

The implication of the hydrogeochemical processes for groundwater chemistry in a semi-arid region: a case study of the Bokoya massif (Central Rif, Morocco)

Ali Errahmouni¹, Jamal Eddine Stitou El Messari¹, Mohammad Ghalit², Daouda Kouotou³, and Morad Taher⁴

¹ Department of Geology, Abdelmalek Essaâdi University, Tétouan, Morocco

² Laboratory of Research and Development in Engineering Sciences, Faculty of Sciences and Techniques of Al-Hoceima (FSTH), Abdelmalek Essaadi University, Tetouan, Morocco

³ Department of Inorganic Chemistry, Faculty of Sciences, University of Yaoundé I, Yaoundé, Cameroon

⁴ Department of Earth and Environmental Sciences, Faculty of Sciences and Technique of Al-Hoceima, Abdelmalek Essaâdi University, Tétouan, Morocco

Abstract. Natural and anthropogenic factors control groundwater chemistry in the semi-arid area in northern Morocco called Bokoya massif. The main goal of this study was to evaluate the geochemical processes that affected groundwater mineralization in the Bokoya massif. As a result, In April 2016, sixty-one (61) water samples were collected from various locations, including wells and springs throughout the Bokoya massif, and analyzed for physicochemical parameters using standard methods. The descriptive study of the physicochemical parameters revealed that the waters were neutral to slightly basic (pH values range between 7,16 and 8,5) and moderately to strongly mineralized (TDS values range between 555,20 and 7980,10 mg/l). Sodium chloride was the dominant hydrochemical facies in the groundwater of the study area, with a percentage reaching (80%) noting the minority of magnesium bicarbonate facies and the absence of sodium bicarbonate and chlorinated calcium type. The tests of the ionic ratio (Cl^-/Na^+ , $\text{Cl}^-/\text{HCO}_3^-$ versus Cl^- , $\text{Ca}^{2+}/\text{Mg}^{2+}$, $\text{Ca}^{2+}/\text{SO}_4^-$, $\text{Ca}^{2+}/\text{Mg}^{2+}$ versus Cl^- , $(\text{Ca}^{2+} \text{ Mg}^{2+})/\text{HCO}_3^-$), indicate that the order of the dominant cations is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and of the dominant anions is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. It suggests that the dominant factors controlling water chemistry are rock dissolution and evaporation, silicate weathering, and ion exchange. Gibbs diagram defines the relationship between water chemistry and the lithology of the aquifer. It showed that most of the groundwater composition in this area is linked to the geochemical processes of evaporation and crystallization, and carbonates and silicate alteration control the minority.

Keywords: Bokoya, Central Rif, Groundwater, Hydrogeochemistry, Mineralization.

1 Introduction

The study of groundwater chemistry is of great interest in karst hydrogeology. It enables us to understand the phenomena controlling water mineralization in this type of aquifer system, such as water-rock exchange, dissolution, and alteration of reservoir rock minerals.

By studying groundwater chemistry, it is also possible to i) follow the spatial evolution of the various dissolved elements ii) estimate their origin, iii) estimate the depth of water circulation, and iv) assess water quality for different types of use. To this end, several researchers have contributed to understanding the hydrology and hydrogeology of the groundwater in the Bokoya massif, including [1–5]

In the Rif belt, Due to the lack of precipitation in recent decades, groundwater resources have been overused [6]. Moreover, water supply has become a significant concern in the Moroccan central Rif, which the Bokoya massif is a part of, due to a scarcity of this valuable resource. The groundwater is experiencing more and more qualitative and quantitative degradation resulting from natural (climatic and tectonic) and anthropogenic constraints. In this context, the current study aims to understand the Bokoya Massif's groundwater mineralization processes using hydrogeochemical technics.

2 Settings

In the northern Moroccan Rif chain, the Bokoya massif is a distinct coastal mountain range (Fig. 1). Its climate is semi-arid with an average annual precipitation of less than 330 mm and a temperature range between 5 and 29°C. Geologically and structurally, it belongs to the internal domain[7], which is highly individualized in the Rif belt's northern central region. It is marked by a stack of several structural units separated by anomalous contacts from each other [8]. It is dominated by the external dorsal limestone formation, which supports lands belonging to the internal limestone dorsal and Ghomaride Paleozoic strata in tectonic klippees. The entire massif crosses over to the south on a sequence of Tizirenean sandstone flyshs through a Predorsalian marly layer (tertiary sole), which is carried on the external Rif units to the south[7, 9–12] .

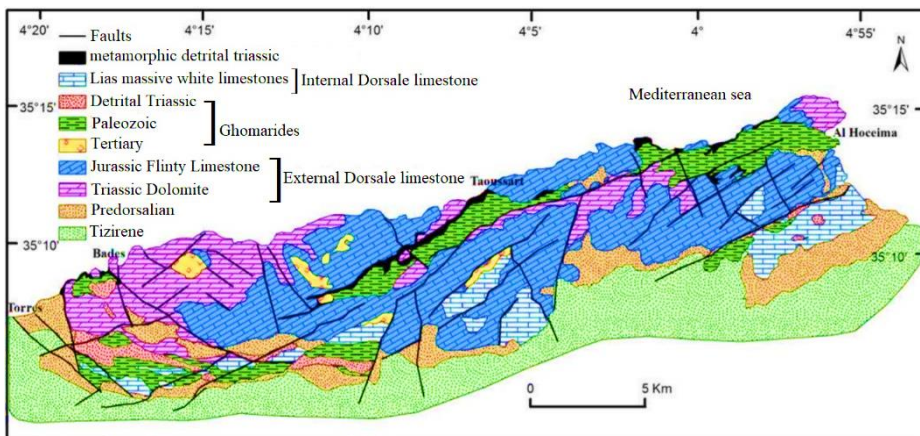


Fig. 1. Geological and structural map of the study area [13].

3 Materials and methods

The study was based first on fieldwork, which consisted of measuring "in situ" parameters and collecting 61 groundwater samples in total. (wells and sources) throughout the entire study region. Using one-liter (1L) polyethylene bottles, these water samples were gathered. Before sampling, the bottles were first rinsed with pre-sampled water. Thereafter bottles were kept in coolers and immediately subjected to analyses after the sampling. By interviewing people from Bokoya massif, they confirmed that the piezometric level of the groundwater in the said area varied during the earthquakes that the region experienced in 1994 and 2004 and other previous tremors. And how the landslides affect this piezometric level. In addition, these people guided us to easily find the water sources and to know the use of each source (agriculture, drinking, daily domestic use...). The second step was in the laboratory, wherein multiple analytical techniques were employed. The EDTA volumetric method was used to titrate calcium (Ca^{2+}), magnesium (Mg^{2+}) ions, and water total hardness. Silver nitrate solution was used to measure chloride (Cl^-) ions and hydrochloric acid solution for bicarbonate (HCO_3^-) ions determination. Colorimetric methods were performed for nitrates (NO_3^-), sulfates (SO_4^{2-}), ammonium (NH_4^+), orthophosphates (PO_4^{3-}), and silicates (SiO_2) determination using a UV 9200 spectrophotometer. Sodium (Na^+) and potassium (K^+) ions were determined by flame atomic absorption spectrophotometry. Finally, the last step is to analyze the results obtained using different hydrochemical software. This step is based on interpreting the various diagrams and tables obtained.

4 Results and discussion

4.1 Hydrogeochemical evaluation

The following table shows the descriptive statistics of the physicochemical parameters of the analyzed groundwater.

Table 1. Statistical summary of physicochemical parameters in the study.

Variables	Minimum	Maximum	Average
pH	7,160	8,5	7,711
E.C ($\mu\text{S}/\text{cm}$)	784,00	15420	2984,33
TH ($^\circ\text{F}$)	15,20	173,60	53,49
TDS (mg/l)	555,20	7980,10	1644,43
Cl^- (mg/l)	81,650	4863,50	616,83
HCO_3^- (mg/l)	146,40	744,20	361,40
Ca^{2+} (mg/l)	36,84	496,62	117,69
Mg^{2+} (mg/l)	10,48	224,407	57,77
Na^+ (mg/l)	61,00	1950,00	360,39
K^+ (mg/l)	0,60	94,00	11,22
SO_4^{2-} (mg/l)	6,65	267,83	58,038

4.2 Hydrogeochemical facies

The results of the Bokoya massif groundwater study, as seen on the triangular Piper's diagrams (Fig. 2), illustrated that Sodium chloride was the dominant hydrochemical facies in the groundwater of the study area with a percentage reaching (80%), the same results obtained by [14]; noting the minority of magnesium bicarbonate facies and absence of sodium bicarbonate and chlorinated calcium type.

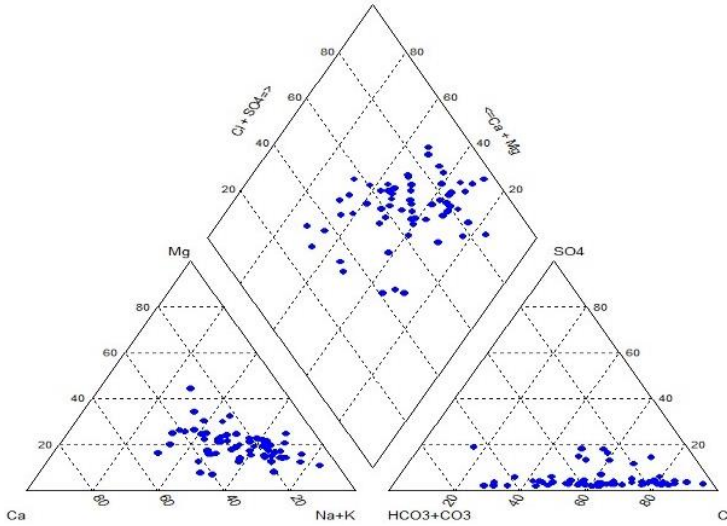


Fig. 2. Piper diagram of groundwater samples.

4.3 Contribution of ions to water mineralization

The relative contribution of ions to the mineralization of groundwater in the Bokoya massif is illustrated in figure 3. It appears that chlorides account for a large proportion (almost 40%) of the mineralization of the sampled water, followed by sodium (22%). Bicarbonate content is around 22%. Sulfate content is around 3%, and nitrate content is 4%. This high level of nitrates is due to anthropogenic causes, as many of the wells are open-cast, which makes them vulnerable to waste discharge, and also due to the infiltration of wastewater from the pits.

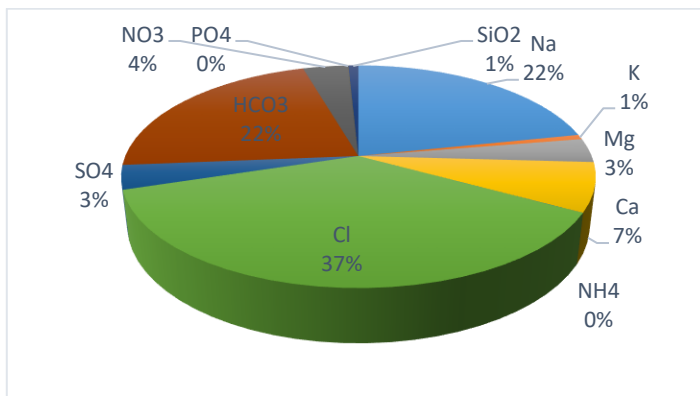


Fig. 3. Relative contribution of ions to groundwater mineralization.

4.4 Processes identification

Ion scatter plots, as seen in Figure 4, are utilized to assess the abundances of the main cationic and anionic varieties in various groundwater within the Bokoya massif.

As observed in (Fig.4a), the majority of sampled points indicate a ratio <1, which signifies a dominance of evaporation and/or ion exchange processes [15]. The $\text{Cl}^-/\text{HCO}_3^-$ ratio versus Cl^- (Fig. 4b) illustrates that most samples showed a ratio range between 0.5 and 6.6 means that salinization mildly polluted these waters. The $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio was more significant than 1 in most of the water points studied (Fig. 4c). It showed that calcium was abundant compared to magnesium. The $\text{Ca}^{2+}/\text{SO}_4^-$ ratio in (Fig. 4d) confirmed that the calcium came from calcite dissolution (CaCO_3) and gypsum (CaSO_4). It also revealed that all groundwater samples were placed above the gypsum dissolution line (1:1).

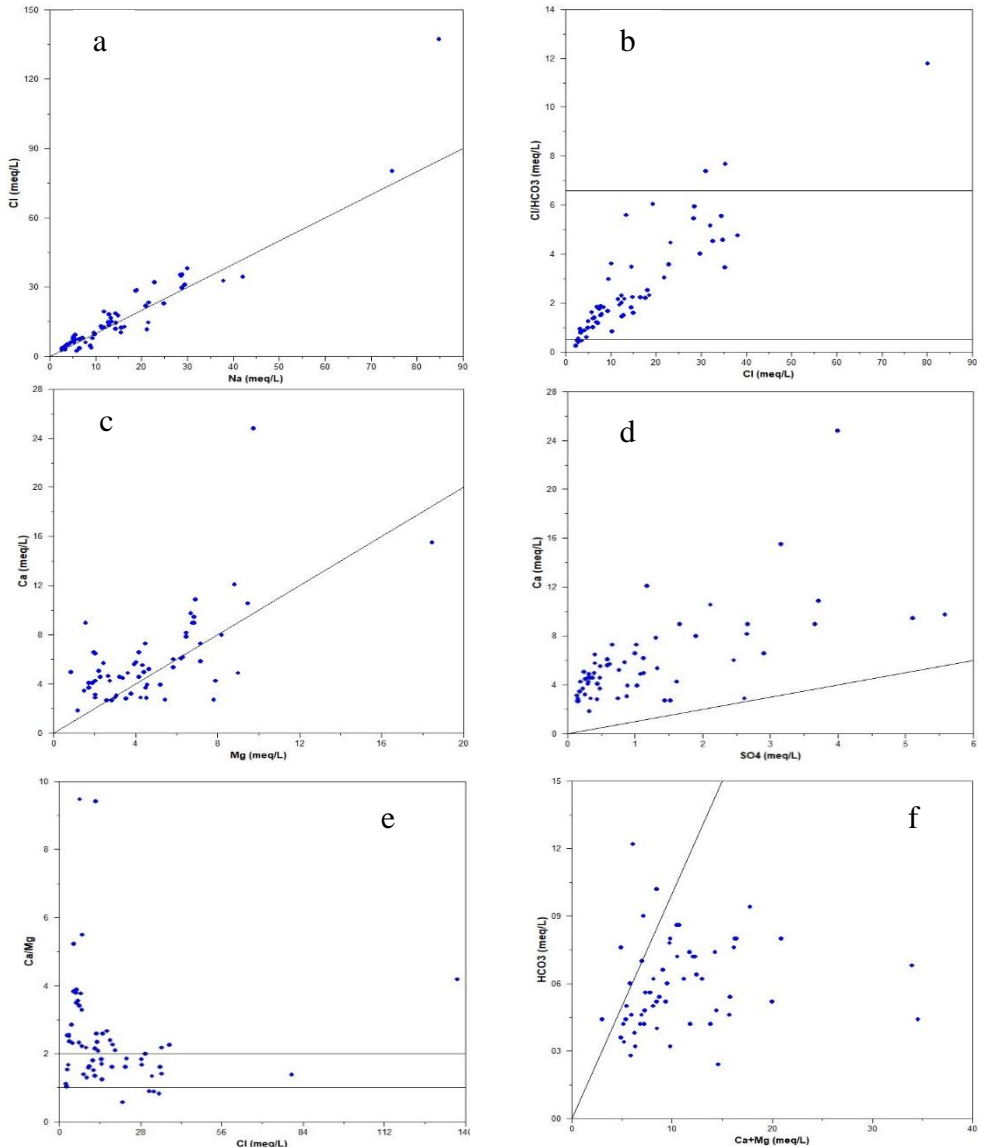


Fig. 4. Groundwater ion scatter diagrams in the study area.

Most sampled water has a higher $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio (> 2) (Fig. 4e), which indicates that silicate minerals have an impact on groundwater chemistry and therefore contribute calcium and magnesium to groundwater [16]. A ratio of 1 to 2 in the water samples indicates dolomite dissolution [17] in the second rank. To evaluate the origins of Ca^{2+} and Mg^{2+} in groundwater, the $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ ratio had to be used (Fig. 4f). This figure indicates that the majority of the sampled water in the Bokoya massif is distinctly below the 1:1 line, suggesting that it is not from the same source. Furthermore, the alkalis Na^+ and K^+ produced by silicate weathering stabilize too much alkalinity in these waters.

The Bokoya massif groundwater Basic Exchange Index (BEI) measurement shows positive values were present in 64% of measured indices, while negative values were found in 36%. The BEI was linked to minerals clay, which fixed Na^+ and K^+ ions in waters during Ca^{2+} and Mg^{2+} releases, as shown by the predominance of positive values.

The Gibbs diagram [18] was used to determine the relationships between water chemistry and the lithological characteristics of aquifers. Figure 5 illustrates groundwater samples from the Bokoya massif, showing that these waters were predominantly present in evaporation-precipitation dominance zones. The studied point minorities, on the other hand, were located in water-rock contact dominance zones. The composition of this area's groundwater seemed to be primarily linked to the geochemical processes of evaporation and crystallization.

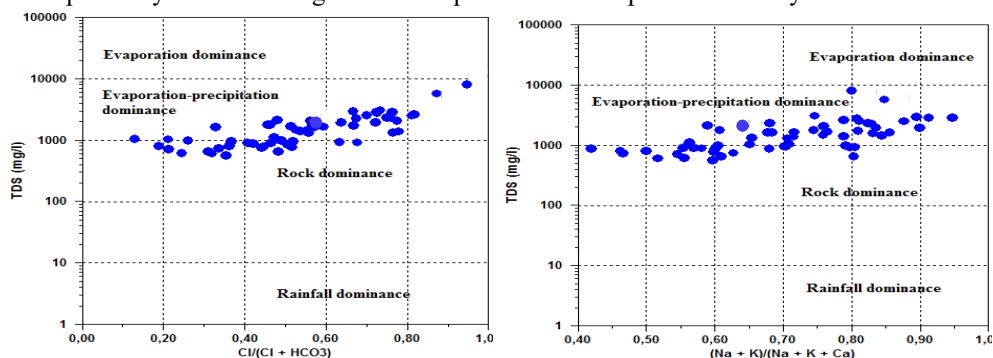


Fig. 5. Gibbs diagram.

5 Conclusion

A combination of hydrochemical and hydrogeological techniques was used to investigate the hydrochemical properties of the groundwater of the Bokoya massif. This study focuses on the various physicochemical properties of the waters under investigation. We noted that the waters of the Bokoya massif are very saline. The classification of chemical analyses obtained from the Piper diagram identifies that Sodium chloride water is the majority of this study area (80%). The principal geochemical processes controlling the water chemistry of the study area are ion exchange and evaporation-crystallization. In addition to the anthropogenic activities.

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