

HYDROCHEMISTRY OF KARST SPRINGS FROM TWO CARBONATIC UNITS IN ZAGROSIDES OF IRAN

E. Raeissi* and F. Moore¹

¹*Department of Geology, College of Sciences, Shiraz University, Shiraz, Islamic Republic of Iran*

Abstract

One hundred and nineteen karst springs, all with electrical conductivity of less than 500 $\mu\text{mhos/cm}$, discharging two carbonatic aquifers in Zagrosides of Iran are chosen and studied. The results indicate that the lithology of each unit is well reflected in the chemistry of the springs and the overall mineralogical composition of the aquifer can successfully be reconstructed from the hydrochemistry of the springs using a mass balance approach. A comparison of the chemistry of the springs reveals that the significant difference is due to the dolomitic nature of one of the studied aquifers.

Introduction

The hydrochemistry of ground water is mainly a function of the lithology and mineral composition of the aquifer that it passes through. In fact, differences in the chemistry of aquifers are the main reason behind the observed differences in ground water hydrochemistry [2, 5, 6]. In carbonatic units, as infiltrating rain and meltwater passes through pore spaces and secondary structures of various sizes, a reaction takes place between the CO_2 bearing groundwater and the carbonatic host. As a result, the chemistry of groundwater continuously changes as a function of time and the distance travelled by the water. Subsequently, considerable dissolution of carbonatic and dolomitic units will also take place. There is no doubt that if other soluble phases such as evaporitic minerals are also present as interlayers or some other form, these too will react and modify the major-ion chemistry of the groundwater. This is why the chemistry of groundwater is traditionally taken by the hydrogeologists as a good representation of the lithology of the aquifer through which the water flows. Therefore, direct analysis of the geological units is preferred for the following reasons:

a) The lithology of sedimentary units is usually so

variable that a large number of samples should be analyzed in order to obtain an average composition.

b) The exposed and available sections of the formations are generally weathered and thus analysis would not reflect the true chemistry of the fresh rock unit.

c) Sampling from depth is expensive and uneconomical.

In this paper, the hydrochemistry of the springs discharging from two carbonatic units in Zagrosides of Iran, namely Sarvak and Asmari-Jahrom Formations is studied and compared to see whether the differences in lithology of the two aquifers is also discernable from the hydrochemistry of their respective discharging springs.

Geological Setting

The stratigraphy and structural characteristics of Zagros sedimentary sequence has been described in detail by James and Wynd [3] and Falcon [1]. The geological map of the study area is presented in Figure 1. The formations of interest in a decreasing order of age consist of Kazhdomi bituminous shale (Aptian to Cenomanian), Sarvak limestone (Albian to Turonian), Gurpi shales (Santonian to Maestrichtian) and Asmari-Jahrom carbonates (Paleocene to Early Miocene).

Keywords: Hydrochemistry; Karst

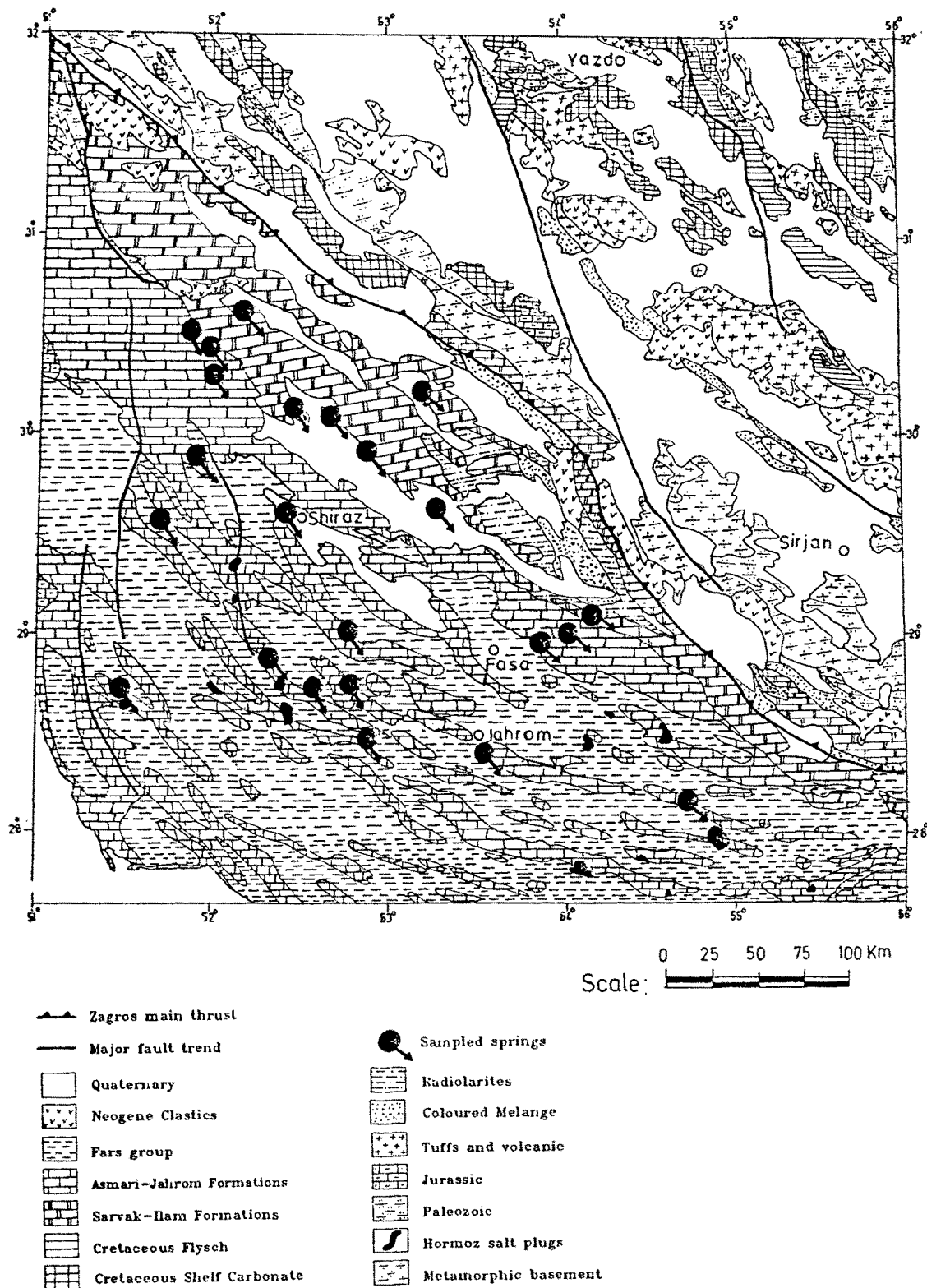


Figure 1. General geological map of the study area showing the location of the sample springs (modified from the map of south-central Iran. Published by the National Iranian Oil Company, [4])

Sarvak Formation with a thickness of about 800 m is a neritic, massive feature-forming limestone containing in some parts siliceous nodules and thin interlayers of marl. The undifferentiated Asmari-Jahrom Formations with a thickness of 700 to 900 m in the study area is also a massive feature-forming dolomitic limestone with shaly interlayers.

Considerable karstification occurred both in Sarvak and Asmari-Jahrom Formations and many karst springs are found at the local base of erosion, especially at the contact between the carbonatic units and the impermeable marly and shaly formations that overlie and underlay these formations.

Data and Methods

Seventy-two karst springs from Asmari-Jahrom Formations and forty-seven karst springs from Sarvak Formation were sampled. Figure 1 shows the location of the sampled springs. The electrical conductivity of all sampled springs is below 500 $\mu\text{mhos/cm}$ and care was taken to select those springs that have no apparent connection with the adjacent evaporitic Formations. pH and electrical conductivity of the samples was measured and the major ions Na^{++} , K^{+} , Mg^{++} , Ca^{++} , HCO_3^{-} , SO_4^{--} and Cl^{-} were also determined using standard wet chemical methods. Table 1 represents the mean, maximum and minimum of the measured ion in each formation. The contribution of each ion to the total dissolved solids is also presented in percent values.

Hydrochemistry of Asmari-Jahrom Springs

Table 1 indicates that 85.7% of the total dissolved ion consists of Ca^{++} , Mg^{++} and HCO_3^{-} , the rest being made up of SO_4^{--} , Cl^{-} , Na^{+} and K^{+} in that order.

The correlation coefficient of measured cations and anions are calculated using Student's *t* test and the results are presented in Table 2. It is clear that in Asmari-Jahrom springs a good correlation exists between HCO_3^{-} and Ca^{++} and Mg^{++} ; SO_4^{--} and Ca^{++} , Mg^{++} , Na^{+} ; and between Cl^{-} and Na^{+} .

Using a mass balance approach and assuming that all bicarbonates are used up by Mg^{++} and Ca^{++} , and that excess Mg^{++} and Ca^{++} is consumed by SO_4^{--} anion, and also considering that Na^{+} is mainly used up by Cl^{-} , the source minerals of Asmari-Jahrom aquifer were reconstructed from the data in Table 1 and are presented in Table 3. Hence, the mass balance approach reveals that the mineralogical composition of the aquifer should predominantly consist of calcite and dolomite with minor amounts of gypsum, halite, and probably epsomite. Although this is a rather perfect reflection of what is seen in the field, it must be noted

Table 1. Mean, maximum, minimum, sum and percent of concentration of measured ions from karst springs of Sarvak and Asmari-Jahrom Formation

	Asmari-Jahrom Formations (N=72)	Sarvak Formation (N=47)
Ca:		
Mean	2.196	2.233
Maximum	3.800	3.700
Minimum	1.000	0.800
% Ca	28.400	31.790
Mg:		
Mean	1.386	1.059
Maximum	2.400	1.800
Minimum	0.200	0.035
% Mg	17.298	15.074
Na:		
Mean	0.239	0.213
Maximum	1.050	1.120
Minimum	0.029	0.026
% Na	3.096	3.026
K:		
Mean	0.017	0.014
Maximum	0.097	0.110
Minimum	0.000	0.000
% K	0.219	0.203
HCO_3^{-} :		
Mean	3.046	2.668
Maximum	4.000	4.000
Minimum	1.700	1.300
% HCO_3^{-}	39.934	37.985
SO_4^{--} :		
Mean	0.582	0.531
Maximum	1.900	1.824
Minimum	0.000	0.060
% SO_4^{--}	7.350	7.560
Cl:		
Mean	0.265	0.306
Maximum	0.600	0.600
Minimum	0.020	0.100
% Cl	3.433	4.362
pH:		
Mean	7.387	7.544
Maximum	8.430	8.140
Minimum	6.400	6.800
EC:		
Mean	377.514	347.532
Maximum	494.000	486.000
Minimum	244.000	220.000

Concentration in meq/l; pH in units; EC is electrical conductivity in $\mu\text{mhos/cm}$.

that this is a somewhat simplified picture of the true situation, as there are undoubtedly minor minerals of various composition that are present in insignificant amounts and are not accounted for here. The original

Table 2. Correlation coefficient between the chemical variables

		HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻
As-Ja	Ca ⁺⁺	0.58*	0.27*	0.12
	Mg ⁺⁺	0.39*	0.46*	-0.08
	Na ⁺	0.12	0.74*	0.52*
	K ⁺	0.08	0.03	0.04
Sa	Ca ⁺⁺	0.67*	0.02	-0.06
	Mg ⁺⁺	0.06	0.37*	0.29*
	Na ⁺	0.25	0.37*	0.39*
	K ⁺	0.18	0.21	0.28

* Significant at the 0.05 level

Table 3. Reconstruction of source minerals for Asmari-Jahrom Springs

	Ca ⁺⁺ + Mg ⁺⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻
Concentration in spring water	2.20+1.39	0.24	0.02	3.05	0.58	0.27
CO ₃ Ca+CO ₃ Mg	-3.05			-3.05		
	0.54	0.24	0.02	0.00	0.58	0.27
SO ₄ Mg+SO ₄ Ca	-0.54				-0.54	
	0.00	0.24	0.02	0.00	0.04	0.27
ClNa	0.00	0.24				0.24
	0.00	0.00	0.02	0.00	0.04	0.03

Concentrations are in meq/l.

composition of the rain water should also be considered.

The relation between electrical conductivity and the concentration of various ions is presented in Figure 2. It can be seen that Ca⁺⁺, Mg⁺⁺, HCO₃⁻, Na⁺ and SO₄²⁻ show good correlation with electrical conductivity, while Cl⁻ and K⁺ reveal a very poor correlation. Using a multiple regression method, the relation between the dissolved ions and electrical conductivity is calculated as logarithmic, semilogarithmic and non logarithmic equations. The F test and the coefficient of determination (R²) show that the nonlogarithmic calculated equation (F=210.72, R²=0.941) is the best. The significant factor of F was also calculated and it was indicated that K⁺ and Cl⁻ hold no significance and so were omitted from the equation. After all these considerations, the equation of the line defining the relation between electrical conductivity and the dissolved ions may be expressed as follows:

$$EC = 41.42 Ca^{++} + 39.25 Mg^{++} + 72.85 Na^{+} + 47.55 HCO_3^{-} + 46.56 SO_4^{2-} + 42.10$$

Hydrochemistry of Sarvak Springs

As can be seen from Table 1, Ca⁺⁺, Mg⁺⁺, and HCO₃⁻ comprise 84.80% of the total dissolved solids, the rest being made up of SO₄²⁻, Cl⁻, Na⁺ and K⁺, respectively. The same mass balance approach is used

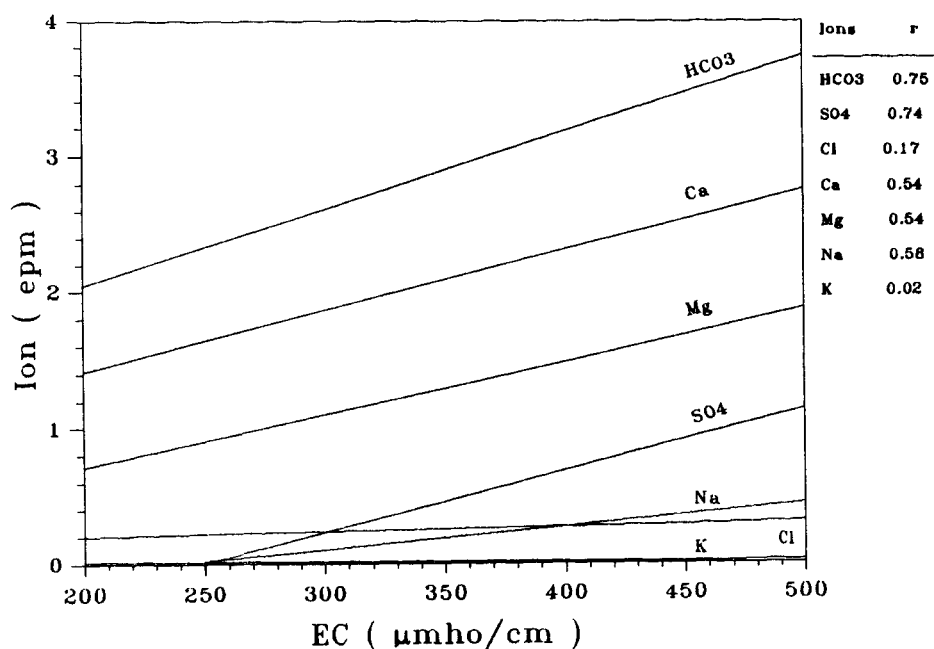


Figure 2. Relation between electrical conductivity and the concentration of various ions in Asmari-Jahrom Karst Springs

and the results are presented in Table 4. It is obvious that the mineralogical compositions of Sarvak aquifer should predominantly be made of calcite with some minor amounts of gypsum, epsomite, dolomite and halite. Here again we can see a perfect agreement between the reconstructed mineralogical compositions and field observations.

The relation between electrical conductivity and the concentration of different ions is presented in Figure 3. It can be seen that electrical conductivity shows a maximum correlation with HCO_3^- while Ca^{++} , Na^+ , SO_4^{--} , K^+ and Mg^{++} all show moderate correlation with EC. Similar statistical treatment of the data as that of Asmari-Jahrom indicates that the non-logarithmic equation ($F=67.177$, $R^2=0.891$) of the line best

Table 4. Reconstruction of source minerals for Sarvak Springs

	$\text{Ca}^{++}+\text{Mg}^{++}$	Na^+	K^+	HCO_3^-	SO_4^{--}	Cl^-
Concentration in spring water	2.23+1.06	0.21	0.01	2.66	0.53	0.31
$\text{CO}_3\text{Ca}+\text{CO}_3\text{Mg}$	-2.66			-2.66		
	0.66	0.21	0.01	0.00	0.53	0.31
$\text{SO}_4\text{Mg}+\text{SO}_4\text{Ca}$	-0.53				-0.53	
	0.13	0.21	0.01	0.00	0.00	0.31
ClNa		0.21				0.21
	0.13	0.00	0.01	0.00	0.00	0.11

Concentrations are in meq/1.

defining the relation between EC and dissolved ions is as follows:

$$\text{EC} = 42.97 \text{ Ca}^{++} + 45.60 \text{ Mg}^{++} + 68.22 \text{ Na}^+ + 45.18 \text{ HCO}_3^- + 45.15 \text{ SO}_4^{--} + 44.26$$

Comparison of Chemical Characteristics of Asmari-Jahrom and Sarvak Springs

The measured ions, pH and electrical conductivity

Table 5. Nonparametric comparison of chemical characteristics of karst springs from Asmari-Jahrom and Sarvak Formations

	Z	Z **	H***	Result of comparison
Ca^{++}	+0.23	0.23	0.052	$\text{Ca}_{\text{Sa}} = \text{Ca}_{\text{As-Ja}}$
Mg^{++}	-3.49	-3.49*	12.205*	$\text{Mg}_{\text{Sa}} < \text{Mg}_{\text{As-Ja}}$
Na^+	-1.92	1.92	3.694	$\text{Na}_{\text{Sa}} = \text{Na}_{\text{As-Ja}}$
K^+	-1.89	1.89	3.560	$\text{K}_{\text{Sa}} = \text{K}_{\text{As-Ja}}$
HCO_3^-	-3.28	3.28*	10.743*	$\text{HCO}_3 \text{ Sa} < \text{HCO}_3 \text{ As-Ja}$
SO_4^{--}	-1.20	1.20	1.431	$\text{SO}_4 \text{ Sa} = \text{SO}_4 \text{ As-Ja}$
Cl^-	+1.91	1.91	3.633	$\text{Cl}_{\text{Sa}} = \text{Cl}_{\text{As-Ja}}$
pH	+1.59	1.59	2.532	$\text{pH}_{\text{Sa}} = \text{pH}_{\text{As-Ja}}$
EC	-2.05	2.05*	4.200*	$\text{EC}_{\text{Sa}} < \text{EC}_{\text{As-Ja}}$

* Indicates that the compared parameters in the two formations are unequal at 0.05 significant level.

** |Z| Mann-Whitney method

*** H Kruskal-Wallis method

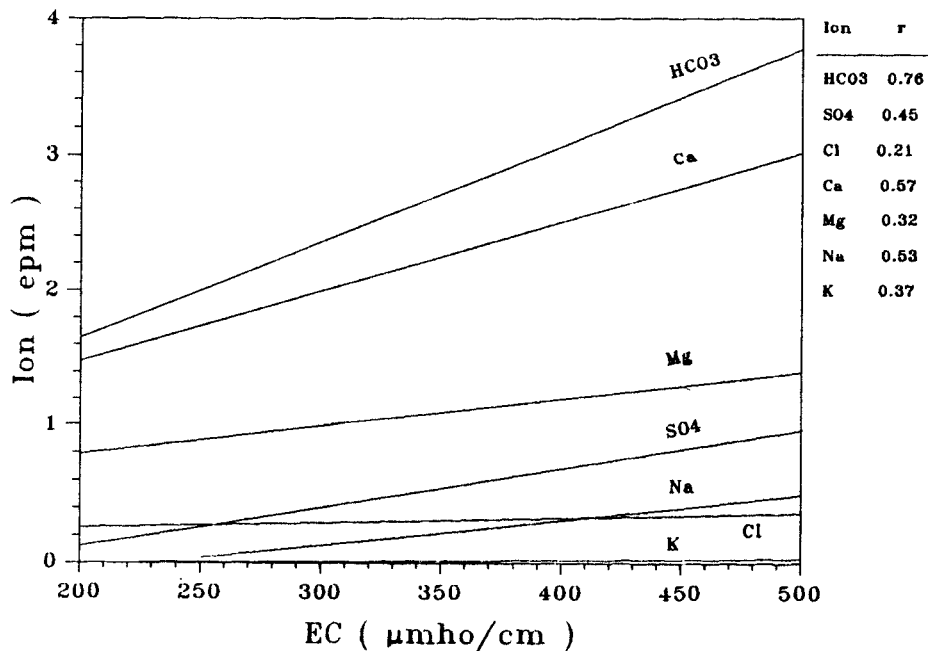


Figure 3. Relation between electrical conductivity and the concentration of various ions in Sarvak Karst Springs

of sampled karst springs from both formations were compared using nonparametric Kruskal-Wallis and Mann-Whitney methods [7]. The results are presented in Table 5. It can be seen that the differences in electrical conductivity, Mg^{++} , HCO_3^- of karst springs of these two formations is significant while the difference between other determined ions and pH does not bear any important significance. The higher Mg^{++} , HCO_3^- and electrical conductivity values in Asmari-Jahrom Formations seem to arise from its dolomitic lithology.

Acknowledgements

The authors would like to thank the research council of Shiraz University for financing this research. Thanks are also due to Mr. M. Bostani for his help in computer data processing.

References

1. Falcon, N.L. *Southern Iran: Zagros mountains in Mesozoic - Cenozoic orogenic belts*. Geol. Soc. London, Spec. Pub. 4, pp. 199-211, (1974).
2. Flint, R.F. *Glacial and quaternary geology*. John Wiley, New York, p. 892, (1971).
3. James, G.A. and Wynd, J.G., Stratigraphic nomenclature of Iranian Oil Consortium agreement area. *Bull. of AAPG*, 49, (12), 64, (1965).
4. National Iranian Oil Company, Tectonic map of South Central Iran 1:2500000, (1975).
5. Palmer, C.D. and Cherry, J.A. Geochemical evolution of groundwater in sequence of sedimentary rocks. *J. Hyrol.* 75, 27-65, (1985).
6. Rogers, J.R. Geochemical comparison of groundwater in areas of New England, New York and Pennsylvania. *Groundwater*. 27, 5, 690-712, (1989).
7. Walpole, R.E. and Mayers, R.H. *Probability and statistics for engineers and scientists*. Macmillan, New York p. 506, (1972).