and  $\text{SiO}_2$  with percentage of variance 21.13%.

The second factor (F2) shows high loading on  $\text{HCO}_3^-$  and  $\text{SiO}_2$ . Factor scores of the springs such as Biname and Naineh have positive value over second factor (Table 8). The compositions of these springs are similar to the thermal spring. Meanwhile, there is also travertine rock around the Biname and Naineh springs.

Table 7: Factor loading of hydrochemical data for non-thermal springs

Hydrochemical parameters	Factor1	Factor2
Temperature	-0.66	-0.54
EC	-0.99*	-0.02
Ca	-0.99*	0.06
Mg	-0.92*	-0.13
Na	-0.99*	0.04
K	-0.97*	-0.18
$\text{HCO}_3$	-0.99*	-0.09
Cl	-0.88*	0.25
$\text{SO}_4$	-0.23	0.94*
$\text{SiO}_2$	-0.24	0.90*
Eigenvalues	7.05	2.10
Percentage of variance	70.50	21.13
Cumulative percentage of variance	70.50	91.63

Table 8: Factor scores based on hydrochemical parameters in non-thermal springs

Spring Name	Naineh	Ziaratgah	Siagohar	Talkheh	Biname
Factor 1	0.75	1.23	-0.15	-1.12	-0.74
Factor 2	0.72	-0.94	0.61	-1.23	0.84

**Geothermometry**

This study identified SiO<sub>2</sub> is the best geothermometer for determining of temperature of Mahalat reservoir (Ghorbani, 2009; Karakuş & Şimşek, 2013). Chemical composition of the spring waters is used to estimate the reservoir temperature. For this reason the solubility and exchange reactions of various phases must be taken into account. Application of Na-K and Na-K-Ca

geothermometers yielded inconsistent and unrealistic estimates due to the lack of equilibrium between the water and rocks (Fig. 3). Using the Quartz and Chalcedony geothermometers (Fournier 1981; Arnorsson *et al.*, 1983; Forcella, 1982), a range of reservoir temperatures from 121°C to 131°C and 93°C to 104°C were obtained for thermal springs respectively (Table 9).

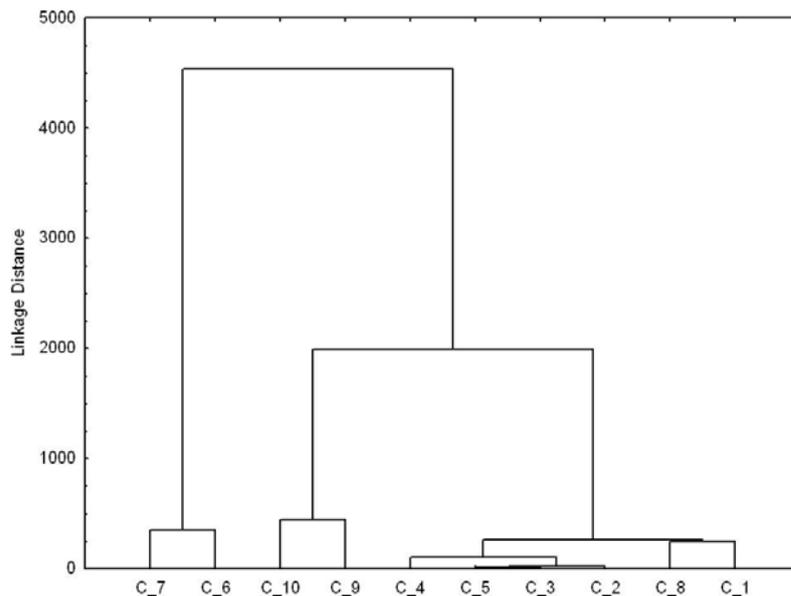
Table9. Estimated reservoir temperature based on different geothermometers

Geothermometer	Estimated temperature(°C)				
	Shafa	Dombeh	Solimani	Soda	Abgarm
Na-K (Arnorsson <i>et al.</i> , 1983)	171	160	169	161	184
Na-K-Ca (Forcella, 1982)	42	40	45	39	43
Chalcedony ( Arnorsson <i>et al.</i> , 1983)	101	102	104	193	96
Quartz (Fournier, 1981)	128	130	131	121	124

**Conduit rock**

To determine conduit rock in the study area, it is necessary to use hydrochemical components. For observing mixing, there are many methods such as cluster pattern and principal component pattern (Davis, 1986). In cluster pattern if total of springs are ordered in one part of diagram, therefore there is one conduit but for several conduit, there are two or several clusters. Based on Fig. 5 there is one cluster for thermal springs (springs C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub>)

but non-thermal springs (springs C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub> and C<sub>10</sub>) have three cluster and several conduit rocks. Conduit rock for thermal springs is limestone but for non-thermal springs are limestone, shale, sandstone and marl. Principle component pattern showed one group for thermal water similar to cluster pattern (Fig.6). Therefore, principal component pattern authorized cluster pattern and there is one conduit rock for thermal waters.



**Fig.5.** Diagram of cluster pattern for springs (thermal water includes C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> and non-thermal springs are C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub> and C<sub>10</sub>)

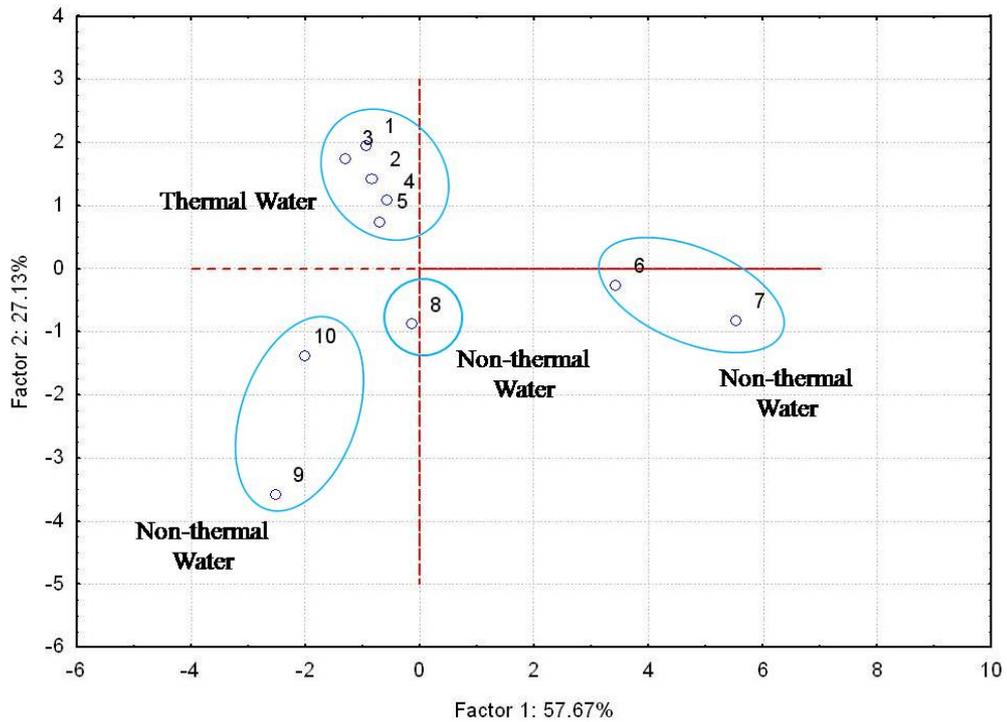


Figure 6: Principal components pattern results. Axis 1 versus axis 2 plot for thermal and non-thermal springs

**Conceptual model**

Hydrochemical and isotopical compositions of springs suggest the main geochemical process in the study area. Therefore, by coupling these results with hydrogeological setting, it is possible to draw a conceptual model to explain the origin of thermal springs in the Mahalat (Fig.7). The Mahalat host rock of thermal springs located in the Permian limestones (Araghi, 2009). The measured surface

temperatures of thermal springs and non-thermal springs are not exceeding 48°C and 25°C, respectively. These values suggest a circulation of shallow depths (Mirzaei et al., 2010) for thermal springs. Temperature of thermal springs at the depths is maximum 131 °C based on Quartz thermometry and decreases their ascent to the surface.

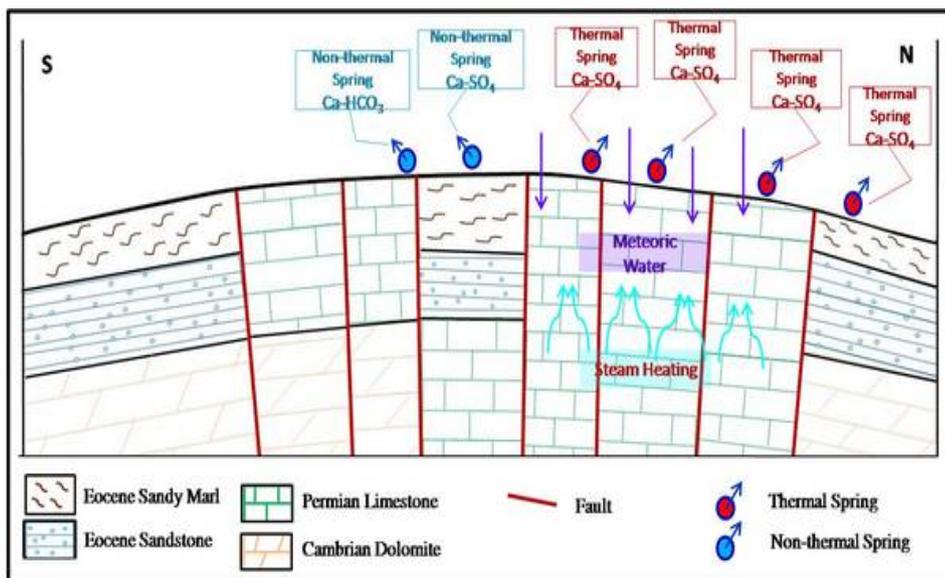


Figure 7: Conceptual model for the thermal and non-thermal springs in Mahalat

Because of the presence of Mahalat fault (Araghi, 2009) and numerous associated fractures in the study area, the meteoric waters infiltrate to great depths. Due to the increasing of thermal gradient in depths (Mirzaei *et al.*, 2010) the temperature of the descending waters increases. Deep, active faults act as permeable conduits for the fast ascent of the now thermal waters to the surface. The mineralization of infiltrated waters increases as they contact and react with Permian limestone host rocks and probably with Eocene marl and sandstone. Therefore, we infer that a shallow regional fluid circulation system has developed in the study area.

### Conclusion

Chemical analysis of springs in Mahalat showed that concentrations of the major ions belong to  $\text{SO}_4$  and Ca. Different plots of springs suggested that thermal and non-thermal springs are immature water and are not in equilibrium with the host rock. The high  $\text{SO}_4$  content, relatively low Cl content and moderate temperature indicate that the most probable mechanism for high Ca content is mixing with shallow cold groundwater. The preliminary hydrochemical of Mahalat springs were analyzed

by the application of multivariate analysis. The results of factor analysis showed that in the study area, leaching of cations in the rocks by thermal waters were the major contributor of hydrochemical variables. Gypsum dissolution is the source of  $\text{SO}_4^{2-}$  in springs. High  $\text{HCO}_3^-$  values is the result of dissolution of deep limestone aquifer due to the interacting with shallow water of meteoric origin. While, the possible alteration of silicate mineral formed  $\text{SiO}_2$ . Hydrochemistry of non-thermal springs were affected by the water-rock interaction.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  originate from the dissolution of marl and limestone.  $\delta^{18}\text{O}$  enrichment with respect to the meteoric water line (WML), indicated that thermal waters have been diluted by shallow waters of meteoric origin. Based on Quartz and Chalcedony thermometer, the temperature of the Mahalat reservoir is estimated the range of 96°C to 131 °C.

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