

## THE CHEMICAL ORIGIN AND GEOTHERMOMETRY OF HOT SPRINGS WATERS IN THE REGION OF KHENCHELA, ALGERIA

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**Abstract:** Our study is carried out on the trio of thermomineral waters in the region of Khenchela - Hammam Salhin, Hammam Knif, and Hammam Djaarir - Northeast of Algeria. The purpose of this study is to determine the physicochemical and geothermal origin of the thermal spring (temperature, pH, and electrical conductivity). The temperatures of the thermal water samples which were being studied varied from 38 to 72°C; therefore, this variation has a direct relation to the climatic conditions and/or the combination of the water which is derived from various sources in the formation of the thermal spring. Additionally, the pH value of the spring under study is of a neutral to slightly alkaline quality, while its electric conductivities are high, ranging from 3059  $\mu\text{S}/\text{Cm}$  to 5007  $\mu\text{S}/\text{Cm}$ . The Piper diagrams presented the domination of sodium chloride (Na-Cl) and sodium sulfate (Na-SO<sub>4</sub>) facies as two types of water in the hydrochemical facies. These facies indicate the mineral composition of the thermal waters, a product from the reservoir by way of geological formations in the subsurface. This is a plausible reason from the chemical changes observed in the fluids and can well be associated with the high influence of water-rock interaction, that is, the formation of sodium bicarbonate water to sodium-chlorinated water formation, where it is linked with the effects of dissolution and salinity in the formation of saliva found in regions with semi-arid climatic conditions. Evaporation would play a major role in increasing the sodium content, while the IIRG plots closer to the industry "α" standard than the other plots. These are the characteristic features of an evaporation-based system. The crucial parameter C serves as a strong indicator of circulation in carbonate reservoirs subject to evaporation.

**Keywords:** Thermomineral, waters, physicochemical parameters, hydrogeochemistry, Algeria

### 1. INTRODUCTION

Thermal waters are defined as those with temperatures above the temperature of the air in their environment. Generally, by the concept of a hot spring, an emergent discharge of water from the earth's surface, in the form of vapor or liquid heated by geothermal processes, is represented. The phenomenon manifests not only on the Earth's continents but also beneath the ocean bed (Espinosa-Paredes & Garcia-Gutierrez, 2004). Deeply percolating water undergoes heating through convective circulation and the geothermal gradient process. They identify behavior reservoirs, groundwater circulation, and thermal water resources. This means that

geothermal systems have been a point of interest to researchers from time immemorial, as evidenced in the works of (Elster et al., 2022. and Déri-Takács et al., 2015.) In Maghreb countries, numerous studies on hydro-environment and the potential of geothermal water resources have been conducted: north Africa has seen pertinent studies on hydrothermal issues, as indicated by (Barkaoui et al., 2014 and Jilali et al., 2018). In Algeria, notable research has delved into characterizing the potential of hydrothermal reservoirs, though some aspects of their emergence have been overlooked (Berkani et Houha, 2017; Chenaker et al., 2018; Benmarce et al., 2023). Numerous studies conducted in Tunisia by various researchers have explored like the study explored by (Trabelsi et al.,

2015 and Bouroubi et al., 2021). Algeria boasts significant thermal potential, featuring 282 thermal springs, with 100 sites available for new projects, 60% are concentrated in the northern regions of the country, while the remaining 40% are situated in the southern areas. (Lakrouit et al., 2022) Given its immunity to seasonality, thermal tourism could serve as a robust instrument for the country's socio-economic development. With a historical lineage dating back to Roman times, thermal baths such as aquae Chibilita, aqua Mauretaniae, and aquae Sirenes continue to thrive in modern times, including sites like Hammam Guergour, Hammam Ouled Ali, and Hammam Salehines (Kifouche et al., 2023).

Distributed across Algeria, these thermal springs exhibit emergence temperatures ranging from 19°C in Hammam Benharoun to 98°C in Hammam Meskoutine. Deposit conditions are intricately linked to diverse hydrologic and morphostructural contexts. Isotopic studies rank the hyper-thermal waters of Guergour as the world's third, following Brembach baths (Germany) and Jachimov baths (Czechoslovakia), boasting a radioactivity level of 122 millimicrons-curies/l. Their chemical composition aligns with sulphate-calcium and sodium chloride water (Benmarce et al., 2021).

From the extensive Algerian thermo-mineral heritage, encompassing over 200 listed thermal springs or sources, this work focuses on three thermal springs located in Khenchela region. Specifically, the Thermal resorts of Hammam Essalihine (35.4401, 7.0845), Hammam El Kenif (35.4871, 7.2526), and Hammam Djaarir (35.2795, 6.7893) are the subjects

of attention. The aim is to align them with professional standards in the field, enhancing their reputation, elevating the quality of services and care offered. This strategic effort intends to position these thermal resorts on the global hydrotherapy market, gradually integrating them into international trade channels.

The objective of paper is to delve into the various chemical processes that impact the distinctive traits of thermal waters by utilizing advanced analytical techniques of chemical analysis. Through this, we hope to uncover valuable insights on the origins, makeup, and geothermal properties of thermal waters, ultimately contributing to a more comprehensive understanding of their geochemical development, heat source, and potential for therapeutic use.

## 2. MATERIALS AND METHODS

### 2.1. Study area

The Aures is the region of the Saharan Atlas located in the central part of the Constantine department. It is the highest massif in Eastern Berberia: Chellia peaks at 2,329 meters at Irfen n'Keltoume, and Kef Mahmel rises to 2,311 meters.

It thus significantly dominates the High Plains of Constantine to the north, whose altitude is only 800 to 1000 meters, and especially the plain of the Chott Melrhir which descends at its southern foot below sea level, forming the most depressed part of the Lower Sahara (Lafitte, 1939).

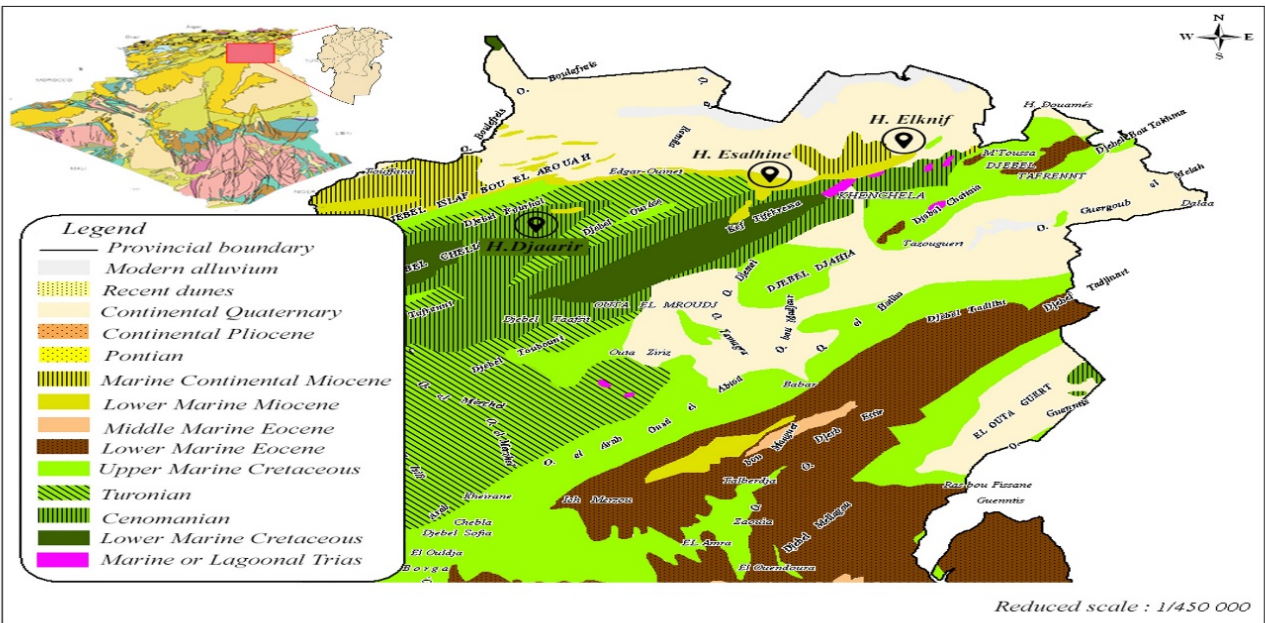


Figure 1 Geographical location of the sampled hotwater springs

The Aures Massif is a part of the eastern Algerian Alpine chain, predominantly consists of a series of autochthonous and parallel ranges extending from southwest to northeast. It is notable for its substantial Mesozoic sedimentary layers dating back to the Cretaceous period. During the Mesozoic era, the Aures Massif experienced significant subsidence, followed by vigorous folding towards the end of the Middle Eocene (Houha, 2007). This geological activity coincided with the formation of the Khenchela and Djebel Krouma diapirs. Khenchela anticline, which represents a vast and regular structure, is dominated by thick series, largely continental, of the Lower Cretaceous period, widely exposed in the mountain chains surrounding the Remila depression (Houha, 2007), (Figure 2).

Farther east, however, they are commonly monotonic, with episodes of marly-sandstone or clayey-sandstone alternating over great thickness with episodes of carbonate, generally of lesser importance, facies containing limestone, marly-limestone, and marly-clay-limestone deposits. The outcrops from the Triassic are very localized toward Khenchela and separate from the Cretaceous along a strip 4 to 5 km long and 300 to 400 m wide to isolate the Miocene. The Trias represents chaotic masses of evaporates (gypsum and halite), chaotic banded marls, varicolored clays, and cargneules in the subsurface (Houha, 2007). The development of structural phenomena is related to the distribution of the hydrological system in the research region. During the rainy season, this hydrological network's high density temporary water flow is what makes it unique. The Boulfrice stream Drain the whole region, starting from its southwest source and ending in the northeast when it empties into the Sabkha. still possessing more smaller, less significant stream, the Baghai Oued River, flows eastward and the middle of the area is drained by Gueis and Maarouf streams.

These streams have a transient flow, then they pour into the Garaat Etarf Sabkha, a closed depression (DHWK,1984).

The study area aquifer (Remila) is located in the sandy-marly limestone substratum of the mio-plio-quaternary. Lithostratigraphy and depth of the aquifer influence Geochemistry and the aquifer recharging mode. The aquifer's replenishment is preserved by draining runoff water from the northern slope of Aures, (CGG,1969).

Warm, dry summers and cold, wet winters with some snow generally typify Khenchela's climate. Khenchela presents one of the cold areas within Algeria. Temperatures in Khenchela fluctuate by great margins during the year. The hottest months are July and August, ranging between high averages of 34 degrees Celsius in July. The coldest months are January and February, with averages at around 10.6 degrees Celsius in January and slightly higher in February. As for precipitation, the region receives about 41mm of rainfall in the month that registers the highest amount, which is April. Conversely, the month of July is the driest in the sense that the little rain that falls is just never enough. Most significantly, the city receives normal snowfall, ranging between January and April, November, and December, where in those times, snowfall falls at its highest in February (Kadri et al., 2023).

## 2.2. Sampling and Analytical Techniques

One crucial aspect of thermal waters is the need to collect samples as close to the spring as possible and accurately identify the source of the spring (IAEA, 2008). The collection process for chemical analysis involved two stages, beginning with field observation. The first stage consisted of storing the thermal spring waters in 150-ml new polyethylene bottles for major ion analysis.

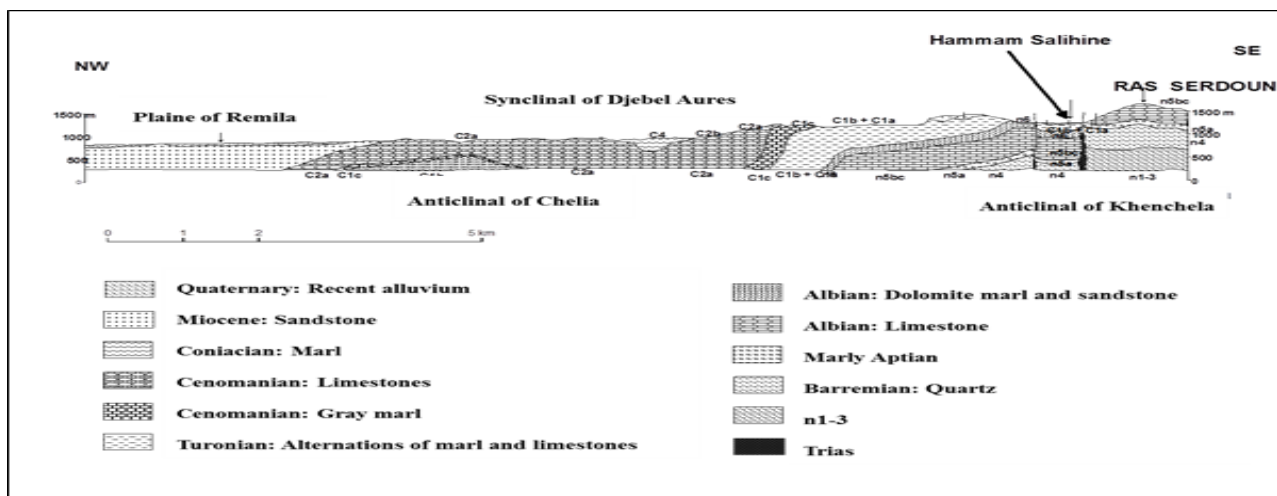


Figure 2: Geology of studied area (Khenchela region)

These bottles were capped and sealed with paraffin film, rinsed three times with the sampling water, and then carefully transported in a cooler. Before being analyzed, the samples are stored in a refrigerator at 4°C for a maximum of one week to ensure accuracy.

In April 2023, three thermal water samples were collected from designated bathing areas for chemical analysis (Figure 1). To maintain sterility, the samples were immediately sent to the water quality laboratory. To measure physical parameters such as temperature, pH, and electrical conductivity (EC), a Consort C931 portable handheld digital multi-parameter device was utilized. The chemical analysis was carried out by the LACIP lab located in Ain-Mlila, Algeria. An advanced Dionex Ion Chromatograph, equipped with an automated sampler and boasting a precision of up to  $\pm 5\%$ , was utilized to analyze the anions. The silica (SiO<sub>2</sub>) was evaluated using reliable colorimetric techniques, while cations were analyzed using a highly accurate atomic absorption spectrophotometer. To identify the chemical layers present in the groundwater, the skilled researchers employed the renowned Piper diagram. The task was made easier with the aid of advanced computer programs such as "Diagrammes" (Simler, 2014) and AquaChem

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Physicochemical parameters

##### 3.1.1 Temperatures

Water temperature is affected by air temperature; it plays a key role in the solubility of salts and gases. It can differentiate between water circulating deep and water circulating near the surface. This is one of the factors that affect the speed of chemical reactions. Remarkably, these high temperatures indicate a deep source of water (Table 1).

The temperatures of the north-eastern hot springs from the study area were calculated using the following geothermometers: a Na–K–Ca geothermometer with Mg-correction, a cationic composition geothermometer (CCG), silica, and Na/Li (Nieva & Nieva, 1987). The CCG is considered to be a good method of temperature estimation (Figure 6) estimates the reservoir temperatures of the samples.

In one hand we know that the path of the thermal water from the original reservoir to the surface most often is accompanied by cooling of the temperature and a change in total mineralization. On the other hand, the concentration of some components

of thermal water is temperature-related, and therefore, it can be utilized to a certain extent in certain relationships either qualitatively or quantitatively as an indicative for the original reservoir temperature. Before these geothermometers are used, there are some preconditions that the models should satisfy first (Fournier, 1979) (Table 1).

Table 1. Physicochemical parameters

Parameters	H. Esalhine	H. Elknif	H. Djaarir
T°C	72	46	38
pH	7.73	7.05	7.27
EC (μS/cm)	3059	4021	5007
Ca <sup>2+</sup> (mg/l)	128	216	234
Mg <sup>+</sup> (mg/l)	47	15	91
Na <sup>+</sup> (mg/l)	664	820	1209
K <sup>+</sup> (mg/l)	16	17	6
Cl <sup>-</sup> (mg/l)	1026	1105	1837
SO <sub>4</sub> <sup>-2</sup> (mg/l)	19	57,7	38
NO <sub>3</sub> <sup>-</sup> (mg/l)	0,83	0,38	0,12
HCO <sub>3</sub> <sup>-</sup> (mg/l)	326	336	243
Li <sup>+</sup> (mg/l)	0,54	0,22	0,08
SiO <sub>2</sub> (mg/l)	61	40	25

##### 3.1.2 pH

The water's pH of the hot springs: Hammam Salhin, Hammam Knif, and Hammam Djaarir, with values of 7.73, 7.05, and 7.27, respectively. These values suggest that the waters are slightly alkaline, which is common for thermal springs due to the dissolved mineral content that can buffer the water's pH. The therapeutic benefits of such mineral-rich alkaline waters are often associated with skin and rheumatic treatments. The slight variations in pH among the springs could be due to differences in geological formations and depths from which the waters emerge, (Table 1).

##### 3.1.3. Electrical Conductivity

The conductivity was found to be quite high. The maximum value of conductivity measured at Hammam Djarir 38°C was recorded as 5007 (μS/cm) while the minimum value measured at Hammam Esalhine was 3059 (μS/cm) as the water contains many minerals and many Salts dissolve more easily at higher temperatures, and these salts and minerals pass into the water through the rocks and sediments they come in contact with. Hot water has relatively high dissolved solids conductivity (TDS) values as well as high overall conductivity (Hayashi, 2004). (Table 1).



## 3.2. Water chemistry

### 3.2.1 Piper and Berkaloff's diagrams

The Piper diagram provides information on the mineralogical trend. It consists of two equilateral triangles at the base (one for the anions and the other for the cations), with a lozenge in the middle. The sides of triangles are divided into 100 equal parts. Each element is represented on the triangle in relation to its pairs of the same nature, (Figure 3).

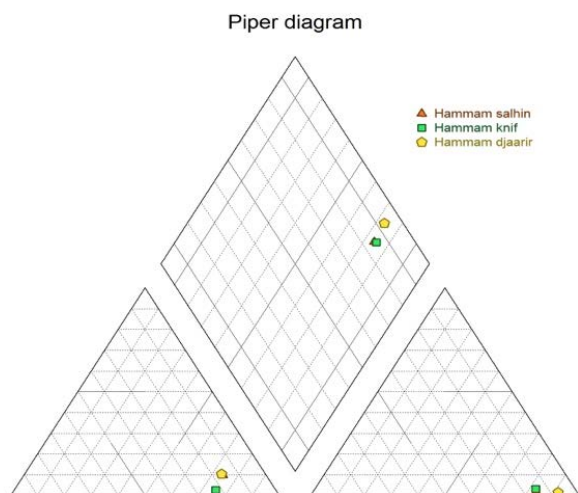


Figure 3. Piper diagram of thermal waters

The projection of the points on the lozenge by two lines led from the triangles corresponds to the chemical facet (Simler, 2014). This graphic representation is used to determine the chemical facet of the water and track its variations in space and time. It also allows to see the evolution of a water, moving from one face to another, through time-spaced analyses or analyses of samples taken from different locations.

The Piper diagram is very useful to represent all other types of analysis groups (Figure 3). The chemical facet of the waters was determined using the Piper diagram using the Diagram of the Hydrogeology Laboratory of Avignon software (Simler, 2014). The data of the major ions, on the Piper diagram, helped to highlight the evolution of the chemical facet of the waters, once the water heated deep in the mountain piedmont; these waters evolve into a calcium sulfate face to sodium chloride.

The waters evolve from one facet to another, moving from calcium bicarbonate water to sodium chlorinated water with intermediate mixed facies of the type chloride and calcium sulfate.

The origin of chloride is mainly linked to the dissolution of halite formations present in our study area. Evaporates are the main source of this element.

Endorheic basins, fossil or tap water. Generally, chlorine-rich waters are sodium-rich, sometimes calcium replaces sodium.

The origin of sodium is linked to the dissolution of the halite formations found in the region and the effect of salinity in areas with semi-arid climates.

The existence of evaporative inclusion in the form of salt rocks rich in NaCl and CaSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> shows that each water source crosses a different path from the other, and it is noted that thermo-mineral waters do not have the same origin because their straight lines collide with one another in Berkaloff's graphic representation (Figure 4).

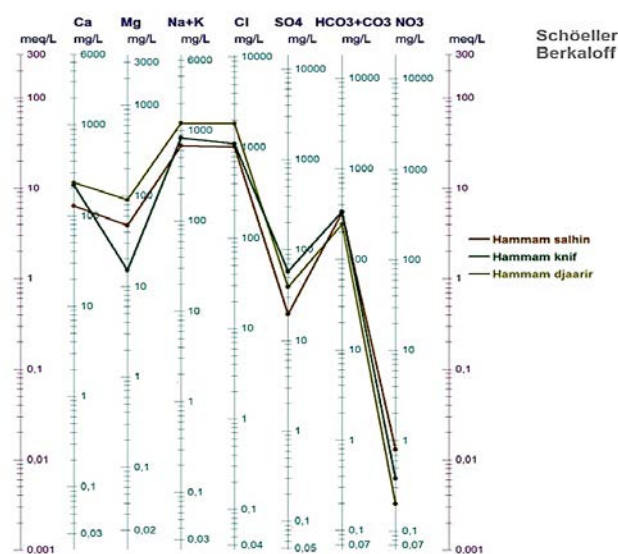


Figure 4. diagram representation of Berkaloff.

### 3.2.2 Geothermometers

The validity of these geothermometers is, however, subject to a number of conditions, the most important of which is the establishment of the balance between the chemical element present in the solution and the mineral that controls it. Furthermore, it is assumed that the system studied is isochemical between the reservoir and the surface (Magnúsdóttir et al, 1972). Components (SiO<sub>2</sub>, Na, K, Ca, and Mg) are passed through a number of conventional geothermometers using temperature-dependent chemical calculations.

Equilibrium and the presumption that the chemical composition remains unchanged from the source to the surface. The temperature of the reservoir that yields the deep waters can be determined using geothermometric analysis, and geothermometers reflect the equilibria of these temperature-dependent reactions. (El-Fiky, 2009).

The literature describes a variety of chemical geothermometer types (Rybach & Muffler, 1981; Kharaka & Mariner, 1989; Fournier, 1979). Due to

specific hydrogeological conditions, the application of geothermometers may be questioned in situations where the underlying assumptions and calibration circumstances, such as those dominated by carbonate and/or evaporated rocks, do not match (Lopez-Chicano et al., 2001).

The expression of CCG is mainly related to the Na/K ratio. Considering this ratio, the qualitative results of the geothermometer are as follows: The outcomes from various solute geothermometry analyses presented in (Figure 6) indicate that the temperature estimates for the subsurface reservoir, as determined by different geothermometers, range from 12 °C (using the Na/K ratio as proposed by Arnórsson in 1983) (Arnórsson et al., 1983) to 158 °C (based on the Na–K–Ca method developed by Fournier & Truesdell in 1973). The temperature estimates derived from Quartz-Chalcedony geothermometers ranged from 40 to 111 °C (Figure 6).

The accuracy of temperature estimates provided by geothermometers may be compromised, either resulting in underestimation or overestimation, due to discrepancies between the actual hydrogeological conditions and the fundamental assumptions required for their use.

Additionally, the reliability of these estimates is contingent upon the equilibrium state of the minerals involved in the geothermometry process (Chenaker et al., 2018).

### **3.2.3 The IIRG**

The IIRG method (International Geothermal Research Institute) developed by (D'amore et al., 1983) was applied. The principle of this method is based on the use of concentration ratios of the major elements and the sum of cations ( $\Sigma^+$ ) and anions ( $\Sigma^-$ ) expressed in meq/l.

Six new parameters (A, B, C, D, E and F) are well defined and standardized between -100 and 100 whose values allow to set the rectangular patterns and compare them with reference patterns ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) (Figure 6a) established by the authors (Figure 5).

The IIRG diagram in the region is adapted to the " $\alpha$ " standard reference, a characteristic of evaporitic series. Parameter C shows water circulation in evaporates-rich carbonated reservoirs.

### **3.2.4 The Stabler Diagram**

The Stabler diagram (Figure 7) method offers a systematic approach to interpreting the mineralogical composition of water sources, providing insights into the geological processes that influence water chemistry. This method facilitates the understanding of how water interacts with its

surrounding geology, particularly in terms of the dissolution of various rock types and the consequent mineral constituents found within the water (Remmani et al., 2021).

For Hammam Essalhine, the water's mineralogical composition includes  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ , KCl, and NaCl, suggesting the dissolution of carbonated rocks and evaporites, such as calcite, gypsum, sylvite, epsomite, and halite. This indicates a complex interaction between water and its geological environment, leading to a rich mineral profile reflective of the dissolution of both carbonate and evaporative rock types, (Figure 6).

The waters of Hammam el-Knif are characterized by a mineral composition of  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , KCl, and NaCl. This composition points to the dissolution processes involving carbonated rocks and evaporates, including calcite, gypsum, and halite. The presence of these minerals in the water is indicative of the geochemical processes that dominate the area, suggesting a significant influence of both carbonate rocks and soluble evaporates on the water chemistry.

For Hammam Djaarir, the mineralogical composition is noted as  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and NaCl. This composition underscores the dissolution of carbonated rocks and highlights the interaction between the water and its geological context, primarily influenced by the presence of calcite and gypsum, along with other soluble minerals. It is the dissolution of carbonated and evaporated rocks: calcite, gypsum, calcium chloride and Halite. It is the chemical composition of sedimentary rocks spread in the regions of the high Constantine plains with dominance of calcite rocks and evaporative inclusions in the filling Mio-Plio-Quaternary.

Overall, this Stabler diagram shows that the three water sources have similar chemical profiles, with a notable dominance of sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ), which classifies them as sodium chlorinated waters, often associated with ancient or deep waters and sometimes with evaporation processes or the influence of seawater.

Regarding the relationship between calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and other ions, the differences between the three samples may be related to regional changes in geology or the chemistry of mineral dissolution in aquifers. The water at Hammam Elknif and Hammam Djarir has slightly higher calcium content than the water in Hammam Esalhine, which could be a sign of a stronger contact with carbonated rocks or the presence of calcic minerals.

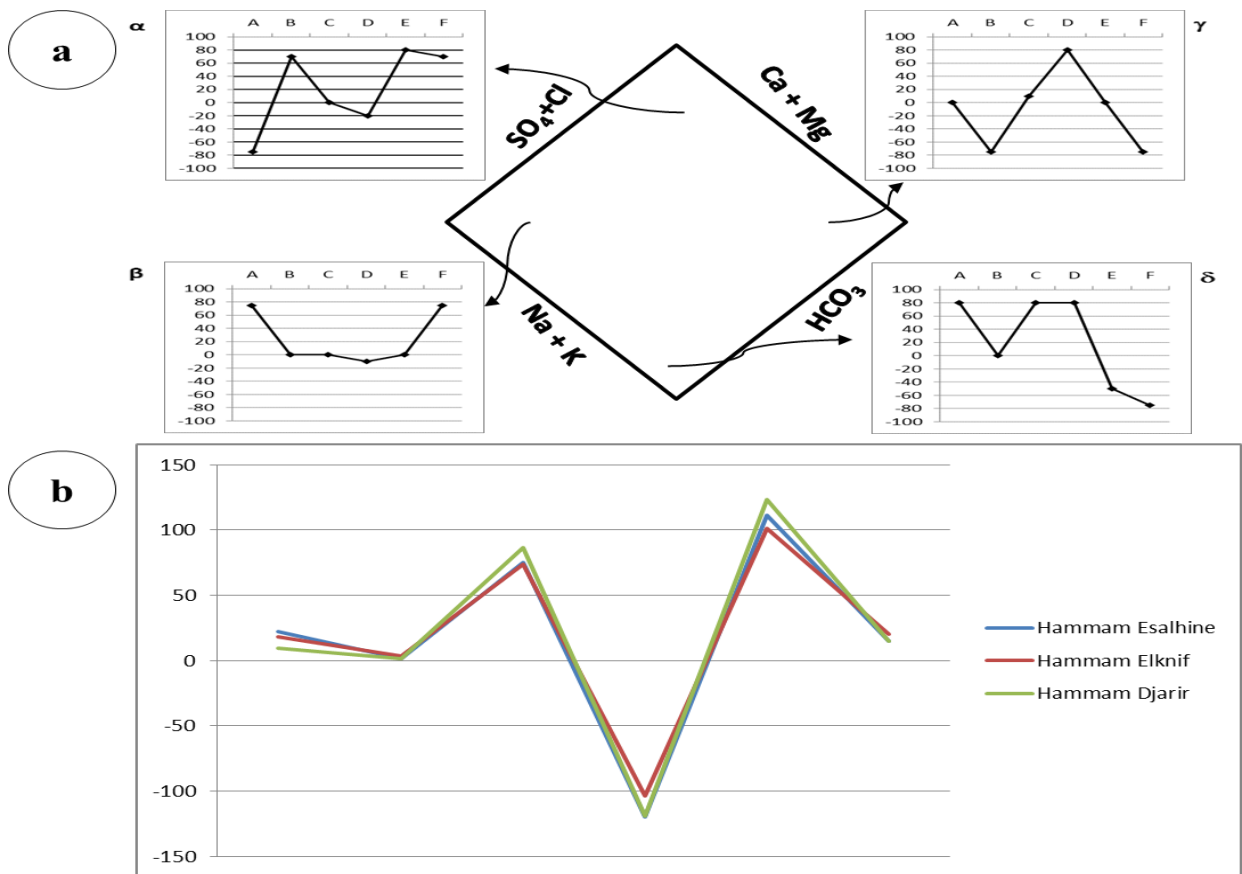


Figure 5. Diagrams of: (a) the international institute of geothermal research applied to the thermal waters (IIRG), ( $\alpha$ : Evaporative sequence;  $\beta$ : Circulation in limestone;  $\gamma$ : Deep circulation through a crystalline basement;  $\delta$ : Argillaceous formation); (b) IIRG applied to sampled waters.

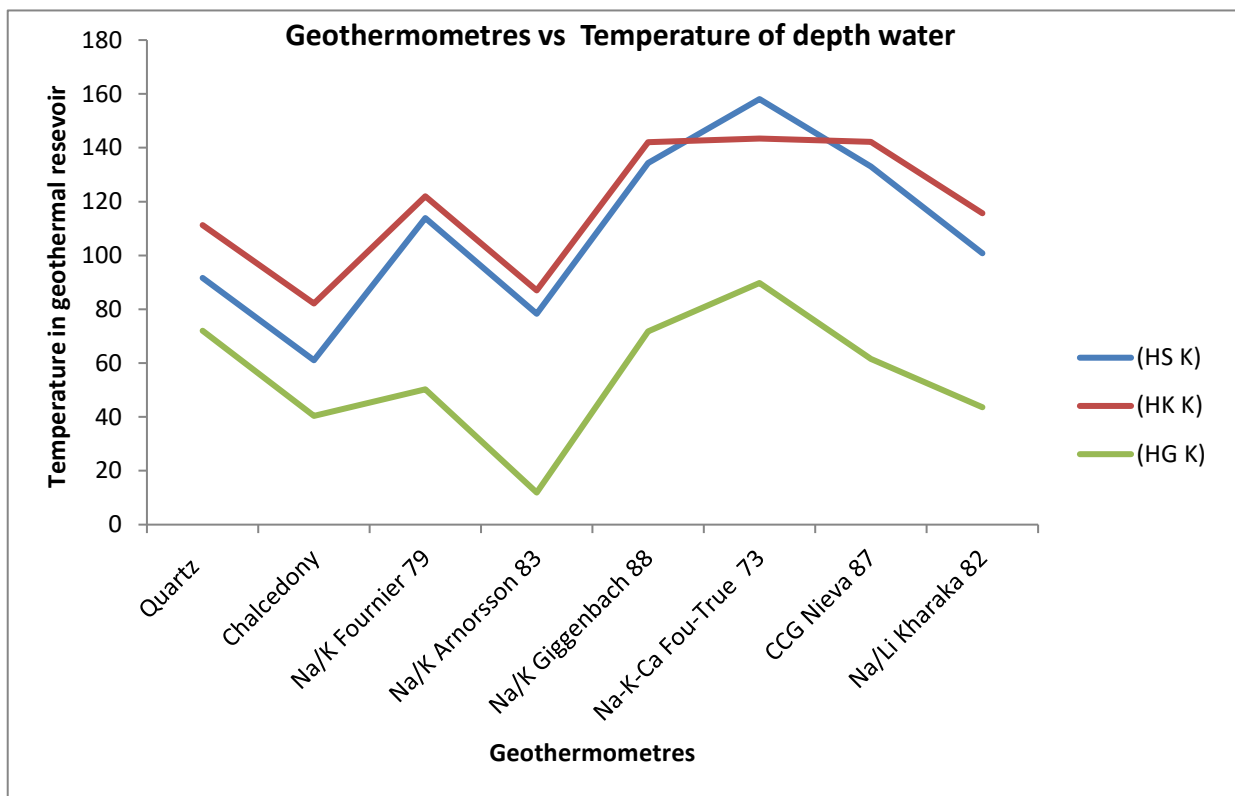


Figure 6. geothermometers vs temperature of water in depth

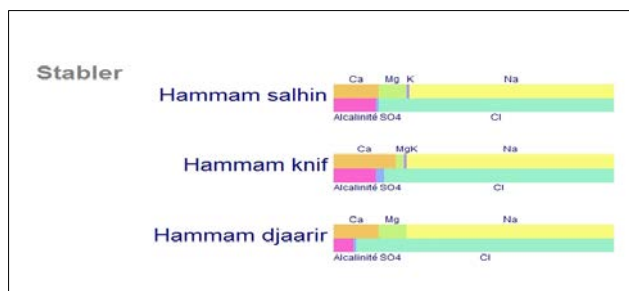


Figure 7. Stabler diagram of thermal waters sampled from the region of Khenchela

#### 4. CONCLUSION

The springs Water's flows through different hydrogeological pathways and its sources vary significantly. This diversity is illustrated by the observation that, as shown in Berkaloﬀ's graphical analysis, thermal mineral waters exhibit overlapping trajectories indicating their different origins and evolutionary histories.

The mineralogical compositions of the waters from Hammam el-Knif and Hammam Djaairir reveal a distinct geochemical signature characterized by the presence of carbonate and evaporite minerals, as indicated in the Piper diagram. The prevalence of dissolution processes targeting calcite, gypsum, and halite underscores the profound impact of both carbonate formations and soluble evaporites on the aqueous geochemistry of the region. These findings highlight the intricate interactions between the aquifer's waters and its geological framework, reflecting the dominant influence of dissolution phenomena in shaping the chemical character of the hydrology. Overall, this study underscores the importance of understanding the geochemical dynamics driven by carbonate and evaporite dissolution processes in evaluating the water quality and geological context of the region.

The geothermometers assessments reveal significant variation in subsurface reservoir temperatures. Estimations range from 12°C to 158°C from Na/K (Arnorsson 1983) and Quartz-Chalcedony geothermometers show a range of 40-111°C. These findings highlight the variability in geothermometric analysis methodologies.

The region's IIRG diagram is adjusted to the "α" standard reference, which is a feature of evaporitic series. Water circulation in carbonated reservoirs with high evaporation is depicted in Parameter C. The dissolution of the halite formation present in the study area is related to the origin of chloride, with evaporates being the primary source.

The findings of the current study demonstrate a strong relation between the hot springs' chemistry and the geology of the region, the water's path in the

underground predicate about the water's facies. The chemical compositions show an important therapeutic potential of the studied waters for different disease and lead us to recommend a serious investigation about a possible use of those waters in a medical purpose.

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