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Geochemical Study of Mineralization of the Thermo-Mineral Sources in the North East of Algeria

Dounia Nechem[1*], Mani Hannouche[1], Nabil Bougherira[2], Hicham Chaffai[2]

[1] Geology Research Laboratory (LRG), Faculty of Earth Sciences Badji Mokhtar, Annaba University, P.O. Box 12, Annaba, Algeria

[2] Water Resource and Sustainable Development Research Laboratory (REDD), Faculty of Earth Sciences Badji Mokhtar, Annaba University, P.O. Box 12, Annaba, Algeria

* Corresponding author's e-mail: ndannaba@gmail.com

ABSTRACT

The majority of thermal sources in northeastern of Algeria, is home to a large number of Hammams (spas) with high geothermal potential (El Tarf; Guelma, Souk Ahras, and Skikda). These thermal springs fall into the low temperature category (between 30°C and 150°C), however Hammam Debagh's source being the warmest at about 90°C. Multiple field campaigns from 12 thermal springs were conducted in northeastern Algeria between 2020 and 2021 to highlight the geochemistry of these waters. The results show that these geologically protected waters have a totally stable geochemical composition, i.e., they have not undergone any chemical treatment or disinfection before being used thermally. Understanding the origin and mineralization of thermal waters in a continental Mediterranean environment is the focus of this investigation. The monitoring of physical indicators, including pH, temperature (°C), water conductivity, dissolved oxygen, flow, and turbidity, in conjunction with the use of the hydrochemical tool, chemical facies, and the saturation index, was done on the 12 of sites studied. Geological evidence has shown that these waters are typically found in deep aquifers and are subject to brittle tectonics. The findings of the investigations performed on the thermal waters revealed that for the evaporitic carbonated components, an enrichment in (Na^{+2}) and in (Cl^{-}) mostly attributable to a geological origin, on the other hand, a depletion of halite (under-saturated) and to a lesser extent, gypsum.

Keywords: thermo-mineral waters; North East of Algeria; Hammams; mineralization; water facies; saturation index.

INTRODUCTION

There is geothermal potential in North Africa, which explains why the north of Algeria has seen a lot of geothermal research [Aliouane, 2023]. In Turkey, hydothermal reservoirs are used for the treatment of musculoskeletal or skin health problems and for relaxation activities [Muazzez, 2018]. Due to its healing properties, natural thermo-mineral waters have been used by the Algerian people for generations, on the national scale, most studies carried out took part in the presentation of the thermalism of the Algerian North and its complex geological and tectonic mechanisms. Let us quote [Bekkouche, 2016; Belhai, 2017; Djemmal, 2018; Benmarce, 2021]. There are also other valuable works which contains a list of 51 springs, including 27 hot springs. This remains an important reference in the research of thermal stations in Algeria [Bouaicha, 2018]. We can learn more about the nature and chemical composition of thermal spring fluids by studying them through chemical analyses. The contribution of the analyzes also gives us other information on the origin of the water. In

order to do this, we simultaneously conducted a hydrogeochemical study focused on 12 of thermal spring control study, distributed over 04 district of the northeast of Algeria. The final objective of this work is to put hydrothermalism in the context of the region and to determine for each thermal spring; temperature at emergence; we found a significant number of thermal springs emerge with low or medium temperatures (ranging between 35.5°C and 85° to 90°C). Hammam Debagh's hot springs baths [Benamara, 2022].

The chemical facies, by the acquisition of the mineralization (mineral salts naturally dissolved in water), evaluate the index of saturation, which is done by the interaction between water and rock during the progression of groundwater. This will allow a better understanding of the mechanisms linked to the lithology and the nature of the thermal reservoir, hot spring baths of Hammam Meskoutine

METHODS

Geology overview

The study area represents a part of the alpine folded zone of North Africa which whose structure is extremely complex. The geology of the region, is conditioned by the existence, of several complexes formations of different structural. Facial zones, in most cases superimposed and trongly brought together by tectonic movements. Also, this area is included in the Tellian geological domain being part of the Tellian atlas. It is a domain of great thrusts, belonging to the alpine chain, which constitutes the frame of the reliefs of all northern Algeria, in the North of the South Atlas accident. The zone of the junction of these two structures of northern Algeria which received the name of the limestone chain has a complex constitution. The sub-autochthonous unit of the Kabyle ridge forms a narrow zone (4 to 8 km), subdivided two (2) sub-zones namely:

- The interior sub-zones which confine the Kabyle unit to the north;
- The outer sub-zone which confines the flysch units to the south.

Sampling and analysis method

The water's physical parameters (temperature (°C), pH, dissolved O_2, rate of salinity (TDS) and electrical conductivity) employing a multi-parameter Type WTW multi 3420 equipment and a WTW cond 3110 device to measure conductivity in situ. The fieldwork consisted in evaluating the quality of the thermo-mineral waters of 12 hot springs in the North-East region of Algeria. The water samples filled in special bottles in order to bring them to the analysis laboratory were taken during two periods (depending on the season): a period of high water during the month of April 2020. A period during the month of January 2021. The coordinates of the various water stations were positioned using a Garmin Wap (72H) global positioning system (GPS). The sources to be the subject of this study (Figure 1); belong to the meso and hypothermal classes.

The US Geological Survey disseminates the PHREEQC software [Parkhurst and Appelo, 2013] in natural and polluted waterways, PHREEQC is used to simulate chemical interactions and transfer. The best approach for assessing the lithological makeup of a thermal water reservoir is the IIRG method (International Institute for Geothermal Research). The basis for this method's operation is the use of concentration ratios for the principal elements, given in meq./l and as the sum of cations (+) and anions (-). As a result, the following six dimensionless parameters (*A*, *B*, *C*, *D*, *E*, and *F*) are established and standardized between -100 and +100:

$$A = 100 \times ((HCO_3 - SO_4)/\Sigma(-)) \quad (1)$$

This variable aids in differentiating between waters through evaporite layers and those traversing calcareous soils.

$$B = 100 \times ((SO_4/\Sigma(-)) - (Na/\Sigma(+)) \quad (2)$$

The ability to distinguish between sodium-rich waters found in sedimentary marly clay soils and sulphate-rich waters flowing in evaporitic soils is provided by parameter *B*.

$$C = 100 \times (Na/\Sigma(+) + Mg/\Sigma(-)) \quad (3)$$

The parameter *C* tends to differentiate between water obtained from flyschs or volcanic rocks and that originating from an evaporitic carbonate series or a schisto-quartzitic basement. Both types of water include significant amounts of sodium (Na^+), but the former has far less chloride (Cl^-) than the latter, which has a Na/Cl ratio near to 1.

$$D = 100 \times ((Na - Mg)/\Sigma(+)) \quad (4)$$

This variable distinguishes between the waters that flow through dolomitic limestones.

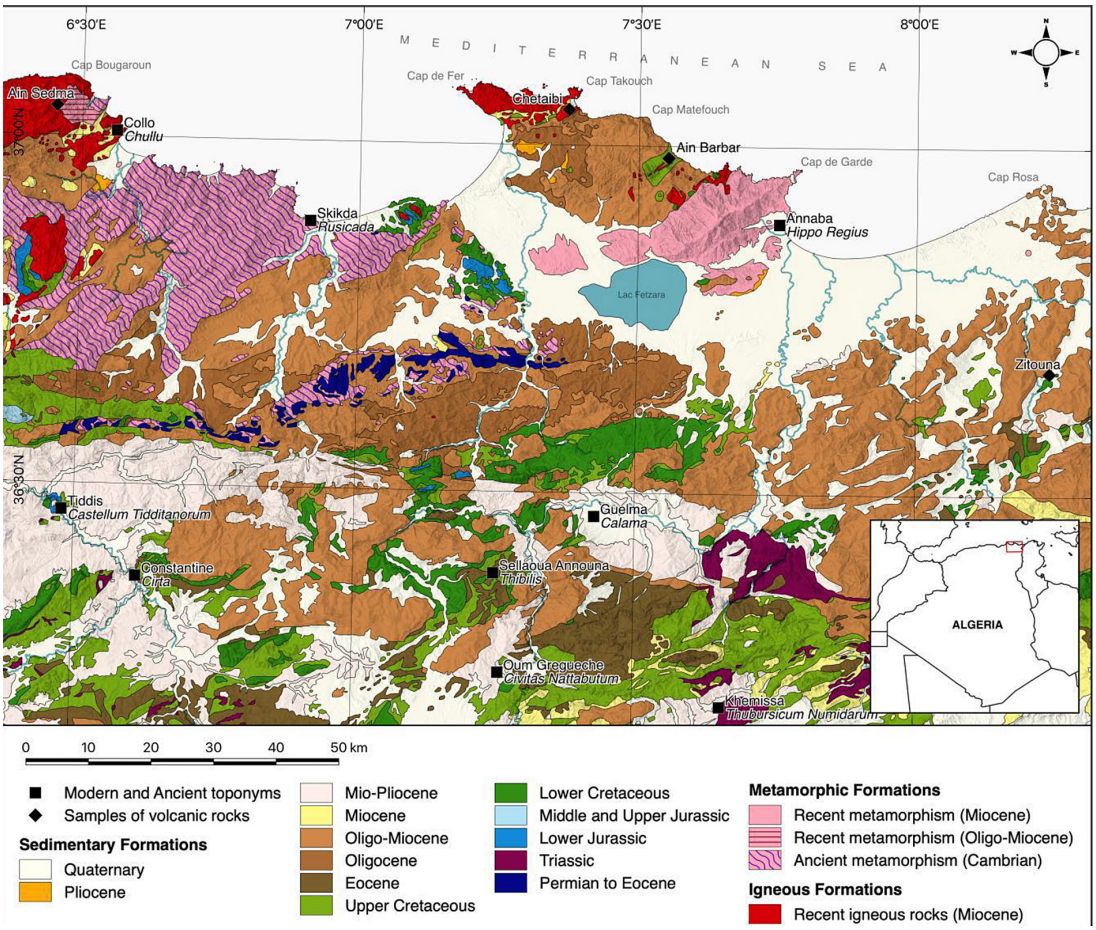

Fig. 1. North-east geological map (adapted by Djerad, 2022)

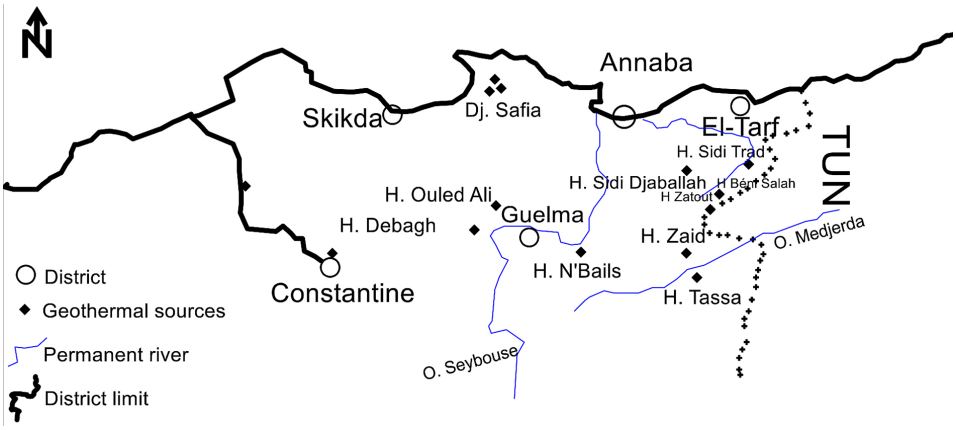

Fig. 2. Thermo mineral sources of northeastern of Algeria

$$E = 100 \times ((Ca + Mg)/\Sigma(+) - HCO_3/\Sigma(-)) \quad (5)$$

The major distinction between carbonate reservoir circulations and sulfated reservoir circulations is made by parameter *E*.

$$F = 100 \times (Ca - Na - K)/\Sigma(+) \quad (6)$$

The increase in potassium (K+) content in the water samples is revealed by parameter *F*.

RESULTS AND DISCUSSION

Geochemistry results

Table 1 presents the physical parameters of water samples from the study area. The pH varies between 6.40, and 7.43. The resulting pH is low, and water can dissolve large amounts of silicate minerals. The electrical conductivity of water

Table 1. The physic parameters

Springs	pH	Temp. °C	Cond.	Q(l/s)	Disso .O_2	Trb. (NTU)
H. N'Baîl	6.50	42.0	9540 µS/cm	NA	7.78	NA
H. Ouled Ali	6.64	51.3	1488µS/cm	NA	2.32	2.18
H. Debagh	6.60	85.0–90.3	2.02mS/cm	NA	5.05	2.60
H. Sidi Djabbalh	7.04	35.5	1661µS/cm	0.5	5.60	2.87
H. Sidi Trad	7.16	60.4	1.0 m.S/cm	1	4.90	2.43
H. Beni Salah	7.43	49.5	1.5 m.S/cm	0.8	6.38	2.31
H. Zatout	7.32	40.0	2.2 m.S/cm	0.6	5.46	2.62
H. Tassa	6.57	38.7	3.5m.S/cm	NA	0.88	13.2
H. Zaid	7.08	36.8	1858µS/cm	NA	3.60	9.51
H. Dj. Safia 1	6.75	39.6	2.59 m.S/cm	5.8	5.49	NA
H. Dj. Safia 2	6.40	42.3	1.6 m.S/cm	4.8	4.44	NA
H. Dj. Safia 3	6.50	44.4	2.57 m.S/cm	4.6	2.38	NA

Note: NA = not available.

increases as the concentration of dissolved salts rises, providing a broad indication of water quality [Gaur, 2022].

The electrical conductivity, which varies from 1488 S/cm to 3.5 m S/cm, is related to the salinity of the water. The development of such a comparatively low salinity demonstrates that the majority of water movement occurs in non-saliferous soils, most likely due to a fault system that is likely impacting the carbonate deposits. EC value is often greater than 1600 S/cm.

The values enable the creation of rectangle diagrams that may be compared to the authors' predefined reference diagrams (Figure 3a). This method displays two intermediate distinct rectangular configurations between the theoretical standards of reference for hot waters in Algeria's northeast (Figure 3b).

THEORETICAL PROPERTIES AND DISCUSSION

Carbonates are solids containing the carbonate ion: CO_3^{2-}. Three are essential:

- Calcite; mineral with formula $CaCO_3$ crystallizing in the rhombohedra system (diamond faces);
- Aragonite; a mineral with same chemical formula as calcite ($CaCO_3$) but crystallizing in the orthormbic system (usually in the form of small needles);

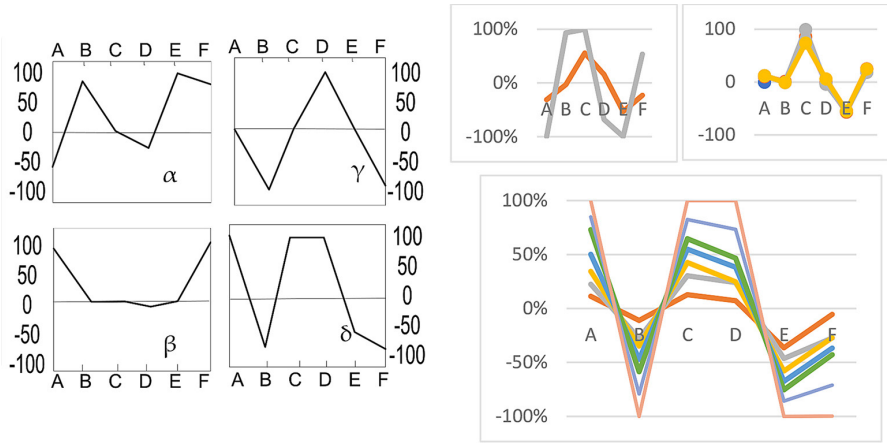

Figure 3. Schemes follow another format. If there are multiple panels, they should be listed as: (a) IIGR reference graphic (α: evaporative sequence, β: limestone circulation, and γ: deep circulation through a crystalline basement; δ: clayey formation); (b) application of the IIGR diagram to the thermal waters of the Northeast of Algeria

- Dolomite; mineral with the formula (Ca, Mg) CO_3 in which calcium and magnesium share the association with CO_3^{2-} ion.

In natural solutions, interactions with minerals are the main controls on alkalinity and calcium, calcite being the first mineral concerned. The calco-carbonic equilibrium reaction can be written:

$$CaCO_3(s) <=> Ca^{2+} + CO_3^{2-},\ \text{calcite} \quad (7)$$

or:

$$CaCO_3(s) + 2H^+ <=>$$

$$Ca^{2+} + CO_{2\,(g)} + H_2O,\ \text{calcite} \quad (8)$$

The calculation of the saturation index (SI) of minerals dissolved by water at the sampling point of Hammam's, during the period of April 2020 and January 2021 by the PHREEQC software, shows that several chemical elements are likely to be involved in precipitation/dissolution processes (see simulations in Table 2) in particular aragonite, calcite and dolomite. These carbonate minerals for the source of Hammam Tassa, Hammam Zaid, have a high saturation index respectively (1.26, 1.40 and 2.80) and (1.17, 1.31 and 2.68) for (aragonite, calcite and dolomite).

On the other hand, we find the SI of the other mineral species largely negative (-5.31) to (-6.05) for halite and finally anhydrite and gypsum are negative respectively. Finally, in this analysis no index close to equilibrium is presented. The CO_2, in the waters of Hammam's, produced by the decomposition of dolomite and/or calcite at high temperature that releases the gas, and we witness their decomposition. The amount of dissolved CO_2 remains proportional to pressure.

On the other hand, as soon as the total pressure becomes less than the partial pressure in CO_2, the latter begins to change phase. From a certain stage, the saturation index with respect to these minerals becomes positive and the water

Table 2. The saturation index

Springs	Anhydrite	Aragonite	Calcite	CO_2 (gas)	Dolomite	Gypsum	H_2 (gas)	Halite
H. N'Baîl	-1.00	0.02	0.15	-0.79	0.39	-0.87	-21.00	-4.49
H. Ouled Ali	-0.68	0.42	0.56	-1.85	1.25	-0.46	-22.60	-5.75
H. Debagh	-0.87	0.20	0.34	-1.75	0.88	-0.65	-22.40	-5.89
H. Sidi Djabbalh	NA	0.51	0.66	-2.42	1.76	NA	-24.00	-5.78
H. Sidi Trad	NA	-1.07	-0.92	-1.18	NA	NA	-20.80	-6.76
H. Beni Salah	-2.30	-0.44	-0.30	-1.34	-1.15	-2.08	-22.00	-5.51
H. Zatout	-2.37	-0.28	-0.13	-1.15	-0.82	-2.15	-22.00	-5.40
H. Tassa	NA	1.26	1.40	-1.75	2.80	NA	-23.20	-5.31
H. Zaid	NA	1.17	1.31	-2.30	2.68	NA	-23.80	-6.05
H. Dj. Safia 1	-0.96	-0.26	-0.12	-1.41	-0.41	-0.74	-21.4	-6.55
H. Dj. Safia 2	-1.24	-0.84	-0.69	-1.21	-1.26	-1.02	-20.80	-6.55
H. Dj. Safia 3	-0.96	-0.85	-0.71	-1.15	-1.84	-0.74	-20.60	-6.42

Note: NA = not available.

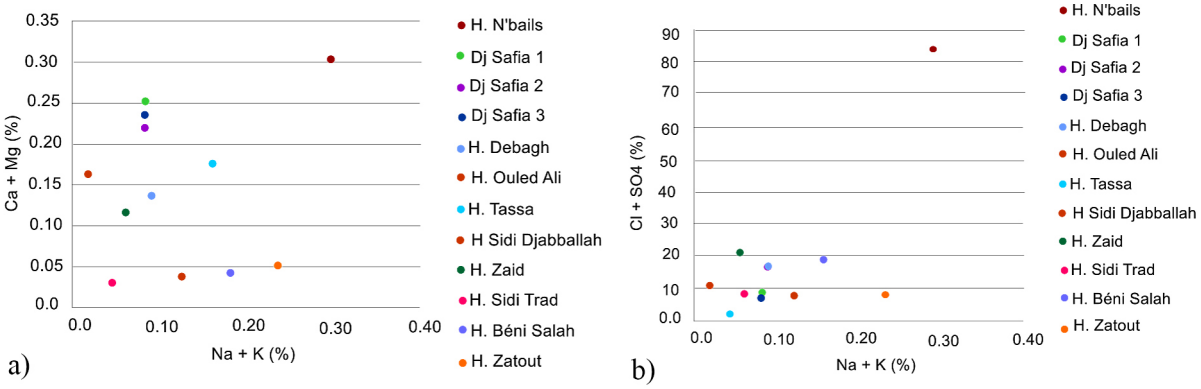

Figure 4. Diagrams created by Langelier and Ludwing and used to analyze the thermal waters in northeastern Algeria; relationships between (a) [Cl + SO4] and (b) [Na + K] and (c) [Ca + Mg].

is super-saturated with respect to dolomite (and/or calcite) which can precipitate. The water becomes encrusting. This encrusting character with the change in pH leads to the deterioration of the installations (pipes, pumps, etc.)

The previous study uses the Langelier-Ludwing diagram to illustrate an instance that has been recorded in the Tamlouka plain in northeast Algeria [Djorfi, 2018];

CONCLUSIONS

According to Algerian national regulations, thermal waters are waters captured from a natural emergence or borehole and which, because of their principle, the stability of their physical characteristics and their chemical composition may have therapeutic properties, prohibited for any agricultural use. There is the strongest relation between the air temperature and soil temperature. This study is a synthesis of 12 sources in North-East Algeria; whose main objectives are: thermal waters, by their physical characteristics, chemical compositions, and geological origin; characterization of mineral sources by their mineral content; the underground origin of thermo-mineral springs.

The deep temperatures recorded during emergence indicate an oscillating temperature range between 35.5°C and 85°C. Hence, the sources' medicinal effects. Natural mineral waters are known to have intrinsic qualities, and this review aims to examine them and their wide-ranging proven impacts on the prevention and treatment of much physiological and pathological status. Very low mineral content is defined as having less than 50 mg/L of mineral salt. Weakly mineralized or trace mineral is defined as having less than 500 mg/L of mineral salt (such as the spring at Sidi Trad); and "rich in mineral salts" is defined as having more than 1,500 mg/L of mineral salt (such as the source of N'bails, Tassa, or Zaid).

It is difficult to analyse the physicochemical properties of thermal waters from sources in North-east of Algeria, Although the aquifer's lithology is carbonate, there are several evaporitic Trias starta, giving it a high degree of variability that likely influences the groundwater's chemistry. Remains to be noted that chloride-sodium is the chemical facies for waters that passed through Triassic salt formations, bicarbonate-calcium is the chemical facies for fluids that have primarily carbonated circulation, and sulfate-calcium is the chemical facies for waters that have leached Triassic gypsum deposits. The study of the saturation index of thermo-mineral waters, showed that the interactions of solutions with minerals is the main origin of mineralization, and the (dolomites, calcites and aragonite) are the first concerned of the equilibrium equations.

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