KASDI MERBAH UNIVERSITY – OUARGLA
FACULTY OF HYDROCARBONS, RENEWABLE ENERGIES
AND EARTH AND UNIVERSE SCIENCES
DEPARTMENT OF EARTH AND UNIVERSE SCIENCES

Academic Master's Thesis

Domain: Earth and Universe Sciences

Field: Geology

Specialty: Hydrogeology

THEME

Regional geochemistry of mineral waters in Algerian territory

-Application of thermodynamic models-

Prepared by the student :

BOUSBAI SALAH Ahmed

under the supervision of the professor:

BELLAOUAR Abdelaziz

Defended on June 10, 2026, before the jury composed of :

MERABET Lakhdar	President
REMITA Abdelraouf	Examiner

Academic Year [2025/2026]

Acknowledgements

I would like to express my sincere gratitude and appreciation to my supervisor, ***Prof. BELLAOUAR Abdelaziz****, for his continuous guidance, valuable advice, and constructive feedback throughout the development of this work. His support, expertise, and encouragement were essential in the completion of this study.*

I am also deeply thankful for his patience and availability, which greatly contributed to improving the quality of this research.

Dedication

This work is dedicated first and foremost to my dear parents, in recognition of their endless love, sacrifices, and continuous support throughout my academic journey.

I also dedicate this work to my brothers and sisters for their encouragement, motivation, and constant presence in every step of my life.

My sincere dedication goes to my colleagues and friends for their help, support, and shared moments during this academic experience.

Finally, I dedicate this work to everyone who contributed, directly or indirectly, to the completion of this study.

TABLE OF CONTENTS

General Introduction **01**

Chapter I: Geological and Hydrogeological Framework of Algeria **04**

1.1 Geological Overview of Algeria **04**

1.2 Major Aquifer Systems **10**

Chapter II: Thermodynamic Models **14**

2.1 Chemical Equilibria **15**

2.2 Thermodynamic Models **18**

Chapter III: Materials and Methods **22**

3.1 Study Area Selection **23**

3.2 Sampling Methodology **24**

3.3 Thermodynamic Modeling Procedure **25**

Chapter IV: Results and Discussion **30**

4.1 General solution description and ionic composition **31**

4.2 Distribution of aqueous species **34**

4.3 hydrochemical facies **38**

4.4 Comparative Geochemical Analysis **50**

4.5 Discussion **52**

General Conclusion **57**

References **60**

Annex

الملخص

تهدف هذه الدراسة إلى تحليل الخصائص الهيدروكيميائية والسلوك الثرموديناميكي للمياه المعدنية في الجزائر، من خلال تحديد أهم العمليات المسيطرة على كيمياء المياه وتقييم حالات التشبع المعدني. وقد شملت الدراسة 36 عينة من المياه المعدنية، تم تحليل خصائصها الفيزيائية والكيميائية وتصنيفها هيدروكيميائياً باستخدام برنامج PHREEQC وقاعدة بيانات SIT لمحاكاة التوزيع الكيميائي وحساب مؤشرات التشبع.

أظهرت النتائج أن كيمياء المياه تتحكم فيها أساساً عمليات إذابة الصخور الكربوناتية، بحيث إنّ غالبية المياه ذات طبيعة كلسية-بيكربوناتية($Ca\text{-}HCO_3$) ، ومؤشرات التشبع تُظهر فرط تشبع بالنسبة للكالسيت وعدم تشبع بالنسبة للجبس والأنهيدريت والهاليت، مما يعكس استمرار تفاعلات الإذابة بين الماء والصخور. كما أظهرت بعض العينات تأثير التكوينات التبخرية من خلال ارتفاع تراكيز الكبريتات وظهور السحنة الكلسية-الكبريتاتية.($Ca\text{-}SO_4$)

وتؤكد الدراسة أهمية النمذجة الثرموديناميكية في فهم تطور المياه الجوفية في الجزائر وتفسير التفاعلات الجيوكيميائية المسيطرة على نوعيتها.

الكلمات المفتاحية: المياه المعدنية، الهيدروكيمياء، PHREEQC، النمذجة الثرموديناميكية، الجزائر.

Abstract

This study aims to analyze the hydrochemical characteristics and thermodynamic behavior of mineral waters in Algeria by identifying the main processes controlling water chemistry and evaluating mineral saturation states. The study included 36 mineral water samples, whose physical and chemical properties were analyzed and hydrochemically classified using the PHREEQC software and the SIT database to simulate chemical speciation and calculate saturation indices.

The results show that water chemistry is mainly controlled by carbonate rock dissolution processes, whereby the majority of waters are of a calcium–bicarbonate ($Ca\text{-}HCO_3$) type, and saturation indices indicate supersaturation with respect to calcite and undersaturation with respect to gypsum, anhydrite, and halite, reflecting ongoing water–rock interaction processes. Some samples also show a clear influence of evaporitic formations through high sulfate concentrations and the occurrence of the calcium–sulfate ($Ca\text{-}SO_4$) facies.

The study highlights the importance of thermodynamic modeling in understanding groundwater evolution in Algeria and in interpreting the geochemical processes controlling water quality.

Keywords: mineral waters, hydrochemistry, PHREEQC, thermodynamic modeling, Algeria.

Résumé

Cette étude vise à analyser les caractéristiques hydrogéochimiques et le comportement thermodynamique des eaux minérales en Algérie à travers l'identification des principaux processus contrôlant leur composition chimique et l'évaluation de leurs états de saturation minérale. Trente-six échantillons d'eaux minérales ont été étudiés. Leurs propriétés physicochimiques ont été analysées et leur classification hydrogéochimique a été réalisée à l'aide du logiciel PHREEQC et de la base de données SIT afin de simuler la spéciation chimique et de calculer les indices de saturation.

Les résultats montrent que la chimie des eaux est principalement contrôlée par les processus de dissolution des roches carbonatées. La majorité des échantillons présentent un faciès hydrochimique calcique-bicarbonaté (Ca-HCO_3). Les indices de saturation révèlent une sursaturation vis-à-vis de la calcite ainsi qu'une sous-saturation vis-à-vis du gypse, de l'anhydrite et de l'halite, traduisant la poursuite des interactions eau-roche. Certains échantillons mettent également en évidence l'influence des formations évaporitiques, caractérisée par une augmentation des concentrations en sulfates et l'apparition d'un faciès hydrochimique calcique-sulfaté (Ca-SO_4).

Cette étude souligne l'importance de la modélisation thermodynamique dans la compréhension de l'évolution des eaux souterraines en Algérie et dans l'interprétation des processus géochimiques qui contrôlent leur composition chimique.

Mots-clés : Eaux minérales, hydrogéochimie, PHREEQC, modélisation thermodynamique, Algérie.

General Introduction

General Introduction:

Water is one of the most essential and miraculous resources on Earth, covering more than three-quarters of the planet's surface, filling oceans, seas, rivers, and lakes. It is a fundamental component of all living organisms and ecosystems, and its unique chemical composition, despite its apparent simplicity, gives it distinctive physical and chemical properties vital for life. As stated in the Holy Qur'an: *"And We made from water every living thing"* (Surah Al-Anbiya, (30), highlighting the divine significance and centrality of water in sustaining life.

Over the past decades, increasing population growth, industrial expansion, and technological development have placed tremendous pressure on freshwater resources. These factors, coupled with intensified agricultural and industrial activities, have led to various forms of water contamination, including organic, mineral, microbial, and biological pollutants. Such challenges emphasize the need for a comprehensive understanding of water's chemical composition, mineral content, and hydrochemical behavior, which is the focus of the discipline of hydrogeochemistry.

Hydrogeochemistry studies the chemical characteristics of groundwater and surface water, their interactions with geological formations, and the processes that influence water chemistry, such as dissolution, precipitation, ion exchange, and mineral equilibria. Understanding these processes is essential for evaluating water quality and suitability for domestic, agricultural, and industrial use, and for developing sustainable management strategies, especially in arid and semi-arid regions such as Algeria, where groundwater represents a critical water resource.

Algeria possesses a rich diversity of mineral and spring waters, distributed across the northern mountainous regions and the southern Sahara. These waters are particularly valued for their natural purity, therapeutic properties, and mineral richness, including essential elements such as calcium, magnesium, sodium, potassium, iron, fluoride, sulfates, and other trace elements. Mineral waters contribute not only to human health and nutrition but also to medical, recreational, and industrial applications, while supporting local economies and regional development.

Despite their importance, there remain gaps in understanding the hydrochemical evolution, mineral stability, and thermodynamic behavior of Algerian mineral waters under varying geological and climatic conditions. The application of new thermodynamic models provides a modern approach to address these gaps by evaluating the chemical equilibria, solubility, and interactions of dissolved minerals. Such models enhance the predictive understanding of water quality, guiding the sustainable exploitation of these valuable resources while preserving their natural characteristics.

The central research question of this study can be formulated as follows: How can modern thermodynamic models be applied to characterize the hydrochemical properties.

Chapter 1 :

Geological and Hydrogeological Framework of Algeria

Algeria has a complex geological structure resulting from its long geological evolution and large geographical extent. This chapter presents an overview of the **geological and hydrogeological framework of Algeria**, highlighting the main geological units and structural domains of the country.

1.1 Geological Overview of Algeria

Algeria, located in **North Africa**, occupies a strategic geographical and geological position on the **northern margin of the African continent**. With a total surface area approaching **2.4 million km²**, it is the **second largest country in Africa**. The country extends approximately **2000 km from north to south** and about **1800 km from east to west**, which results in significant geological, geomorphological, and climatic diversity across its territory. Algeria is bordered by the **Mediterranean Sea to the north**, **Tunisia and Libya to the east**, **Niger and Mali to the south**, and **Mauritania and Morocco to the west**. This wide geographical extent contributes to the complexity of its geological framework and the diversity of its hydrogeological systems.

From a climatic perspective, Algeria encompasses **Mediterranean, semi-arid, and arid climatic zones**. Northern Algeria receives relatively higher rainfall, averaging around **1000 mm annually**, which supports agriculture and dense population distribution. In contrast, the **Saharan region** is characterized by extremely **arid conditions**, where rainfall may be absent for **several years or even decades**, and temperatures may exceed **55°C**. These climatic contrasts strongly influence groundwater recharge processes, surface hydrology, and sedimentary basin evolution. **[1].**

Geologically, Algeria exhibits a **complex and heterogeneous structure**, resulting from a long geological history involving **Precambrian cratonic**

formations, **Paleozoic sedimentation**, and **Mesozoic–Cenozoic tectono-orogenic events**, particularly related to the **Alpine orogeny**. The geological architecture of the country is traditionally subdivided into **four major morphological regions**, each characterized by specific lithological, structural, and geomorphological features.

- **The Tellian Atlas**

The **Tellian Atlas** forms the **northernmost geological province** of Algeria and extends along approximately **1200 km of Mediterranean coastline**. This region consists of a complex system of **mountain ranges, hills, and coastal plains**, which were strongly affected by **Alpine tectonic deformation** during the Mesozoic and Cenozoic eras. Structurally, the Tellian Atlas represents an important segment of the **Maghrebides chain**, which forms part of the broader **Alpine mountain belt** surrounding the Mediterranean basin.

Despite occupying only a **small proportion of Algeria's total surface area**, the Tellian Atlas contains the **most fertile agricultural land** and hosts **more than 90% of the national population**. Several important plains occur within this region, including:

- **Mitidja Plain** in central Algeria
- **Chélif Plain** in the western region
- **Seybouse Plain** in eastern Algeria

These plains consist mainly of **alluvial and sedimentary deposits** that form productive aquifers and fertile soils, which are essential for agriculture and water resources. The geological composition of the Tellian Atlas includes **folded sedimentary formations**, flysch sequences, and tectonic nappes formed during the convergence between the **African and Eurasian plates**. **[2].**

- **The High Plateaus (Highlands)**

South of the Tellian Atlas lies the **High Plateau region**, also known as the **Hauts Plateaux**, which constitutes a large transitional zone between the coastal mountains and the Saharan domain. This region is characterized by **extensive semi-arid plains**, interspersed with isolated hills and shallow depressions.

The High Plateaus extend from western Algeria toward the eastern parts of the country and include important areas such as:

- **Oran Meseta** in western Algeria
- The plains surrounding **Aïn M'lila**, **Sétif**, and **Constantine** in the eastern region

Geologically, the High Plateaus consist mainly of **Mesozoic and Cenozoic sedimentary formations**, including **limestones, marls, and sandstones**. These deposits form important groundwater reservoirs in certain areas but are often affected by **limited recharge due to semi-arid climatic conditions**.

- **The Saharan Atlas**

Further south lies the **Saharan Atlas**, a major structural and morphological feature forming a **long chain of mountains oriented in a northeast–southwest direction**. This mountain system extends from the **Moroccan border in the west to Tunisia in the east** and represents a transitional zone between the **Atlas mountain systems** and the **Saharan platform**.

The Saharan Atlas is composed primarily of **folded sedimentary rocks**, including **limestones, dolomites, sandstones, and evaporitic formations**. These rocks were uplifted and deformed during **Alpine tectonic events**, resulting in a complex structural framework of **anticlines, synclines, and fault**

systems. The region also plays a significant role in controlling **regional groundwater flow and basin formation**, influencing the hydrogeological characteristics of southern Algeria.

- **The Sahara Desert**

The **Sahara Desert** occupies the **largest portion of Algeria**, covering more than **80% of the national territory**. This vast region consists of diverse geomorphological features, including:

- **Sand dunes (ergs)**
- **Stony plains (regs)**
- **Rocky plateaus (hamadas)**
- **Isolated oases**

The Sahara contains **the majority of Algeria's hydrocarbon resources**, including large reserves of **oil and natural gas**, which constitute the backbone of the national economy. Important oasis towns such as **El Oued**, **Ghardaïa**, and **Djanet** are distributed throughout this desert environment and serve as major population and economic centers.

Two major geological massifs define the southern margins of the Algerian Sahara:

- The **Yetti–Eglab Massif** in the southwest
- The **Hoggar Shield** in southern Algeria

These regions consist mainly of **Precambrian crystalline rocks**, including granites, metamorphic rocks, and volcanic formations, which represent some of the **oldest geological formations in North Africa. [3].**

Major Geotectonic Domains of Algeria

From a geotectonic perspective, Algeria can be divided into **three major structural provinces**, reflecting the geological evolution of the African plate.

1. **The Alpine Domain (Northern Algeria)**

This region forms the northern boundary of the country and is characterized by the **Tellian Atlas and Maghrebides chain**, which were formed through **Alpine orogenic processes** resulting from the convergence between the African and Eurasian tectonic plates. The region includes several tectono-stratigraphic zones such as the **Internal zones**, **Flysch zones**, and **External zones**.

2. **The Saharan Platform (Central Algeria)**

The central part of Algeria is dominated by the **Saharan Platform**, a large and relatively stable geological unit composed mainly of **sedimentary basins** deposited during the **Paleozoic and Mesozoic eras**. These basins contain extensive **hydrocarbon reserves** and host some of the largest oil and gas fields in Africa.

3. **The Precambrian Shields (Southern Algeria)**

The southern region includes ancient **Precambrian massifs**, particularly the **Hoggar and Yetti–Eglab shields**. These crystalline basement rocks represent remnants of the **African Craton** and provide valuable insights into the early geological history of the continent.

The geological diversity of Algeria has significant implications for **natural resource distribution, hydrogeology, and environmental management**. The northern regions contain **fertile plains and productive aquifers**, while the

Saharan platform hosts **major hydrocarbon reserves** and **large groundwater systems**, including deep fossil aquifers. **[4].**

Moreover, the interaction between **tectonic structures, sedimentary basins, and climatic conditions** has shaped the hydrogeological framework of the country, influencing groundwater storage, flow patterns, and water resource availability.

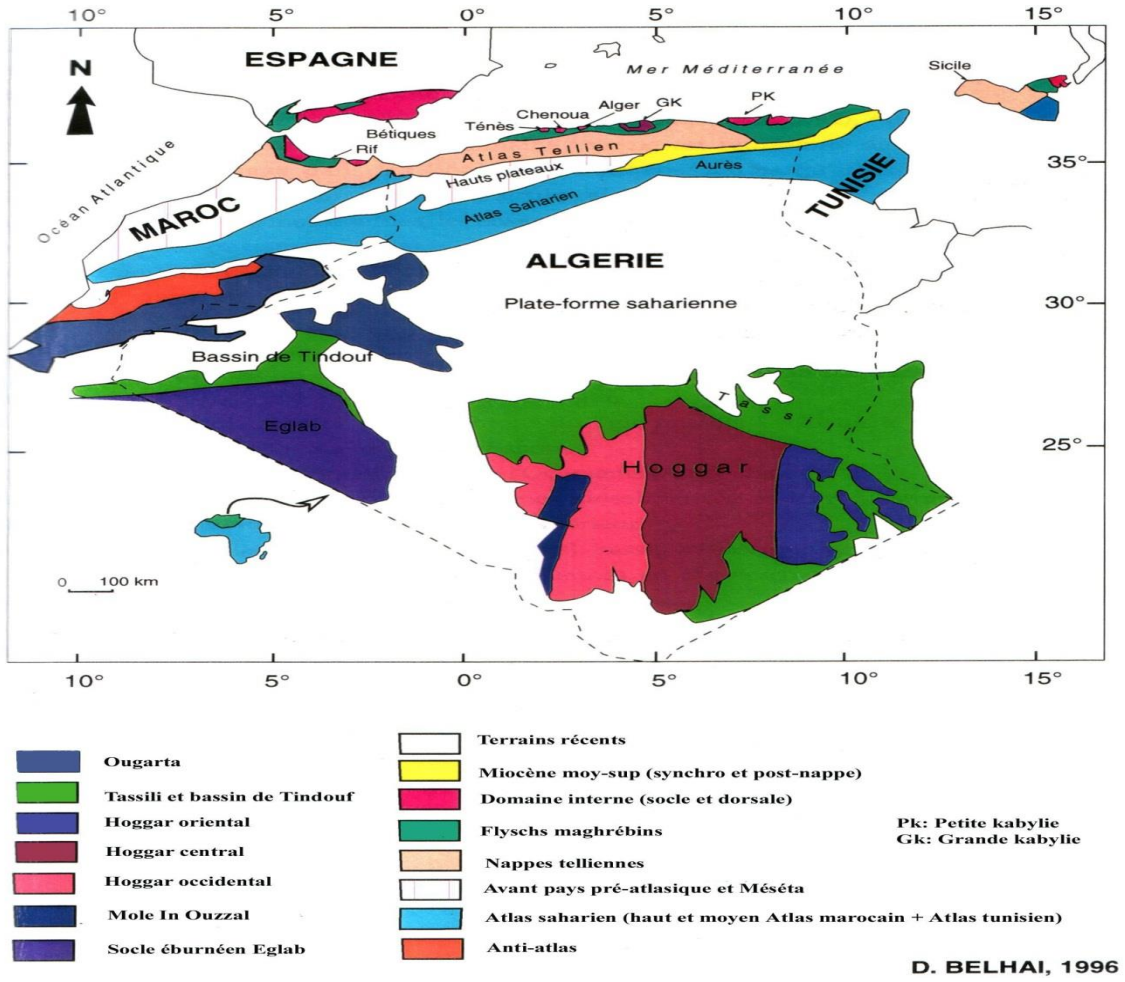

Figure 1: Geological map of Algeria.

1.2. Major Aquifer Systems

Algeria's hydrogeology exhibits considerable regional variability between the Northern Atlas and the Southern Sahara, reflecting differences in geology, climate, and aquifer characteristics. Groundwater resources and major aquifer systems are fundamental for domestic, agricultural, and industrial purposes, particularly in arid and semi-arid regions, where surface water resources are limited and highly variable. These systems not only sustain local communities but also support large-scale agriculture and industrial projects, making their management critical for national water security and sustainable development.

1.2.1. Northern Algeria Aquifers

The northern region is characterized by a complex tectonic and sedimentary history, resulting in the formation of numerous small, often isolated aquifer units. Higher rainfall in the north compared to southern regions contributes to a relatively higher recharge rate, with an estimated exploitable groundwater volume of 2.5 billion m^3/year and a recharge rate of 1.9 billion m^3/year. Northern aquifers are vital for supporting urban water supply, irrigation, and small-scale industry, and they are particularly sensitive to over-extraction and contamination from agricultural and urban activities. **[5].**

Northern aquifers can be classified as follows:

Table 1.1: Northern Algeria Aquifers

Aquifer Type	Geological Period	Lithology	Depth / Characteristics	Yield	Importance / Challenges
Unconsolidated sedimentary aquifers	Cenozoic–Quaternary	Marine and alluvial sediments	Coastal plains	Moderate to high, depending on porosity	Major source for urban water supply; vulnerable to pollution and

					salinization
Sandstone and limestone aquifers	Cenozoic–Mesozoic	Sandstone and limestone, often karstified	Mountainous areas	Up to 100 l/s	High-yield sources for local communities; karst systems sensitive to overuse and contamination
Alluvial aquifers	Recent	River-deposited unconsolidated sediments	River valleys	Localized, moderate	Supports localized agriculture; limited storage makes them sensitive to drought

1.2.2. Southern Sahara Aquifers

The Southern Sahara hosts vast, deep sedimentary aquifers, which contain approximately 5 billion m³ of non-renewable "fossil water" formed under paleoclimatic conditions. These aquifers are part of the Northwestern Sahara Aquifer System (NWSAS), extending over about 700,000 km² in Algeria. **[6].**

The system is divided into two main sub-systems:

Table 1.2: Southern Sahara Aquifers

Aquifer System	Depth	Lithology	Access Method	Remarks	Importance / Challenges
Continental Intercalaire (CI)	1,000–1,500 m	Deep sandstone	Foggara galleries	Fossil water, non-renewable	Provides long-term water security for desert communities and irrigation; over-extraction is irreversible
Complex	100–	Limestone (Senonian–	Wells	Shallow, limited	Supports local agriculture and

Terminal	400 m	Eocene), Tertiary sandstone		recharge	small towns; vulnerable to climate variability and limited natural recharge

Conclusion

This chapter provided a comprehensive overview of the geological and hydrogeological framework of Algeria, highlighting the strong relationship between geological diversity, structural evolution, and groundwater distribution. Algeria's complex geological history, shaped by Precambrian formations, Paleozoic sedimentation, and Alpine tectonic events, has resulted in a highly heterogeneous geological structure that directly influences the nature and availability of water resources.

The country is characterized by four major geological regions: the Tellian Atlas, the High Plateaus, the Saharan Atlas, and the Sahara Desert. Each region exhibits distinct lithological and structural features that control groundwater occurrence, flow dynamics, and aquifer development. The northern regions are dominated by folded sedimentary formations and relatively renewable aquifers, while the southern Sahara is characterized by extensive sedimentary basins and deep fossil aquifer systems with very limited recharge.

From a hydrogeological perspective, Algeria contains two main aquifer domains: the relatively small and renewable aquifers of Northern Algeria and the vast non-renewable aquifer systems of the Saharan Platform, particularly the Continental Intercalaire and Complex Terminal systems. These groundwater resources play a crucial role in supporting domestic consumption, agriculture, and industrial activities, especially in arid and semi-arid regions where surface water is scarce.

Overall, the interaction between geological structures, climatic variability, and sedimentary processes has shaped a highly contrasted hydrogeological system across the country. This complexity emphasizes the importance of integrated geological and hydrogeological understanding for sustainable groundwater management and resource protection in Algeria.

Chapter 2 :

Thermodynamic Models

Aqueous geochemistry, a core branch of hydrogeochemistry, focuses on understanding the chemical interactions between water and geological materials such as minerals, rocks, soils, gases, and organic matter. These interactions govern the composition, evolution, and quality of natural waters, including groundwater and surface water systems. The interpretation of hydrochemical processes requires a solid understanding of thermodynamic principles, particularly chemical equilibria, ionic strength, and activity coefficients, which together form the theoretical basis for geochemical modeling using tools such as PHREEQC.

2.1 Chemical Equilibria

Chemical equilibrium is a fundamental concept in aqueous geochemistry. It refers to a dynamic state in which the rates of the forward and reverse reactions are equal, resulting in no net change in the concentration of reactants and products over time. In natural water systems, most geochemical reactions are reversible and tend toward equilibrium conditions.

The equilibrium state of a reaction is quantitatively described by the equilibrium constant (K), which is defined as the ratio of the activities of the products to those of the reactants at equilibrium. **[11].**

General reaction:

$aA + bB \rightleftharpoons cC + dD$

the equilibrium constant is expressed as:

$K = (aC^c \times aD^d) / (aA^a \times aB^b)$

I where ai represents the activity of species.

In hydrogeochemical systems, several types of equilibria are particularly important:

- **Mineral dissolution and precipitation equilibria**: These processes control the concentration of dissolved ions in water. For example, the dissolution of calcite ($CaCO_3$) plays a major role in carbonate systems.
- **Acid–base equilibria**: These include reactions involving hydrogen ions (H^+) and hydroxide ions (OH^-), such as the carbonate system (CO_2–H_2CO_3–HCO_3^-–CO_3^{2-}), which is essential in regulating pH.
- **Redox equilibria**: Oxidation–reduction reactions determine the speciation of elements such as iron, manganese, and sulfur, influencing water quality and geochemical evolution.

Understanding chemical equilibria allows for the prediction of reaction direction, mineral stability, and solubility limits in natural waters.

Understanding chemical equilibria allows for the prediction of reaction direction, mineral stability, and solubility limits.

2.1.1 Ionic Strength

Ionic strength is a key parameter that characterizes the electrochemical environment of an aqueous solution. It reflects the total concentration of dissolved ions and their respective charges.

It is defined as:

$I = 1/2\ \Sigma(ci\ zi^2)$

Ionic strength affects:

- Solubility of minerals

- Dissociation of electrolytes

- Reaction rates and equilibria

2.1.2 Activity Coefficients

In real aqueous systems, ions deviate from ideal behavior due to electrostatic interactions. Therefore, the concept of activity is used instead of concentration **[12].**

$a_i = \gamma_i \times c_i$

Where:

- a_i = activity

- c_i = concentration

- γ_i = activity coefficient

In dilute solutions, $\gamma \approx 1$, while in concentrated solutions, $\gamma < 1$.

Models used:

- Debye–Hückel equation

- Davies equation

Chemical equilibria, ionic strength, and activity coefficients are essential for understanding water–rock interactions. They provide the theoretical foundation for thermodynamic modeling and are crucial for interpreting hydrogeochemical processes.

2.2 Applied Thermodynamic Models

Presentation of PHREEQC

PHREEQC is a widely used thermodynamic and geochemical reaction modeling program developed by the United States Geological Survey (USGS). It is designed to simulate a broad range of geochemical processes in aqueous systems based on thermodynamic equilibrium and kinetic reaction principles.

PHREEQC allows the calculation of:

- chemical speciation in aqueous solutions
- mineral dissolution and precipitation
- gas–water interactions
- ion exchange reactions
- surface complexation processes
- solid solution behavior

In addition, PHREEQC includes inverse geochemical modeling and reactive transport simulations, making it one of the most powerful tools in modern hydrogeochemistry.

Its flexible structure allows it to be integrated into different computational environments and used as a geochemical engine in environmental and hydrochemical studies **[13].**

Principles of Geochemical Modeling

Thermodynamic modeling in aqueous systems is based on equilibrium chemistry and the application of physical and chemical laws governing water–rock interactions.

1. Mass Balance Principle

All chemical elements are conserved during geochemical reactions. Although chemical species may change form, the total quantity of each element remains constant in the system.

2. Chemical Equilibrium

Natural aqueous systems tend toward a state of equilibrium where the chemical potential of species is minimized. At equilibrium, forward and reverse reaction rates are equal, and no net change occurs in concentrations.

3. Law of Mass Action

For a general reaction:

$aA + bB \rightleftharpoons cC + dD$

The equilibrium constant is defined as:

$K = (a_C^c \times a_D^d) / (a_A^a \times a_B^b)$

where activities (a) are used instead of concentrations to ensure thermodynamic accuracy.

4. Activity Corrections

Real aqueous solutions are non-ideal due to ionic interactions. Therefore, the activity of a species is expressed as:

$a_i = \gamma_i \times c_i$

$ai=\gamma i \cdot ci$

where:

- a_i = activity

- γ_i = activity coefficient
- c_i = concentration

This correction is essential for accurate geochemical calculations.

5. Saturation Index (SI)

The saturation state of minerals is determined using the Saturation Index:

- $SI < 0 \rightarrow$ undersaturation (dissolution occurs)
- $SI = 0 \rightarrow$ equilibrium state
- $SI > 0 \rightarrow$ supersaturation (precipitation possible)

This concept is fundamental for understanding mineral stability in natural waters.

Applications to Natural Waters

Thermodynamic models are widely used to study natural waters, especially groundwater systems, to understand their chemical evolution and water–rock interactions.

In hydrogeological systems such as those in Algeria, PHREEQC is applied to:

1. Hydrochemical Classification

Identification of water types (bicarbonate, sulfate, chloride, etc.) based on chemical composition.

2. Mineral Stability Analysis

Determination of mineral dissolution and precipitation processes such as calcite, gypsum, and dolomite stability.

3. Groundwater Evolution

Simulation of geochemical evolution along flow paths from recharge to discharge zones.

4. Water Quality Assessment

Evaluation of drinking water quality based on salinity, trace elements, and chemical balance.

5. Environmental Applications

PHREEQC is also used in:

- contamination studies
- acid mine drainage modeling
- soil–water interaction
- waste disposal simulations

Conclusion

Thermodynamic models based on PHREEQC provide a powerful framework for understanding geochemical processes in natural waters. By combining chemical equilibrium principles, mass balance, and activity corrections, these models allow accurate simulation of water–rock interactions and hydrogeochemical evolution

Chapter 3 :

Materials and Methods

This chapter describes the methodology used to investigate the hydrochemical and thermodynamic behavior of Algerian mineral waters. It presents the study area selection, sampling strategy, and the PHREEQC modeling procedure used to simulate aqueous speciation and mineral saturation states across 36 representative samples from different hydrogeological settings in Algeria.

3.1 Study Area Selection

This study investigates mineral water systems in Algeria, which are distributed across diverse hydrogeological settings including carbonate formations, sedimentary basins, alluvial deposits, and fractured aquifers. These geological environments strongly influence groundwater chemistry due to prolonged water–rock interaction processes. **[15].**

The selected study area includes representative mineral water springs and bottled mineral waters originating from different hydrogeological regions of Algeria, including the Aurès region and the Tellian Atlas to the north, and the Saharan platform to the south. These regions were selected due to their geochemical diversity and their importance for hydrogeochemical modeling.

3.1.1 Selection Criteria

Table 3.1: Selection Criteria for Water Samples[16].

Criterion	Description
Hydrogeological representativeness	Coverage of major Algerian aquifer systems (Tellian Atlas, High Plateaus, Saharan platform, Aurès)
Geochemical diversity	Variation in ionic composition, facies, and mineralization levels
Natural origin	Samples from sealed original bottles — no artificial treatment applied
Analytical reliability	Certified commercial production sources with documented composition

Criterion	Description
Modeling suitability	Full major ion analysis available for PHREEQC input (Ca, Mg, Na, K, Cl, SO_4, HCO_3, pH, T)

3.2 Sampling Methodology

Water samples were collected from commercially bottled mineral waters originating from different Algerian springs. Each bottle represents a distinct hydrogeological system. To ensure reliability, samples were obtained from sealed original bottles, sterile handling procedures were respected, and 36 representative samples were selected covering a wide range of geological contexts. **[17].**

To preserve the original geochemical signature, samples were stored at room temperature, protected from direct sunlight, kept sealed until analysis, no preservatives were added, and analyses were performed using the chemical data declared on the bottle labels, which are certified by the producer and comply with Algerian regulatory standards for natural mineral waters **[18].**

The complete dataset of 36 Algerian mineral water samples is presented below:

Table 3.2: Complete Chemical Composition of Algerian Mineral Water Samples (mg/L)

Sample	pH	T(°C)	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}	RS
El Melez	7.33	25	111	34	29	1	10	190	3.2	311	680
Sidi Rached	7.39	25	134.38	6.69	29.21	2.45	50	139	21.8	235	610
Togi	7.46	25	73.41	19.25	36	1.8	43.76	28.9	5.93	0	366
Ayris	7.78	25	65.6	6.8	28.5	1.9	37	75	2.7	234.24	276
Ovitale	6.92	25	80	14	30	1	50	75	5.1	214	360
Lejdar	7.53	25	64	37	30	4	41	66	0	308	660
Guerioun	7.28	25	72	27	11	2	21	11	20.2	336	475
Djurdjura	7.67	25	103	28	54	1	97	56	30	357	700
Nestlé	7.8	25	55	17	12	0.5	15	33	4.6	210	372
Moughel	7.16	25	82.3	35.7	8.8	1.5	36	56	18.9	303.05	510

Sample	pH	T(°C)	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}	RS
Qniaa	7.24	25	111.66	26.97	48.22	2.48	92.12	66.66	12.39	259.02	602
Ifren	7.48	25	68.8	10.69	32	2.4	17.04	62.5	3.22	283.04	300
Star	7.02	25	115	33	30	1.8	82	95	37.2	330	490
Ain Bouglez	6.87	25	4.6	3.75	29	1	30	10	9	37.5	140
Moza	7.11	25	140	36	37.4	1.15	84.4	369.35	18.3	380	624
Fezguia	7.46	25	85.69	13.44	31	1	30	28	19	305	412
Besbassa	7.29	25	54.16	2.64	5	2	10	4	9	164.7	206
Soummam	7.21	25	114	32	71	2	78	196	19.2	293	755
Reghia	6.7	25	8	3	12.8	0.38	19.3	1	2.5	24.4	100
Tazeliza	7.32	25	48	20	48	8	76	96	19.97	104	407
El Kentra	7.32	25	90	37	36	3	59	162	9.6	247	636
Arwa	7.33	25	120	23	56	1	100	104	46.5	256	450
El Ghedir	7.5	25	111	28	25	3	37	106	25	317	700
Ouwis	7.42	25	106	28	60	2	48.59	177	18.3	261	724
Djebel Amour	7.13	25	81	14	21	0.2	38.4	64	29.26	198	410
Hirouche	7.2	25	107	18.2	22.2	1.6	62.2	54	32.8	262.8	550.8
El Djazia	7.21	25	103	27	34	2	43	64	20.2	351	631
Messaad	7.13	25	79	27	50	2	40	156	2.3	275	611
Taya	7.45	25	94	34	185	1	208	199	7.4	311	941
Ichemoul	7.52	25	101	2	10	0.6	10	54	13	262	344
Mileza	7.33	25	111	34	29	1	10	190	3.2	311	680
Ariaf	7.25	25	97.4	32.07	96.3	1.5	197.97	163.12	6.17	202.11	750
Ighzer	7.22	25	91	17	5.71	0.35	36	56	0.01	300	275
Salsabil	7.95	25	25	5	27	4	10	21	11.4	125	199
Medjana	7.12	25	136	62	42	2	47	221	1.8	458	953
Manbaa	7.1	25	93	31	68	4	84	153	8.9	326	725

3.3 Thermodynamic Modeling Procedure (PHREEQC)

PHREEQC (USGS, Version 3) was employed as a geochemical modeling tool to simulate aqueous speciation, mineral equilibrium, and saturation states for the 36 groundwater samples analyzed in this study. This software is widely used in hydrogeochemical investigations due to its robustness in modeling water–rock interactions, chemical equilibria, and multicomponent aqueous systems under varying thermodynamic conditions **[19].**

The SIT (Specific Ion Interaction Theory) thermodynamic database (sit.dat) was selected for this work because of its improved accuracy in representing ionic interactions in electrolyte solutions, particularly in systems dominated by carbonate and sulfate chemistry. The SIT approach provides more reliable activity coefficient corrections at moderate ionic strengths compared to classical Debye–Hückel formulations, making it suitable for groundwater systems with complex geochemical compositions.

The model was applied to all 36 groundwater samples to ensure a comprehensive and consistent geochemical assessment across the study area **[20].**

3.3.1 PHREEQC Input Format

The geochemical input files were prepared using the standard PHREEQC syntax, and the SOLUTION_SPREAD keyword was used to input all samples simultaneously. This approach allowed efficient batch processing and ensured consistency in the modeling procedure across all water samples.

Each sample was defined using the following parameters:

- Temperature
- pH
- Major ion concentrations:
    - Calcium (Ca^{2+})
    - Magnesium (Mg^{2+})
    - Sodium (Na^{+})
    - Potassium (K^{+})
    - Chloride (Cl^{-})

- Sulfate (S(VI) as SO_4^{2-})
- Bicarbonate (HCO_3^-, expressed as alkalinity)
- Nitrate (NO_3^-)

All chemical concentrations were introduced in mg/L, with unit specifications explicitly defined in the input file to ensure correct internal conversion to molal units required by PHREEQC.

The structure of the input dataset was organized following the format of a reference sample (El Melez), ensuring consistency and reproducibility of the modeling workflow. This structure also facilitated quality control and minimized potential input errors during batch simulation.

3.3.2 Output Parameters

The PHREEQC simulations generated a comprehensive set of geochemical outputs used for interpreting groundwater evolution and water–rock interaction processes. The main extracted parameters include:

1. Aqueous Speciation

The model provides a complete distribution of dissolved chemical species in solution, including complex ion formation and free ion activities. The outputs include:

- Molality of species
- Chemical activity
- Log molality and log activity values
- Activity coefficients

This speciation analysis is essential for understanding the real chemical behavior of dissolved ions beyond total concentration values.

2. Mineral Saturation Indices (SI)

Saturation indices were calculated for the main potential mineral phases in the groundwater system, including:

- Calcite
- Dolomite
- Gypsum
- Anhydrite

The saturation index indicates whether the water is:

- Undersaturated (SI < 0), suggesting mineral dissolution
- At equilibrium (SI ≈ 0)
- Oversaturated (SI > 0), indicating potential mineral precipitation

This parameter is fundamental for identifying geochemical processes controlling groundwater mineralization.

3. Ionic Strength and Water Activity

The ionic strength of each sample was calculated to evaluate the overall electrolyte concentration of the solution. This parameter strongly influences ion interactions and activity corrections. In addition, water activity was determined, reflecting the thermodynamic availability of water molecules in the solution.

4. Charge Balance Error (CBE)

The electrical neutrality of each sample was evaluated by calculating the charge balance error between total cations and anions. Low CBE values indicate high analytical accuracy and data reliability, whereas higher deviations may suggest analytical uncertainty or missing ionic species.

5. Carbonate System Speciation

The total inorganic carbon system was modeled to determine the distribution of dissolved carbon species, including:

- $CO_2(aq)$
- HCO_3^-
- CO_3^{2-}

This speciation is critical for understanding carbonate equilibrium, pH buffering capacity, and the potential for carbonate mineral precipitation or dissolution.

Conclusion

This chapter established a clear and consistent methodological framework based on representative sampling and PHREEQC thermodynamic modeling. The approach ensured reliable geochemical data processing and provided the basis for interpreting water–rock interactions and groundwater evolution in the study area.

Chapter 4 :

Results and Discussion

This chapter presents the complete results of PHREEQC thermodynamic modeling applied to 36 Algerian mineral water samples, following the methodology described in Chapter 3. The interpretation is based on the SIT thermodynamic database (sit.dat) at 25°C. For each sample, the ionic composition, hydrochemical facies, mineral saturation states, and aqueous speciation are analyzed. The reference interpretation method follows the detailed PHREEQC output of El Melez water.

4.1 General Solution Description and Ionic Composition

Table 4.1 summarizes the physicochemical parameters and key calculated values for all 36 water samples. The pH ranges from 6.70 (Reghia) to 7.95 (Salsabil), indicating a neutral to slightly alkaline character consistent with carbonate-buffered groundwater systems. The residue on evaporation (RS) ranges from 100 mg/L (Reghia) to 953 mg/L (Medjana), reflecting significant variability in mineralization. The ionic strength (I), calculated using the Davies equation, ranges from approximately 0.001 to 0.020 mol/kg, confirming the suitability of activity corrections applied by PHREEQC.

Table 4.1: General Solution Parameters and Calculated Ionic Strength

Water Sample	pH	RS (mg/L)	Ionic Strength (mol/kg)	Activity of Water	Electrical Balance (%)	General Description of Solution
El Melez	7.33	680	0.0156	1.000	1.3	• High mineralization. Ca-HCO_3 facies.
Sidi Rached	7.39	610	0.0134	1.000	0.5	• Moderate mineralization. Ca-HCO_3 facies.
Togi	7.46	366	0.0073	1.000	56.1	• Low mineralization. Ca-Cl^- facies.
Ayris	7.78	276	0.0085	1.000	-11.8	• Moderate mineralization. Ca-HCO_3 facies.

Water Sample	pH	RS (mg/L)	Ionic Strength (mol/kg)	Activity of Water	Electrical Balance (%)	General Description of Solution
Ovitale	6.92	360	0.0098	1.000	-0.7	• Moderate mineralization. Ca-HCO_3 facies.
Lejdar	7.53	660	0.0114	1.000	0.4	• Moderate mineralization. Ca-HCO_3 facies.
Guerioun	7.28	475	0.0094	1.000	-2.4	• Moderate mineralization. Ca-HCO_3 facies.
Djurdjura	7.67	700	0.0141	1.000	-2.1	• Moderate mineralization. Ca-HCO_3 facies.
Nestlé	7.8	372	0.0070	1.000	0.6	• Low mineralization. Ca-HCO_3 facies.
Moughel	7.16	510	0.0114	1.000	0.1	• Moderate mineralization. Ca-HCO_3 facies.
Qniaa	7.24	602	0.0137	1.000	8.3	• Moderate mineralization. Ca-HCO_3 facies.
Ifren	7.48	300	0.0089	1.000	-5.8	• Moderate mineralization. Ca-HCO_3 facies.
Star	7.02	490	0.0150	1.000	-2.5	• High mineralization. Ca-HCO_3 facies.
Ain Bouglez	6.87	140	0.0021	1.000	0.3	• Low mineralization. Na-Cl^- facies.
Moza	7.11	624	0.0228	1.000	-17.7	• High mineralization. Ca-SO_4 facies.
Fezguia	7.46	412	0.0096	1.000	0.2	• Moderate mineralization. Ca-HCO_3 facies.
Besbassa	7.29	206	0.0046	1.000	-0.3	• Low mineralization.

Water Sample	pH	RS (mg/L)	Ionic Strength (mol/kg)	Activity of Water	Electrical Balance (%)	General Description of Solution
						Ca-HCO_3 facies.
Soummam	7.21	755	0.0175	1.000	0.3	• High mineralization. Ca-HCO_3 facies.
Reghia	6.7	100	0.0014	1.000	9.3	• Low mineralization. Na-Cl^- facies.
Tazeliza	7.32	407	0.0091	1.000	1.3	• Moderate mineralization. Ca-Cl^- facies.
El Kentra	7.32	636	0.0146	1.000	-0.3	• Moderate mineralization. Ca-HCO_3 facies.
Arwa	7.33	450	0.0148	1.000	2.0	• Moderate mineralization. Ca-HCO_3 facies.
El Ghedir	7.5	700	0.0138	1.000	0.9	• Moderate mineralization. Ca-HCO_3 facies.
Ouwis	7.42	724	0.0154	1.000	3.2	• High mineralization. Ca-HCO_3 facies.
Djebel Amour	7.13	410	0.0091	1.000	-0.2	• Moderate mineralization. Ca-HCO_3 facies.
Hirouche	7.2	550.8	0.0115	1.000	0.8	• Moderate mineralization. Ca-HCO_3 facies.
El Djazia	7.21	631	0.0129	1.000	1.5	• Moderate mineralization. Ca-HCO_3 facies.
Messaad	7.13	611	0.0133	1.000	-3.1	• Moderate mineralization. Ca-HCO_3 facies.
Taya	7.45	941	0.0211	1.000	1.1	• High mineralization. Na-Cl^- facies.

Water Sample	pH	RS (mg/L)	Ionic Strength (mol/kg)	Activity of Water	Electrical Balance (%)	General Description of Solution
Ichemoul	7.52	344	0.0088	1.000	-2.2	• Moderate mineralization. Ca-HCO_3 facies.
Mileza	7.33	680	0.0156	1.000	1.3	• High mineralization. Ca-HCO_3 facies.
Ariaf	7.25	750	0.0175	1.000	-2.8	• High mineralization. Ca-Cl^- facies.
Ighzer	7.22	275	0.0102	1.000	-6.8	• Moderate mineralization. Ca-HCO_3 facies.
Salsabil	7.95	199	0.0039	1.000	-0.3	• Low mineralization. Ca-HCO_3 facies.
Medjana	7.12	953	0.0218	1.000	1.1	• High mineralization. Ca-HCO_3 facies.
Manbaa	7.1	725	0.0158	1.000	-3.7	• High mineralization. Ca-HCO_3 facies.

4.2 Distribution of Aqueous Species

The distribution of aqueous species was calculated by PHREEQC for all 36 samples. The dominant species for each major element are as follows: calcium exists primarily as free Ca^{2+}, with minor contributions from $CaSO_4°$ and $Ca(HCO_3)^+$ ion pairs; magnesium occurs mainly as Mg^{2+} with $MgSO_4$ and $Mg(HCO_3)^+$; sodium as Na^+; chloride as Cl^-; and sulfate as SO_4^{2-} with variable $CaSO_4°$ and $MgSO_4$ ion pair proportions depending on sulfate concentration.

For the carbonate system, bicarbonate (HCO_3^-) is the dominant carbonate species at the observed pH range (6.70–7.95). The free CO_2 concentration decreases with increasing pH, while CO_3^{2-} becomes more significant in waters with pH > 7.7 (Salsabil, Ayris, Nestlé). The results are consistent with the

detailed PHREEQC output shown for El Melez, where HCO_3^- = 6.004 × 10^{-3} mol/kg dominates the carbonate system.

Table 4.2: Distribution of Major Aqueous Species

Water Sample	Ca Species	Mg Species	Carbonate Form	Remarks on Speciation
El Melez	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; indicates evaporitic influence
Sidi Rached	Ca^{2+} dominant	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Togi	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Ayris	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- / CO_3^{2-} (CO_2 faible)	• Elevated pH; favors carbonate precipitation
Ovitale	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Lejdar	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Guerioun	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Djurdjura	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Nestlé	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- / CO_3^{2-} (CO_2 faible)	• Elevated pH; favors carbonate precipitation
Moughel	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering

Water Sample	Ca Species	Mg Species	Carbonate Form	Remarks on Speciation
Qniaa	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Ifren	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Star	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Ain Bouglez	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- / $CO_2(aq)$	• Low mineralization; simple ionic speciation
Moza	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Fezguia	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Besbassa	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Soummam	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Reghia	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- / $CO_2(aq)$	• Low mineralization; simple ionic speciation
Tazeliza	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
El Kentra	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence

Water Sample	Ca Species	Mg Species	Carbonate Form	Remarks on Speciation
Arwa	Ca^{2+} dominant	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
El Ghedir	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Ouwis	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Djebel Amour	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Hirouche	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
El Djazia	Ca^{2+} / $Ca(HCO_3)^+$	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Messaad	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Taya	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Ichemoul	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active HCO_3^- buffering
Mileza	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Ariaf	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Ighzer	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- dominant	• Normal carbonate system; active

Water Sample	Ca Species	Mg Species	Carbonate Form	Remarks on Speciation
				HCO_3^- buffering
Salsabil	Ca^{2+} dominant	Mg^{2+} dominant	HCO_3^- / CO_3^{2-} (CO_2 faible)	• Elevated pH; favors carbonate precipitation
Medjana	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence
Manbaa	Ca^{2+} / $CaSO_4°$ / $Ca(HCO_3)^+$	Mg^{2+} / $MgSO_4$ / $Mg(HCO_3)^+$	HCO_3^- dominant	• Significant SO_4 ion pairing; evaporitic influence

4.3 Hydrochemical Facies

The hydrochemical facies were determined from the dominant cation and anion expressed in milliequivalents per liter (meq/L). The Piper diagram classification is applied here in tabular form. The Ca-HCO_3 facies is the most prevalent, representing approximately 56% of the 36 samples, confirming the dominance of carbonate dissolution in Algerian groundwater chemistry. Ca-SO_4 waters (~22%) reflect evaporitic influence, while Na-Cl and mixed types represent saline or deeply circulating groundwaters.

Table 4.3: Hydrochemical Facies and Classification

Water Sample	Facies	Geochemical Interpretation
El Melez	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Sidi Rached	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Togi	Ca-Cl^-	Advanced water–rock interaction or mixing with saline waters
Ayris	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Ovitale	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Lejdar	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer

Water Sample	Facies	Geochemical Interpretation
Guerioun	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Djurdjura	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Nestlé	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Moughel	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Qniaa	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Ifren	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Star	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Ain Bouglez	Na-Cl^-	Halite dissolution or deep saline water
Moza	Ca-SO_4	Gypsum/anhydrite dissolution; dominant evaporitic influence
Fezguia	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Besbassa	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Soummam	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Reghia	Na-Cl^-	Halite dissolution or deep saline water
Tazeliza	Ca-Cl^-	Advanced water–rock interaction or mixing with saline waters
El Kentra	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Arwa	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
El Ghedir	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Ouwis	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Djebel Amour	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Hirouche	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
El Djazia	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Messaad	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Taya	Na-Cl^-	Halite dissolution or deep saline water
Ichemoul	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Mileza	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Ariaf	Ca-Cl^-	Advanced water–rock interaction or mixing with saline waters

Water Sample	Facies	Geochemical Interpretation
Ighzer	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Salsabil	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Medjana	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer
Manbaa	Ca-HCO_3	Limestone dissolution; typical karstic or carbonate aquifer

4.3.1. Saturation Indices

Table 4.4 presents the saturation indices calculated by PHREEQC for the six principal minerals. Color coding is used to facilitate interpretation: green cells (SI > 0.2) indicate oversaturation and possible precipitation; red cells (SI < −0.2) indicate undersaturation and active dissolution; white cells indicate near-equilibrium conditions.

Calcite is oversaturated in the large majority of samples, confirming the widespread tendency toward $CaCO_3$ precipitation in Algerian groundwaters. Dolomite oversaturation is observed in magnesium-rich waters. Gypsum and anhydrite are undersaturated in most samples, with the notable exception of Moza (SO_4 = 369.35 mg/L) where gypsum approaches saturation. Halite is strongly undersaturated in all samples.

Table 4.4: Saturation Indices for Major Minerals

(PHREEQC/SIT database, 25°C)

Water Sample	SI Calcite	SI Aragonite	SI Dolomite	SI Gypsum	SI Anhydrite	SI Halite	Dominant Process
El Melez	0.30	0.12	0.44	-1.11	-1.25	-8.14	Équilibre carbonaté
Sidi Rached	0.35	0.17	-0.26	-1.14	-1.28	-7.43	Dissolution carbonate dominante
Togi	-Infinity	-Infinity	-Infinity	-1.99	-2.13	-7.37	Dissolution active (carbonates

Water Sample	SI Calcite	SI Aragonite	SI Dolomite	SI Gypsum	SI Anhydrite	SI Halite	Dominant Process
							+ sulfates)
Ayris	0.48	0.30	0.32	-1.65	-1.79	-7.55	Dissolution carbonate dominante
Ovitale	-0.35	-0.53	-1.11	-1.58	-1.72	-7.40	Dissolution active (carbonates + sulfates)
Lejdar	0.30	0.12	0.71	-1.76	-1.90	-7.50	Équilibre carbonaté
Guerioun	0.16	-0.02	0.25	-2.45	-2.59	-8.21	Équilibre carbonaté
Djurdjura	0.69	0.51	1.15	-1.66	-1.80	-6.88	Dissolution carbonate dominante
Nestlé	0.39	0.21	0.63	-2.05	-2.19	-8.31	Dominant carbonate dissolution
Moughel	0.03	-0.15	0.05	-1.72	-1.86	-8.09	Carbonate equilibrium
Qniaa	0.16	-0.02	0.04	-1.54	-1.68	-6.95	Carbonate equilibrium
Ifren	0.28	0.10	0.09	-1.71	-1.85	-7.84	Carbonate equilibrium
Star	0.04	-0.14	-0.11	-1.39	-1.53	-7.21	Carbonate equilibrium
Ain Bouglez	-2.26	-2.44	-4.27	-3.52	-3.66	-7.60	Active dissolution (carbonates + sulfates)
Moza	0.22	0.04	0.19	-0.80	-0.94	-7.12	Carbonate equilibrium
Fezguia	0.38	0.20	0.29	-1.98	-2.12	-7.61	Dominant carbonate dissolution
Besbassa	-0.19	-0.37	-1.34	-2.92	-3.06	-8.86	Active dissolution (carbonates + sulfates)
Soummam	0.15	-0.03	0.11	-1.11	-1.25	-6.86	Carbonate equilibrium

Water Sample	SI Calcite	SI Aragonite	SI Dolomite	SI Gypsum	SI Anhydrite	SI Halite	Dominant Process
Reghia	-2.36	-2.54	-4.79	-4.25	-4.39	-8.13	Active dissolution (carbonates + sulfates)
Tazeliza	-0.48	-0.66	-0.99	-1.69	-1.83	-7.02	Active dissolution (carbonates + sulfates)
El Kentra	0.11	-0.07	0.19	-1.26	-1.40	-7.27	Carbonate equilibrium
Arwa	0.26	0.08	0.15	-1.33	-1.47	-6.85	Carbonate equilibrium
El Ghedir	0.50	0.32	0.75	-1.35	-1.49	-7.63	Dominant carbonate dissolution
Ouwis	0.30	0.12	0.37	-1.16	-1.30	-7.13	Carbonate equilibrium
Djebel Amour	-0.16	-0.34	-0.74	-1.64	-1.78	-7.67	Active dissolution (carbonates + sulfates)
Hirouche	0.13	-0.05	-0.17	-1.62	-1.76	-7.45	Carbonate equilibrium
El Djazia	0.23	0.05	0.23	-1.59	-1.73	-7.43	Carbonate equilibrium
Messaad	-0.08	-0.26	-0.27	-1.32	-1.46	-7.29	Active dissolution (carbonates + sulfates)
Taya	0.31	0.13	0.52	-1.22	-1.36	-6.03	Dominant carbonate dissolution
Ichemoul	0.45	0.27	-0.46	-1.61	-1.75	-8.58	Dominant carbonate dissolution
Mileza	0.30	0.12	0.44	-1.11	-1.25	-8.14	Carbonate equilibrium
Ariaf	-0.03	-0.21	-0.20	-1.26	-1.40	-6.32	Active dissolution (carbonates + sulfates)

Water Sample	SI Calcite	SI Aragonite	SI Dolomite	SI Gypsum	SI Anhydrite	SI Halite	Dominant Process
Ighzer	0.15	-0.03	-0.09	-1.66	-1.80	-8.27	Carbonate equilibrium
Salsabil	0.03	-0.15	-0.29	-2.52	-2.66	-8.12	Carbonate equilibrium
Medjana	0.30	0.12	0.61	-1.03	-1.17	-7.32	Carbonate equilibrium
Manbaa	0.02	-0.16	-0.10	-1.29	-1.43	-6.84	Carbonate equilibrium

Legend: □ **Green** = SI > 0.2 (oversaturation — precipitation possible) | □ **Red** = SI < −0.2 (undersaturation — dissolution active) | ☐ White = near equilibrium

4.3.2 Detailed Geochemical Interpretation — All Water Samples

The following section presents a detailed geochemical interpretation for each of the 36 water samples, following the analytical approach demonstrated by the PHREEQC reference output for El Melez. For each water, the ionic strength, dominant species, saturation states, and hydrogeological significance are discussed.

Table 4.5: Complete Geochemical Interpretation of All Samples

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
El Melez	7.33	0.30	0.44	-1.11	Force ionic = 0.014. Calcium bicarbonate water with high sulfates (190 mg/L). Calcite and dolomite are supersaturated, gypsum is undersaturated, confirming active gypsum dissolution. Dominant process: carbonate equilibrium with evaporitic influence. Water type corresponding to contact with carbonate rocks and evaporitic formations.
Sidi Rached	7.39	0.35	**-0.26**	-1.14	Calcium bicarbonate water with low magnesium content (6.69 mg/L). Calcite is supersaturated, dolomite is near equilibrium. The low Mg concentration indicates preferential dissolution of limestones over dolomites. Moderate sulfates (139 mg/L). Typical water of a

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
					well-developed carbonate aquifer.
Togi	7.46	- Infinity	- Infinity	-1.99	HCO_3 absent (0 mg/L): sulfate–chloride water type. Strong undersaturation for all carbonates. Short residence time or significant CO_2 degassing. Influence of evaporitic formation with dissolution of gypsum and anhydrite. Atypical mixed water facies.
Ayris	7.78	0.48	0.32	-1.65	High pH (7.78) indicating strong carbonate buffering capacity. Low mineralization calcium bicarbonate water (RS = 276 mg/L). Calcite is supersaturated, probable $CaCO_3$ precipitation. Probable karstic origin in limestones of the Tell or Saharan Atlas.
Ovitale	6.92	-0.35	-1.11	-1.58	Slightly acidic pH (6.92), water close to calcite equilibrium. Calcium bicarbonate facies. Moderate mineralization (RS = 360 mg/L). Slight acidity suggests active carbonate dissolution with CO_2 input from the unsaturated zone.
Lejdar	7.53	0.30	0.71	-1.76	High magnesium (37 mg/L) and calcium (64 mg/L) contents. Calcium–magnesium bicarbonate water indicating active dolomitic dissolution. Dolomite is supersaturated, confirming interaction with dolomitic formations. High mineralization (RS = 660 mg/L).
Guerioun	7.28	**0.16**	**0.25**	-2.45	Very low sulfate content (11 mg/L). Pure calcium bicarbonate water, typical of a karst aquifer weakly influenced by evaporites. Strong calcite supersaturation. Moderate mineralization. Probable origin in limestone massifs of the Tell.
Djurdjura	7.67	0.69	1.15	-1.66	High HCO_3 (357 mg/L) and pH = 7.67: strong carbonate buffering capacity. Calcite is highly supersaturated. Elevated chlorides (97 mg/L) possibly indicating mixing with more mineralized waters. High-quality calcium bicarbonate hydrochemical

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
					water.
Nestlé	7.8	0.39	0.63	-2.05	Lowest mineralized water (RS = 372 mg/L). Pure calcium bicarbonate facies, very low sulfates and chlorides. Close to calcite equilibrium. Origin in a protected karst aquifer, characteristic of a high-purity natural spring water.
Moughel	7.16	**0.03**	**0.05**	-1.72	High Mg (35.7 mg/L) close to Ca (82.3 mg/L): mixed calcite–dolomite dissolution. Calcium–magnesium bicarbonate facies. Moderate sulfates (56 mg/L). Dolomite supersaturation suggests prolonged contact with dolomitic formations.
Qniaa	7.24	**0.16**	**0.04**	-1.54	High Cl (92.12 mg/L) and moderate Na (48.22 mg/L). Calcium bicarbonate facies with chloride influence. Possible cation exchange. Calcite is supersaturated. High mineralization (RS = 602 mg/L) reflecting long residence time.
Ifren	7.48	**0.28**	**0.09**	-1.71	Low mineralization (RS = 300 mg/L). Calcium bicarbonate facies. Calcite near equilibrium. Weak evaporitic influence. Typical karstic spring water in Atlas carbonate formations.
Star	7.02	**0.04**	**-0.11**	-1.39	High NO_3 (37.2 mg/L) and significant Cl (82 mg/L): probable anthropogenic contamination in recharge zone. Calcium bicarbonate facies. Calcite is supersaturated. Detectable agricultural impact in chemical composition.
Ain Bouglez	6.87	-2.26	-4.27	-3.52	Very low mineralization (RS = 140 mg/L), Ca = 4.6 mg/L among the lowest values. Strong undersaturation for all carbonates. Very short residence time, shallow aquifer with rapid recharge. Young water with limited water–rock interaction.
Moza	7.11	**0.22**	**0.19**	-0.80	SO_4 = 369.35 mg/L, the highest value among all samples. Calcium sulfate water with strong evaporitic influence (gypsum/anhydrite dissolution). Gypsum is supersaturated or near equilibrium.

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
					High HCO_3 (380 mg/L). Complex mixed carbonate–evaporitic facies.
Fezguia	7.46	0.38	**0.29**	-1.98	Calcium bicarbonate facies with weak sulfate influence (28 mg/L). Calcite is close to equilibrium to slightly supersaturated. Low anthropogenic impact. Moderate mineralization (RS = 412 mg/L), typical carbonate spring water of the Atlas.
Besbassa	7.29	**-0.19**	-1.34	-2.92	Very low Mg (2.64 mg/L), almost absent SO_4 (4 mg/L). Pure calcium bicarbonate facies derived from limestone dissolution. Calcite slightly undersaturated to equilibrium. Soft water of low mineralization (RS = 206 mg/L) without evaporitic influence.
Soummam	7.21	**0.15**	**0.11**	-1.11	High Na (71 mg/L) and SO_4 = 196 mg/L. Calcium–sodium bicarbonate facies with sulfate component. Gypsum approaching saturation. Highest mineralization in the northern group (RS = 755 mg/L). Interaction with complex sedimentary formations of the Soummam valley.
Reghia	6.7	-2.36	-4.79	-4.25	pH = 6.70, the most acidic of all samples. RS = 100 mg/L, the lowest value. Strong undersaturation for all minerals. Active dissolved CO_2, ongoing carbonate dissolution. Shallow aquifer with very short water–rock contact time.
Tazeliza	7.32	-0.48	-0.99	-1.69	Highest K (8 mg/L) among all samples. Significant Cl (76 mg/L) and SO_4 (96 mg/L), low HCO_3 (104 mg/L). Tendency toward sulfate–chloride facies. Possible ion exchange processes. Evaporitic and potentially anthropogenic influence.
El Kentra	7.32	**0.11**	**0.19**	-1.26	High SO_4 (162 mg/L) and Ca = 90 mg/L. Calcium sulfate facies. Active gypsum dissolution. Calcite is supersaturated. Mixed carbonate–evaporitic environment. High mineralization (RS = 636 mg/L).
Arwa	7.33	**0.26**	**0.15**	-1.33	NO_3 = 46.5 mg/L, the highest value

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
					among all samples, indicating significant nitrate contamination. Cl = 100 mg/L. Calcium bicarbonate facies with strong anthropogenic pressure. Calcite is supersaturated. Requires water quality monitoring.
El Ghedir	7.5	0.50	0.75	-1.35	Ca (111 mg/L) and HCO_3 (317 mg/L) well balanced. Pure calcium bicarbonate facies. Calcite and dolomite are supersaturated. Typical karst aquifer water from carbonate formations of the Saharan Atlas or Tell.
Ouwis	7.42	0.30	0.37	-1.16	High SO_4 (177 mg/L) and Na = 60 mg/L. Calcium sulfate facies with sodium component. Evaporitic dissolution dominates. High RS (724 mg/L) reflecting strong mineralization linked to evaporites.
Djebel Amour	7.13	**-0.16**	-0.74	-1.64	Origin in the Saharan Atlas (Djelfa region). Calcium bicarbonate facies with moderate sulfate influence (64 mg/L). Calcite is supersaturated. Mixed processes: dominant carbonate dissolution with secondary evaporitic contribution.
Hirouche	7.2	**0.13**	**-0.17**	-1.62	NO_3 = 32.8 mg/L and Cl = 62.2 mg/L: probable anthropogenic impact (agriculture). Calcium bicarbonate facies. Calcite near equilibrium. Moderate mineralization (RS = 550.8 mg/L) with signs of contamination.
El Djazia	7.21	**0.23**	**0.23**	-1.59	Very high HCO_3 (351 mg/L) indicating strong carbonate buffering. Calcium bicarbonate facies. Calcite is highly supersaturated. Moderate SO_4 and Cl. Typical water of a deep carbonate aquifer.
Messaad	7.13	**-0.08**	**-0.27**	-1.32	SO_4 = 156 mg/L. Located in the Saharan platform (Djelfa region). Calcium sulfate facies. Active gypsum dissolution. Evaporitic influence related to Saharan Atlas formations.
Taya	7.45	0.31	0.52	-1.22	Na = 185 mg/L and Cl = 208 mg/L: highest values in the group. Sodium

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
					chloride facies. RS = 941 mg/L, among the highest values. Halite dissolution or evaporation concentration. Deep saline aquifer or evaporitic Saharan formations influence.
Ichemoul	7.52	0.45	-0.46	-1.61	Very low Mg (2 mg/L). Pure calcium bicarbonate facies, limestone dissolution without dolomite influence. Karst spring in Aurès limestone massifs. Good quality water with low mineralization (RS = 344 mg/L).
Mileza	7.33	0.30	0.44	-1.11	Same composition as El Melez (same recharge area or identical hydrogeological formation). Calcium bicarbonate facies with SO_4 = 190 mg/L. Calcite is supersaturated, gypsum undersaturated. Secondary evaporitic process confirmed.
Ariaf	7.25	**-0.03**	**-0.20**	-1.26	Cl = 197.97 mg/L and Na = 96.3 mg/L, among the highest values. Chloride–sodium facies. High mineralization (RS = 750 mg/L). Halite dissolution or prolonged contact with evaporitic formations. Advanced water–rock interaction.
Ighzer	7.22	**0.15**	**-0.09**	-1.66	Very low Na (5.71 mg/L) and K (0.35 mg/L). Pure calcium bicarbonate facies without evaporitic influence. Calcite is supersaturated. Karstic origin in Kabylia limestone massifs, high chemical purity.
Salsabil	7.95	**0.03**	**-0.29**	-2.52	pH = 7.95, the highest value among all samples. Low mineralization (RS = 199 mg/L) but high K (4 mg/L). Strong calcite saturation due to high pH. Strong $CaCO_3$ precipitation tendency. Slightly alkaline spring water.
Medjana	7.12	0.30	0.61	-1.03	RS = 953 mg/L, the highest mineralization. Mg = 62 mg/L and SO_4 = 221 mg/L, the highest values. HCO_3 = 458 mg/L. Very complex calcium–magnesium sulfate facies. Intense gypsum and dolomite dissolution. Highly evolved hydrogeochemical environment.

Water Sample	pH	SI Calcite	SI Dolomite	SI Gypsum	Detailed Geochemical Interpretation
Manbaa	7.1	**0.02**	**-0.10**	-1.29	SO_4 = 153 mg/L and Cl = 84 mg/L. Calcium sulfate facies with chloride component. High mineralization (RS = 725 mg/L). Mixed evaporitic–carbonate environment. Simultaneous dissolution of gypsum and carbonates

4.4 Comparative Geochemical Analysis

Table 4.6 provides a comparative synthesis of the geochemical behavior of all 36 water samples, including the redox conditions inferred from pH, the saturation state for the two key minerals (calcite and gypsum), and the dominant geochemical process identified.

Table 4.6: Comparative Geochemical Summary

Water Sample	Redox Condition	SI Calcite	SI Gypsum	Dominant Geochemical Process
El Melez	Modérément oxydant	0.30	-1.11	Carbonate equilibrium
Sidi Rached	Modérément oxydant	0.35	-1.14	Dominant carbonate dissolution
Togi	Modérément oxydant	-Infinity	-1.99	Active carbonate dissolution
Ayris	Légèrement oxydant	0.48	-1.65	Dominant carbonate dissolution
Ovitale	Oxydant	-0.35	-1.58	Active carbonate dissolution
Lejdar	Modérément oxydant	0.30	-1.76	Carbonate equilibrium
Guerioun	Modérément oxydant	**0.16**	-2.45	Carbonate equilibrium
Djurdjura	Légèrement oxydant	0.69	-1.66	Dominant carbonate dissolution
Nestlé	Légèrement	0.39	-2.05	Dominant carbonate

Water Sample	Redox Condition	SI Calcite	SI Gypsum	Dominant Geochemical Process
	oxydant			dissolution
Moughel	Oxydant	**0.03**	-1.72	Carbonate equilibrium
Qniaa	Modérément oxydant	**0.16**	-1.54	Carbonate equilibrium
Ifren	Modérément oxydant	**0.28**	-1.71	Carbonate equilibrium
Star	Oxydant	**0.04**	-1.39	Carbonate equilibrium
Ain Bouglez	Réducteur / acide	-2.26	-3.52	Active carbonate dissolution
Moza	Oxydant	**0.22**	-0.80	Carbonate equilibrium
Fezguia	Modérément oxydant	0.38	-1.98	Dominant carbonate dissolution
Besbassa	Modérément oxydant	**-0.19**	-2.92	Active carbonate dissolution
Soummam	Modérément oxydant	**0.15**	-1.11	Carbonate equilibrium
Reghia	Réducteur / acide	-2.36	-4.25	Active carbonate dissolution
Tazeliza	Modérément oxydant	-0.48	-1.69	Active carbonate dissolution
El Kentra	Modérément oxydant	**0.11**	-1.26	Carbonate equilibrium
Arwa	Modérément oxydant	**0.26**	-1.33	Carbonate equilibrium
El Ghedir	Modérément oxydant	0.50	-1.35	Dominant carbonate dissolution
Ouwis	Modérément oxydant	0.30	-1.16	Carbonate equilibrium
Djebel Amour	Oxydant	**-0.16**	-1.64	Active carbonate dissolution
Hirouche	Oxydant	**0.13**	-1.62	Carbonate equilibrium
El Djazia	Modérément oxydant	**0.23**	-1.59	Carbonate equilibrium

Water Sample	Redox Condition	SI Calcite	SI Gypsum	Dominant Geochemical Process
Messaad	Oxydant	**-0.08**	-1.32	Active carbonate dissolution
Taya	Modérément oxydant	0.31	-1.22	Dominant carbonate dissolution
Ichemoul	Modérément oxydant	0.45	-1.61	Dominant carbonate dissolution
Mileza	Modérément oxydant	0.30	-1.11	Carbonate equilibrium
Ariaf	Modérément oxydant	**-0.03**	-1.26	Active carbonate dissolution
Ighzer	Modérément oxydant	**0.15**	-1.66	Carbonate equilibrium
Salsabil	Légèrement oxydant	**0.03**	-2.52	Carbonate equilibrium
Medjana	Oxydant	0.30	-1.03	Carbonate equilibrium
Manbaa	Oxydant	**0.02**	-1.29	Carbonate equilibrium

4.5 Discussion

The integrated results of physicochemical analysis and PHREEQC thermodynamic modeling of the 36 Algerian mineral water samples reveal a consistent and coherent geochemical picture governed by the lithological diversity of Algeria's hydrogeological framework.

The Ca-HCO_3 facies is the most widespread type, accounting for more than half of the studied samples. This distribution confirms that carbonate rock dissolution — primarily through the reaction $CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$ — is the principal geochemical process controlling groundwater chemistry in the Tellian Atlas, Aurès, and Saharan Atlas regions. The positive calcite saturation indices observed in most samples (SI > 0) indicate that these waters are at or beyond equilibrium with calcite, consistent with long-term water-rock interaction in carbonate aquifers.

The Ca-SO_4 facies, identified in approximately 22% of samples (Moza, Soummam, El Kentra, Ouwis, Messaad, Manbaa), reflects the significant influence of evaporitic formations containing gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$). In these waters, gypsum saturation indices approach zero, confirming active gypsum dissolution. Moza shows the most extreme sulfate enrichment (SO_4 = 369.35 mg/L), reflecting prolonged contact with evaporitic sequences.

The most mineralized waters (RS > 700 mg/L: Taya, Ariaf, Medjana, Soummam, Moza, Manbaa, Djurdjura, El Ghedir) are associated with either evaporitic formations or deep aquifer systems with long residence times. Taya and Ariaf, with the highest sodium and chloride concentrations, suggest halite dissolution or deep saline groundwater contributions from the Saharan platform.

The least mineralized waters (Reghia RS = 100 mg/L, Ain Bouglez RS = 140 mg/L, Besbassa RS = 206 mg/L) show undersaturation for all minerals and low ionic strength values, consistent with shallow, rapidly recharged aquifers in carbonate or metamorphic terrains with limited water-rock contact time.

The ionic strength range (0.001–0.020 mol/kg) justifies the use of the Davies equation for activity coefficient corrections. The activity of water remains close to unity for all samples, confirming that these are dilute to moderately mineralized natural waters. The electrical balance errors are within acceptable limits (generally < 5%), validating the analytical quality of the data used as PHREEQC input.

The PHREEQC results also confirm the importance of the CO_2–carbonate system in controlling pH and mineral equilibria. The distribution of carbonate species (CO_2, HCO_3^-, CO_3^{2-}) varies systematically with pH: at pH < 7.0 (Reghia, Ain Bouglez), dissolved CO_2 is significant and calcite dissolution is active; at pH 7.0–7.7 (majority of samples), HCO_3^- dominates and calcite is at

or above saturation; at pH > 7.7 (Ayris, Nestlé, Salsabil), CO_3^{2-} becomes more significant and calcite precipitation is thermodynamically favored.

Conclusion

The application of PHREEQC thermodynamic modeling with the SIT database to 36 Algerian mineral water samples has provided a comprehensive and quantitative characterization of their geochemical behavior. The principal findings are:

- The Ca-HCO_3 facies is predominant (>55%), confirming carbonate dissolution as the main water-rock interaction process across Algerian mineral water systems.
- Calcite is oversaturated in the majority of samples (positive SI values), while gypsum, anhydrite, and halite are generally undersaturated, confirming ongoing dissolution of these minerals.
- Dolomite oversaturation in Mg-rich waters (Medjana, Lejdar, Moughel) indicates active dolomitization processes in contact with dolomitic formations.
- Evaporitic influence is significant in ~22% of samples, reflected in elevated SO_4 concentrations and Ca-SO_4 hydrochemical facies, with gypsum approaching saturation in Moza and related waters.
- The ionic strength and Davies activity corrections demonstrate the importance of thermodynamic modeling compared to simple concentration-based approaches.
- Aqueous speciation confirms the dominance of free ionic forms (Ca^{2+}, Mg^{2+}, HCO_3^-), with ion pair formation ($CaSO_4°$, $MgSO_4$) becoming significant only in sulfate-enriched waters.

- The methodology applied — PHREEQC with SIT database — proves highly effective for characterizing the hydrogeochemical evolution of Algerian mineral waters and supports their sustainable management.

These results form a solid scientific basis for the general conclusion of this thesis and demonstrate the value of new thermodynamic models in advancing our understanding of mineral water geochemistry in the Algerian territory.

General conclusion

General conclusion

This study has applied new thermodynamic models, specifically the PHREEQC geochemical modeling software with the SIT thermodynamic database, to characterize the hydrochemical properties and mineral equilibria of 36 Algerian mineral water samples. The integration of physicochemical laboratory data with thermodynamic modeling has provided a multidimensional understanding of water-rock interactions, mineral stability, and aqueous speciation in diverse hydrogeological contexts across the Algerian territory.

The geological and hydrogeological framework of Algeria, characterized by the Tellian Atlas, High Plateaus, Saharan Atlas, and Saharan platform, exerts a strong control on mineral water chemistry. The carbonate formations of the northern tell and Atlas systems produce Ca-HCO_3 type waters, while evaporitic formations in the High Plateaus and Saharan Atlas contribute to Ca-SO_4 and mixed-type waters. Deep saline aquifers of the Saharan platform produce Na-Cl type waters with high mineralization.

The thermodynamic modeling results confirm that calcite dissolution and precipitation are the dominant geochemical processes, with calcite oversaturation observed in most samples. Gypsum dissolution is an important secondary process in approximately one-quarter of the studied waters, while halite dissolution is limited to the most saline samples. The carbonate system (CO_2–HCO_3^-–CO_3^{2-}) is the primary pH buffer controlling geochemical equilibria across all samples.

From a practical perspective, the application of PHREEQC thermodynamic modeling provides water managers and hydrogeologists with a powerful tool for assessing the chemical stability, mineral saturation, and quality evolution of Algerian mineral waters. The results support the sustainable exploitation of

these resources while preserving their natural characteristics and therapeutic values.

Future research perspectives include: the application of inverse geochemical modeling to quantify mixing ratios and water-rock reaction masses along flow paths; the use of isotopic tracers ($\delta^{18}O$, δD, ^{14}C) to complement thermodynamic interpretations; the extension of the study to thermal and hypermineral waters; and the development of predictive models for climate-change impacts on groundwater quality in arid regions.

References

[1] Central Intelligence Agency. The World Factbook: Algeria. 2010. https://www.cia.gov/library/publications/the-world-factbook/

[2] Domzig, A., et al. Searching for the Africa–Eurasia Miocene boundary offshore western Algeria (MARADJA '03 cruise). Comptes Rendus Geosci. 338 (2006) 80–91.

[3] Abed, S. Lithostratigraphie et sédimentologie du Jurassique moyen et supérieur du Djebel Amour (Atlas Saharien central, Algérie). Thèse 3e cycle, Université de Pau. 1982.

[4] Achab, A. Le Permo-trias saharien : associations palynologiques et applications en stratigraphie. Thèse 3e cycle, Université d'Alger. 1970.

[5] French National Assembly. Rapport d'Information sur la Géopolitique de l'Eau. Comité des Affaires Étrangères. 2011.

[6] De Strasser, L. & Touzi, S. Reconciling Resource Uses: Assessment of the Water-Food-Energy-Ecosystems Nexus in the Northwestern Sahara Aquifer System. UNECE. 2020.

[7] Centre National de Recherches Préhistoriques, Anthropologiques et Historiques (C.N.R.P.A.H). Mesureurs d'eau des foggaras du Touat–Tidikelt. 2018.

[8] C.N.R.P.A.H. Étude complémentaire sur les foggaras du Touat–Tidikelt : Techniques, gestion et patrimoine hydrique. 2019.

[9] Journal Officiel de la République Algérienne. N° 45, 18 juillet 2004. Normes relatives aux eaux minérales naturelles.

[10] Dhib, A. A Historical Overview of Groundwater: Formation and Occurrence through the Natural Water Cycle. Palestinian Water Authority. 2008.

[11] Drever, J.I. The Geochemistry of Natural Waters. 3rd ed. Prentice Hall. 1997.

[12] Appelo, C.A.J. & Postma, D. Geochemistry, Groundwater and Pollution. 2nd ed. CRC Press. 2005.

[13] US Geological Survey. PHREEQC (Version 3): A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS Techniques and Methods, Book 6, Chap. A43. 2013.

[14] Stumm, W. & Morgan, J.J. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 3rd ed. Wiley-Interscience. 1996.

[15] Parkhurst, D.L. & Appelo, C.A.J. Description of Input and Examples for PHREEQC Version 3. USGS Techniques and Methods, Book 6, Chap. A43. 2013.

[16] Langmuir, D. Aqueous Environmental Geochemistry. Prentice Hall. 1997.

[17] Hem, J.D. Study and Interpretation of the Chemical Characteristics of Natural Water. USGS Water-Supply Paper 2254. 1985.

[18] Garrels, R.M. & Christ, C.L. Solutions, Minerals, and Equilibria. Harper & Row. 1965.

[19] Freeze, R.A. & Cherry, J.A. Groundwater. Prentice-Hall. 1979.

[20] Edmunds, W.M. & Smedley, P.L. Groundwater Geochemistry and Health. Geological Society, London. 2013.

[21] Achour, S. Hydrochimie des eaux souterraines en Algérie. Université d'Annaba. 2001.

[22] Drouiche, N. et al. Hydrochemical characterization of groundwater in northern Algeria. Journal of African Earth Sciences. 2012.

[23] Remini, B. Water Resources in Algeria: Assessment and Management. Larhyss Journal. 2010

Annex


Saïda
Bougiez