Journal of Materials and
Environmental Sciences
ISSN: 2028-2508

J. Mater. Environ. Sci, 2017, Volume 8, Issue 12, Page 4253-4263

http://www.jmaterenvironsci.com/

Isotope studies and chemical investigations of hot springs from North-Eastern Algeria

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Received 20 Jun 2016,
Revised 17 Oct 2016,
Accepted 23 Oct 2016

Keywords

- ✓ Algeria
- ✓ Geochemistry
- ✓ Geothermometers
- ✓ IIRG
- ✓ Isotopes
- ✓ PCA
- ✓ Thermal Waters

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Abstract

To improve our understanding of the origin of thermal water from North-Eastern Algeria, hydrochemical facies, isotopic characteristics to identify the major geochemical processes that affect water composition, for this purpose, a multidisciplinary approach was adopted, including hydrogeochemistry, isotope hydrology and principal component analysis (PCA). Eleven samples collected from thermal springs in 2015 vary in temperature between 38 and 96 ◦C, a near neutral pH and very high values of electrical conductivity. Two groundwater types were identified: highly mineralized Na-Cl type representing the deep thermal waters and Ca-SO_4 type determined the presence of evaporite deposits (Triassic) along the circuit of upwelling. The application of IIRG method illustrates three rectangular configurations which the first corresponds perfectly to the standard diagram γ, indicating a deep circulation of fluids, second corresponding to water circulation through the evaporate sequences, and the last belongs to intermediate between the standard α and γ, due to possible mixing in thermal waters with surrounding groundwater.The isotopic results (δ O18, δD) (respectively −9.95 to −7.72 ‰ and from −61.99 to −38.20 ‰) fall on the Global Meteoric Water Line (GMWL) indicate a meteoric origin of the thermal water (rains at higher altitude). In order to know the state of fluid-mineral equilibrium, saturation index (SI) was used; the most of the thermal waters have Chalcedony and quartz near or slightly above the saturation limit for equilibrium. In present study, multivariate statistical method - Principal component analysis PCA - is used; PC1 (41%) explains the minerality, (ionic composition), for which temperature is of secondary importance PC2 (18%).

1. Introduction

Because of the various uses that can be made of hot waters, thermal springs have attracted considerable attention since antiquity [1]. Ancient civilizations revered thermal springs because they were believed to have supernatural and healing powers [2].

Geothermal fields are widely being studied to understand the mechanism of hot springs that is why; many countries have conducted research into geothermal resource exploitation in recent decades. The chemistry of thermal waters has attracted the attention of numerous studies, Most of these studies have focused on three aspects: (i) the interaction between thermal waters and wall rock has a fundamental control on the chemical characteristic of thermal waters (e.g. Gemici et al. 2004; Cruz and Franca, 2006); (ii) the origin of geothermal waters can be traced by using stable isotope composition (Papp and Nitoi, 2006; Hamed et al., 2014); and (iii) the reservoir can be estimated through the use of chemical geothermometry (Houha 2007; Ben Abidate, 1998).

There more than 200 thermal springs on the Algerian territory, situated in different areas with complex geological structure [3], this number increases regularly moving eastward. The regional geology marked by sedimentary rocks inherited from marine transgressions of the secondary and tertiary [4]. Hydrothermal systems can be found in various geological settings and are hosted in different types of wall-rocks, but generally are found in high heat flow and volcanic regions associated with tectonic plate boundaries, and/or in the areas with sedimentary rocks of high porosity and permeability, the water in the sediments is heated by the regional heat flow.

The major goals of geochemical studies in geothermal systems are to predict the subsurface temperatures, to understand the circulation of the thermal fluids and to have information on their origin [5]. Hydrogeochemistry, including isotope geochemistry, has greatly contributed to the present understanding of geothermal systems. The chemical and isotopic composition of the geothermal fluids provides information about their origin, recharge areas and flow patterns. In addition, geochemical analysis for major ions revealed fair assessment about chemical nature and sub-surface reservoir temperatures of thermal waters [6].

The present study is focused on the isotopic signatures and geochemical analyses of the thermal springs from North-Eastern of Algeria to understand the origin, determine the chemical processes governing the composition and circulation of these fluid s giving rise to salinities of these waters and estimation of the subsurface reservoir temperatures. To verify this, a combination of physically based tools, hydrogeochemistry including isotope, geochemistry and conventional chemical geothermometers and multivariate statistical analysis will have to be used. This combined approach is essential because none of these techniques alone is able to provide definite answers. The study area in northeastern Algeria appears as a slightly waved landscape, extending between the Saharien Atlas from South, the Mediterranean Sea to the North and by the Tunisian border to the east (Figure 1). Eleven samples of thermal spring's water samples were collected between November 2013 and April 2015. For this purpose, fieldwork and laboratory analyses were performed. The temperature, pH and conductivity of spring's water was measured directly in the field using a portable equipment, while isotopic and hydrochemical properties were analyzed in hydrogeology laboratory, Avignon (LHA), France. Thermals springs are frequently developed as spas and bathing facilities, have also been used for medical therapy and improving social and economic well-being. Other useful applications of thermal springs in volcanic regions are related to direct application of heat production for domestic use, greenhouse heat supply, and power production [7]. The applications depend on the discharge volume and temperature of geothermal resources.

2. Study area

The sampling locations were carefully selected according to their locations on the geographical, geological and thermal considerations.

2.1. *Geographical context*

Our study area is located in the Northeastern of Algeria, is limited by the Mediterranean Sea to the north, by the Northwestern part of Algeria to the west, by The Saharan Platform to the south, and by the Tunisian border to the east (Figure 1).

2.2. *Geological and hydrological context:*

The geology of Algeria is divided into two main structural units: the folded Tellian Domain in the north, and the Saharian Platform in the south, separated by the South Atlasic Flexure [8]. Our study area (Figure 1) is delineated by the following features: the Tellian Atlas to the north, large plains in the center and the Saharan Atlas to the south, is belongs to the Alpine structural domain (unstable) with significant seismic activity, it is characterized by complex geology of over thrusting allochthonous terrains; the geological formations are mainly carbonates and marls.

The northeastern domain made up of young mountains formed during Tertiary times by the Alpine orogeny. Alpine Algeria consists of a number of structural-sedimentary units, from north to south [9]:

- The Tellian Atlas is the nappe domain, with mountain basins, and a sedimentary column ranging from Jurassic to Miocene.
- The High Plateaus are the fore-land of the Alpine range bearing a thin sedimentary cover. Local distension mechanisms allowed the formation of intra-mountain basins
- The Saharan Atlas was formed from an elongated trough pinched between the High Plateaus and the Saharan Platform. During the Mesozoic times, the trough was filled by a powerful sedimentary series (7000-9000 m).

Eastern Algeria, the rainiest region of the country, is characterized by major climatic contrasts and semi-arid influence. It juxtaposes two opposed hydrologic systems: Mediterranean Sea basins at the north and closed sub-arid basins connected to Chotts and Sebkhas at south [10].

2.3. *Climate context:*

Due to its geographical position and climatic characteristics, Algeria is highly vulnerable to climate change [11]. In Our study area, the climate is transitional, has a temperate Mediterranean climate in the northern part, which includes the coast and the Tell Atlas (hot and dry summers, wet and fresh winters); semi-arid with irregular and low precipitation on high plateau in the center; and arid desert with extremely low annual precipitation beyond the Saharan Atlas. The temperatures range from very high to very low, over 45°C by day and - 5°C by night.

2.4. *Geothermal gradient*

Geothermal gradients are very useful; as indicators of subsurface temperature distribution; in the understanding of regional and sub-regional tectonics and in the assessment of geothermal resource potentials of an area. The distribution of geothermal gradient is directly related to the overburden thickness, lithology, tectonic activities (growth faults), and hydrodynamics of the basin [12]. In Our study area, the local geothermal gradients range from 25 to 45 °C/km. According to the relationship between water temperature and depth, the geothermal gradient for the Albian reservoir is about 4.1°C/100m [4].

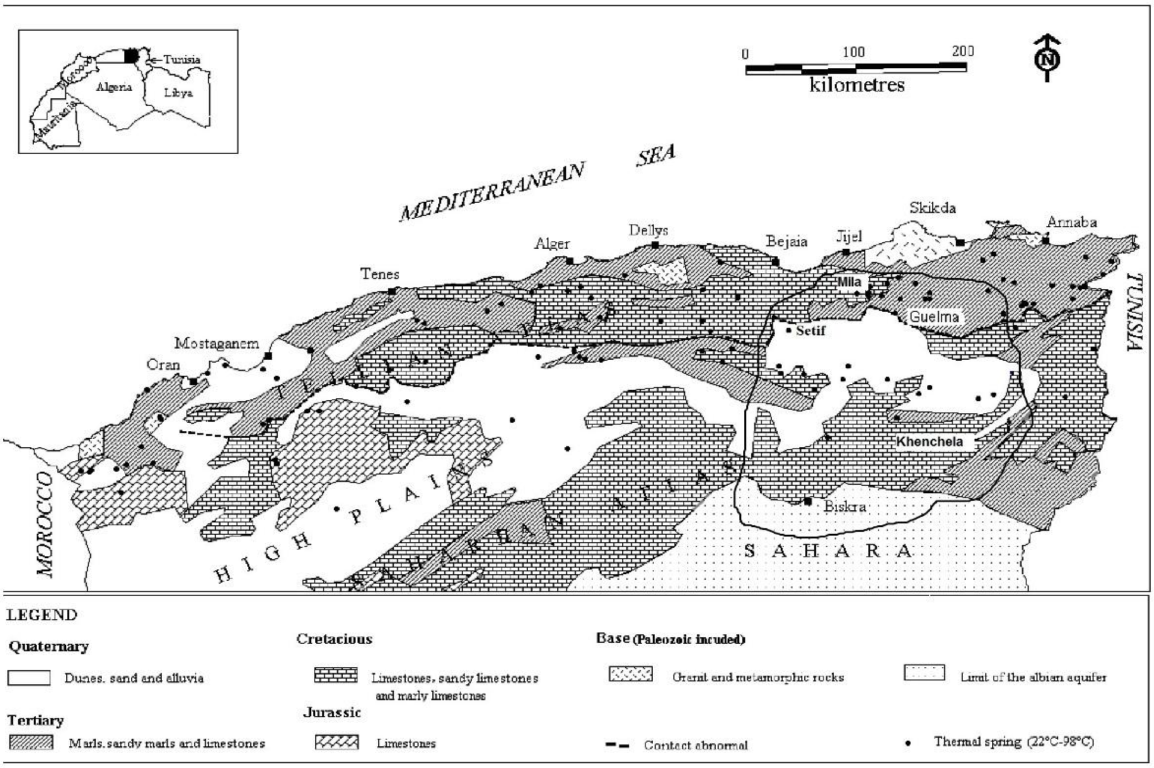

Figure 1: Geological sketch map of Northern Algeria [13], showing location of the thermal springs.

3. Methodology and materials:

Particularly critical for thermal waters is the need to identify the source of the spring and to sample as close to the spring as possible [14]. The collection of samples for chemical analysis is the first step in a long process was conducted in three stages; (a) field observation; (b) sampling and storing of the thermal spring waters in 150 ml new polyethylene bottles (for major ions analysis) and water samples for isotope determinations were stored in 50 ml high-density polyethylene bottles with small necks and caped and sealed with paraffin film, rinsed three times with the water to be sampled then transported in a cooler, Once arrived at the laboratory, the water samples are filtered at 0.45 µm. Then, the samples are stored in the dark, in a fridge, at 4°C, maximum one week before being analyzed; and (c) analysis, data processing and interpretation of results.

Eleven thermal waters were sampled in November 2013 and April 2015 for chemical and isotopic characterization, and were immediately bought to the laboratory in sterile conditions, all samples collected used in the spa. At all sampling points, physicochemical parameters of the waters, such as electrical conductivity (EC), pH and temperature were measured using a portable handheld digital multi-meter. The samples were analyzed for their major ion concentration as well as for their isotope contents (δ18O, δD).

Chemical and isotopes (δ18O and δD) analyses were carried out at Laboratory of Hydrogeology, University of Avignon (France). Anion species were analyzed using a Dionex Ion Chromatograph equipped with an automatic sampler with a precision better than ± 5%. Silica (SiO_2) was analyzed using colorimetric methods, Cations species were analyzed using Atomic Absorption Spectrometer, for δ18O and δD isotope analyses using an isotopic ratio mass spectrometer.

Groundwater chemical facies were determined from the Piper diagram using the computer software “Diagramme” developed by Simler, 2014 and AquaChem 2014.2 for ternary diagrams. We use the GeoT code, which uses as input the chemical composition of water and saturation indices of minerals to calculate water-rock equilibrium over a temperature and Principal Component Analysis (PCA) has been achieved with the use of Hydro AQUA software [15].

4. Results and discussion

4.1. *Physicochemical parameters*

The in-situ parameters are reported in Table 1. The temperatures of thermal waters are between 38◦C measured in spring of Hammam Garir and 96◦C including the hottest spring in Algeria (96°C) situated in the Hammam Meskhoutine area. These springs have been classified with respect to their temperatures: 45% are Orthothermal 37-45°C and 55% are Hyperthermal above 45°C. The different outlet temperatures of the thermal springs are attributed to local conditions depends on the velocity of water flow, time of circulation and fracture characteristics. The high temperature of a spring depends on both the depth and the upwelling speed [16]. The temperature of the thermal spring thus reflects the depth of penetration of the water and the rate at which it ascends to the surface [17]. The lowest temperatures are due to cooling caused by mixing between the deep thermal waters and the shallow meteoric waters and may be due to greater meteoric recharge or greater heat conduction due to shallow reservoir depths.

The pH values of these springs vary from slightly acidic to slightly alkaline. The maximum value of pH was recorded as 7.7 at (HM M) Hammam Mechta Smara Mila and the minimum value of pH was recorded as 6.7 at (HS K) Hammam Salihine khenchela. As per the findings, it was observed that the water was slight alkaline in nature which might be due to the presence of the dissolved salts in the water

The electrical conductivity was found to be quite high, the maximum value of conductivity measured at temperature of sample was recorded as 14780S/cm at Hammam Salihine Biskra and the minimum value was recorded as 2040 S/cm at Hammam Mechta Smara (Table 1). Due to the presence of high amounts of minerals in the water and many salts are more soluble at higher temperatures, these salts and minerals enter the water from rocks and sediment in contact with it, the hot springs showed higher conductivity value related to the high total dissolved solids (TDS).

Table 1: Chemical and isotopic composition of sampled waters [a]

Springs		T°C	pH	c25°C	Ca	Mg	Na	K	HCO3-	F	Cl	Br	SO4	NO3	SiO2	Li+	18O	2H
H Elkenif Khenchela	**HK K**	46	7.5	4310	189.08	16.73	695.93	16.79	314.76	0.79	879.54	0.57	469.67	5.04	49.2	0.341	-8.88	-58.31
H Salihine Khenchela	**HS K**	72	6.7	3550	119.40	21.78	568.17	17.89	284.26	0.37	779.54	0.40	227.14	1.84	45.3	0.192	-9.00	-56.70
H Gaarir Khenchela	**HG K**	38	7.6	6440	261.31	44.48	1020.86	6.35	201.30	0.38	1847.71	0.42	551.30	0.25	26.9	0.059	-9.18	-57.06
H Salihine Biskra	**HS B**	45	7.2	14780	339.46	45.56	2936.65	79.58	386.74	1.75	4512.43	5.69	1485.09	n.d.	34.5	1.147	-8.83	-61.99
H El hadjeb Biskra	**HE B**	42	6.9	4410	434.23	79.54	461.76	43.75	134.20	0.66	538.67	1.78	1742.92	0.55	31.9	0.146	-7.72	-54.76
H Guerfa Guelma	**HG G**	60	7.5	2390	344.38	59.96	113.07	10.34	339.12	1.84	176.32	0.42	883.33	0.64	47.3	0.07	-7.99	-53.21
H Debagh Guelma	**HD G**	96	7.3	2190	222.43	20.09	209.58	22.51	345.26	2.86	314.77	0.45	391.92	0.45	68.99	0.20	-7.91	-48.94
H Ouled Ali Guelma	**HO G**	55	7.05	2494	244.10	43.00	35.685	6.02	250.22	2.30	190.20	1.25	310.00	0.22	50.20	0.10	-9.95	-59.23
H Guergour Setif	**HG S**	46	6.8	3920	162.00	93.55	476.09	11.7	310.23	1.45	794.74	1.22	374.4	0.10	32.25	0.50	-8.56	-51.01
H Soukhna Setif	**HS S**	42	7.6	3380	156.85	89.29	439.66	10.19	261.08	0.98	766.86	1.39	318.49	0.10	26.9	0.06	-8.84	-58.10
H Mchta Smara Mila	**HMM**	53	7.7	2040	108.45	41.82	102.56	4.62	200.10	0.56	180.56	2.20	210.28	0.35	15.50	0.04	-8.22	-38.20

[a] Values are expressed in mg/l except SiO_2 in mg/kg. Temperature is expressed in °C, pH in pH units. EC=electrical conductivity in S/cm at 25°C. The isotopic composition of oxygen and hydrogen are reported in δ unit per mil vs V-SMOW standard. n.d. =not determined.

4.2. *Water chemistry*

4.2.1. *Piper diagram*

The physical and chemical properties of the thermal water depend on the composition of the infiltrating solution, the migration depth, the residence time of the thermal water in the migration pathway, and rock/water interactions in deep formations (and mixing with fresh precipitation). The physico-chemical characteristics of waters are connected to their underground path, temperature depth, the nature of the crossed rocks and the time residence. The thermal springs have a variety of chemical types; this variability is due to the lithological composition of the collection sites, which lie over several different geological and complex structures [3].

The different water samples have been classified according to their chemical composition using the Piper diagram [18], by using the software Diagram. This diagram (Figure 2.a) shows that the overall chemical character falls within the following two water types:

i) Most waters belong to the sodium-chloride type Na-Cl (Hammam Essalhine Khenchela), in general, all these are derived from the sodium-chloride waters as a result of physical environment or of reactions with wall rocks, which can be related to water–rock interaction [17] in the region of sampling and due the near-surface reaction of the thermal water with shallower salt-flat water, associated with Tertiary rocks Na-Cl type probably due to the Triassic halite dissolution [20]. According to the Piper diagram, it appears that the composition of circulating shallow waters is influenced by the halite layers.

ii) Secondly, we identify a typical SO_4-type composition for the thermal waters from the Saharan domain (HS B) and at the sprigs of Guelma (Hammam Debagh) probably due to the presence of gypsum and/or anhydrite ($CaSO_4$) in this aquifer and the clay fraction of the aquifer (Plio-Quaternary series) and sedimentary rocks. Aqueous sulfate and sulfate obtained by dissolution of minerals were precipitated as Baryte ($BaSO_4$). Samples are very high SO_4 contents and high Ca + Mg suggest a carbonate source with anhydrite. Similarly, the probable additional production of CO_2 originating from the reduction of sulfates would also contribute; under reducing conditions, a small amount of H_2S and CO_2 can be released during the bacterial reduction of SO_4 and hydrocarbons as follows [21]:

$$SO_4\ (\text{solid}) + CnHm\ (\text{gas}) \rightarrow CO_2\ (\text{gas}) + H_2O(\text{liquid}) + H_2S(\text{gas})$$

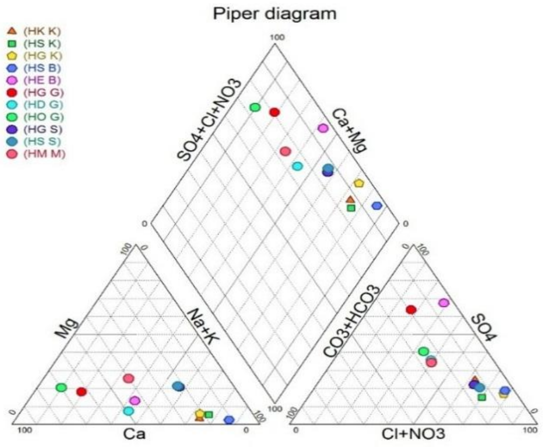

Figure 2.a: Piper diagram showing the chemical facies

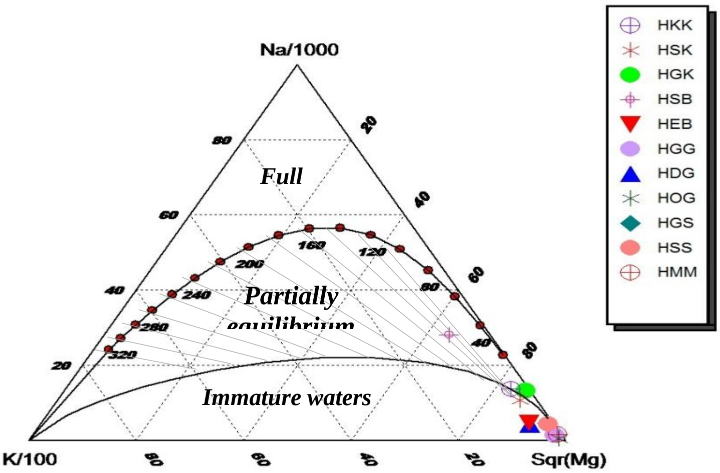

Figure 2.b: Na–K–Mg ternary diagram

4.2.2. *The Na-K-Mg ternary diagram*

Triangular diagrams are introduced as powerful tools in the interpretation of geothermal geochemistry. The Na–K–Mg ternary diagram proposed by Giggenbach (1988) was used to evaluate water–mineral (feldspars, clay) equilibrium status and distinguish different types of water originating in deep reservoirs. This method only describes equilibration processes at different levels and upflow rates in a thermal reservoir [22]. Chemical equilibration was tested with Giggenbach's (1988) ternary diagram using relative Na/1000, K/100 and $Mg^{1/2}$ contents, and works better for a more reliable estimate of reservoir temperatures (Figure 2.b), showed that the most thermal waters samples corresponded to immature water and are rather close to the Mg-corner, indicating that these waters have not attained full equilibrium. However, the samples of Khenchela plot only slightly above the Mg1/2 corner, closely to the boundary between mature waters and partly equilibrated. Triangular diagrams are introduced as powerful tools in the interpretation of geothermal geochemistry. The Na–K–Mg ternary diagram proposed by Giggenbach (1988) was used to evaluate water–mineral (feldspars, clay) equilibrium status and distinguish different types of water originating in deep reservoirs. This method only describes equilibration processes at different levels and upflow rates in a thermal reservoir [22].

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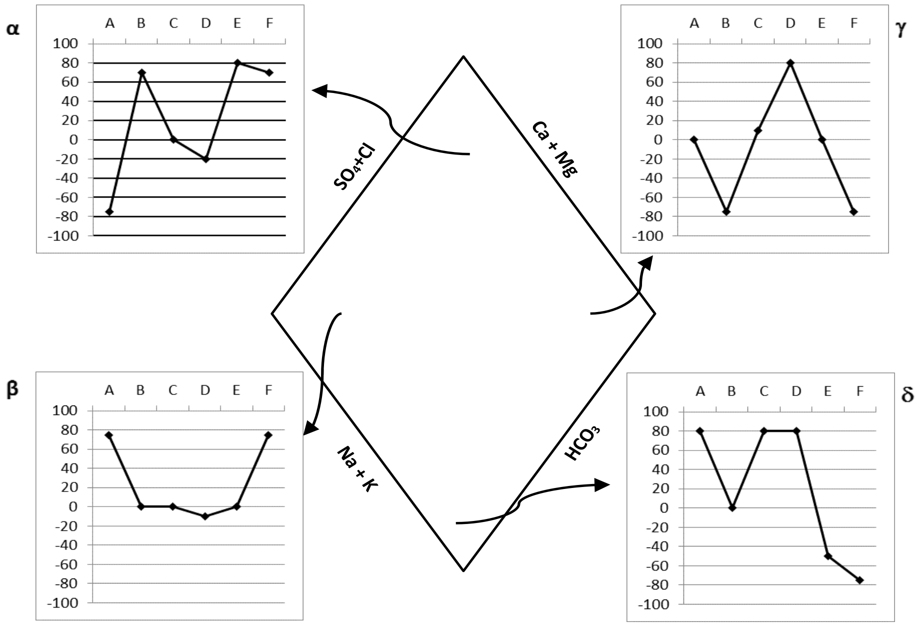
4.2.3. *The IIRG method*

International Institute of geothermal research IIRG, developed by D'Amore et al. (1983), constitutes the most used tool for the determination and identify the lithological nature of the origin reservoir of thermal waters [23]. Using meq/1 of the major chemical components of some water samples, we defined six new parameters for distinguishing water groups, on the basis of the geological and hydrogeological features of the main reservoir crossed by each water sample [24]. Using basic cations and anions determined six new parameters for distinguishing water groups based on the geological features of the main reservoir crossed by each water sample (Figure 3.a). Hydrochemical parameters are marked by letters from A to F. All the parameters discussed below are normalized between + 100 and - 100, so as to widen the range of values as much as possible. Σ (+) and Σ (-) represent the sum of the cations and anions, respectively, also expressed in meq/l.

The calculated values of the parameters A-F for the water samples have been plotted in rectangular D'Amore diagrams (Figure 3.b), almost all the samples (group a) corresponds to the standard rectangular diagram γ which is characterized by Na-Cl type water, indicates the flowing of thermal fluids through fractured levels, mainly the cretaceous limestone and indicating a deep circulation of fluids related to major tectonic discontinuities. The calculated values of the parameters A-F for the water samples have been plotted in rectangular D'Amore diagrams (Figure 3.b), almost all the samples (group a) corresponds to the standard rectangular diagram γ which is characterized by Na-Cl type water, indicates the flowing of thermal fluids through fractured levels, mainly the cretaceous limestone and indicating a deep circulation of fluids related to major tectonic discontinuities.



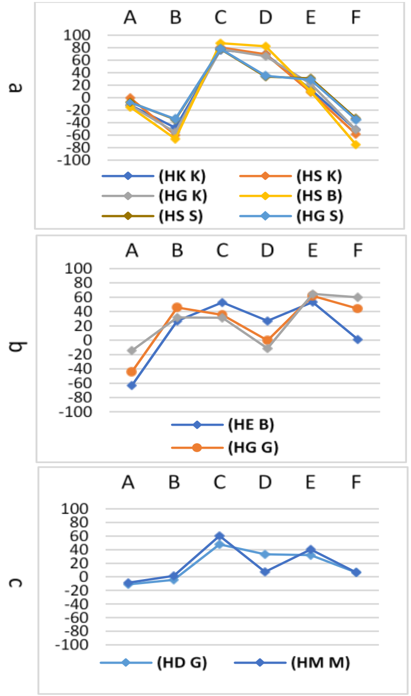


Figure 3.a: IIRG Reference diagram of the International institute of geothermal research

Figure 3.b: I.I.R.G. diagram applied to studied waters

α: Evaporative sequence
β: Circulation in limestone
γ: Deep circulation through a crystalline basement
δ: Argillaceous formation

The specters are characterized by high contents of parameters C and D indicate waters deriving from 'flysch' or 'volcanites', and low values of the parameters B and F points out that Na and K concentration in the water is higher in relation to Ca concentration (Na-Cl water type). However, the samples (group b) related to the Ca–SO4 type shows a rectangular configuration α corresponding to water circulation through the evaporate sequences (Figure 3.b), and heated in depth and acquire sulfates mineralization by leaching of evaporitic minerals contained in the Triassic formation located in the hydrothermal conduit (fault), and/or by oxidation of pyrites, giving rise to the Ca–Na–SO4 water type [25]. The specters are characterized by high contents of parameter E distinguishes between circulations in carbonate reservoirs and those in sulphate-bearing reservoirs. According to the Piper diagram, the spring HDG and HMM (group c) belongs to intermediate between the standard α and γ, we suggest that this similarity is probably due to mixed facies in the field probably due to the presence not only of chloride minerals but also of gypsum and/or anhydrite (CaSO4) in this aquifer.

4.3. *Chemical isotopes*

For several decades now, stable isotopes of the water molecule have been used as powerful tool for tracing precipitation, groundwater recharge and origin, river/ groundwater exchange, hydrograph separation, basin-water hydrology, the mixing of waters from different origins, evaporation, and the impact of climate change on groundwater. Isotopic compositions of hydrogen and oxygen of hot spring are regarded as effective proxies to trace water origin [26]. The δD and δ18O values of waters, especially when combined with the concentrations of conservative solutes are the best geochemical indicators of the origins, recharge locations, and flow paths of subsurface waters. Isotopic data can differentiate between the three possible types of origin of thermal water i.e. magmatic, oceanic and meteoric.

In order to know the origin of the geothermal fluid, the isotopic signature [27], constitutes a good indicator for any magmatic or meteoric contribution in geothermal waters. Both δ18O and δ D contents depend on many factors such as altitude, latitude, and precipitation in the study area [28]

The results of stable isotope analyses in thermal waters are presented in Table 1. The values for ^{18}O and ^{2}H range from −9.95 to −7.72 ‰ and from −61.99 to −38.20 ‰ with respect to SMOW, respectively. The isotope analyses were reported in ‰ relative to the SMOW standard. Further, the relationship between δ18O and δD (Figure 4) for the thermal waters from the study area shows that these waters fall on and just below the global meteoric water line (GMWL), δ2H=8 δ18O+10, given by Craig (1961), while the second one is the Mediterranean meteoric water line (MMWL): δD= 8 δ18O+22 [29] and the regional meteoric water line (RMWL) calculated from the weighed annual mean of precipitation at Tunis-Carthage station, follows a linear regression: δ2H = 8δ18O + 12,4 [30]. Measurement reproducibility of duplicates was better than ±0.15‰ for δ18O and ±1‰ for δ2H.

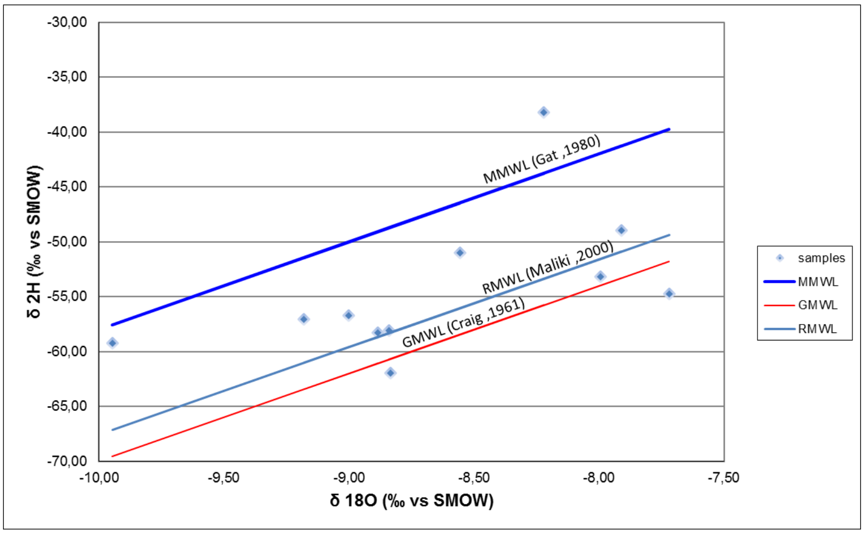


Figure 4: Isotopes plots for thermal waters together with GMWL [27], MMWL [29] and RMWL [30]

Figure 4, shows that most waters in the study area lie close to the Global Meteoric Water Line (GMWL) and (RMWL), but away from the Mediterranean meteoric water line (MMWL), which indicates a meteoric origin and may be from a higher altitude with increasing temperature with the exception of HMM water, which represents modern Mediterranean precipitation. Indicates also that precipitation of the dry and intermediate zones recharges the springs without significant evaporation prior to the infiltration as illustrated in figure for Biskra's waters (HSB and HEB) (climatic conditions).

The scale of the d18O shift is dependent on the reservoir temperature, the residence time and the degree of water–rock interaction, this negative δ18O shift is caused by the large water content of CO2 rich in the heavy oxygen isotope, which indicates less precipitation and a more arid climate. The changes in oxygen isotope composition of thermal waters between a deep reservoir and the surface may be caused by steam loss (boiling) or by dilution with near surface waters with different oxygen isotope compositions.

In a dry climate, the evaporation of surface waters (soil, lakes, ...), led couples 2H/18O to move away from their meteoric line according to evaporation line. The gap in relation to the Mediterranean meteoric water line MMWL is somewhat correlated with the electrical conductivity, the data points of Biskra deteriorates the quality of this correlation which is very good. In effect, by removing these singular points, the R² goes from 0.4321 to 0.6674. These basins can, therefore, be considered as well enough defined (all are perched systems) and the infiltration of the water is rapid (very weak evaporation) [30].

The physical structure of study area characterized by very heterogeneous terrain, although the diversity of the relief provides sharp contrasts in temperature, where it goes from Tell Atlas area (dominant high mountain range well-watered with rainfall ranging from 700 to 1200 mm per year, where the highest peak is Mount Chelia in the Aures mountain ranges which sits at 2,328 metres), to steppe landscape and pre-Saharan region of the Saharan Atlas, where rainfall rarely exceeds 200 mm per year, It lies almost entirely below the sea level and contains the lowest point in Algeria, −40 meters (Chott Melghir, Biskra)

4.4. *Mineral equilibration*

It is known that thermal waters have different temperatures and chemistry at subsurface conditions. By using the saturation index approach, it is possible to predict the reactive minerals in the subsurface from the groundwater chemical data without examining samples of the solid phases, can use it as geothermometers [32], this approach is called multi-component geothermometry, especially in the presence of carbonate and evaporate host rocks. All minerals in equilibrium at the same temperature converge to $SI = 0$; $SI < 0$ for an undersaturated solution, and $SI > 0$ for a supersaturated solution, if the mineral saturation index is below zero, the solution is undersaturated and the mineral will continue dissolving [34], but they are assumed to be ± 0.5 accurate [33].
Geochemical modeling using PHREEQC [33] interfaced with AquaChem 2014.2 enabled the prediction of the saturation state of minerals. Calculated saturation indexes for selected minerals are presented in Table 2, which may suggest different mineral–solution interactions. Thermal waters from the springs of the area are undersaturated with respect to gypsum, anhydrite, silica (amorphous) and halite. They are oversaturated or nearly in equilibrium with respect to calcite, aragonite, dolomite, quartz, calcite and chalcedony indicating that these minerals will have a thermodynamic tendency to precipitate at the point of sampling.

Table 2: Calculated saturation index (SI) for thermal waters samples

Mineral name	Anhydrite	Gypsum	Halite	SiO2(a)	Chalcedony	Quartz	Dolomite	Calcite	Aragonite
Chemical formula	**CaSO4**	**CaSO4:2H2O**	**NaCl**	**SiO2**	**SiO2**	**SiO2**	**CaMg(CO3)2**	**CaCO3**	**CaCO3**
HKK	-1	-0.9	-4.93	-0.53	0.24	0.61	1	0.79	0.66
HSK	-1.15	-1.28	-5.11	-0.74	-0.04	0.26	-0.06	0.13	0.01
HGK	-0.97	-0.81	-4.45	-0.73	0.06	0.45	1.05	0.68	0.55
HSB	-0.65	-0.54	-3.69	-0.66	0.12	0.49	0.8	0.6	0.47
HEB	-0.32	-0.19	-5.34	-0.69	0.1	0.48	-0.32	0	-0.14
HGG	-0.4	-0.42	-6.43	-0.65	0.08	0.41	2.08	1.21	1.08
HDG	-0.3	-0.72	-5.97	-0.7	-0.06	0.19	1.67	1.31	1.2
HOG	-0.89	-0.87	-6.86	-0.59	0.16	0.5	0.87	0.57	0.45
HGS	-1.19	-1.09	-5.13	-0.71	0.06	0.43	0.36	0.06	-0.07
HSS	-1.28	-1.15	-5.17	-0.77	0.02	0.4	1.67	0.72	0.59
HMM	-1.33	-1.28	-6.4	-1.09	-0.34	0.01	1.64	0.78	0.66

The gypsum SI, which is below zero is unsaturated, causing dissolution slowly, far from equilibrium, indicates that the waters from these springs have reached equilibrium with anhydrite (CaSO4) and are characteristic of waters circulating in gypsum aquifers. Anhydrite is under saturated in all spring waters, indicating that dissolution of SO4 is still going on in the reservoir [35], and increase until saturation is almost reached. Any increase in $SO4^{-2}$ accompanied by rising Cl^{-} describes the same dissolution reactions with halite [26], halite is found as less than zero, means all type of waters are undersaturated, resulting in the dissolution of evaporite deposits of Triassic by the waters during their ascent to the surface. However, the dissolution and precipitation of halite can result in cation and anion exchange of Na and Cl during dominant hydrochemical reactions leading to travertine formation and hot water evolution.
This suggests that the amorphous silica (the most soluble SiO2 polymorph) represent the case of silica dissolution-precipitation equilibria in hydrothermal systems. The reservoir waters are sub-saturated with respect to amorphous silica and they are also nearly in equilibrium is more likely to precipitate, because reaction kinetics for precipitation are relatively fast. The most of the thermal waters have Chalcedony and quartz near or slightly above the saturation limit for equilibrium. Only samples HSK, HDG and HMM have negative values but they are also nearly in equilibrium with calcite. Quartz solubility is a strong function of temperature.
Precipitation of aragonite, dolomite and calcite from a parent solution can be controlled by the temperament, degree of supersaturation caused by C02 degassing and (or) evaporation, the rate of precipitation, and thermophilic microbial factors [36]. Calcite saturation indices based on the ion activity products of Ca2+ and HCO3- indicate that all the thermal waters are super-saturated with respect to calcite, which is probably due to the cationic change of these thermal waters [24]., a saturation index of zero at Sample HEB indicate equilibrium between the solid and the solution phases with respect to a calcite. The thermal water springs are oversaturated with the dolomite, is possible to cause precipitation from the thermal waters, except the HSB and HSS. Aragonite is also under or near the saturation state, indicating that calcium carbonate deposits easily around the spring and due to loss of CO2 [37].

4.5. *Principal component analyses (PCA)*

The statistical methods used for data analysis of the samples were principal component analysis (PCA) [38]. Multidimensional data analysis methods are very useful when large quantities of data need to be analyzed for a target area. Principal component analysis (PCA) is a kind of factor analysis, which is useful to reduce the number of variables in a data set to a few components or factors that represent most of the variation in the original data simplifying multiple variable interpretations [39]. PCA is used for understanding the characteristics of water qualities in many fields [40]. These methods have been widely used to identify geochemical controls on the groundwater composition.

In present study, multivariate statistical method - Principal component analysis PCA - is used (Figure 5) , four data sets of the selected physical parameters (pH, T and EC), major ions (Ca, Mg, Na, K, HCO_3, Cl, SO4 and NO_3), trace elements (F, Br, NH_4, Li and SiO_2) and stable isotopes (18O and 2H) were used for PCA to identify the main hydrogeochemical processes governing the groundwater chemistry and to find their origin.

It indicates that the first three principal components together account for 72 % of the total variance in the dataset, in which the first principal component is 41 %, second principal component is 18%, and the third principal component accounts for 12 % of the variability much less important than the first two, have been eliminated and we use only two principal components would account for a meaningful amount of variance.

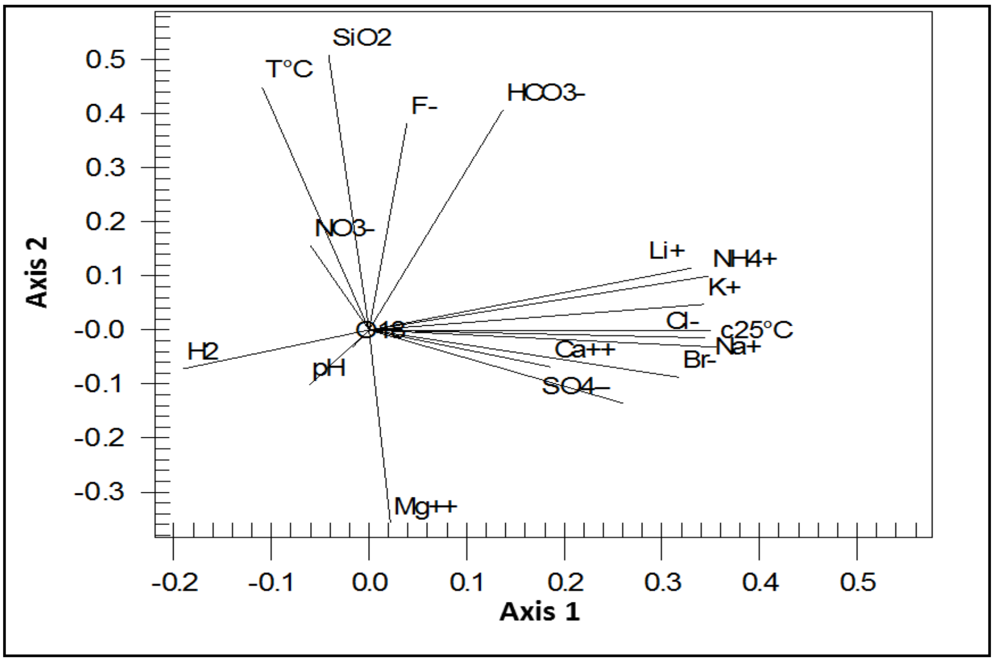


Figure 5: Biplot of the first two components of the PCA made with 18 variables

The first factor axis PC1 (41%) (Figure 5) opposes the major elements (soluble) and other parameters, the temperature hardly contributing to this axis. This is an axis of minerality, which opposes waters with low mineralization on those with high mineralization. This axis often comes first for hydrochemistry of the major elements in arid area.

This result confirms the effect of climate aridity, which is responsible for the concentration of major and some minor constituents in water. In this case, we have two possibilities were considered: either while recharging (during the infiltration process), or the thermal waters ascending from a geothermal reservoir may be cooled by mixing with cold, shallow waters, which tends to occur where there is a change in rock permeability. The answer to this problematic is going to be provided in the next paper

The second factor axis PC2 (18%) (Figure 5) is mainly influenced by temperature, silica and fluorine. This is the axis of thermalism, for which temperature is of secondary importance.

Conclusions

The application of isotope and geochemical techniques in North-Eastern of Algeria is an important tool to understand the chemical composition, origin, the chemical processes of the hydrothermal system. Geologic map and geothermal resource map were combined to show the locations of hot springs relative to local geologic, structural features and permeability. 11 Samples taken from hot springs has its temperature ranged between 38-96°C, the elevated temperature depends on the depth, the upwelling speed and the assumed thermal gradient. The pH values of these springs vary from slightly acidic to slightly alkaline, high conductivity due to the increased mineral and many salt ions which are more soluble at higher temperatures. Chemically, the thermal waters are of Na-Cl and Na-SO4 facies, which confirms the influence of the geological formations dominated by tertiary, carbonate and evaporate rocks, attributable to the variability of the lithological composition and related to different hydrogeological systems.

The higher contents of Na, K, Ca, Cl, SO4 and SiO_2 in thermal waters are attributed to a prolonged interaction between water and its wall rock during longer subsurface circulation and cation exchange in the carbonate and evaporate host rocks. Water–rock interaction under high temperatures in the geothermal reservoirs is responsible for the hydrochemical composition of thermal water, as the dissolution of anhydrite, gypsum, and dolomite controlled the water chemistry. Stable isotopic results (δ18 O and δ D) indicate that the thermal waters are of meteoric origin as they plot on the Global Meteoric Water Line GMWL, deeply infiltrated and heated by advective heat anomalies and raised up to the surface through deep-seated faults acting as hydrothermal conduits. Therefore, in estimating the oxygen-18 composition of deep geothermal water, two factors must be considered: (1) steam loss and (2) dilution by waters above the deep reservoir [41].

Principal component analyses PCA revealed that strong correlation coefficients between the elements and their close relation influence on the thermal waters. The two main factors: The dry zone, which is responsible for the concentration of chemical constituents in thermal water (PC1 41%), for which temperature of the thermal springs is of secondary importance PC2 (18%). It is the exception in this area. This aridity affects the chemical and isotopic chemical properties of thermal waters of this area complicating somewhat the chemical tracing [4]. We hope that this research will provide a scientific basis and additional information on the evaluation and sustainable exploitation for thermal water and contributes to ecotourism in Algeria.

Acknowledgements- This study was conducted as part of a Ph.D. research project at the University of Khenchela. The author wishes to thank Pr. HOUHA Belgacem (Khenchela University, Algeria) and Pr. Vincent Valles (Avignon university, France), for supervising this study and provided invaluable assistance with the field collection of samples considered and for their helpful discussion and constructive comments, and we would like to thank the research committee and the staff of Laboratory of Hydrogeology, University of Avignon, France, for their help during laboratory work (Chemical and isotopic analyses) in particular Simler, R. Finally, special thanks to the journal editors for their help, patience and constructive guidance during the completion of the manuscript

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(2017) ; http://www.jmaterenvironsci.com