HYDROGEOCHEMICAL CHARACTERIZATION OF THERMAL WATERS IN THE NORTHERN PART OF THE ARGENTINEAN ANDES (NORTHERN PART)

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Advisors: Prof. Dr. Stefan Wohnlich; Ruhr-Universität Bochum
Dr. Andrea Hachenberg; Ruhr-Universität Bochum
Dra. Sofia Pérez Luján; Universidad Nacional de San Juan

María José Rey Ocampo

rey.mariajose@hotmail.com.ar

Abstract

This thesis focuses on the hydrogeochemical characterization of thermal waters in the northern part of the Andes Mountains in Argentina, covering the provinces of Jujuy, Salta, Catamarca, and San Juan. This geographical area, located in a zone of high tectonic activity, is home to a significant number of thermal springs and mineral sources, which are situated within a fault system between the Andes Mountains and the Pre-Andes. The chemical composition of the groundwater in these springs provides valuable information about the hydrogeological and geochemical processes that regulate their origin, evolution, and characteristics. These processes include the deep circulation of fluids, hydrothermal weathering, mineral dissolution, and, in particular, the possible ascension of sodium chloride fluids from the subducted Nazca Plate beneath the South American Plate.

The main objective of this research is to analyze and understand the complex relationships between the deep-water circulation systems, geological faults, groundwater characteristics, and thermal springs on the eastern slope of the northern part of the Andes. In this context, the relationship between the presence and distribution of sodium chloride in the different geological provinces of the region has been explored, hypothesizing that the sodium chloride in the groundwater of the Andes may originate from oceanic sediments deposited in the Pacific Ocean. These sediments, when subducted along with the Nazca Plate, ascend through the tectonic faults of the Andes, reaching higher altitudes. Subsequently, these sediments dissolve in thermal waters and mix with the groundwater, which may explain the high concentration of sodium chloride in thermal springs.

To carry out the hydrogeochemical characterization of thermal waters, the PhreeqC software was used to model the chemical compositions obtained from a total of 388 thermal water samples, of which 282 were selected for detailed analysis. The chemical data were processed and analyzed using tools such as Piper diagrams, Excel, and scatter plots, which allowed for the identification of significant trends and relationships. The geographical coordinates of the samples were correlated with a permafrost zoning map to locate the samples within thermally active zones, consistent with the focus on working with thermal waters.

The results of the research show that the groundwater in the region is generally neutral to slightly alkaline or acidic. According to the Piper diagrams, thermal waters exhibit significant compositional variability, with a prevalence of calcium sulfate and/or chloride waters (Ca^{2+}, SO_4^{2-}), calcium-magnesium bicarbonate (Ca^{2+}, Mg^{2+}, HCO_3^-), or sodium bicarbonate (Na^+, HCO_3^-), and sodium chloride or sulfate waters (Na^+, Cl^-, SO_4^{2-}). The constant presence of a chloride-sodium association, regardless of altitude, suggests that the origin of sodium chloride is linked to a common geological process affecting both the Andes and Pre-Andes. The water-rock interaction, combined with the processes of evaporation and mineral dissolution, are key factors that explain the chemical composition of thermal waters, with these processes being especially influenced by temperature and local geology.

A key finding of this research is the heterogeneity in the chemical data of thermal waters, which shows a nonlinear trend in their behavior over time, highlighting the need to establish a more robust baseline for future studies. The data obtained provide a preliminary view of the chemistry of the waters, so it is proposed to continue monitoring to complete this baseline and more accurately assess the long-term trends in the chemical composition of thermal waters.

The hydrogeochemical analysis performed has significant implications for the sustainable development of water resources in the region. The classification of groundwater based on its geochemical potential provides crucial information for understanding the associated thermodynamic systems, which are influenced by variations in temperature and pressure related to altitude differences. This analysis is not only essential for evaluating the hydric potential of the region but also for guiding the responsible and sustainable exploitation of these resources, ensuring their long-term conservation within the framework of balanced geothermal development that respects the natural environment.

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CHAPTER I: INTRODUCTION

I.1. Generalities

I.1.1. Contextualization of the Study in the Argentine Andes

Thermal waters that emerge from the depths of the Argentine Andes represent not only a natural attraction but also a fundamental key to understanding the geothermal processes and hydrogeological systems of the region (Auge et al., 2006; Hochstein, 1990). This study delves into the hydrogeochemical characterization of thermal springs, investigating their origin, physical characteristics, and behavior in relation to the local geology.

The northern Andes region is one of the most complex and fascinating geological areas on the planet, extending across the provinces of Jujuy, Salta, Catamarca, and San Juan (Allmendinger et al., 1997; Ramos, 1999). This zone presents great lithological diversity, with a combination of volcanic, plutonic, sedimentary, and metamorphic rocks that configure a highly active geothermal system. Among the most prominent components are undifferentiated volcanic rocks, siliciclastic sedimentary rocks, and halite associated with the Llullaico Salt Flat in Salta, along with rhyolites, granitoids, and low- to medium-grade metamorphic formations.

The region’s tectonic dynamics are dominated by the subduction of the Nazca Plate beneath the South American Plate, a phenomenon that generates significant volcanic activity (Allmendinger et al., 1997; Ramos, 1999). This subduction has led to the formation of active volcanoes, such as those located in Salta (Socompa, Tocomar, Llullaico), Jujuy (Tuzgle), and Catamarca (the Cerro Galán caldera and the Antofalla volcano). These volcanoes are key indicators of the geothermal processes influencing the composition of the region's thermal waters, making this an essential study area for understanding the hydrogeological and geochemical mechanisms shaping thermal springs.

The region has an arid climate, with limited precipitation and high evaporation, which influences the chemical composition of both groundwater and thermal waters (Hem, 1985; Domenico & Schwartz, 1990; Abraham de Vázquez et al., 2000). This geological and climatic context creates an ideal setting to study how geothermal characteristics and geological faults affect the composition of thermal waters, offering a unique window into deep hydrogeological and geochemical processes.

The aim of this research is to hydrogeochemically characterize the springs of the Andean region, exploring the interactions between deep circulation systems, geological faults, groundwater, and thermal springs. Using PhreeqC software, the interactions between underground fluids and rocks will be modeled, establishing significant connections that will allow for a better understanding of geothermal processes and chemical variations in thermal waters over time.

I.2. Research Hypothesis

The hypothesis of this study proposes that the hydrogeochemical composition of thermal waters is directly linked to a complex interaction between underground fluids, the fault system, and the geothermal conditions of each region. It is assumed that variations in the chemical composition of thermal waters are influenced by the depth and orientation of geological faults, as well as by the geothermal activity characteristic of the Central Andes. Furthermore, it is expected that a detailed analysis of the waters will reveal distinctive geochemical patterns, originating from the subduction process of the Nazca Plate, thus providing key information on the dynamics of groundwater in geothermal areas.

It is proposed that thermal waters undergo ionic exchange with rocks during their circulation through geological faults, which determines their chemical composition (Appelo & Postma, 2005; Hem, 1985). This interaction process is crucial for understanding the observed differences in the waters, which vary not only due to local geology but also due to factors such as temperature and altitude.

I.3. General Objectives

The main objective of this research is to hydrogeochemically characterize the springs in the Andean regions of Argentina. To achieve this, the study aims to understand the complex relationships between deep circulation systems, fault systems, groundwater, springs, and precipitation. This comprehensive analysis will enable the modeling of hydrogeochemical processes using the PhreeqC program, allowing for the establishment of significant relationships with the geological subsurface and a deeper understanding of the processes influencing these waters.

I.3.1. Specific Objectives

- Produce a detailed geological map of the study provinces (Jujuy, Salta, Catamarca, and San Juan): Link the geological units with regional structures and permafrost zones, identifying spatial relationships associated with the occurrence of geothermal manifestations. This will allow for a more precise analysis of the interaction between geological and geothermal factors, facilitating the identification of key areas for thermal water research.
- Characterize the lithological environment of thermal springs and identify the mineralogical sources of dominant ions.
- Analyze the physicochemical parameters of groundwater, identifying facies evolution, temperature dependence, and altitudinal trends.
- Apply modeling tools (PhreeqC, Piper diagrams) to simulate water–rock interactions and mineral saturation indices.
- Correlate hydrochemical variability with structural features, recharge zones, climatic conditions, cryospheric influence, and regional geothermal gradients.

CHAPTER II: MATERIALS AND METHODS

II.1. Data and Sample Collection

- A total of 388 thermal water samples were initially available, originating from various sources and field sampling campaigns conducted in the years 1985 and between 2015 and 2018, with no records in the intervening years. However, due to the absence of key parameters in a significant portion of the dataset—which compromised data reliability—280 samples were carefully selected based on their analytical quality. The selection followed specific criteria aimed at ensuring the accuracy, consistency, and representativeness of the hydrogeochemical information. These criteria included the analytical completeness of the major ions (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}), the availability of temperature measurements, internal chemical consistency of the analyses, and acceptable charge balance errors. The hydrochemical information used in this study therefore corresponds to previously collected datasets that were compiled, reviewed, and filtered for hydrogeochemical interpretation.
- Collection of thermal water sample analyses by Hydroproyectos S.A. (Year: 1985) [Des-Go-Ba]: These data, corresponding to the Despoblados area in the Frontal Cordillera of San Juan, provided fundamental information on the characteristics of thermal waters and served as a starting point for the research.
- Data presented in the work of Pesce and Miranda (2003) [J-S-Ca-SJ]: These data, derived from the same sampling campaigns conducted by Hydroproyectos S.A. in the provinces of Jujuy, Salta, Catamarca, and San Juan, were used as a complementary source. Pesce and Miranda (2003)'s work compiled and disseminated this previously collected information, providing a more accessible and organized framework for analyzing the hydrogeochemical characteristics of thermal waters in the region.
- Data obtained during the Binational Master's Program in Applied Geothermics Excursions (Years: 2015-2018) [EXC]: These updated and relevant data significantly contributed to the understanding of geothermal conditions in the areas of interest.
- All hydrochemical datasets compiled and processed for this study were organized in spreadsheet format. These files include the original analytical data, calculated parameters, and derived hydrochemical classifications. Due to their size, they are not included in thesis but are available from the author upon request.
- Map provided by Taillant, J. D. (2012) [Email: jdtaillant@cedha.org.ar; Phone: +54 9 351 507 8376]: This map, obtained from the Center for Human Rights and Environment (CEDHA), was used to contextualize both warm temperature conditions and geothermal activity, as well as cold zones that coincide with cryospheric features in Argentina. It was also utilized to correlate these thermal anomalies—both warm and cold—with the locations of thermal water springs.
- Geological Map of South America 2019 (Scale 1:5,000,000) by Gómez, J., Schobbenhaus, C., & Montes, N. E. (2019) [Commission for the Geological Map of the World (CGMW), Colombian Geological Survey, and Brazilian Geological

Survey]: This map was used to contextualize the geological characteristics of the study region, specifically focusing on the provinces of Jujuy, Salta, Catamarca, and San Juan. It enabled the assignment of thermal water discharge points to their corresponding geological formations and structural settings on the surface.

- The Arid Diagonal of South America, documented by UNESCO (2010) and IADIZA-CONICET, was considered to define the climatic background influencing evaporation and recharge conditions.
- The presence of glaciers, rock glaciers, and permafrost, as mapped by IANIGLA-CONICET and Taillant (2012), was used to contextualize the origin of recharge for many high-altitude thermal water springs, particularly in the Frontal Cordillera and The Puna regions (Boni et al., 2019; Villalba et al., 2020).
- Google Earth was used to verify the spatial location and altitude of thermal springs, facilitating the cross-referencing of sample coordinates with geological formations and fault systems visible in satellite imagery.

II.2. Methods of Analysis

II.2.1. Introductory Office Tasks

Thesis Timeline: A detailed schedule was established, outlining activities and estimated deadlines for the development of thesis, providing a structured guide for the research.

Study Area Analysis: A comprehensive analysis of the study area was conducted using satellite imagery, topographic and geological maps, and thematic maps provided by Taillant, J. D. (2012), Gómez, J., Schobbenhaus, C., and Montes, N. E. (2019), the Argentine Institute for Snow Research, Glaciology and Environmental Sciences (IANIGLA–CONICET), and the Argentine Institute of Arid Zones (IADIZA–CONICET). This allowed for a deeper understanding of the geological, geomorphological, and geothermal characteristics of the region, as well as the identification of relevant cryospheric features. Additionally, Google Earth (version 7.3.6.10201; imagery and elevation data: SRTM/NASA) was employed as a visual support tool to examine terrain profiles, estimate altitudes of thermal springs, recognize regional slopes, and assess structural features such as faults and fracture alignments. While not a substitute for technical topographic surveys, it provided a valuable preliminary basis for spatial interpretation and hydrogeological context.

Literature Review and Data Compilation: An extensive review of literature related to geothermal energy, regional geology, geomorphology, geotectonics, geochemistry, structural geology, hydrogeochemistry, and hydrogeology was carried out. The information obtained was integrated with existing data, enriching the knowledge base with initial insights derived from satellite imagery and map studies.

Reconstruction of Geological Evolution: Focused on major geological processes such as magmatic arc development, terrane accretion, and the formation of Andean structural features that shape the circulation and chemistry of thermal waters. The integration of stratigraphic and tectonic information provided the basis for interpreting the origin and evolution of the geothermal systems studied.

Data Inventory Coordination: The data inventory was coordinated within the framework of the Binational Master in Applied Geotherm**ics**, with the support of the Ruhr-

Universität Bochum (RUB). Historical datasets**,** such as those from Hydroproyectos S.A. (1985), Pesce and Miranda (2003) and field campaigns conducted during academic outings 2015-2018, were integrated with cartographic resources, including maps from Taillant (2012), Gómez et al. (2019), the Arid Diagonal Map (UNESCO-IADIZA, 2010) and the cryospheric inventory from IANIGLA (2020). All information was consolidated and systematized in Excel spreadsheets, encompassing laboratory analysis, water classification, rock types, PHREEQC outputs, Piper diagrams and related visualizations. This unified and structured database, organized under strict data reliability criteria, provided the analytical basis for the hydrogeochemical interpretations developed in this thesis

II.2.2. Advanced Office Tasks

Hydrogeochemical Data Quality Control: Prior to the hydrogeochemical analysis, the compiled dataset underwent a quality control procedure. This included verification of analytical completeness, calculation of charge balance errors (CBE) using PHREEQC, and spatial validation of sampling locations through geological maps and satellite imagery. From the initial dataset of 388 thermal water analyses, 280 samples were retained after applying these reliability and consistency criteria.

Detailed data on the concentrations of major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-), initially expressed in mg/L and subsequently converted to meq/L, were collected for standardization. These parameters represent the fundamental ionic components commonly used in groundwater characterization. The dataset also included in situ measurements of pH, electrical conductivity, and temperature, which were carefully selected based on their internal consistency and completeness. Temperature values correspond primarily to measurements taken at the discharge points of thermal springs. In a few cases where temperature data from wells were available, these were considered cautiously and only for general comparison, as they represent measurements at different depths and therefore do not necessarily reflect the same hydrogeological conditions.

To ensure data reliability, charge balance errors (CBE) were calculated using PHREEQC software. Samples with errors exceeding ±10% were excluded from the analysis, following the acceptable margin established in hydrogeochemical literature (Appelo & Postma, 2005). Special attention was given to samples with pH values around 7 which, despite appearing neutral, exhibited significant ionic imbalances. In such cases, the charge balance was reviewed individually and those outside the accepted margin were discarded.

In cases where records lacked information on dissolved inorganic carbon (C(4)), a correction procedure was applied in PHREEQC using the charge command on Ca^{2+}, according to the method outlined in the official manual (Parkhurst & Appelo, 2013). This approach enabled the closure of ionic balances and the retention of samples that would have otherwise been excluded due to incomplete data.

Priority was given to samples with in situ pH measurements, as they are considered to better reflect the actual hydrogeological conditions at the time of sampling. When both field and laboratory pH values were available, they were compared and an average value was adopted as representative.

Because many of the data tables—particularly those from Hydroproyectos S.A. (1985), Pesce and Miranda (2003)—were only available in PDF format, all information was manually transcribed into Excel spreadsheets for further analysis and processing.

All compiled hydrochemical datasets were organized and processed in spreadsheet format, including original analytical values, calculated parameters, and derived hydrochemical classifications. Due to their size, these datasets are not included in thesis but are available from the author upon request. Measurement uncertainties for temperature were not consistently reported in the historical datasets used in this study; therefore, error bars could not be incorporated into the temperature plots and temperature values were interpreted comparatively across geological provinces rather than statistically.

Hydrogeochemical Data Processing and Interpretation: Groundwater classification also considered the total dissolved solids (TDS) concentration, following the criteria proposed by Domenico & Schwartz (1990) and Hem (1985):

0–250 mg/L: Very fresh

250–1000 mg/L: Fresh

1000–10000 mg/L: Brackish

10000–100000 mg/L: Saline

100000 mg/L: Brine

In addition to this classification, the hydrochemical facies of groundwater were interpreted using Piper diagrams, which allow a visual integration of the relative proportions of major cations and anions (Piper, 1944). The plots were created using Excel-based templates specifically designed for hydrochemical analysis, and results were manually validated to ensure consistency. This interpretation was conducted according to the geological provinces, underlying lithologies, and altitudinal settings, enabling the correlation of water types with prevailing rock types and elevation-related hydrogeological contexts.

Additionally, ionic ratios such as Na^+/Ca^{2+}, Mg^{2+}/Ca^{2+}, Cl^-/SO_4^{2-} and Cl^-/HCO_3^- were calculated and interpreted through bivariate diagrams, which complemented the hydrogeochemical analysis and allowed for inferences about dissolution, mixing processes, and geochemical evolution.

Because the dataset integrates hydrochemical analyses from different sampling campaigns and historical sources, the study focuses on comparative hydrogeochemical interpretation rather than on formal statistical modeling. Therefore, the results are interpreted mainly through hydrochemical facies, ionic ratios, saturation indices, and geological context across the studied provinces.

Geochemical Data Visualization: Tools such as PHREEQC, Excel, Google Earth, QGIS, and Corel Draw were used for data processing and visualization. Piper diagrams, scatter plots, saturation index bar charts, and geological overlays helped correlate water composition with lithological and structural settings. The 1:5,000,000 Geological Map of South America (Gómez et al., 2019) provided geostructural and lithologic context for geochemical interpretations, while mapped faults and fracture zones were used to evaluate potential flow pathways.

Climatic and Cryospheric Context: To enhance the understanding of groundwater dynamics in high-altitude and arid zones, thermal zonation and permafrost mapping were integrated. The Permafrost World Map and regional soil temperature maps (Taillant, 2012) allowed the distinction of cold and warm ground zones, influencing the location and intensity of thermal manifestations. Additionally, debris-covered glaciers and rock glaciers mapped by IANIGLA–CONICET were included as key seasonal water reservoirs that influence aquifer recharge and thermal spring flows in the Andes (Boni et al., 2019; Villalba et al., 2020). These features act as delayed-release hydrological systems in arid basins such as the Frontal Cordillera and Iglesia Valley

The study area is located within the South American Arid Diagonal, which affects surface recharge and regional hydrology. This climatic corridor, described by Abraham de Vázquez et al. (2000), is characterized by low annual precipitation (under 100–300 mm), high solar radiation, and intense evapotranspiration. The geographic and climatic framework was integrated using maps from the Argentine Institute of Arid Zones (IADIZA–CONICET) and further informed the hydrogeological interpretation of thermal systems within arid mountain catchments.

Geological and Structural Framework: A chronological geological framework was developed for the provinces of Jujuy, Salta, Catamarca, and San Juan to support the interpretation of lithological influence on thermal water chemistry. The The Puna formed through long-term volcanic and sedimentary processes related to Andean orogenesis and back-arc magmatism (Ramos, 1999). The Eastern Cordillera and the Subandean Ranges developed as foreland fold-and-thrust belts during the Cenozoic. The Precordillera and Bermejo Valley basins were shaped by Paleozoic marine sedimentation followed by synorogenic infill and Neogene thrusting (Jordan et al., 1990, 1993a). The Pampean Ranges, formed by Paleozoic orogenies (Famatinian and Pampean) and later reactivated by Andean tectonics, provided fractured basement rocks with a long record of crustal evolution (Rapela et al., 1998; SEGEMAR, 2019). This stratigraphic and tectonic synthesis enhances the interpretation of geothermal systems conditioned by lithological inheritance and structural reactivation.

CHAPTER III: CHARACTERIZATION OF THE STUDY AREA

III.1. Geographic Location of the Study Area

The study area is located in northwestern Argentina, a geologically diverse region characterized by geological provinces that are essential for understanding regional hydrogeology and hydrogeochemistry. This area includes important geological provinces such as the The Puna, Sub-Andean System, Famatina Range, Pampean Ranges, Frontal Cordillera, Eastern Cordillera, Precordillera, and the structural depressions of Iglesia Valley and Bermejo Valley in San Juan. Geographically, it is located between latitudes 22° and 31° south and longitudes 65° and 67° west.

National Route 40, which crosses the region from north to south, connects the provinces of Jujuy, Salta, Catamarca and San Juan, facilitating access to the various study areas. This route also hosts several relevant thermal manifestations that will be analyzed in this research, which makes it a central corridor for monitoring thermal resources in the región (Figure 1).

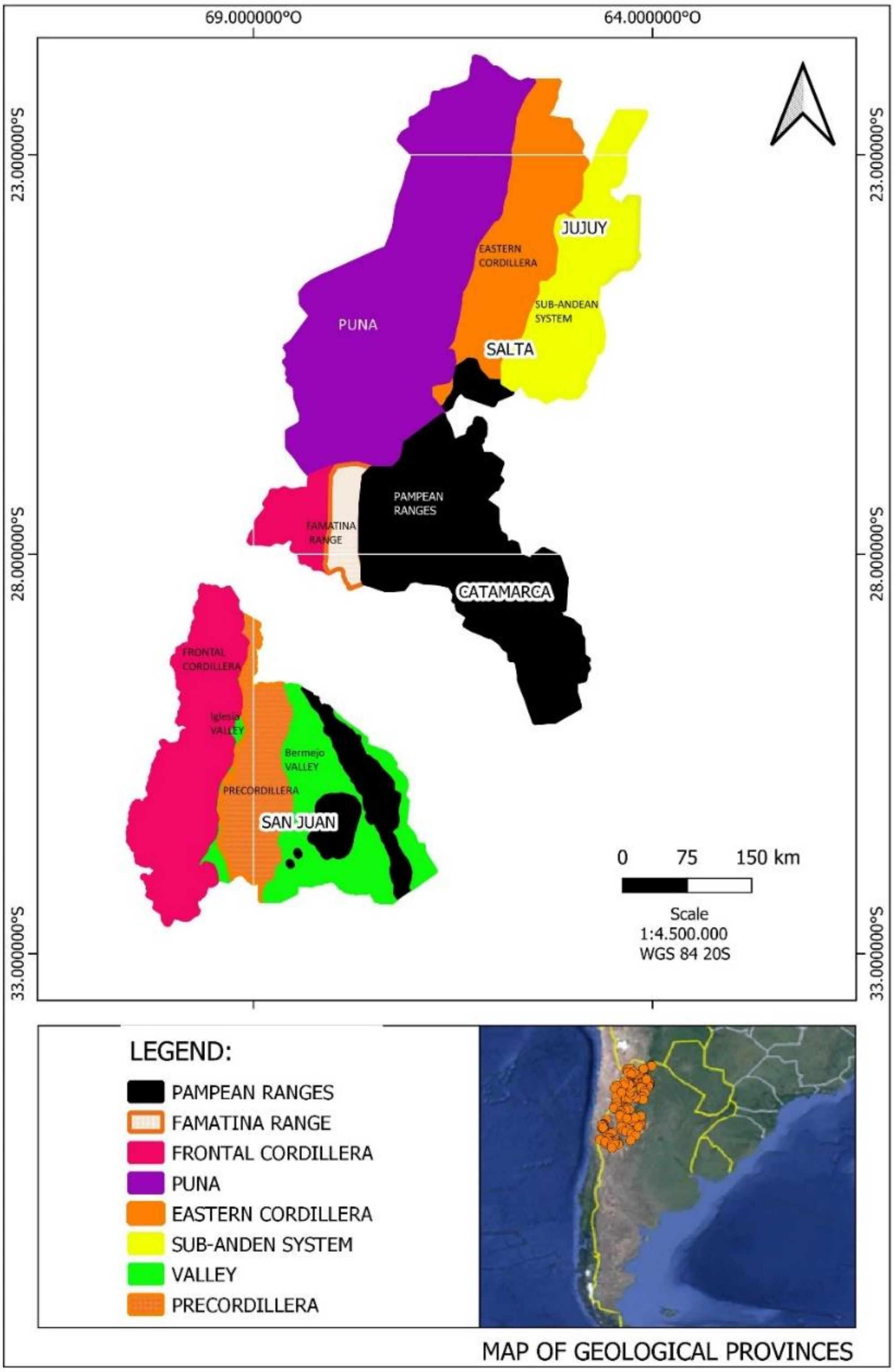

Figure 1. Geological provinces of the study area and regional location.

This map was created by the author of this thesis to represent the main geological provinces involved in the study area: the The Puna, the Eastern Cordillera, the Sub-Andean System, the Famatina Range, and the Pampean Ranges. Each geological province was delimited based on its structural and lithological identity and overlaid onto a simplified administrative background showing current provincial boundaries. The geographic provinces (Jujuy, Salta, Catamarca, and San Juan) were labeled from north to south to facilitate spatial reading. A regional map of Argentina is also included, highlighting the study area and the location of the hydrogeochemical samples analyzed. This representation highlights that administrative boundaries do not accurately reflect the natural units that control geodynamics, hydrogeology, and groundwater chemistry. On the contrary, geology defines the true functional limits of the territory. This understanding led to the hydrogeochemical analysis being structured around longitudinal correlations between geological provinces, grouping them according to their relative position and structural continuity beyond administrative limits. As a result, three main geological associations were established: (1) The Puna and Frontal Cordillera, (2) Eastern Cordillera, Famatina Range, and Precordillera, and (3) Pampean Ranges and Sub-Andean System.

Source: Autor based on SEGEMAR (2019) and INTA (2023).

III.2. Geological Evolution

The present-day configuration of the geological provinces in northwestern Argentina results from a long and intricate tectonic, magmatic, and sedimentary history spanning from the Proterozoic to the Quaternary. Each province represents a structural domain with a distinct lithological and chronological identity, shaped by successive orogenic events, accretionary processes, and continental collisions (Ramos, 1999; Astini, 1998).

The story begins in the deep Proterozoic, when the crystalline basement of the Pampean Ranges was formed. These ancient rocks were later uplifted and fractured during the early Paleozoic Pampean and Famatinian orogenies (Rapela et al., 1998; San José Rodríguez, 2008). Around 490–440 million years ago, the Famatina Range rose, forming part of a magmatic arc linked to the eastward subduction of oceanic crust beneath the Gondwanan margin. This arc left behind Ordovician volcanic, plutonic, and sedimentary sequences that were later intensely deformed (Aceñolaza & Toselli, 1973; Astini, 1998).

Simultaneously, the Precordillera began to take shape as a passive continental margin. It accumulated thick carbonate and siliciclastic marine sequences during the Paleozoic, which were subsequently deformed and uplifted by Andean tectonics. According to the Laurentian terrane model, this block would have collided with Gondwana during the Ordovician, becoming an exotic addition to the South American margin (Astini et al., 2005; Ramos, 1999).

To the west, the Frontal Cordillera records a younger but equally complex evolution. It consists of volcanic and sedimentary units from the Permian to the Tertiary, linked to back-arc and forearc environments during Andean orogenesis. Deep crustal faults and Neogene intrusive bodies have enabled the development of active geothermal systems such as those in the Valle del Cura (Barcelona, 2015; Hovland et al., 2015; SEGEMAR, 2023). Its elevated relief and fractured lithologies are key to understanding the current distribution of thermal manifestations in this region.

Further west, the The Puna began to rise during the Miocene as a result of continued Nazca plate subduction beneath the South American plate. Crustal thickening, Neogene volcanism, and compressive tectonics created a high-altitude plateau (>5000 m) composed of intermontane basins filled with volcanic, sedimentary, and evaporitic successions (Gómez Tapias et al., 2023; SEGEMAR, 2023).

To the east, the Eastern Cordillera originated from Paleozoic siliciclastic marine units. These sediments were deformed first during the Oclóyic Cycle and later reactivated by Andean compression, giving rise to a classic fold-and-thrust belt (Ramos, 1999; Mon, 2005).

At the Andean front, the Subandean Ranges represent the most recent orogenic development. This active fold-and-thrust belt comprises Cretaceous to Quaternary foreland basin deposits deformed into thin-skinned tectonic structures during Neogene to Quaternary compressional phases (Allmendinger et al., 1997; SEGEMAR, 2023).

In San Juan, tectonic uplift generated intermontane depressions such as the Valle de Iglesia and Valle de Bermejo. These structural basins, filled with Neogene and Quaternary sediments, reflect synorogenic accommodation formed by the rise of adjacent blocks. Their structural geometry favors aquifer development and the ascent of thermal waters (Hinzer et al., 2021; Jordan et al., 1993a).

To identify the lithological units at each sampling site, the 1:5,000,000 Geological Map of South America by Gómez Tapias et al. (2019) was used. This map allowed correlation of thermal water samples with dominant rock types, including magmatic, volcanic, sedimentary, carbonate, and evaporitic formations. These rock types are crucial for understanding the source of solutes, the degree of water–rock interaction, and thermal characteristics of the groundwater systems.

The integration of geological, hydrogeological, and hydrogeochemical data demonstrates that the lithological diversity and structural complexity of each province directly influence the hydrothermal systems analyzed in this thesis. Interestingly, the hydrogeological classification by Auge et al. (2006) adopts the same nomenclature as the geological provinces described throughout this section, highlighting a remarkable convergence between structural domains and groundwater behavior (see Figure 2).

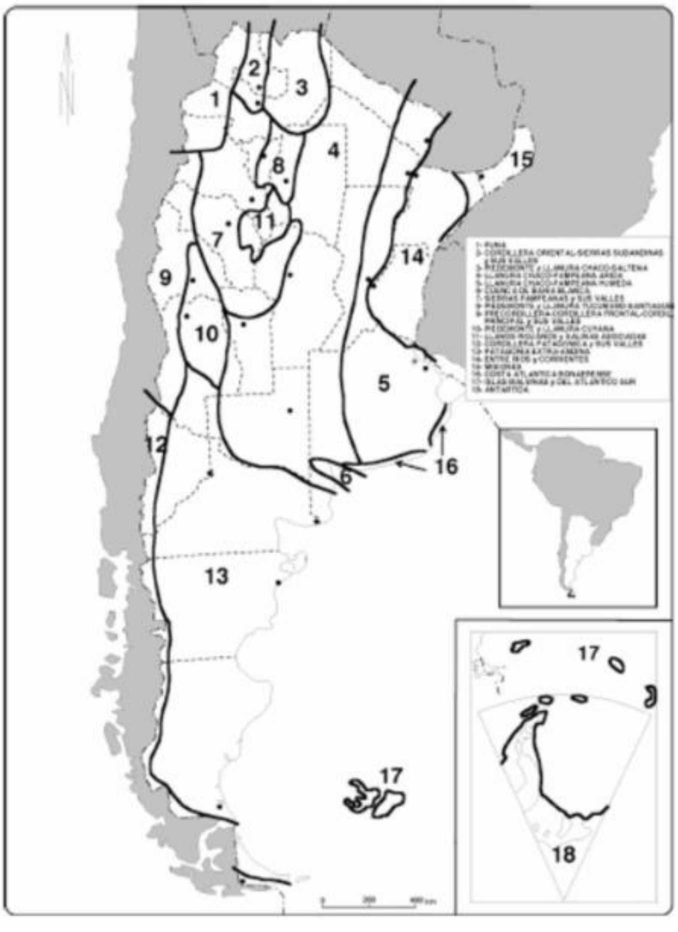

Figure 2. Regional hydrogeological map of Argentina showing main structural units.

The map presents the hydrogeological provinces defined by Auge et al. (2006), including sedimentary basins, mountain blocks, fault systems, and volcanic regions. The The Puna (1), located in the northwestern part of the country, is characterized by its endorheic basin configuration, high elevation (up to >6000 m a.s.l.), and strong volcanic influence. Other key provinces relevant to this study include the Eastern Cordillera (2), the Sub-Andean System (3), the Frontal Cordillera (4), the Precordillera (7), and the Pampean Ranges (10). Within the latter, the Famatina system has been included based on structural criteria, despite being geologically differentiated in other classifications. A particularly striking aspect is the fact that the hydrogeological provinces defined by Auge et al. (2006) share the same names as the geological provinces analyzed in this thesis. This coincidence is not merely nominal but reflects a genuine correspondence between structural, tectonic, and functional domains of the Andean system. As such, the use of common designations like The Puna, Eastern Cordillera, Sub-Andean System, or Pampean Ranges underscores the close interrelation between geological framework and the hydrogeological and hydrogeochemical behavior of the region. The lower right inset shows the location of the Malvinas (Falkland) Islands and South Georgia.

Source: Auge, M., Pacino, M.C., Benedetto, A., Degiovanni, S., Ercolano, A., & Custodio, E. (2006). "Hydrogeología de Argentina". Boletín Geológico y Minero, 117(1): 7–23. ISSN: 0366-0176. https://ri.conicet.gov.ar/handle/11336/76016

III.3. Climatic and Environment Conditions

The Andean region of northwestern Argentina, encompassing the provinces of Jujuy, Salta, Catamarca, and San Juan, is traversed by the so-called Arid Diagonal—a climatic corridor that connects the Andean Altiplano with the Patagonian steppe. This zone is characterized by low precipitation (less than 100 mm annually in hyper-arid sectors) and high evapotranspiration rates, significantly limiting meteoric recharge and shaping groundwater availability and hydrological processes (See Figure 3).

According to the Atlas de Zonas Áridas de América Latina y el Caribe (UNESCO, 2010), mean annual precipitation ranges from less than 100 mm in the The Puna to up to 300 mm in the more humid eastern piedmont areas. This heterogeneity is driven by altitudinal differences, orographic exposure, and local geographical configurations. At the continental scale, the Arid Diagonal lies between two opposing atmospheric domains: the humid tropics to the north and the temperate-humid influences of the south, reinforcing its dry nature (Abraham de Vázquez et al., 2000).

The persistent water deficit, together with endorheic basins and tectonic subsidence, has favored the formation of salt flats (salars), where evaporation far exceeds recharge. In these systems, the progressive concentration of dissolved salts and mineral precipitation (e.g., halite, gypsum, borax) generate extensive evaporitic environments. Notable examples include the Antofalla, Hombre Muerto, and Arizaro salars—located in high-altitude sectors of the The Puna with scarce vegetation and intense solar radiation. These sites not only serve as key paleoclimatic archives but also represent strategic reservoirs of lithium, boron, and other critical elements (Houston et al., 2011; Alonso et al., 2022).

In regions such as the The Puna, the combination of extreme aridity, endorheic drainage, and volcanic activity creates ideal conditions for sodium chloride (Na^+–Cl^-) enrichment in groundwater. The closed basins function as salinity concentration systems, where progressive evaporation, halite dissolution, and prolonged residence of groundwater in contact with altered volcanic rocks result in distinctive mineralization. This phenomenon explains the higher prevalence of Na^+–Cl^- type thermal waters in the The Puna compared to other geological provinces of the Argentine Northwest (Giggenbach, 1992; Hovland et al., 2015; Boni et al., 2019).

The climate map developed by the Instituto Argentino de Zonas Áridas (IADIZA–CONICET) graphically illustrates the longitudinal distribution of this dry belt, helping contextualize the studied provinces within one of the driest regions of South America.

In this context, a recent report by the Interinstitutional Committee for Monitoring the Water Crisis (CIGIAA, 2024) warned of a worsening hydrological situation in the province of San Juan. According to the report, the region is transitioning from a hydrological drought to a structural socio-economic crisis, characterized by a critical reduction in groundwater recharge, decreasing surface runoff, and progressive depletion of high-mountain cryogenic bodies and glaciers. This issue is especially acute in areas like Valle de Iglesia, where water supply depends on seasonal meltwater from debris-covered glaciers and permafrost.

This climatic and cryospheric degradation has also impacted irrigation systems, regional economies, agricultural production, and rural livelihoods. Reduced glacial and snowmelt inputs, combined with higher temperatures and persistent drought, have triggered cascading effects that exacerbate water scarcity, social vulnerability, and conflicts over resource allocation.

From west to east, across all provinces, there is a consistent increase in precipitation and a transition in hydroclimatic conditions. While the western domains (The Puna and Frontal Cordillera) are characterized by hyper-arid or arid environments with low recharge potential, the eastern domains (Sub-Andean System and Pampean Ranges) receive more rainfall (up to 300 mm) and are more favorable to direct meteoric recharge. This trend reflects the influence of orographic precipitation and decreasing elevation, as well as exposure to humid air masses from the Atlantic basin.

In summary, the Arid Diagonal represents a fundamental climatic and environmental framework for interpreting the distribution, functioning, and evolution of hydrothermal systems in the northern part of the Argentine Andes—particularly in the NOA (northwestern Argentina) and Cuyo regions. Its influence determines not only water availability and groundwater recharge but also the growing vulnerability of these systems to climate change, desertification processes, and anthropogenic pressures on mountain water resources.

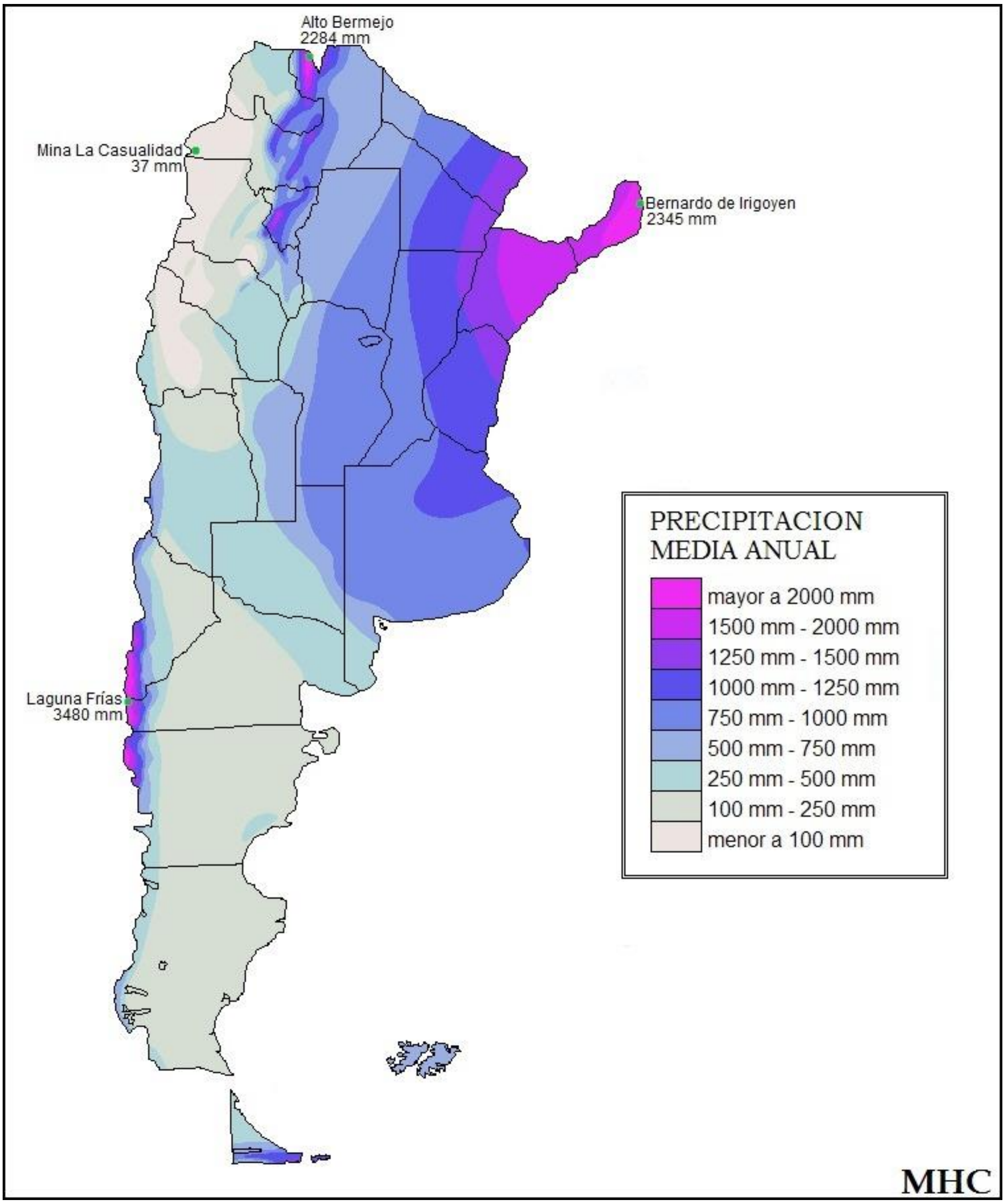

Figure 3. Map of the Arid Diagonal in Argentina.

The map shows the distribution of the arid corridor that crosses Argentina from the northwestern Andes to Patagonia, as defined by IADIZA-CONICET. It can be seen that the provinces of Jujuy, Salta, Catamarca, and San Juan are entirely encompassed within this dry belt, highlighting their climatic vulnerability and the environmental constraints affecting groundwater recharge and thermal manifestations.

Source: Adapted from Restauremos Argentina (2016), based on IADIZA-CONICET Retrieved from https://restauremos-ra.blogspot.com/2016/08/diagonal-arida.html

III.4. Cryosphere and Permafrost Influence

The study of the cryosphere and permafrost in arid Andean regions is essential for understanding hydrogeological processes related to the origin and dynamics of thermal waters. Soil temperature—strongly influenced by altitude, solar exposure, and the presence of permafrost—directly affects groundwater circulation pathways, mineralization, and temperature (Boni et al., 2019; Villalba et al., 2020).

Permafrost is defined as ground that remains at or below 0 °C for at least two consecutive years (Taillant, 2012). In the Andean context, the distribution of permafrost and other cryogenic bodies is not homogeneous, but rather follows an altitudinal thermal zoning that clearly separates cold areas from warm ones. This zoning allows for direct correlations between ground thermal behavior and its hydrogeological function: in warm zones, higher ground temperatures favor deep infiltration and the subsequent emergence of thermal waters; whereas in cold zones, the presence of the cryosphere—glaciers, debris-covered glaciers, and permafrost—acts as a barrier to deep recharge (IANIGLA-CONICET, 2018; Villalba et al., 2020).

In fact, the surveyed hydrothermal springs are consistently located in the warmest zones of the regional thermal gradient, where the absence of permafrost allows meteoric waters to infiltrate to greater depths, become heated through interaction with deep rocks, and later reemerge as thermal springs. In contrast, glaciers and permanent ice bodies—such as debris-covered glaciers or areas of discontinuous permafrost—are concentrated in higher, colder zones. This distribution not only supports the hydrogeological interpretation of observed thermal features but also highlights the critical role of ground temperature as a controlling factor in high-altitude hydrothermal systems (Boni et al., 2019; Villalba et al., 2020; Taillant, 2012).

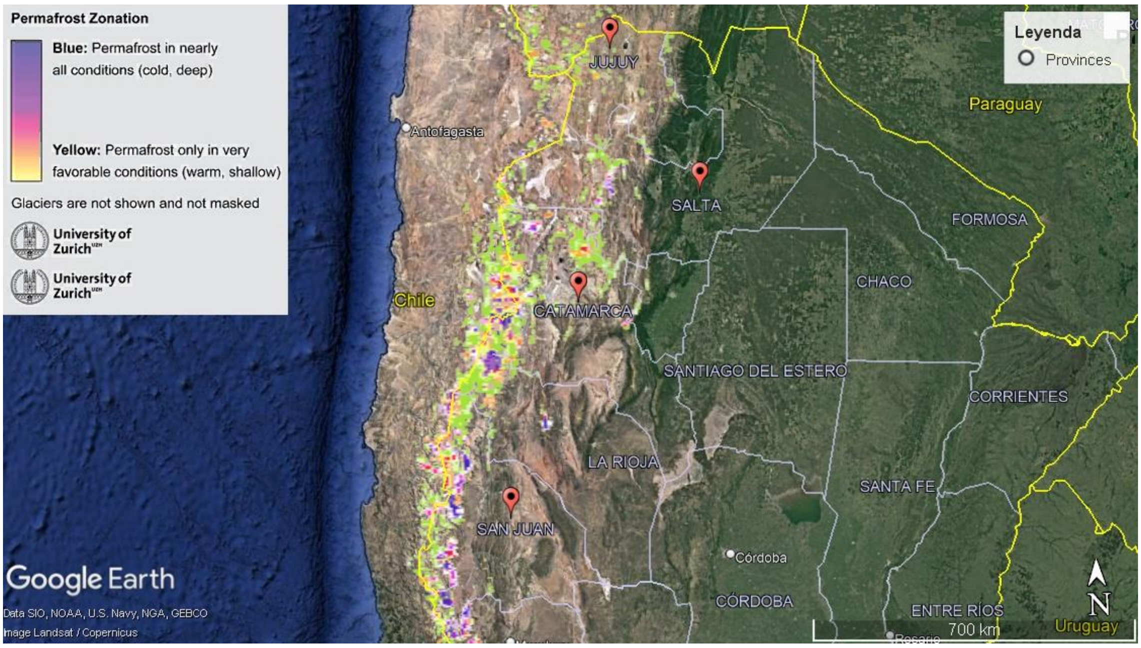

Figure 4. Permafrost zonation in the provinces of Jujuy, Salta, Catamarca, and San Juan

The map was generated using the Global Permafrost Zonation Index Map developed by the University of Zurich (Switzerland), which combines elevation and air temperature data to estimate the potential distribution of permafrost. The color scale in the upper left corner indicates that blue shades represent colder and deeper areas with a high probability of permanent permafrost, while yellow and pink tones correspond to warmer or shallower areas where permafrost is sporadic or absent. This map was incorporated into thesis to validate the spatial consistency of the analyzed hydrothermal samples. The zonation confirmed that thermal springs are systematically located in warm zones (yellow/pink), supporting their deep meteoric origin and circulation through unfrozen subsurface environments. In contrast, blue areas match the highest and coldest sectors, where active cryospheric bodies such as uncovered or debris-covered glaciers are concentrated.

Source: Global Permafrost Zonation Index Map, University of Zurich, available via Google Earth https://center-hre.org/wp-content/uploads/2012/11/El-Ambiente-Periglacial-y-la-Mineria-en-la-Argentina-English.pdf.

III.5. Climate–Cryosphere–Groundwater Interactions

To comprehensively understand hydrogeological processes in arid mountainous environments, key climatic and cryospheric variables from the Central Andes were integrated. Ground temperature and permafrost maps developed by Taillant (2012), the National Glacier Inventory by IANIGLA-CONICET (2012), and recent studies by Forte et al. (2016, 2021) were used to spatially contextualize the distribution of cryogenic bodies—exposed glaciers, debris-covered glaciers (rock glaciers), and permafrost zones—relative to thermal spring occurrences in the provinces of San Juan, Catamarca, Salta, and Jujuy (Figure 5).

This mapping allowed the distinction of warm, discontinuous, and periglacial soil zones, which are critical for interpreting recharge mechanisms and the presence of confined systems. In high-altitude areas of the Frontal Cordillera and the Altiplano (6770 m a.s.l.), permafrost zones act as thermal barriers, generating hydrostatic pressures that favor the development of deep hydrothermal systems. These frozen bodies induce seasonal discharge dynamics, regulating baseflows of thermal springs and ephemeral streams in structurally controlled basins such as Valle de Iglesia or the high-altitude depressions of the The Puna (Forte et al., 2016; Villarroel et al., 2021; Trombotto Liaudat & Sileo, 2020).

In the province of San Juan, more than 5,000 cryogenic bodies have been inventoried, mainly in the Frontal Cordillera between 3,800 and 6,200 m a.s.l., where the combination of altitude, slope orientation, and precipitation enables their preservation. In contrast, despite its high elevation (>4000 m), the The Puna region does not exhibit active glaciers. This absence is not due to cartographic omission but rather to a real physical limitation: hyper-arid conditions—with annual precipitation below 100 mm, high solar radiation, and low atmospheric humidity—prevent the accumulation of snow required to form and sustain glaciers (Bookhagen & Strecker, 2008). Instead, smaller cryogenic features are observed, such as snow patches, penitentes, seasonal frozen soils, and melt-driven springs, which may contribute to episodic recharge, though with negligible volumetric significance compared to actual glaciers.

On the other hand, glaciers and debris-covered glaciers have been mapped at elevations above 5,000 m a.s.l. in high sectors of the Eastern Cordillera, Sierra de Famatina, and volcanic zones of Catamarca, Salta, and Jujuy, where orographic moisture allows limited snow accumulation. While their surface area is small, they play a critical role as seasonal recharge reservoirs.

Although no direct hydrodynamic modeling has confirmed a functional hydraulic connection between cryogenic landforms and thermal spring systems, the observed spatial proximity between permafrost zones and geothermal discharges, coupled with thermal and structural characteristics of the terrain, support the formulation of a new hypothesis. Such hypothesis proposes that frozen reservoirs may act as delayed storage systems, gradually releasing meltwater that buffers seasonal recharge of shallow and deep aquifers. This potential interaction deserves further investigation to assess its implications on geothermal flowpaths and long-term water availability in arid Andean basins.

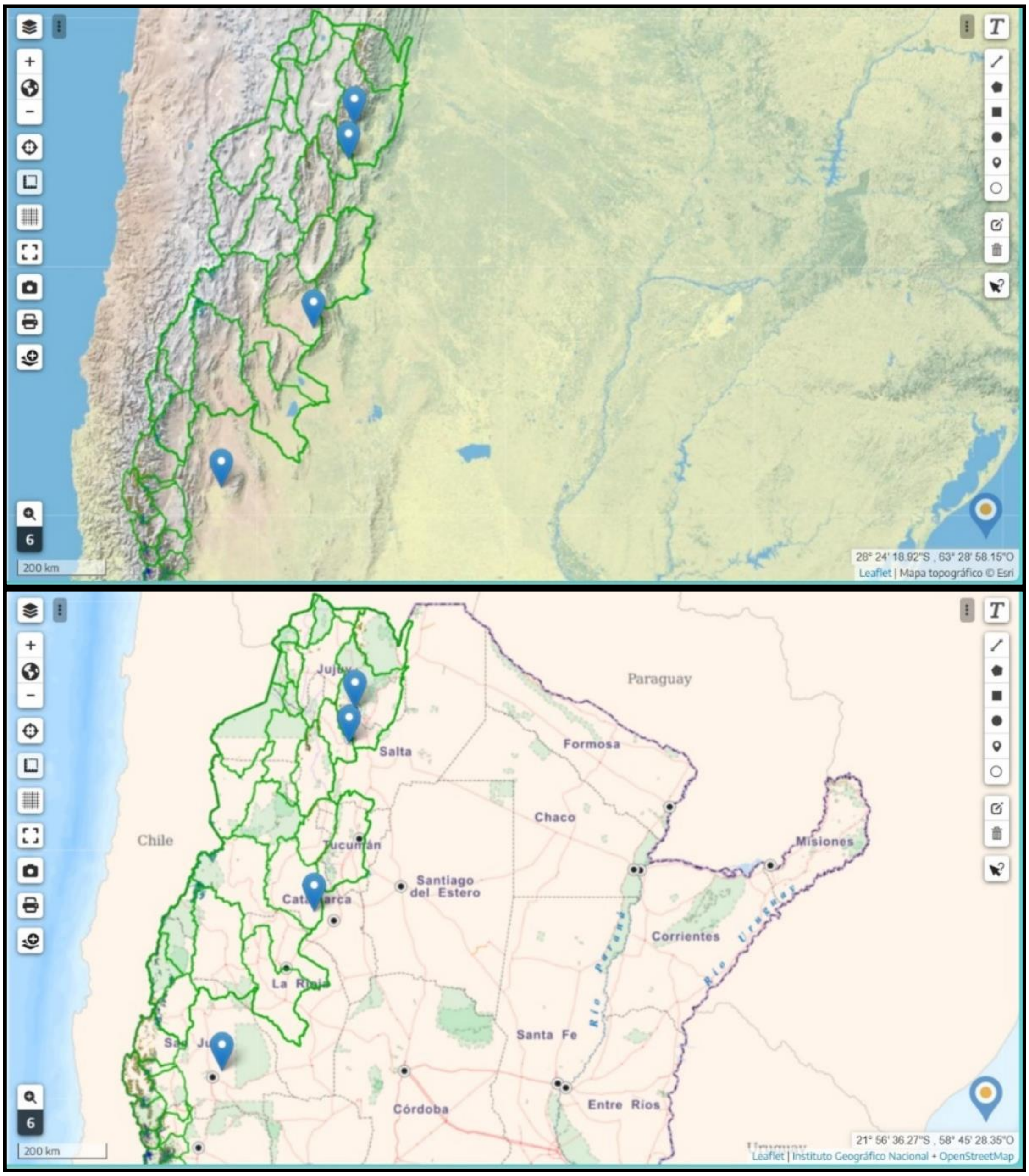

Figure 5. Spatial and typological distribution of glacial bodies in the arid Andes.

The maps illustrate the geographic and typological distribution of inventoried glacial bodies in the arid Andes of northwestern Argentina, according to the National Glacier Inventory (Law 26.639). The images were extracted from the official mapping platform of IANIGLA-CONICET (http://maping.glaciaresargentinos.gob.ar/visor_ing_v122024/index.html?zoom=4&lat=-

40.8803&lng=-
60.6445&layers=argenmap,glaciares_pais_v12,glaciares_pnlg_v2,limite_subcuencas_pais_v17)
, using the "Glaciares Andes Desérticos v1" and "Límite de subcuencas Andes Desérticos v1" layers, with topographic (top) and satellite (bottom) backgrounds. Green lines delineate hydrographic sub-basins belonging to a large endorheic Andean watershed extending through the provinces of Jujuy, Salta, Catamarca, and San Juan. Blue markers indicate exposed glaciers (GE), while brown markers correspond to debris-covered glaciers (GEI) or rock glaciers (GEA), following the official classification by IANIGLA.A key observation is the complete absence of inventoried glaciers in the The Puna, despite its high altitudes (>4000 m a.s.l.), due to hyperarid conditions (precipitation <200 mm/year, high radiation, strong sublimation), which prevent glacier development and persistence. In contrast, glacial bodies are concentrated in steep, shaded, and rugged terrain such as the Frontal Cordillera, Famatina Range Precordillera, and higher sectors of the Pampean Ranges, between 4000 and 6000 m a.s.l. These maps are essential tools for analyzing the regional cryospheric context and integrating it into the hydrogeological interpretation of mountain systems in arid regions.

Source: IANIGLA-CONICET (2023).

III.6. Groundwater Flow and Hydrothermal Circulation

Understanding hydrogeological processes in arid mountain environments requires a conceptual framework that explains how meteoric water infiltrates high-altitude areas, circulates deep through fractured rocks and tectonic structures, and discharges into thermal springs within intermontane valleys. These schematic flow paths reveal the influence of topography, lithology, fault structures, and thermal gradients on groundwater behavior in structurally complex regions such as the northwestern part of the Argentine Andes.

A valuable framework for this is the distinction between mountain front recharge (MFR) and mountain block recharge (MBR), as conceptualized by Manning and Solomon (2003). In MFR, groundwater recharge occurs near the mountain front—through streams, surface runoff, or alluvial fans—and typically generates short flow paths, low residence times, and relatively fresh chemical signatures. In contrast, MBR involves groundwater recharge within the mountain massif itself, where water migrates through deep fractures and structural conduits, resulting in longer flow paths, prolonged residence times, and more evolved hydrochemical characteristics.

Bresciani et al. (2018) offer a robust methodology for differentiating between MFR and MBR using three key parameters: hydraulic head, chloride concentration, and electrical conductivity. According to their results, MBR systems tend to show higher chloride levels and greater conductivity due to prolonged interaction between water and rock and the accumulation of solutes. In contrast, MFR systems are characterized by lower chloride content, indicating more recent recharge and limited hydrochemical evolution. This distinction is particularly useful in arid regions where recharge is sporadic and structural controls dominate groundwater circulation.

Geothermal systems in these environments can be further classified as convective or conductive, depending on the dominant heat transfer mechanism (Hochstein, 1990; Giggenbach, 1991). Convective systems, often associated with active volcanism or residual magmatic heat, drive the upward flow of fluids through permeable structures, typically producing high-temperature springs. In contrast, conductive systems operate without direct magmatic heat input, relying on high geothermal gradients and heat transport by conduction through the rock mass, often resulting in low-enthalpy thermal springs. Both types can coexist in Andean regions, depending on local tectonic, lithological, and thermal conditions.

Notably, Christiansen et al. (2021) documented a low-enthalpy conductive geothermal system in Pismanta (San Juan, Argentina), where deep groundwater circulation is enhanced by structural controls and a normal to anomalous geothermal gradient, with no evidence of recent volcanism. This case highlights how structurally guided deep flow can generate thermal emergence even in non-volcanic mountainous terrain.

Seasonal recharge from snowmelt and cryosphere melting (permafrost, glaciers, debris-covered glaciers) also plays an essential role in high mountain hydrology. Studies by IANIGLA (2023) and analyses by Somers and McKenzie (2020) highlight that the timing and volume of recharge in these environments are strongly influenced by the cryosphere, which in turn affects both shallow and deep groundwater systems.

Together, these conceptual models—MFR vs. MBR, convective vs. conductive thermal regimes, and cryosphere-driven seasonal recharge—provide a solid theoretical basis for interpreting groundwater flow and thermal circulation in arid, structurally controlled mountain environments. They also provide the necessary framework for analyzing hydrogeochemical data and inferring flow pathways, recharge sources, and thermal drivers in complex Andean systems.

These conceptual distinctions are illustrated in Figure 6, which presents schematic diagrams of MFR and MBR systems. The figure highlights the contrasting flow mechanisms, recharge locations, and structural controls that define each regime, including a mixed scenario where both processes operate simultaneously. This model is particularly valuable for interpreting the hydrogeological behavior of thermal waters in structurally complex intermontane basins, such as those found in Frontal Cordilera, Iglesia Valley and Bermejo Valley.

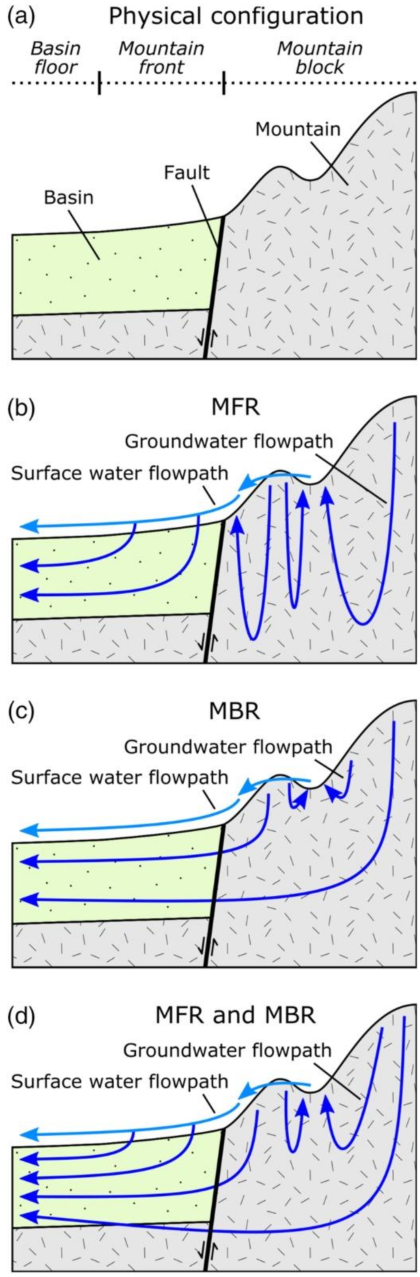

Figure 6. Conceptual diagrams illustrating MFR and MBR systems.

Conceptual diagrams illustrating Mountain Front Recharge (MFR) and Mountain Block Recharge (MBR) systems. a) A schematic example showing the physical transition between mountain and basin, with a fault acting as a controlling structure. b) A system dominated by MFR, where surface and groundwater flow from the mountain directly toward the basin. c) A system dominated by MBR, where infiltration occurs higher in the mountain block and follows deeper pathways. d) A mixed system with coexistence of both MFR and MBR components. This model is particularly useful for interpreting hydrothermal systems in the arid Andes of northwestern Argentina. In regions such as Iglesia Valley, Cura Valley, and Bermejo Valley, groundwater circulation occurs under structural and topographic conditions analogous to those illustrated here featuring high-altitude recharge, deep flow through fractured geological formations, and discharge at lower elevations. The presence of thermal springs associated with faults suggests a combined MFR–MBR dynamic, where topography, lithology, and structural control strongly influence flow trajectories and water chemistry. This conceptual framework supports the hypotheses presented in this thesis regarding the origin, circulation, and mineralization of Andean hydrothermal systems.

Source: Bresciani et al. (2018), in Somers & McKenzie (2020), *WIREs Water*. https://wires.onlinelibrary.wiley.com/doi/10.1002/wat2.1475

CHAPTER IV: RESULTS, INTERPRETATION AND DISCUSSION

In this chapter, the discussions about the results obtained from the analysis of the hydrochemistry of thermal waters in the provinces of Jujuy, Salta, Catamarca, and San Juan are addressed. The data acquired through analytical tools, such as Piper diagrams, mineral saturation indices, and ion relationship analyses, allow for a deeper understanding of the variations in the chemical composition of groundwater and the underlying geological and tectonic causes.

The ions analyzed in this study include the following parameters: Temperature (°C), Electrical Conductivity (E.C.) [µS/cm], in situ pH, Ca^{2+} [mg/L] and Ca^{2+} [meq/L], Mg^{2+} [mg/L] and Mg^{2+} [meq/L], Na^{+} [mg/L] and Na^{+} [meq/L], K^{+} [mg/L], HCO_3^{-} [mg/L] and HCO_3^{-} [meq/L], Cl^{-} [mg/L] and Cl^{-} [meq/L], SO_4^{2-} [mg/L] and SO_4^{2-} [meq/L], and F^{-} [mg/L]. These measurements provide key information about the chemical composition of thermal waters and their potential interactions with the geological and tectonic formations in the region.

Additionally, other data such as altitude, temperature, pH, and TDS (Total Dissolved Solids) are interpreted, providing a more complete overview of the hydrogeochemical system in the provinces of Jujuy, Salta, Catamarca, and San Juan. The information obtained allows for an observation of how geological, altitudinal, and thermal factors interact in the behavior of thermal waters. The discussions include the relationships of these variations with the geological activity of the region, the influence of geological formations, and their connection with the geochemical characteristics of the observed thermal waters.

The geological groups of provinces referenced in this analysis are as follows:

- JUJUY: The Puna, Sierras Subandinas, and Eastern Cordillera.
- SALTA: The Puna
- CATAMARCA: The Puna, Sierras Famatina, Pampean Ranges.
- SAN JUAN: Frontal Cordillera, Precordillera, Pampean Ranges, and the structural depressions of Iglesia Valley and Bermejo Valley.

One of the key aspects influencing the dynamics of groundwater and its hydrochemical composition is the flow path through the geological structures of the region. Fault and fracture systems play a fundamental role in the circulation of groundwater, acting as preferential pathways for water migration. Thermal waters in these provinces follow paths controlled by these fault systems, which affects the mixing and exchange of dissolved ions in the waters. Faults, being structural weak zones, provide direct access to minerals found in the surrounding rocks, which can alter the chemical composition of the water as it flows through them.

The flow path in relation to the fault systems helps to understand how groundwater is recharged, circulates, and emerges at thermal springs. Ionic composition data reveals how flows through these faults contribute to the variability in water chemistry, influenced by factors such as mineralization and ion exchange processes. Variations in the concentrations of certain ions may be directly related to the flow paths and the interactions these flows have with fractured or tectonically altered rocks.

This analysis provides key insights into understanding the mechanisms behind the circulation of groundwater, its relationship with thermal springs, and the aquifer dynamics. It is observed that the ionic composition of thermal waters varies according to the characteristics of the geological formations present in each province, reflecting a complex interaction between geological processes, regional geology, and groundwater chemistry.

The analysis of ionic relationships such as Na^{+}/Ca^{2+}, Mg^{2+}/Ca^{2+}, Cl^{-}/SO_4^{2-}, and Cl^{-}/HCO_3^{-} has also shown trends suggesting the influence of interactions between groundwater and rocks, as well as hydrothermal alteration processes in the studied thermal springs. These ionic relationships are fundamental to understanding the processes of ion exchange and mineralization of thermal waters in this region, which are controlled by the geological characteristics of each group of provinces.

IV.1. JUJUY

In the hydrogeological exploration of Jujuy (Figure 7), significant patterns emerge when analyzing various aspects, starting with the relationship between temperature and altitude in its three geological provinces: The Puna, Eastern Cordillera and Sub-Andean System.

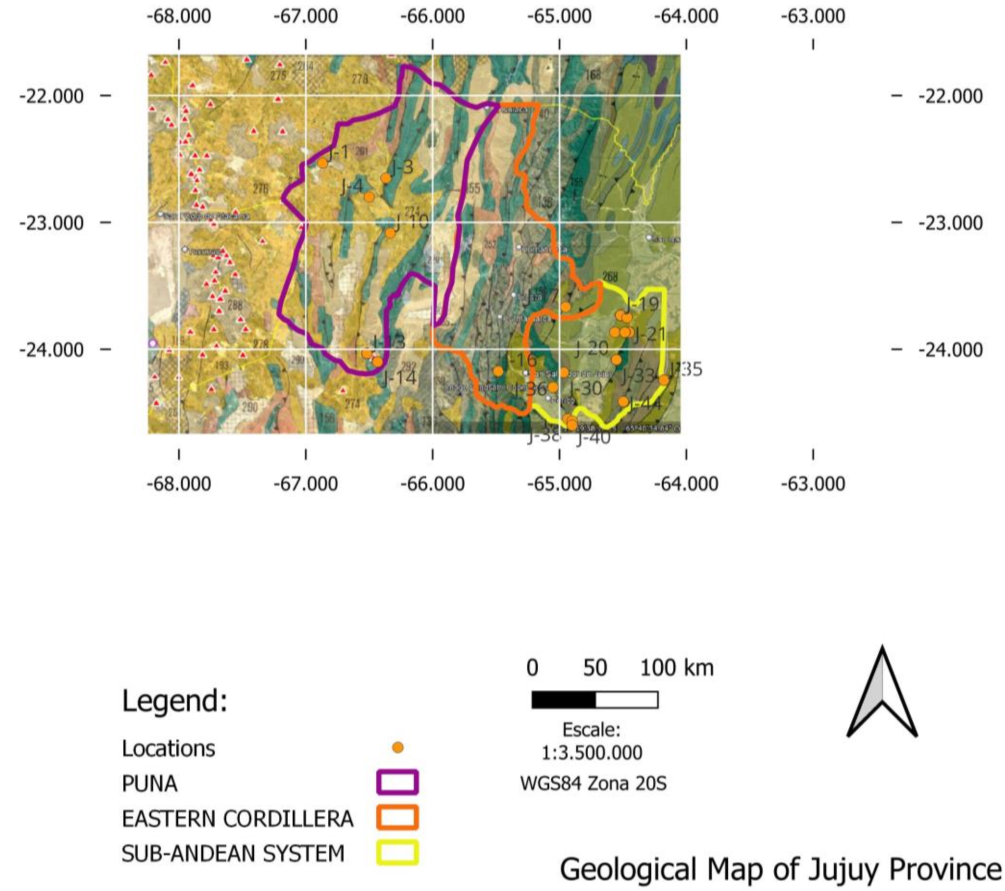

Figure 7. Location of the analyzed samples in Jujuy Province on the geological map.

The figure displays the spatial distribution of 72 thermal water samples collected in Jujuy Province, grouped by geological province: The Puna, Eastern Cordillera, and Subandean System. Samples are georeferenced on a geological base derived from the *Geological Map of South America* (CGMW, 2019), with tectonic fault traces included to highlight structural controls on groundwater flow. In the The Puna, samples are mainly located on Quaternary rhyolitic volcanic rocks (code 286), Tertiary undifferentiated volcanics (274), and Ordovician granitic plutonics (154). Most samples (e.g., J-13-1 to J-13-24) lie in the middle of two faults, indicating a strong structural control on hydrothermal upflow. Additional units include Quaternary (J-1) and Ordovician (J-3) siliciclastic sediments, as well as granitic intrusions that may align with deeper fault continuations (J-14 series). In the Eastern Cordillera, samples J-16-1, J-16-2, and J-17 lie on Cambrian (140) and Ordovician (156) siliciclastic sediments, all situated between two major faults, suggesting a structurally controlled discharge system typical of this folded and faulted belt. The Subandean System contains the largest group of samples, mostly on Tertiary siliciclastic sediments (279), with additional Cretaceous (252), Ordovician (156), Silurian (168), and Quaternary (292) units. Nearly all of these samples (e.g., J-19 to J-22, J-33 to J-44) are either located between two faults or directly on fault traces, demonstrating the role of compressional tectonics in guiding groundwater pathways. Thrust faults and associated ramp structures appear to act as conduits for ascending thermal waters. This figure provides a high-resolution view of the lithological, chronological, and structural setting of each sample, offering a solid foundation to interpret deep fluid flow, recharge zones, and hydrothermal mineralization across the province of Jujuy. Source: Commission for the Geological Map of the World – CGMW (2019). *Geological Map of South America*. Paris: UNESCO-CGMW.

Figure 8 illustrates the relationship between temperature and elevation/depth of thermal waters in the different geological provinces of the study area. The highest recorded temperature (85 °C) corresponds to a sample from the Sub-Andean System obtained from a borehole located at approximately 556 m a.s.l., with a depth of about 1085 m below ground surface. Because this measurement was obtained from a deep borehole, it is not directly comparable to temperatures measured in surface thermal springs.

Nevertheless, relatively high temperatures (around 60 °C) are also observed in the Sub-Andean System at elevations close to 370 m a.s.l., while comparable temperatures occur in the The Puna region at elevations around 4190 m a.s.l. These differences highlight the influence of geological setting and fluid circulation depth on thermal characteristics of the hydrothermal systems in the region.

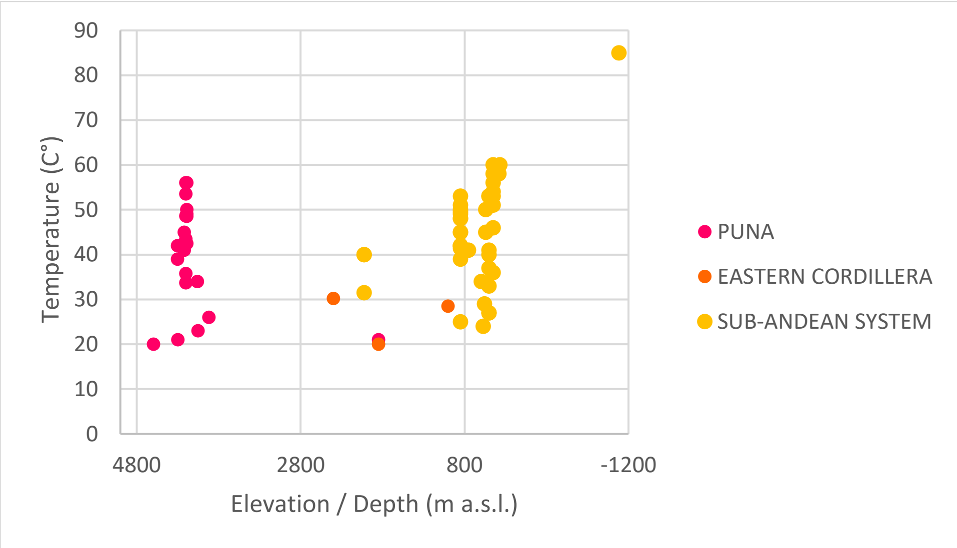

Figure 8. Relationship between temperature and elevation/depth of thermal waters from different geological provinces of the study area (The Puna, Eastern Cordillera and Sub-Andean System).

Figure 9. illustrates the relationship between total dissolved solids (TDS) and elevation/depth of thermal waters from the different geological provinces of the study area. The horizontal axis is arranged approximately from west to east across the Andean geological provinces. The highest TDS value reaches 14,700 mg/L and occurs in the Sub-Andean System at an elevation of approximately 500 m a.s.l. According to standard hydrochemical classifications, this value corresponds to saline water, as it exceeds 10,000 mg/L.

At the other end of the spectrum, minimum TDS values ranging between 208 and 907 mg/L indicate the presence of very fresh to fresh waters. However, most samples fall within the range of 1000 to 3500 mg/L, corresponding to brackish waters.

In the Eastern Cordillera, TDS values generally vary between 250 and 1000 mg/L, indicating predominantly fresh waters. In contrast, samples from the The Puna commonly exceed 1000 mg/L, suggesting brackish conditions, although a few anomalously low values corresponding to fresh waters are also observed.

TDS classification limits (mg/L)

0–250 mg/L — Very fresh water

250–1000 mg/L — Fresh water

1000–10,000 mg/L — Brackish water

10,000–100,000 mg/L — Saline water

100,000 mg/L — Brine

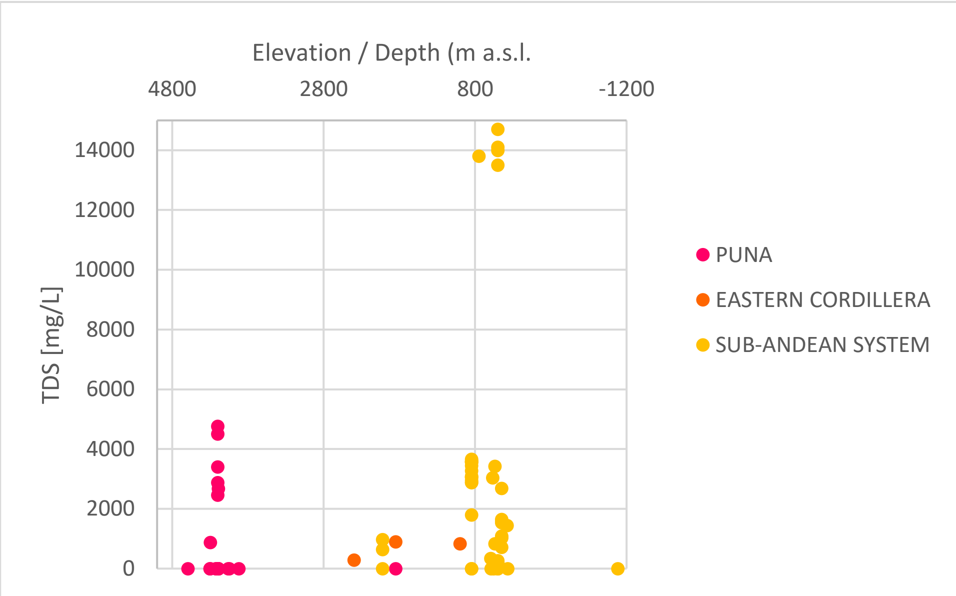

Figure 9. Relationship between total dissolved solids (TDS, mg/L) and elevation/depth of thermal waters from the different geological provinces of the study area (The Puna, Eastern Cordillera and Sub-Andean System).

In the analysis of Equivalent Concentration Ratios in meq/L (see Figure 10) of the Na^+ to Ca^{2+} ratio, distinctive patterns are evident at different altitudes grouped by geological provinces. In the Sub-Andean System, high concentrations of Na^+ stand out compared to lower proportions of Ca^{2+}. In the The Puna, a significant presence of Na^+ in relation to Ca^{2+} is recorded, even more pronounced in the Sub-Andean System, exceeding double the ratio presents in the The Puna. The Eastern Cordillera shows low concentrations of both ions, with a slight predominance of Na^+ in the composition.

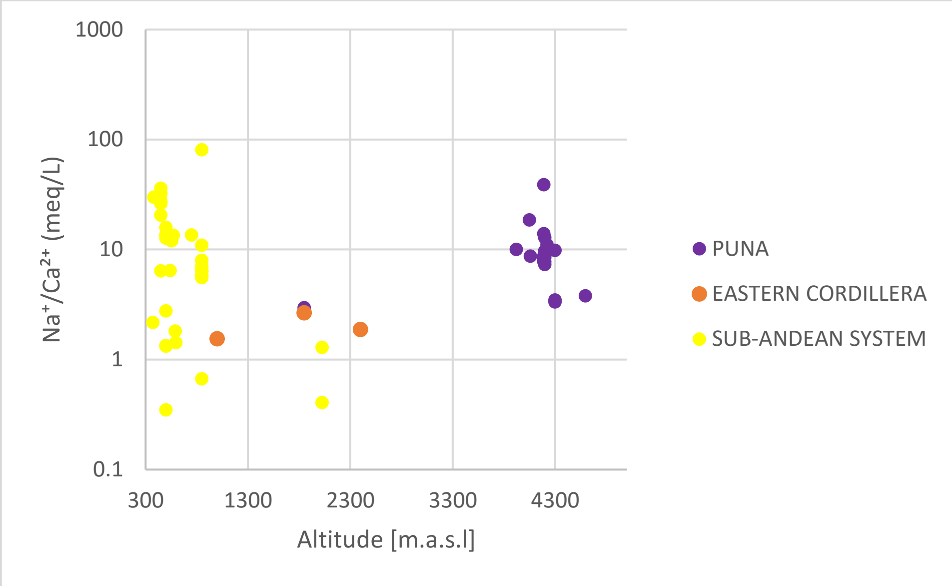

Figure 10. Na^{+}/Ca^{2+} (meq/L) according to geological provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of Mg^{2+} to Ca^{2+} (Figure 11), a minimal anomaly with a slight predominance of Mg^{2+} over Ca^{2+} is observed in the The Puna. In other regions, a higher concentration of Ca^{2+} compared to Mg^{2+} is recorded. This trend is replicated in the Sub-Andean System, where, similar to the The Puna, a minimal anomaly in favor of Mg^{2+} is present. In the Eastern Cordillera a more pronounced ratio of Ca^{2+} to Mg^{2+} is evident.

It is interesting to note that the highest Ca^{2+} anomaly is found in the The Puna, suggesting a unique chemical composition in this region compared to the Sub-Andean System and the Eastern Cordillera.

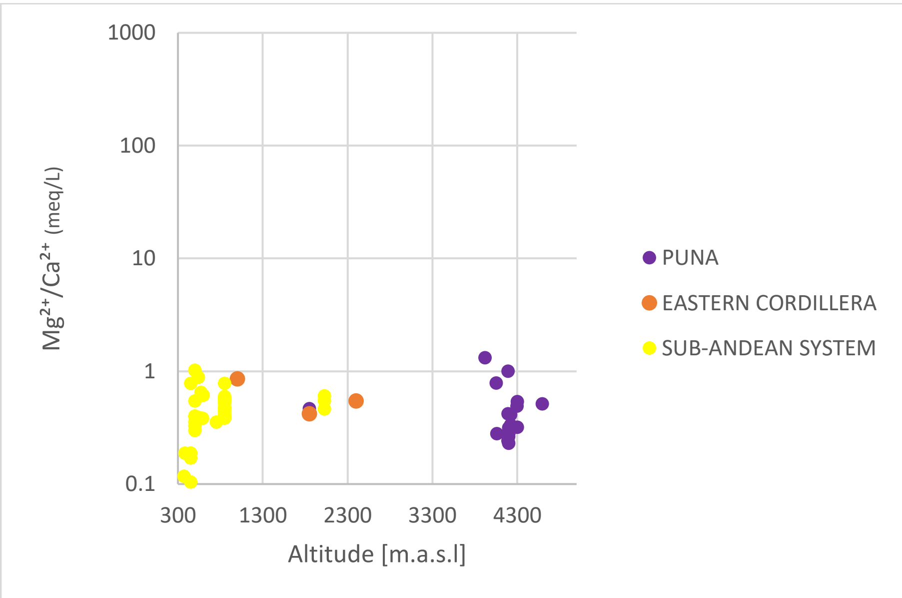

Figure 11. Mg^{2+}/Ca^{2+} (meq/L) according to geological provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of Cl^- to SO_4^{2-} (see Figure 12), the The Puna records the presence of Cl^- in most locations compared to SO_4^{2-}, with a majority of SO_4^{2-}. Conversely, in the Sub-Andean System region, there are mostly SO_4^{2-}, but with the maximum Cl^- anomaly of all regions.

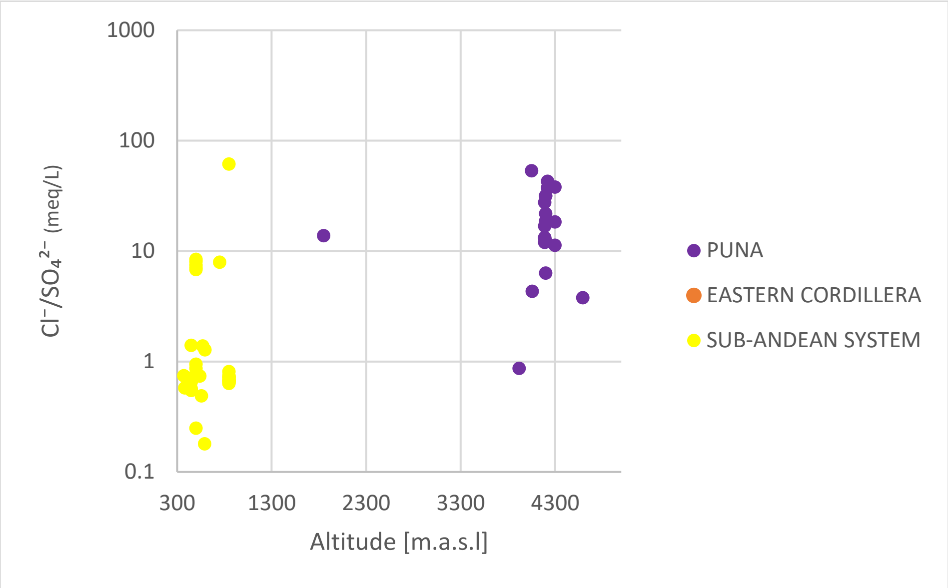

Figure 12. Cl^-/SO_4^{2-} (meq/L) according to geological provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of Cl^- to HCO_3^- (see Figure 13), the The Puna records the presence of Cl^- in most locations compared to HCO_3^-. However, the highest values are found in the Sub-Andean System region. This is indicated at the higher elevations of the Sub-Andean System, where a higher content of HCO_3^- is concentrated, while at intermediate altitudes, the presence of Cl^- predominates, with the most significant anomaly.

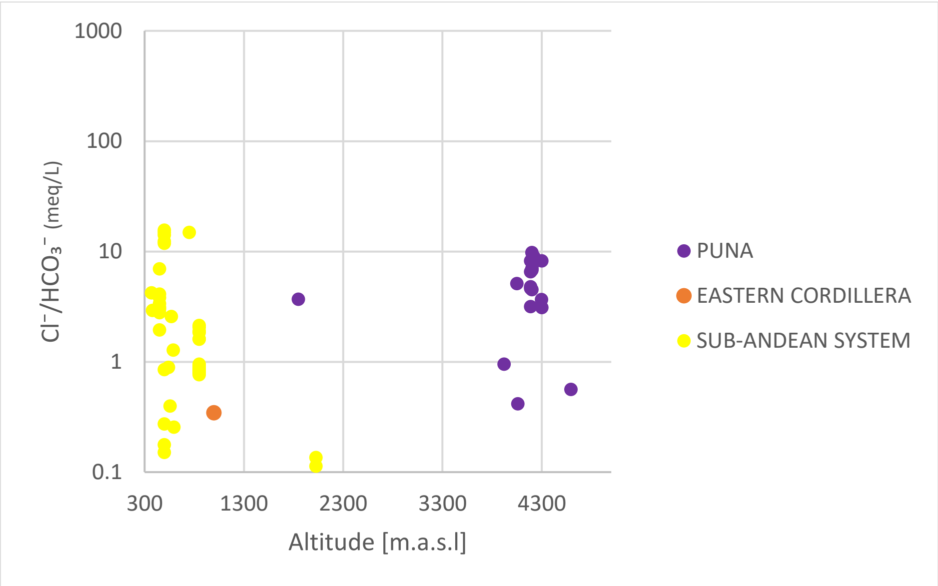

Figure 13. Cl^-/HCO_3^- (meq/L) according to geological provinces.

The calcite saturation index (see Figure 14) shows that it is Undersaturated in the siliciclastic sedimentary rocks of the The Puna and the Eastern Cordillera, where as in the Sub-Andean System, it is mostly oversaturated and occasionally Undersaturated. In the The Puna, there are granitic plutonic rocks where calcite is oversaturated and Undersaturated. In the volcanic rocks of the The Puna, calcite is Undersaturated.

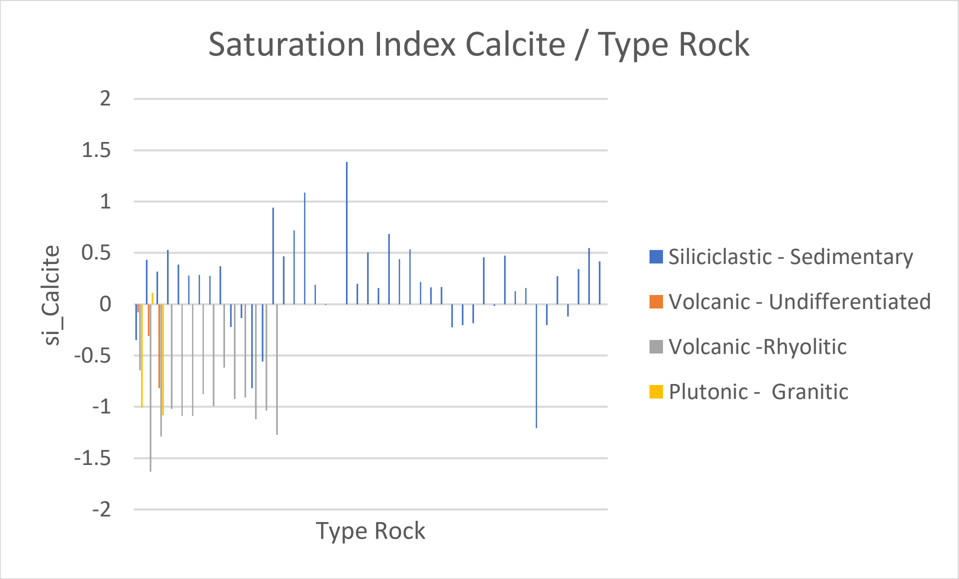

Figure 14. Saturation Index of Calcite phases.

The dolomite saturation index (see Figure 15) indicates that it is Undersaturated in all rocks of the The Puna, except for a sample in the plutonic granitic rock where it is oversaturated, and it is also oversaturated in two samples of undifferentiated volcanic rocks. In all rhyolitic rocks of the The Puna, dolomite is Undersaturated, and the same occurs in siliciclastic sedimentary rocks. In the Eastern Cordillera, dolomite is Undersaturated in siliciclastic rocks, except for one sample that is oversaturated. In the Sub-Andean System, dolomite is mostly oversaturated, except for two samples where it is Undersaturated.

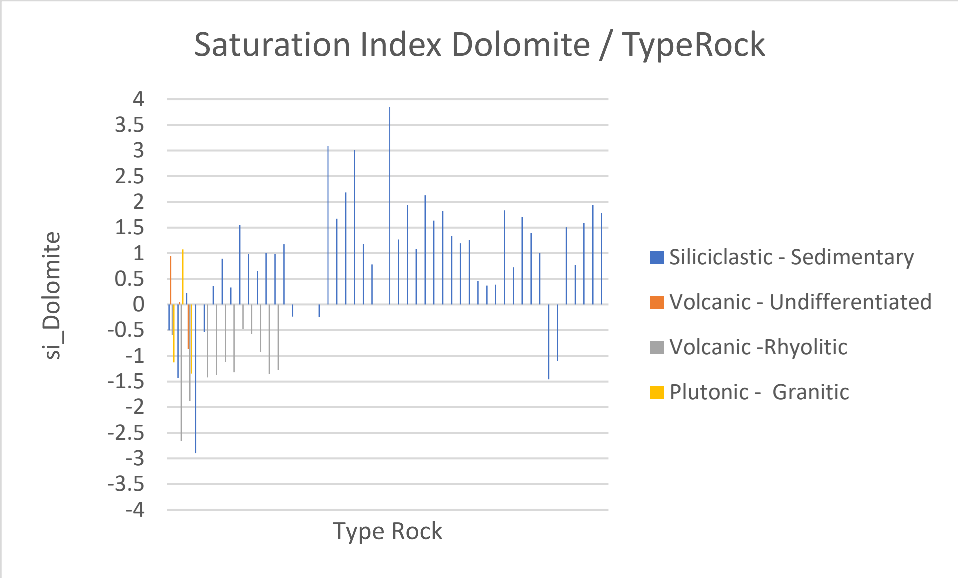

Figure 15. Saturation Index of Dolomite phases.

The saturation index (see Figure 16 and 17) of halite and sylvite is Undersaturated in all types of rocks and at all elevations.

As we ascend from the highest altitudes of the The Puna, through the Eastern Cordillera, and reach the Sub-Andean System at lower elevations, the highest amounts of precipitated calcite and dolomite are detected at lower altitudes, not forgetting the temperatures similar to those of the The Puna. It can be inferred that the Sub-Andean System is characterized by thermal waters surrounded by areas oversaturated by dolomite and calcite. So, if temperatures are similar between the The Puna and the Sub-Andean System, and the only variable is altitude, in general, it can be said that at higher altitudes, there is less oversaturated of dolomite and calcite, and at lower altitudes, there is greater oversaturated, highlighting the importance of altitudinal variability in interpretation.

This interpretation emphasizes variations in mineralogical composition across altitudes and geological provinces, providing a more detailed insight into geochemical processes in the region.

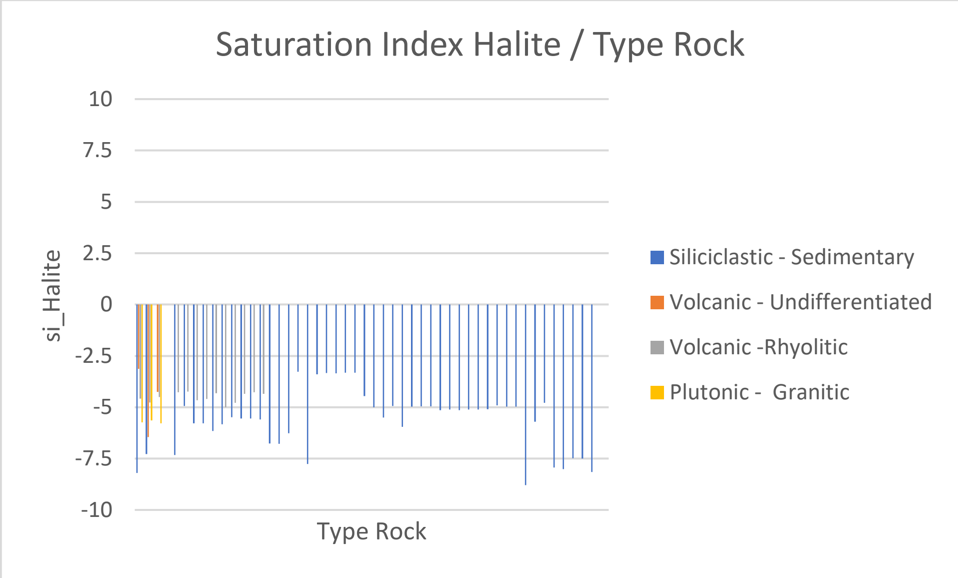

Figure 16.Saturation Index of Halite phases.

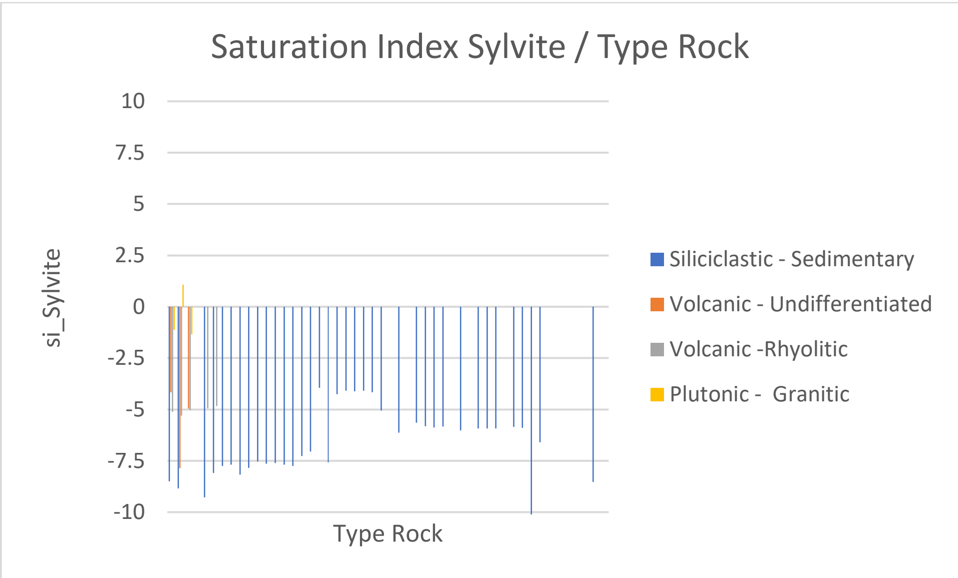

Figure 17. Saturation Index of Sylvite phases.

In Piper's diagram (See Figure 18), which illustrates the distribution of water classifications according to rock type, distinctive patterns can be observed that reveal the geochemical characteristics of emerging waters in the different types of rock formations in Jujuy.

- Volcanic Rhyolitic Rocks: These are mainly characterized by thermal waters with a dominant composition of Na^+ and Cl^-. However, there is a spring sample with a Na^+ and HCO_3^- composition.
- Undifferentiated Volcanic Rocks: The springs present a Na^+ and Cl^- composition.
- Siliciclastic Sedimentary Rocks: They show a variety of compositions in the springs, predominantly Na^+ and Cl^- compositions. In addition, there are springs of Ca^{2+} and Mg^{2+} bicarbonate in smaller proportions. Ca^{2+} and Na^+ sulfate and

Ca^{2+} and Mg^{2+} sulfate waters are also found. Intermediate concentrations of HCO_3^-, SO_4^{2-}, and Cl^- ions are observed, predominantly Na^+ and to a lesser extent Ca^{2+}-Mg^{2+}.

- Granitic Plutonic Rocks: Most have springs with a Na^+ and Cl^- composition. However, there is one sample that shows a Na^+ and HCO_3^- composition.

This analysis reveals the diversity of groundwater chemical compositions, influenced by the geochemical nature of the underlying rocks. Differences in the mineralogy and chemical composition of the rocks emerge as key factors affecting water quality in the region.

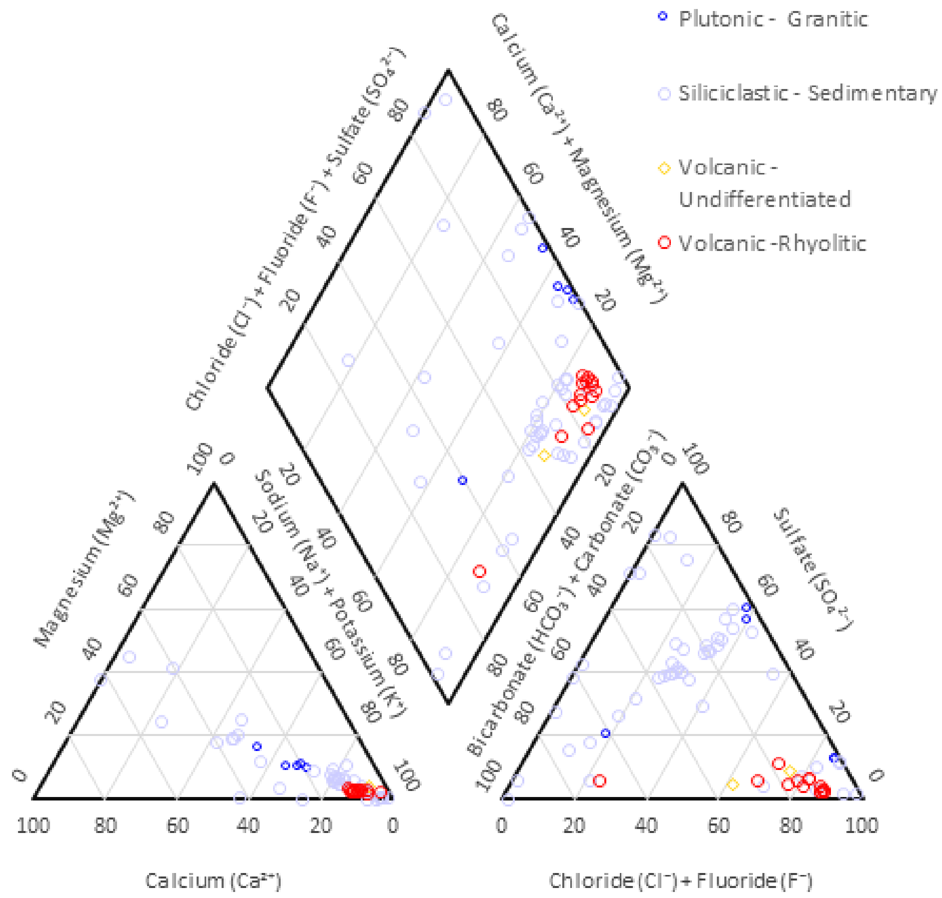

Figure 18. Piper plot of concentration in meq/L of springs in rock types.

In the Piper diagram (see Figure 19), reflecting water classifications according to elevations in the geological provinces, distinctive patterns are observed revealing the chemical composition of waters in different geographical areas of Jujuy.

- The Puna: Thermal waters are mainly Na^+ and Cl^-, Na^+ and Cl^--HCO_3^-, but there are also Na^+ and HCO_3^-, and Na^+ and SO_4^{2-} waters in smaller proportions.
- Eastern Cordillera: Thermal waters are predominantly Na^+ and SO_4^{2-}, and Ca^{2+} and SO_4^{2-}-Na^+.
- In the Sub-Andean System, thermal waters are predominantly Na^+ and Cl^-. However, there are also smaller proportions of Na^+ and SO_4^{2-}, Na^+ and HCO_3^--SO_4^{2-}, and Ca^{2+} and Mg^{2+} and HCO_3^- waters. Based on their composition, the

waters can be classified as: Na^+ and SO_4^{2-}-Cl^-, Na^+ and SO_4^{2-}-HCO_3^-, Na^+ and Cl^-, and Ca^{2+} and Mg^{2+} and HCO_3^-.

This analysis highlights the variability in the chemical composition of thermal waters across elevations and geological regions in Jujuy. The predominance of certain ions in different areas suggests the influence of underlying geology on the local hydrochemistry

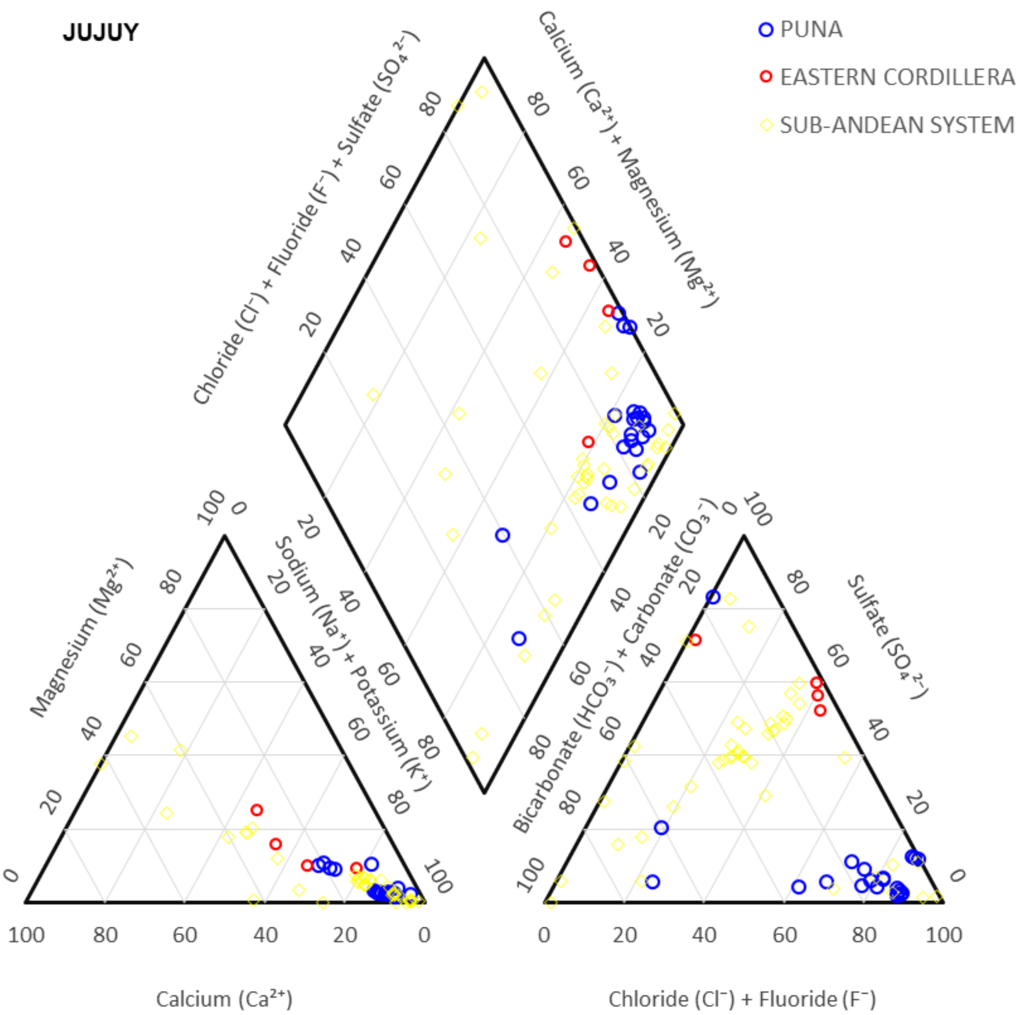

Figure 19. Piper plot of concentration in mg/L of springs in altitudinal regions of Jujuy.

Discussion: Hydrogeochemical classification of thermal waters in the three geological provinces of Jujuy.

In the present study, a hydrochemical characterization of hot springs in the northern Argentine Andes, particularly in the province of Jujuy, which is divided into three geological provinces: the The Puna, the Eastern Cordillera, and the Sub-Andean System, is conducted. Through the analysis of the collected samples, it was possible to classify thermal waters according to their ionic composition. The relationship between local rock formations and the chemical characteristics of the waters was observed. This relationship reflects how the interactions between groundwater and the geological materials present in each region contribute to the variability of its composition. Additionally, the geological context, being located on a subduction edge, plays a key role in shaping these interactions. Tectonic dynamics and related structures, such as major faults, significantly influence the circulation of fluids, their flow trajectories, and the release of minerals. These factors ultimately affect water chemistry, contributing to the variation in ion concentrations observed in thermal waters.

This interplay between fluid dynamics and geological formations highlights the complex hydrogeochemical processes at work in the region, where the pathways of fluid movement are guided by fault systems and the underlying rock types, leading to a wide variety of water compositions across different elevations and geological provinces.

1. The Puna

In the The Puna region, 23 thermal water samples were collected, mainly of the sodium chloride, sodium sulfate, sodium chloride-bicarbonate, and sodium bicarbonate types, at altitudes ranging between 4,300 and 4,050 meters above sea level. Water temperatures vary between 20 and 56°C, reflecting the geothermal activity in the region. The pH of the waters, ranging from 6 to 8, suggests that most waters are neutral to slightly alkaline, with some samples showing slightly acidic values. This pH variability could be related to the interaction of the waters with volcanic rocks, whose hydrothermal alteration can release various metal ions (such as iron (Fe^{2+}) and magnesium (Mg^{2+})) and other volatile elements, such as sulfur (S^{2-}) and fluoride (F^{-}), which affect the acid-base balance in the waters.

The concentration of total dissolved solids (TDS) in the samples ranged between 2,400 and 2,900 mg/L, classifying the water as brackish, except for one sample from the Bety mine, whose value was significantly lower (878 mg/L), classifying it as freshwater. This classification as brackish water is associated with high concentrations of chloride (Cl^{-}) and sodium (Na^{+}) ions, which are linked to the presence of rhyolitic volcanic rocks and hydrothermal activity in the region.

The mineral saturation indices analyzed provide key information about hydrothermal processes and mineral stability in the region. In thermal water samples from the The Puna, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are oversaturated in some samples, especially in areas where the alteration of plutonic granitic and volcanic rocks has released these ions in large quantities. This suggests that hydrothermal systems in these areas have sufficient capacity to dissolve these carbonates, which could favor the precipitation of these minerals under certain conditions. On the other hand, halite (NaCl) and sylvite (KCl) are undersaturated in the waters, indicating that although sodium and chloride ions are present in high concentrations, current temperature and pressure conditions do not favor the precipitation of these minerals on the surface.

In subduction zones, seawater migrating toward hot magmatic bodies in the subducted oceanic plate becomes confined. As it descends into the mantle, this water undergoes an increase in pressure and temperature. However, the salts formed in the depths of a subduction zone are not easily transported to the surface due to the overload of mantle and crustal rocks. Therefore, much of the salts formed during subduction remain hidden in the roots of mountains. The formation of solid salt is an inevitable process associated with Wilson cycles, even without the need for solar evaporation (Hovland, Rueslåtten & Johnsen, 2015).

The distinct solubility of marine salts leads to a refinement of salt types. Upon reaching the seabed, warm brines cool in brine pools, which eventually become saturated with salts, resulting in their precipitation on the seafloor. Dense layers of brine protect the salts from re-dissolution by normal seawater. Magmatic and volcanic processes associated with hydrothermal activity, especially those linked to subduction beneath the Andes, are related to massive salt deposits. Brines are hydrothermally transported from the subduction zone and expelled at altitudes ranging between 3,500 and 4,000 meters above sea level.

On the surface, brines evaporate due to the arid climate, which also helps protect the salts from re-dissolution. The brines that feed hydrothermal systems above the subduction zone originate from the drainage of subducted slabs. This water causes fractional melting of the upper mantle wedge, initiating volcanism (Hovland et al., 2015).

Regarding the geology of the The Puna, it is characterized by the presence of rhyolitic volcanic and plutonic granitic rocks, part of the western The Puna eruptive belt, according to the geological map of South America prepared by Gómez Tapias et al. (2023). The petrology and geochemistry of these rocks have been described as part of a typical magmatic arc (Ramos, 1999).

In the region, all sampled emergent groundwater is associated with geological faults. These tectonic structures act as natural conduits that allow the circulation of fluids from the depths to the surface. Faults facilitate the ascent of mineral-rich hydrothermal fluids, creating a favorable environment for rock alteration and ion dissolution.

The Tuzgle volcano, located near thermal water sampling area, plays a key role in the region's hydrothermal activity. Its location, associated with the Olacapato-El Toro lineament, has been influenced by transtensional processes, facilitating the ascent of geothermal fluids and the formation of hydrothermal reservoirs (Comisión Sitios de Interés Geológico de la República Argentina [CSIGA], 2008).

2. Eastern Cordillera

In the Eastern Cordillera, at an altitude of 1850 meters above sea level, a thermal water sample was collected, classified as sodium sulfate and calcium-sodium sulfate. The water temperature was 30.2°C, indicating moderate hydrothermal activity in the region. The recorded pH was 7.2, suggesting a nearly neutral environment. Regarding the total dissolved solids (TDS) concentration, the obtained value was 895 mg/L, classifying it as freshwater, in contrast to the more mineralized waters of the The Puna.

The low concentration of sodium chloride (NaCl) in this sample may be related to mixing with meteoric water sources or less mineralized tributaries. This dilution affects the concentrations of ions such as sodium (Na^+) and chloride (Cl^-), which are more abundant in other regions with greater hydrothermal influence.

The predominant rocks in the area are siliciclastic sedimentary rocks, which correlate with the presence of calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) in the water, elements that dissolve through the interaction between the hydrothermal fluid and rock formations. The presence of sulfate (SO_4^{2-}) is directly linked to the interaction of fluids with rocks rich in sulfur-bearing minerals, such as pyrite (FeS_2), whose hydrothermal alteration releases sulfate and iron ions (Fe^{2+} or Fe^{3+}) into the solution.

The mineral saturation indices provide key information about the stability and processes of mineral precipitation or dissolution in thermal water. In the analyzed sample from the Eastern Cordillera, the following was observed:

Calcite ($CaCO_3$): Undersaturated, indicating that the water has the capacity to dissolve this mineral rather than precipitate it.

Dolomite ($CaMg(CO_3)_2$): Undersaturated, except in one specific sample where oversaturation was found, suggesting that under certain local conditions, dolomite could precipitate.

Gypsum ($CaSO_4 \cdot 2H_2O$): Near equilibrium, implying that water conditions may favor both its dissolution and precipitation.

Halite (NaCl) and Sylvite (KCl): Undersaturated, indicating that although sodium and chloride ions are present, current conditions do not favor the precipitation of these minerals at the surface.

These results reflect that the hydrochemical conditions in the Eastern Cordillera are strongly controlled by the interaction between hydrothermal fluids and siliciclastic sedimentary rocks, in contrast to the more mineralized hydrothermal systems of the The Puna.

Hydrothermal activity in the Eastern Cordillera is influenced by the subduction of the Nazca Plate beneath the South American Plate, a process that led to the uplift of the Protothe Puna and the formation of a foreland basin. Over 5000 meters of clastic sediments have been deposited in this basin (Ramos, 1999). Tectonic activity generates vapors and gases that ascend through faults and fractures, reacting with rocks and releasing soluble minerals, explaining the observed chemical composition in thermal water sample.

Previous studies have interpreted the geological evolution of this basin in different ways. Ramos (1999) considers it a foreland basin, while Vistalli (1999) proposes that it originated as a rift basin with subsequent thermal cooling. Regardless of its origin, the geological structure and the interaction of hydrothermal fluids with sedimentary rocks explain the chemical composition of the single thermal water sample analyzed in the Eastern Cordillera.

3. Sub-Andean System

The Sub-Andean System exhibits great diversity in the ionic composition of its thermal waters. A total of 45 samples were collected from thermal springs, lagoons, springs, and a well, at altitudes ranging from 450 to 2025 meters above sea level. Based on their composition, the waters were classified as sodium sulfate-chloride, sodium sulfate-bicarbonate, sodium chloride, and calcium-magnesium bicarbonate.

Temperatures ranged from 25°C to 60°C, with an exceptionally high value of 85°C in the well. The pH varied between 6 and 8.9, indicating a wide range of chemical conditions. The waters were primarily slightly acidic (~6), neutral (~7), and slightly alkaline (~8.9).

This pH variability is related to the interaction of thermal fluids with rock formations and, especially, to the influence of volcanic gases. Gases such as carbon dioxide (CO_2), when dissolved in water, can lower the pH, making the waters more acidic in areas with higher gas accumulation. The dissolution of CO_2 also increases the concentration of bicarbonate (HCO_3^-), generating acidic waters, especially in volcanically active areas (Giggenbach, 1992).

The total dissolved solids (TDS) concentrations in the waters of the Sub-Andean System range between 280 mg/L and 14,700 mg/L, classifying them into three types: fresh (low TDS), brackish (medium TDS), and saline (high TDS). The main ions present include sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}), reflecting the interaction between water and rocks in the hydrothermal process.

The region's geology, dominated by siliciclastic sedimentary formations accumulated in the foreland basin and preserved in the Sub-Andean System, crossed by tectonic fault structures, favors the release of cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) due to hydrothermal alteration in the subsurface. Vapors generated at great depth enrich the system with compounds such as sulfate (SO_4^{2-}) and chloride (Cl^-), which react with the rocks, altering their mineral composition and releasing these ions into the solution. These hydrothermal processes explain the complexity of the observed ionic compositions, reflecting the interaction between fluids and rock formations.

In the Piper diagram (Figure 16), which classifies waters according to elevation in geological provinces, distinctive patterns reveal the chemical composition of water in different areas of Jujuy. Thermal waters are predominantly of the Na^+ and Cl^- type, although there are also smaller proportions of Na^+ and SO_4^{2-}, Na^+ and HCO_3^--SO_4^{2-}, and Ca^{2+} and Mg^{2+} with HCO_3^-. Based on their composition, the waters can be classified as Na^+ and SO_4^{2-}-Cl^-, Na^+ and SO_4^{2-}-HCO_3^-, Na^+ and Cl^-, and Ca^{2+} and Mg^{2+} with HCO_3^-.

It can be inferred that the Sub-Andean System is characterized by thermal waters surrounded by zones oversaturated in dolomite and calcite. Thus, if temperatures are similar between the The Puna and the Sub-Andean System, and the only variable is altitude, in general, higher altitudes show lower dolomite and calcite oversaturation, whereas lower altitudes exhibit greater oversaturation, highlighting the importance of altitudinal variability in interpretation.

The waters of the Sub-Andean System exhibit complex ionic compositions, such as chloride-sulfate-sodium, sulfate-chloride-sodium, bicarbonate-sulfate-sodium, chloride-sodium, and bicarbonate with magnesium (Mg^{2+}) and calcium (Ca^{2+}). A notable feature of these waters is the presence of sodium chloride (NaCl), which is also characteristic of thermal waters of the The Puna. This raises a key question: could water chemistry be related to a trajectory of underground flows from the The Puna to the Sub-Andean System The possible connection between both systems suggests that subsurface fluid movement could play a fundamental role in the final composition of these waters.

It is possible that the Sub-Andean System and the The Puna share a common geothermal process that favors the formation of sodium-chloride waters, through the migration of underground fluids that, as they ascend, interact with the minerals of fractured rocks. In addition to sharing sodium chloride chemistry, the The Puna and the Sub-Andean System exhibit similar temperatures in their thermal waters, although they differ significantly in altitude.

Attributing this composition exclusively to volcanic activity does not seem appropriate. Instead, a more plausible explanation is that meteoric waters infiltrate deeply into the Sub-Andean System, where they heat up and ascend again due to hydrostatic pressure generated by fractured siliciclastic sedimentary rocks. Along their path, these waters become enriched with various minerals, mainly calcium, magnesium, sulfates, and chlorides. According to Hovland, Rueslåtten, and Johnsen (2015), in tectonically active areas, hydrothermal fluids derived from meteoric infiltration heat up as they ascend through rock fractures, promoting the dissolution and release of minerals into the solution.

In the Sub-Andean System, dolomite and calcite exhibit notable oversaturation, to a greater extent than in the The Puna and the Sub-Andean System. In contrast, halite and sylvite are undersaturated in all rock types and elevations.

Discussion on Water Circulation in Geological Provinces

The representativeness of the samples is crucial for generalizing the chemical composition of the region's waters, especially when only a limited number of samples are available, as is the case with the three samples from the Eastern Cordillera. With such limited data, it is not possible to be entirely certain that the waters of this region do not contain sodium chloride, as there may be spatial variability within the area. It is likely that in other parts of the Eastern Cordillera, sodium chloride concentrations exist that are not reflected in these three samples.

A key aspect highlighted in this analysis is the water circulation from the The Puna towards lower areas such as the Eastern Cordillera and the Sub-Andean System. This dynamic circulation and mixing of waters between different altitudes and geological formations could have a significant impact on water chemistry and may be a crucial factor in the presence or absence of certain ions, such as sodium chloride. The flow of meteoric or glacial meltwater that infiltrates deep into the The Puna and then circulates through the geological formations of the Eastern Cordillera and the Sub-Andean System may alter the chemical composition as it interacts with the distinct geological characteristics of each zone. Differences in rock types (sedimentary, volcanic, plutonic) and interactions with subsurface minerals are key factors in these changes.

Water recharge in the The Puna plays a key role in this dynamic. At altitudes above 4000 and up to 4850 meters above sea level, the permafrost zone is found, where glaciers, snow, and precipitation significantly contribute to regional water recharge. Although the arid climate of the The Puna limits precipitation, glacial melt remains an important water source, infiltrating through geological faults and circulating through subsurface layers. As this water interacts with ascending fluids linked to the subduction of the Nazca Plate, it mixes with underground saline waters or brines, influencing the The Puna's water chemistry, particularly in the presence of sodium chloride.

In the The Puna, active debris-covered glaciers, indicative of discontinuous permafrost, are found between 4000 and 4850 meters above sea level. These glaciers play a crucial role in the hydrological system, releasing a volume of water comparable to that of ice glaciers but with less suspended material. Their ice core is protected by debris and sediments, making them more resistant to temperature variations at high altitudes, allowing them to function as long-term freshwater reservoirs. These debris-covered glaciers coexist with glacial cirques and permanent snowfields, further increasing their importance as a water source in the region.

As noted by Ahumada, Ibáñez, and Páez (Actas XXIV Reunión Científica de la AAGG Geofísica Aplicada), Andean permafrost is a crucial remnant of the cryosphere on the eastern edge of the The Puna, and its dynamics significantly contribute to the region's hydrogeological processes, particularly in terms of groundwater recharge. This permafrost zone, combined with the dynamics of debris-covered glaciers, directly impacts groundwater composition and the circulation of elements such as sodium chloride within the The Puna's hydrogeological system.

In the Eastern Cordillera and the Sub-Andean System, the mixing of thermal waters with meteoric waters from precipitation is more pronounced. In these areas, precipitation levels are higher, leading to a more intense mixing with fresh waters. This mixing of fresh water with saline or brackish water modifies the concentration of present ions, resulting in a water chemistry distinct from that of the The Puna.

It is important to consider that the number and geographical distribution of samples influence the observed patterns. Ideally, more data would be collected to confirm whether sodium chloride is indeed present in the Eastern Cordillera and to gain a more precise understanding of how waters circulate from the The Puna to these regions.

The circulation of water from the The Puna to the Eastern Cordillera and the Sub-Andean System appears to be a key dynamic, where interactions between different rock types, minerals, and geological formations play a determining role in the final water chemistry, including sodium chloride concentrations. The variability of samples and the lack of more comprehensive data may prevent capturing all the interactions present in the region's hydrogeological system.

IV.2. SALTA

In the hydrogeological exploration of Salta (Figure 20), several geological provinces covering different thermal aspects have been identified. Among them, the The Puna, the Easter Cordillera, Sub-Andean System and the Chaco Plain stand out. However, in this study, thermal water samples come exclusively from the The Puna.

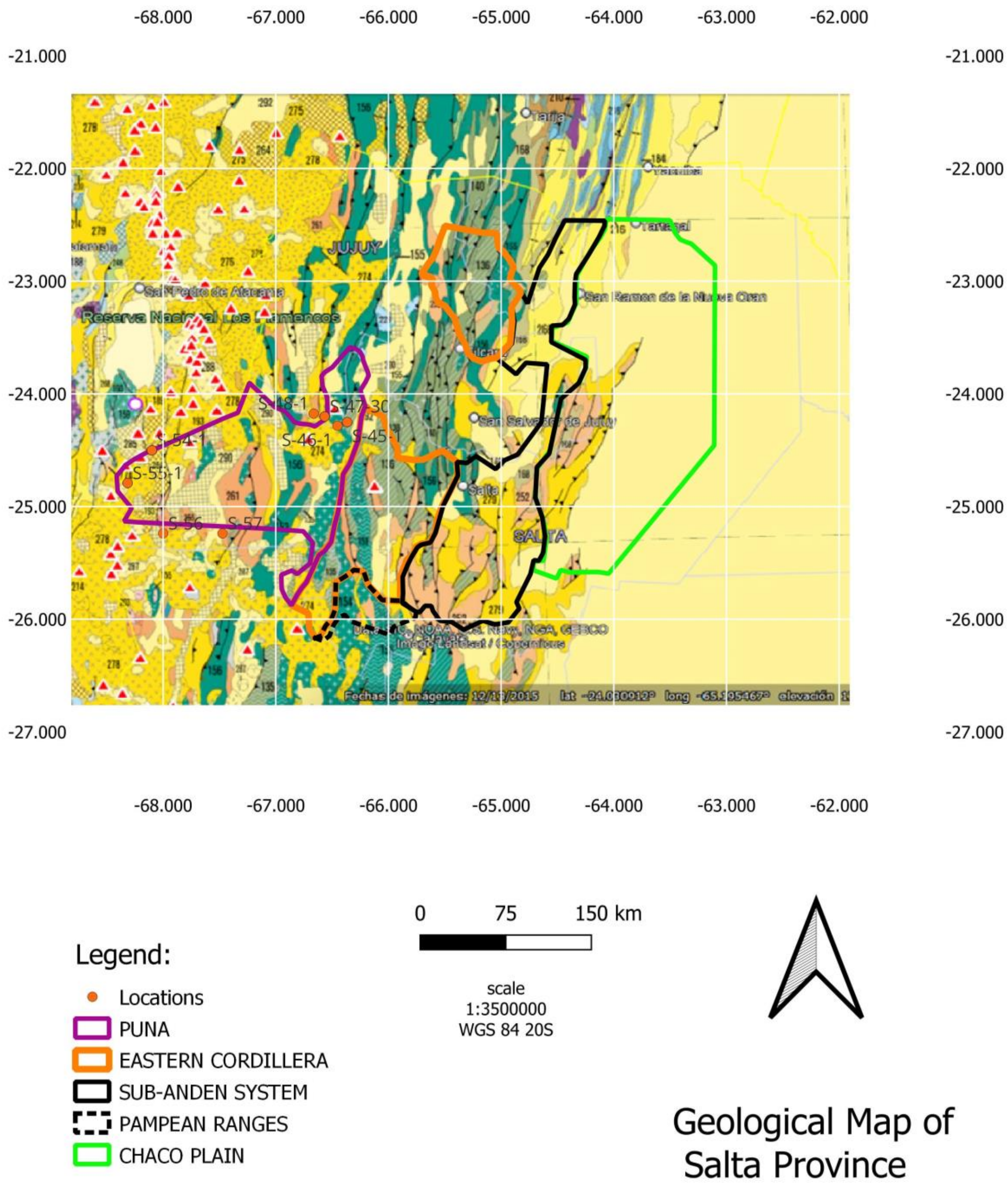

Figure 20. Location of the analyzed samples in Salta Province on the geological map.

The figure shows the location of 45 thermal water samples collected in Salta Province, all of which are situated within the boundaries of the The Puna geological province, according to the Geological Map of South America (CGMW, 2019). The samples, labeled with the prefix "S-" followed by a number, are distributed over volcanic, volcano-sedimentary, evaporitic, and metamorphic lithological units. Most samples (S-46-1, S-47-1 to S-47-30, S-48-1, and S-56) are hosted in Neogene undifferentiated volcanic rocks (code 274), which are representative of recent Andean magmatism typical of the Cenozoic volcanic activity in the The Puna. Paleogene volcano-sedimentary rocks (code 264), associated with samples S-54-1 to S-54-4, are interpreted as mixed volcanic-lacustrine deposits linked to calderas and ancient geothermal systems. Additionally, some thermal discharges (S-55-1 to S-55-3 and S-57) occur in Quaternary evaporitic deposits (code 290), typical of closed high-altitude basins with endorheic drainage, such as salt flats. Finally, samples S-45-1 and S-45-16 to S-45-18 are located on Cambrian low- to medium-grade metamorphic basement rocks (code 136), indicating thermal spring emergence controlled by deep fracturing within ancient structural domains.

Although the dataset includes 45 samples, several of them share identical or very close geographic coordinates, corresponding to repeated sampling at the same thermal discharge sites. For this reason, the number of visible locations in the figure is lower than the total number of analyzed samples.

Since all samples were collected exclusively in the Salta sector of the The Puna, this figure supports a detailed analysis of lithological, tectonic, and hydrochemical interactions in a volcanic and endorheic high-mountain setting.

Source: Commission for the Geological Map of the World – CGMW (2019). *Geological Map of South America*. Paris: UNESCO-CGMW.

Figure 21 shows the relationship between the temperature of thermal waters and the elevation of the springs in the The Puna region. The maximum recorded temperature reaches 78°C and occurs at an elevation of approximately 3900 m a.s.l. The temperatures observed in this region range between approximately 17°C and 78°C, with most values concentrated between 40°C and 60°C at elevations close to 4000 m a.s.l.

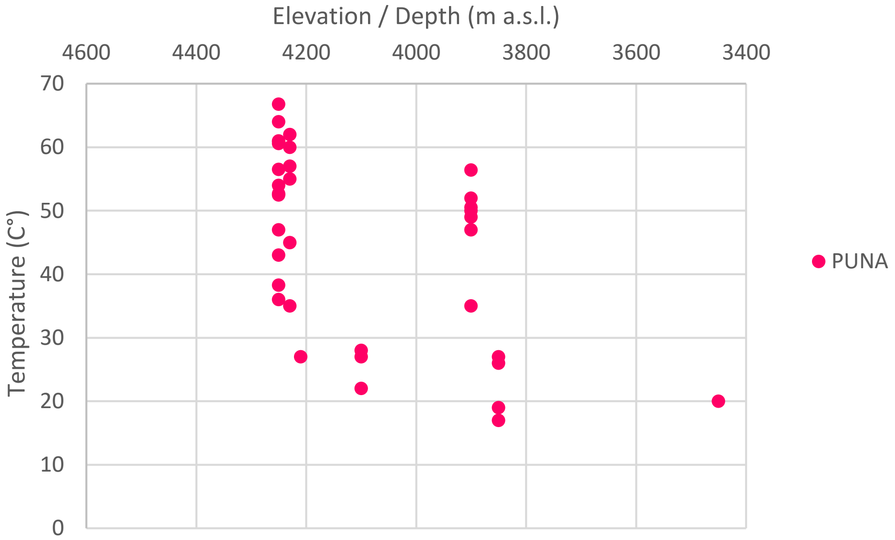

Figure 21. Relationship between temperature (°C) and elevation (m a.s.l.) of thermal springs in the The Puna region.

Figure 22 shows the relationship between total dissolved solids (TDS) and the elevation of thermal springs in the The Puna region. The maximum recorded TDS value reaches approximately 19,167 mg/L at an elevation close to 4200 m a.s.l., corresponding to saline water according to standard TDS classifications.

The remaining samples show TDS values ranging between approximately 1,800 mg/L and 4,500 mg/L, corresponding to brackish waters, and are located at elevations between approximately 3900 and 4000 m a.s.l

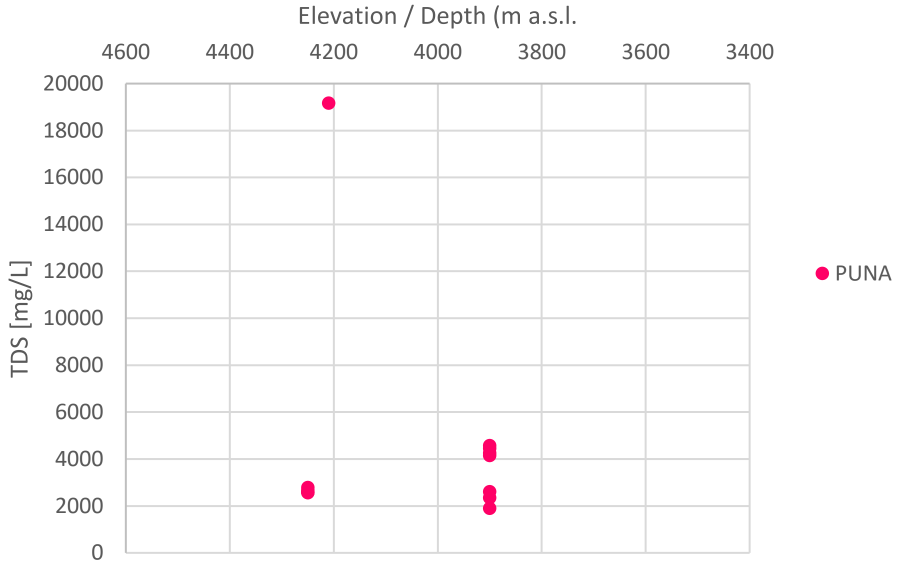

Figure 22. Relationship between total dissolved solids (TDS, mg/L) and elevation (m a.s.l.) of thermal springs in the The Puna region.

In the analysis of Equivalent Concentration Ratios in meq/L (Figure 23) for the Na^+/Ca^{2+} ratio, distinctive patterns are observed at different altitudes, grouped by geological provinces. In the The Puna, there is a significant predominance of Na^+ over Ca^{2+}, with maximum values reaching 117.30 meq/L at 3900 m a.s.l.

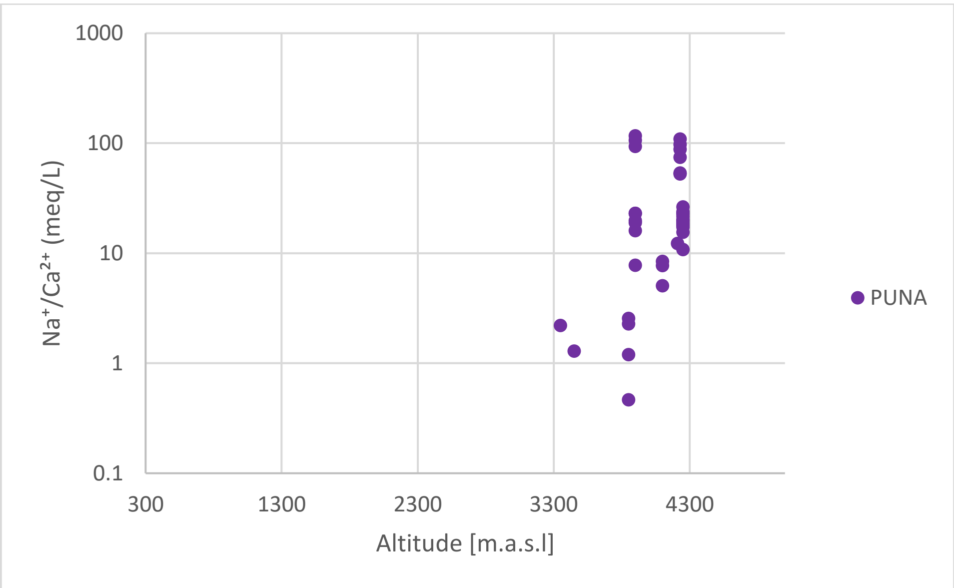

Figure 23. Na^+/Ca^{2+} (meq/L) in The Puna.

In the analysis of Equivalent Concentration Ratios in meq/L of magnesium-to-calcium (Figure 24), some minimal anomalies with a slight predominance of calcium over magnesium are observed in the The Puna, but in May there is a predominance of magnesium over calcium, with maximum values of 0.15 meq/L at 4250 m a.s.l.

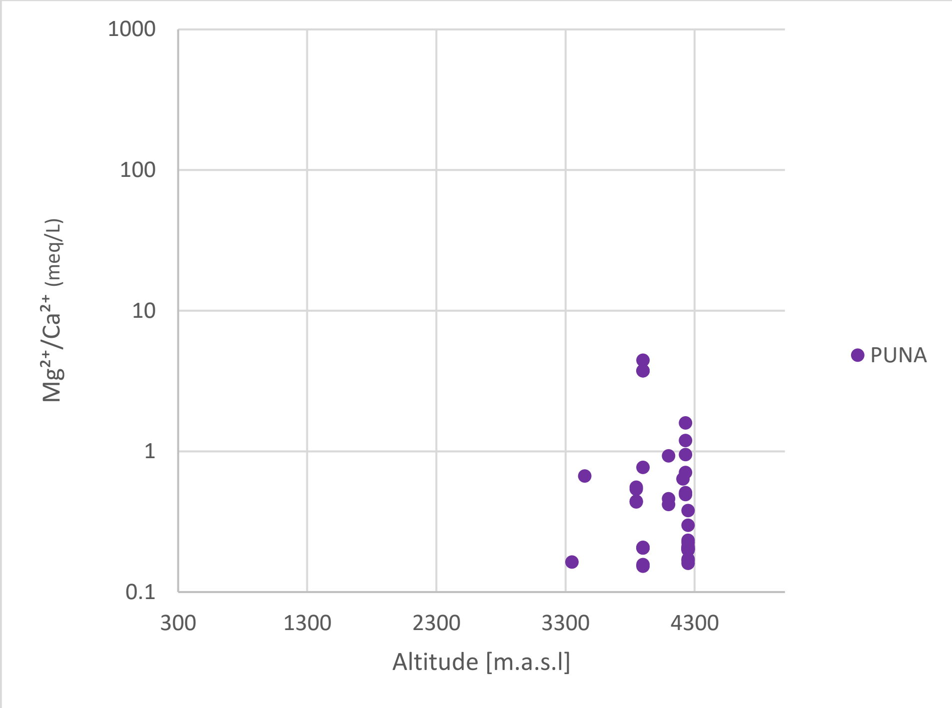

Figure 24. Mg^{2+}/Ca^{2+} (meq/L) in The Puna.

In the analysis of Equivalent Concentration Ratios in meq/L for the Cl^-/SO_4^{2-} ratio (Figure 25), it is observed that in the The Puna, Cl^- values predominate over SO_4^{2-} in most localities. The maximum concentration of Cl^- reaches 219 meq/L at 4100 m a.s.l. However, in general terms, Cl^- values vary between 31 meq/L and 2 meq/L. On the other hand, in contrast to most cases, there are some localities with minimum values where SO_4^{2-} predominates, reaching 0.5 meq/L.

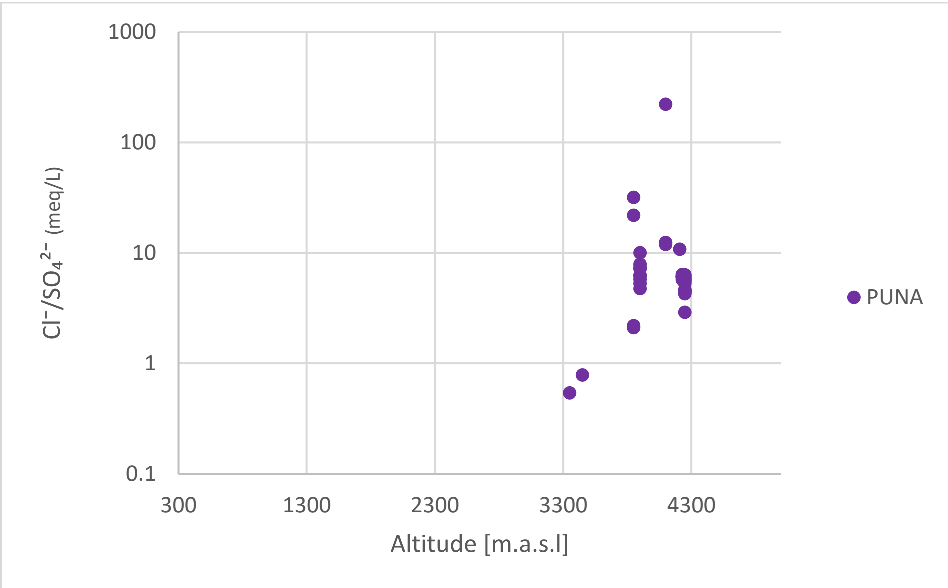

Figure 25. Cl^-/SO_4^{2-} (meq/L) in The Puna.

In the analysis of Equivalent Concentration Ratios in meq/L for the Cl^-/HCO_3^- ratio (Figure 26), it is observed that in the The Puna, Cl^- predominates in most localities compared to HCO_3^-. The maximum concentration of Cl^- reaches 52 meq/L at 4100 m a.s.l. However, in general terms, Cl^- values range between 3 meq/L and 1.1 meq/L. As for HCO_3^-, the minimum values recorded are 0.91 meq/L.

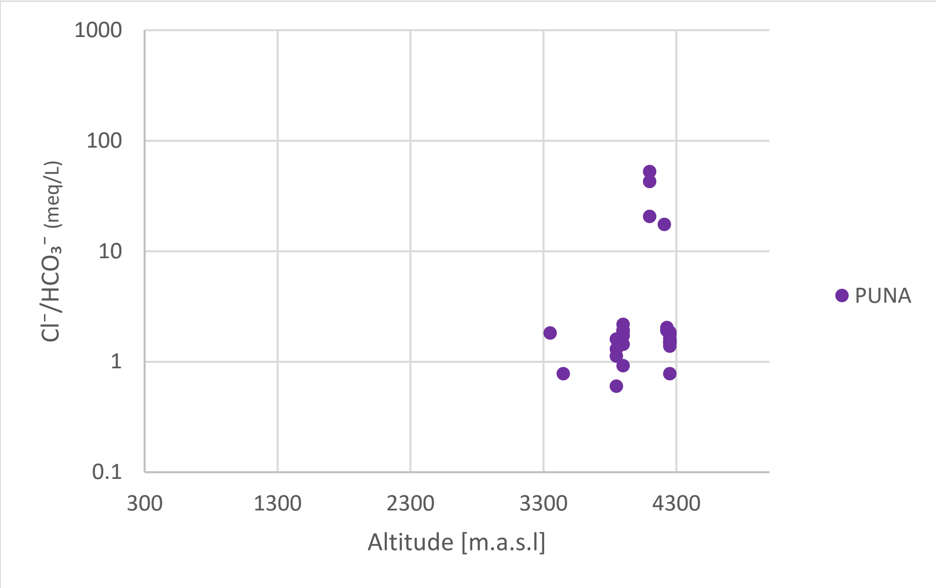

Figure 26. Cl^-/HCO_3^- (meq/L) in The Puna.

The calcite ($CaCO_3$) saturation index (Figure 27) reveals that it is supersaturated in Volcanic (Undifferentiated), Volcanic (Volcano-sedimentary), and Evaporitic rocks. On the other hand, Metamorphic rocks (low to medium grade), together with Volcanic (Undifferentiated) and Volcanic (Volcano-sedimentary) rocks, show undersaturated conditions. In general, subsaturation predominates, except in the mentioned cases where supersaturation is observed.

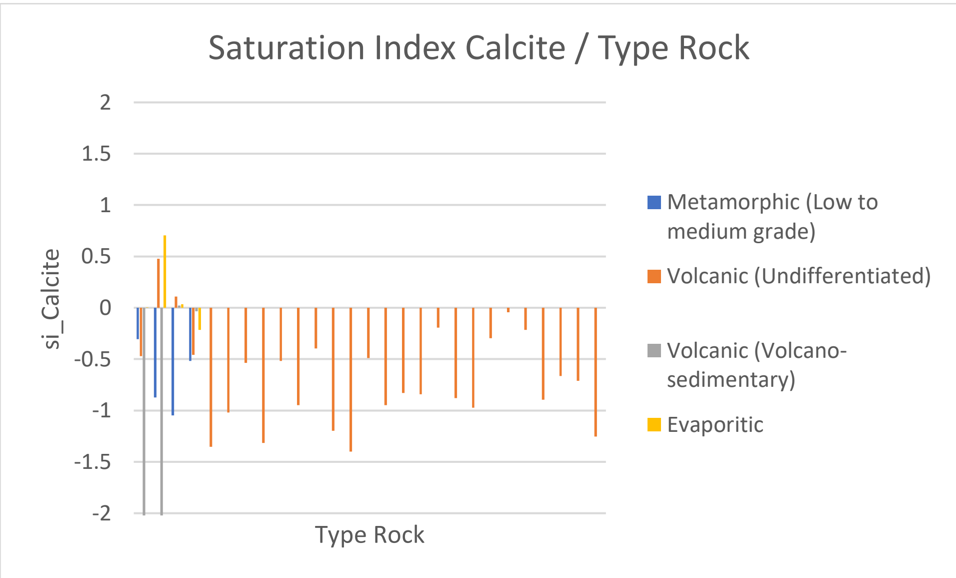

Figure 27. Saturation Index of calcite phases and type rocks in The Puna.

The dolomite saturation index (Figure 28) indicates that Metamorphic (low to medium grade), Volcanic (Undifferentiated), Volcanic (Volcano-sedimentary) and Evaporitic rocks are undersaturated, except in some samples of these same formations, where oversaturation is observed. In general, subsaturation predominates in the water samples.

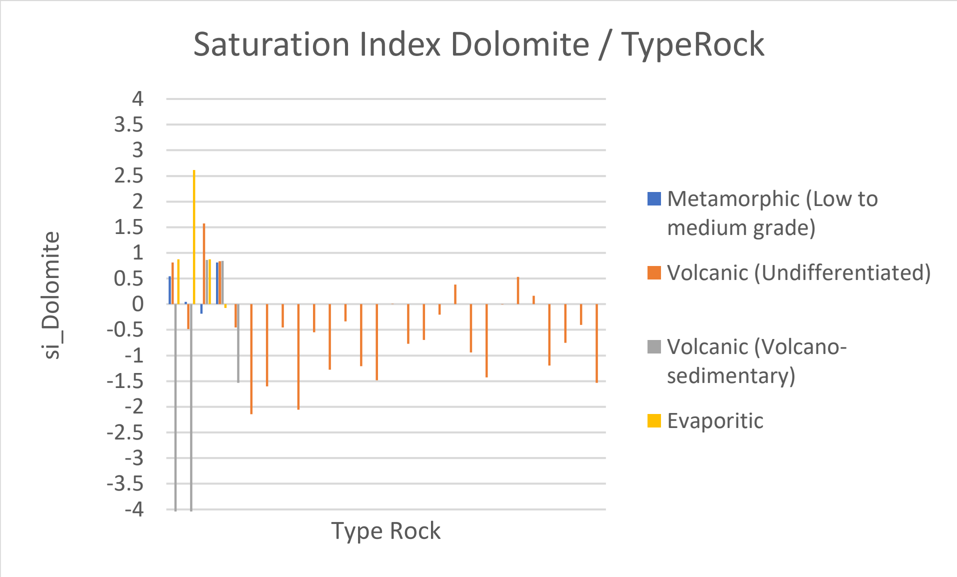

Figure 28. Saturation Index of Dolomite phases.

The saturation index (Figure 29 and 30) of halite and sylvite is unsaturated across all rock types and elevations. Additionally, the saturation index remains consistent, showing no significant dependence on changes in altitude.

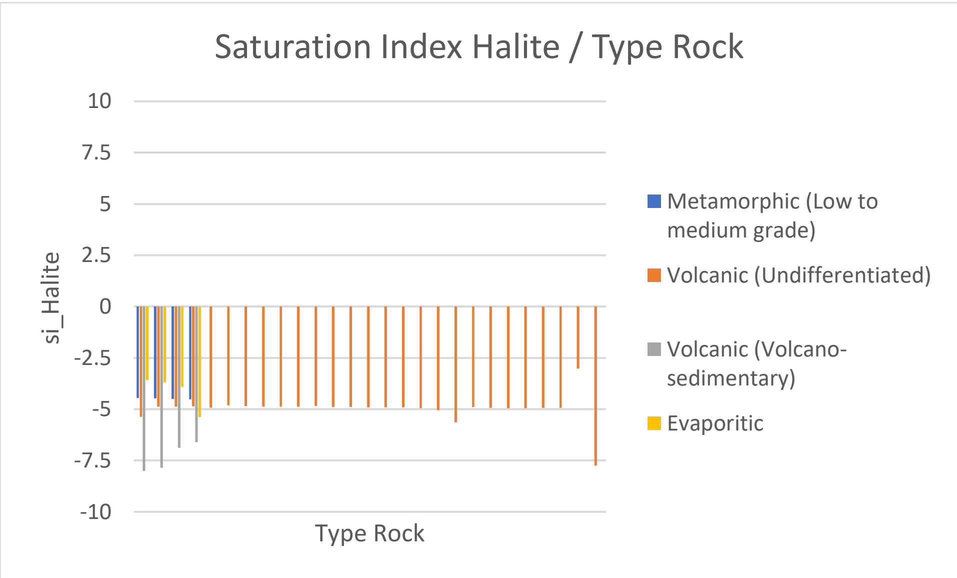

Figure 29. Saturation Index of Halite phases.

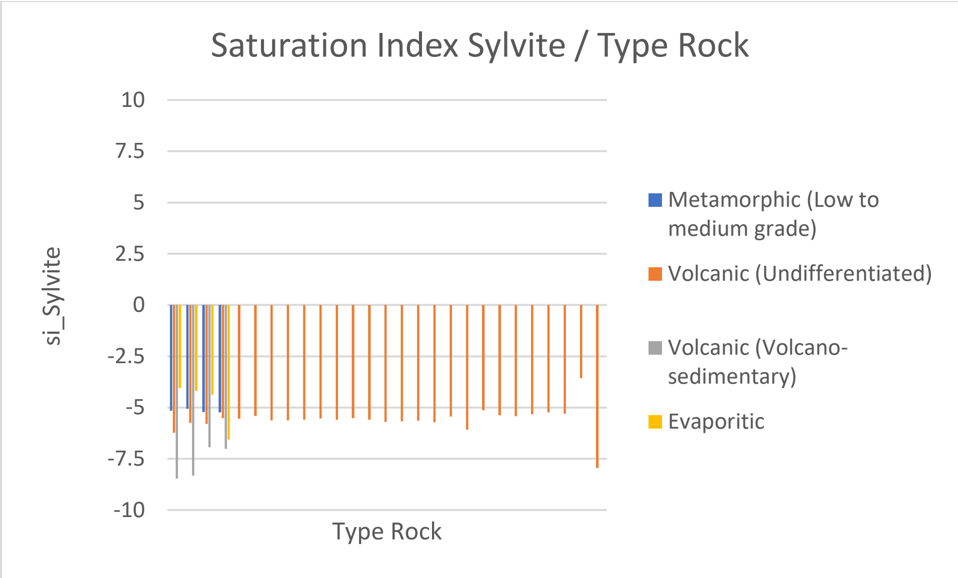

Figure 30. Saturation Index of Sylvite phases.

In the Piper diagram (Figure 31), which illustrates the distribution of water classifications according to rock type, distinctive patterns can be observed that reveal the geochemical characteristics of emerging waters in the different rock formations of Salta.

Evaporitic rocks: They are mainly characterized by thermal waters with a dominant composition of Na^+ - Cl^-.

Undifferentiated Volcanic Rocks: The springs present a majority composition of Na^+ - Cl^-, with a minor presence of HCO_3^- - Na^+ - Ca^{2+} - SO_4^{2-}.

Metamorphic rocks (low to medium grade): Show a variety of compositions in the springs, predominantly Na^+ - Cl^- and Na^+ - HCO_3^-, with some water samples also showing characteristics of Na^+ - HCO_3^- - Cl^-.

Volcanic rocks (Volcano-sedimentary): The waters present a predominantly Na^+ - HCO_3^- composition, with some samples showing a combination of Ca^{2+} - Na^+ - HCO_3^- - Cl^-.

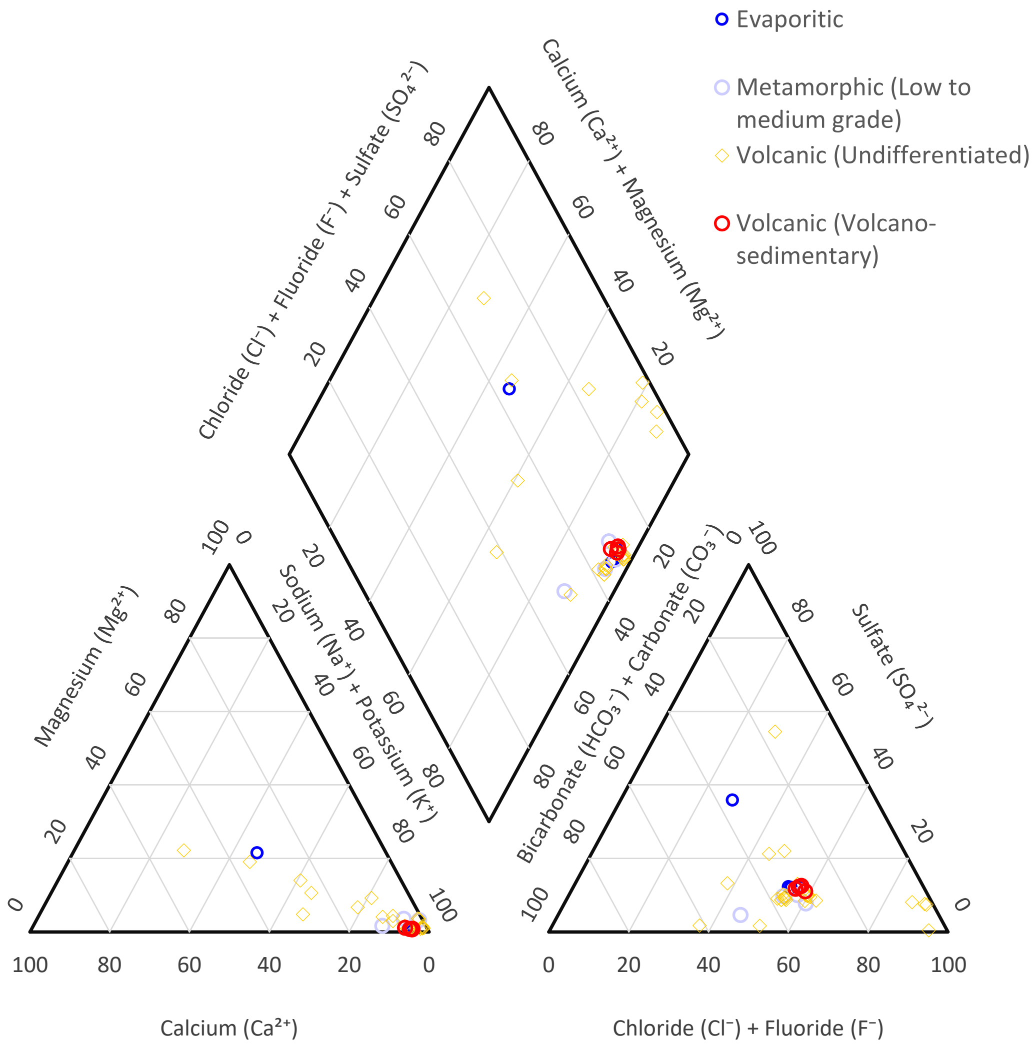

Figure 31. Piper plot of concentration in meq/L of springs in rock types.

In the Piper diagram (Figure 32), which reflects the water classifications according to the elevations of the geological provinces, distinctive patterns can be observed that reveal the chemical composition of the waters in the different geographic zones of Jujuy.

The Puna: Thermal waters in this region show a predominance of Na^+-Cl^- and Na^+-HCO_3^-, with a lower proportion of Ca^{2+}-HCO_3^-, Na^+-SO_4^{2-}, and other combinations of Cl^-, HCO_3^-, and SO_4^{2-}. These variations in chemical composition reflect the influence of geological features and local geochemical processes.

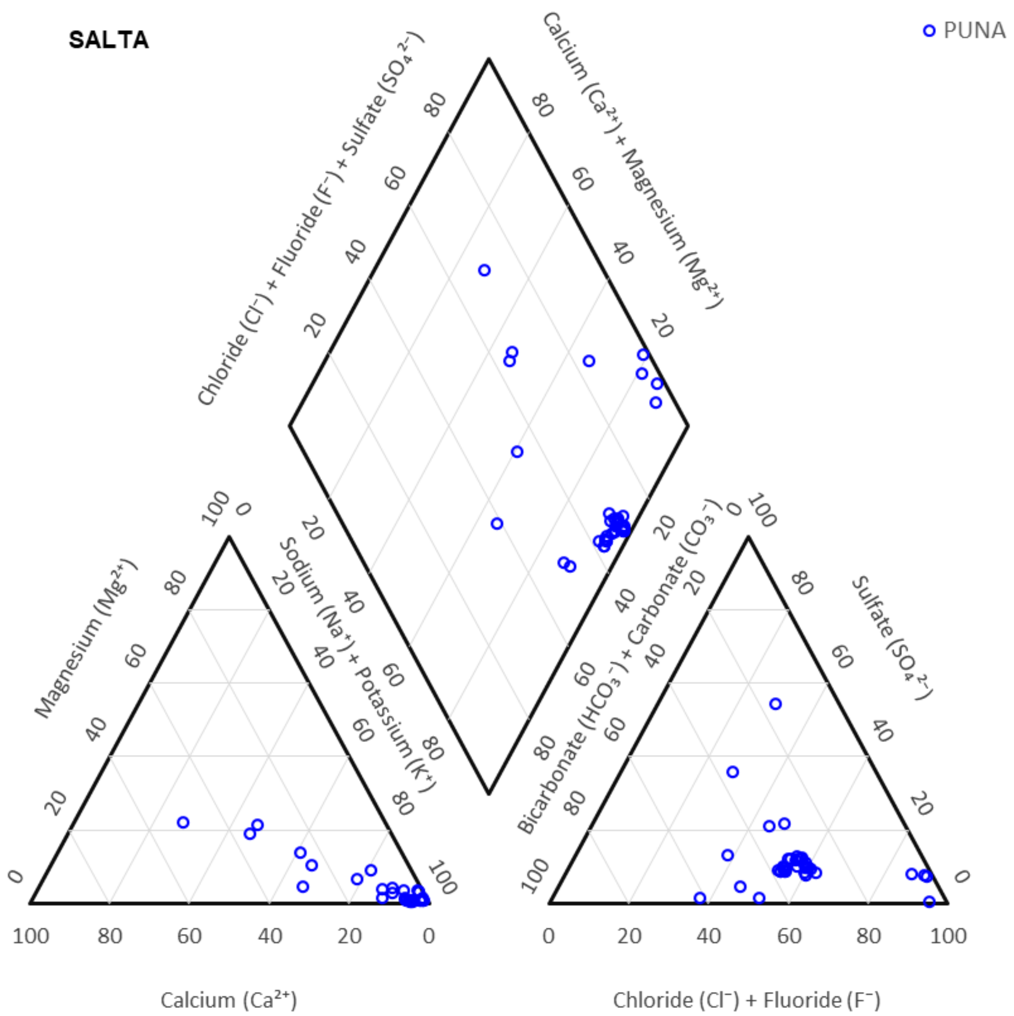

Figure 32. Piper plot of concentration in meq/L of springs in the The Puna.

Discussion: Hydrogeochemical classification of thermal waters in one of the five geological provinces of Salta,The Puna.

In the present study, a hydrochemical characterization of thermal waters of the northern Argentine Andes was carried out, specifically in the province of Salta, which is divided into five geological provinces: the The Puna, the Eastern Cordillera, the Sub-Andean System, the Pampean Sierras and the Chaco Plain. This work focuses only on the analysis of water samples from the The Puna. From the results obtained from the analyses, it was possible to classify thermal waters according to their ionic composition and to identify the relationship between the local rock formations and the chemical characteristics of the waters. This interaction reflects how the circulation of groundwater, in contact with the geological materials present in each region, contributes to the variability of its composition. In addition, the geological context, particularly being on the edge of a subduction zone, plays a key role, as tectonic dynamics and associated structures, such as major faults, influence the circulation of fluids and the release of minerals that alter water chemistry.

1. The Puna

In the The Puna region (Figure 31) , 39 samples of thermal waters were collected, primarily classified into the following types: sodium bicarbonate chloride (Na^+-HCO_3^--Cl^-), bicarbonate chloride (HCO_3^--Cl^-), sodium chloride (Na^+-Cl^-), sodium-calcium sulfate chloride (Na^+-Cl^--Ca^{2+}-SO_4^{2-}), and sodium-calcium sulfate bicarbonate (HCO_3^--Na^+-Ca^{2+}-SO_4^{2-}). These samples were taken at altitudes ranging from 3,350 to 4,250 meters above sea level, with water temperatures varying between 17 and 78°C, reflecting the geothermal activity of the region. The average pH is 6.3, with values ranging from 6 to 7.5, indicating that the waters are generally neutral or slightly alkaline. Although the pH value of 6.3 is close to neutrality, lower values suggest slight acidity, while higher values indicate mild alkalinity.

The concentration of total dissolved solids (TDS) in the water samples varied between 1,892 mg/L and 4,568 mg/L, classifying the waters as brackish, except for a sample from Socompa, which presented an exceptionally high value of 19,167 mg/L, identifying it as saline water. This classification as brackish water is associated with high concentrations of ions such as chloride (Cl^-), sodium (Na^+), and bicarbonate (HCO_3^-), which are linked to low-to-medium-grade metamorphic rocks and undifferentiated volcanic rocks, as well as the hydrothermal activity present in the region.

The minerals present in the volcanic and metamorphic rocks of the region, such as halite (NaCl) and sylvite (KCl), are common and are associated with hydrothermal activity. The dissolution of these minerals in thermal waters contributes to the formation of the observed ionic compositions. The high concentrations of sodium (Na^+) and chloride (Cl^-) detected in the water samples result from the dissolution of these minerals present in the geological environment.

Seawater migrating toward magmatic bodies in a subduction zone becomes trapped in the subducting oceanic plate. As this water descends into the mantle, it undergoes a progressive increase in pressure and temperature. However, the salts formed in the subduction zone are not easily transported to the surface due to the overburden of mantle and crustal rocks. Therefore, much of the salt formed during subduction remains hidden in the roots of the mountains. This process of solid salt formation is inevitable and is associated with the Wilson cycles, even without the need for solar evaporation. The different solubilities of marine salts lead to differentiation in salt types. When hot brines reach the seafloor, they cool in brine pools, which eventually become saturated with salts, precipitating them onto the seafloor. Dense brine layers protect the salts from re-dissolution in normal seawater. Magmatic and volcanic processes associated with hydrothermal activity, especially those related to subduction beneath the Andes, are responsible for the formation of massive salt deposits. Brines are hydrothermally transported from the subduction zone and expelled at altitudes ranging from 3,500 to 4,000 meters above sea level. At the surface, the brines evaporate due to the dry climate, which also helps protect the salts from re-dissolution. The brine that feeds the hydrothermal systems located above the subduction zone originates from the drainage of subducting slabs. This water induces fractional melting of the upper mantle wedge, initiating volcanism (Hovland, Rueslåtten & Johnsen, 2015).

The geology of the The Puna is characterized by the presence of rhyolitic volcanic and granitic plutonic rocks, which are part of the eruptive belt of the western The Puna, according to the geological map of South America by Gómez Tapias et al. (2023). The petrology and geochemistry of these rocks have been described as part of a typical magmatic arc (Ramos, 1999). The hydrothermal alteration of these rocks results in the release of various ions such as potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), and silica (SiO_2). The alkali feldspars present in rhyolitic rocks are an important source of sodium (Na^+) and potassium (K^+), while minerals such as chlorite and other silicates release chloride (Cl^-) and magnesium (Mg^{2+}). These ions, released through mineral alteration, dissolve in thermal waters, explaining the high concentrations of these compounds in the analyzed samples (Lagos Durán, L. V., 2016).

The saturation index of halite and sylvite is undersaturated, indicating that these salts tend to dissolve in water rather than precipitate. However, the waters show oversaturation in dolomite and, to a lesser extent, in calcite, suggesting that carbonate precipitation may occur in certain parts of the hydrothermal system. This is related to the interaction of waters with carbonate rocks present in the region and with fluid mixing processes between hydrothermal waters and lower-temperature waters. The oversaturation of dolomite indicates an environment where hydrothermal activity promotes the release and subsequent precipitation of calcium and magnesium carbonates, which could have implications for the formation of mineral deposits associated with thermal waters.

The Tocomar geothermal field, with maximum recorded water temperatures of 78°C, represents a prominent example of hydrothermal activity in the The Puna. The geochemistry and geothermometry of this system provide valuable information for understanding the geothermal dynamics of the region, where the interaction between magmatic activity, geological faults, and groundwater generates a complex hydrothermal system with potential both for the exploitation of geothermal resources and for the formation of mineral deposits of economic interest. Additionally, in the areas near the sampling sites, the Llullaillaco volcano, the Socompa volcano, and the Antuco volcano are located.

IV.3. CATAMARCA

In the hydrogeological exploration of Catamarca (Figure 33), several geological provinces covering different thermal aspects have been identified. Among them, the The Puna, the Frontal Cordillera, Famatina Range and the Pampean Ranges stand out. However, in this study, thermal water samples come exclusively from the The Puna, Famatina Range and the Pampean Ranges.

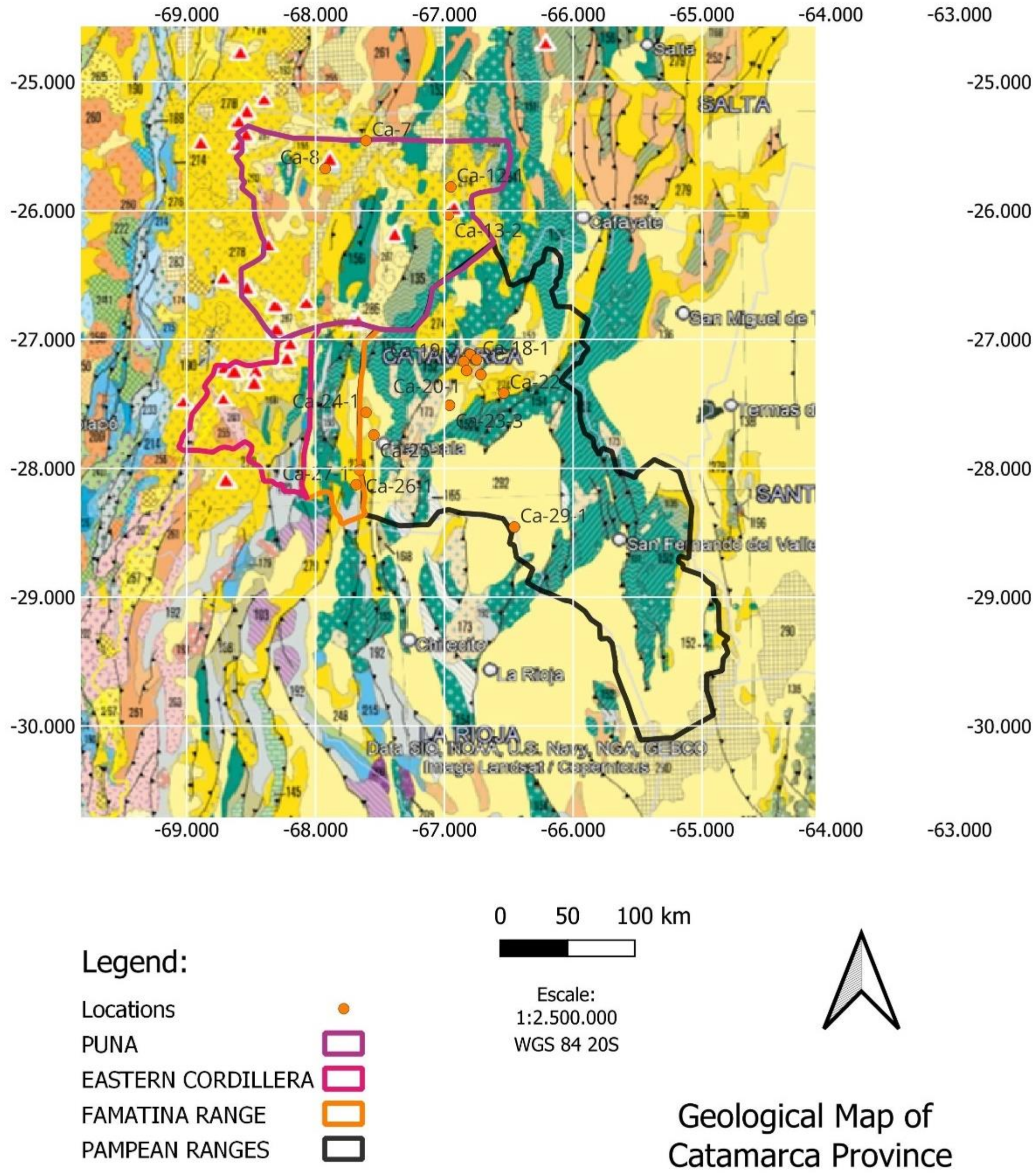

Figure 33. Location of the analyzed samples in Catamarca Province on the geological map.

The figure shows the location of 52 thermal water samples collected in Catamarca Province, distributed across the geological map that distinguishes the main geological provinces of the area: The Puna, Famatina Range, and Pampean Ranges, based on the *Geological Map of South America* (CGMW, 2019). The samples are labeled with the prefixes "Ca-" and "EXC_" followed by their respective numbers.In the The Puna of Catamarca, the dominant lithologies are Neogene undifferentiated volcanic rocks (code 274), present in samples such as Ca-7 to Ca-13 and EXC_28, EXC_30, EXC_32 to EXC_34. Additionally, Ordovician siliciclastic sedimentary rocks (EXC_29, EXC_31) and a Quaternary basaltic volcanic unit (EXC_27) are also represented, reflecting the volcanic and sedimentary diversity associated with high-altitude magmatic arc settings and endorheic basins. In the Famatina Range, represented by sample Ca-27-1, Quaternary siliciclastic sediments (code 292) are observed, suggesting recent depositional environments, possibly related to piedmont or alluvial fan systems in internal basins. The Pampean Ranges host the largest number of samples, encompassing a wide lithological variety. These include Neogene and Quaternary siliciclastic sedimentary rocks (e.g., Ca-17 to Ca-29), Ordovician granitic plutonic rocks (Ca-18, Ca-22), medium- to high-grade metamorphic rocks (Ca-25-1 and EXC_26), and some Neogene volcanic units (Ca-21-1 and Ca-21-2). This lithological diversity reflects the complex geological history of the Pampean basement, influenced by compressional tectonics and Paleozoic magmatism. This figure enables correlations between rock type, geological age, and the location of thermal spring discharges, providing a framework for analyzing groundwater circulation patterns, mineralization processes, and water chemistry within distinct structural domains of the province. **Source**: Commission for the Geological Map of the World – CGMW (2019). *Geological Map of South America*. Paris: UNESCO-CGMW.

Figure 34 shows the relationship between the temperature of thermal waters and elevation across the different geological provinces of the study area, including the The Puna, Famatina Range, and Pampean Ranges. The maximum recorded temperature reaches approximately 85°C and occurs in the The Puna region at an elevation close to 4800 m a.s.l. Temperatures in the dataset range from approximately 4°C to 85°C, with most values concentrated between 20°C and 40°C in the Famatina Range and Pampean Ranges.

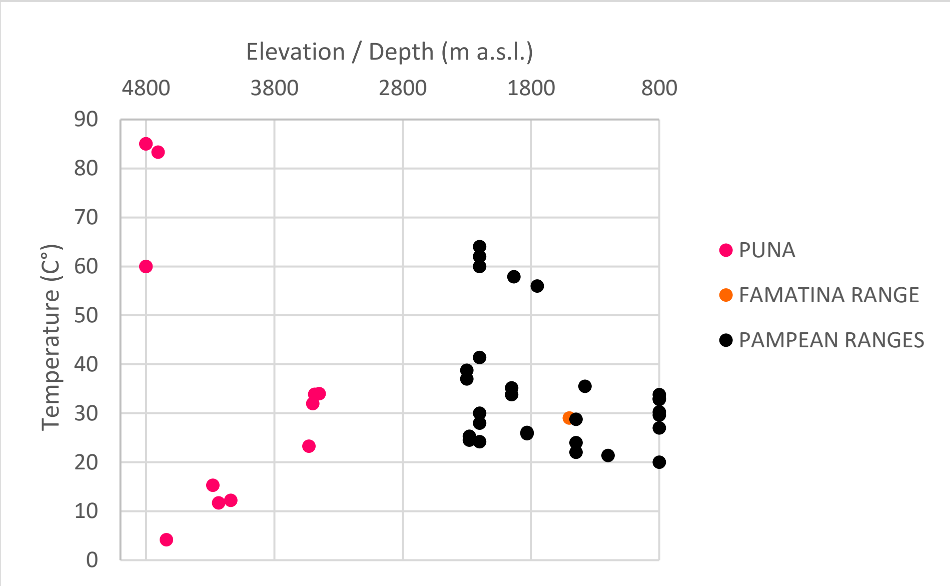

Figure 34. Relationship between temperature (°C) and elevation (m a.s.l.) of thermal waters in the different geological provinces of the study area (The Puna, Famatina Range, and Pampean Ranges).

Figure 35 shows the relationship between total dissolved solids (TDS) and elevation/depth of thermal waters in the geological provinces of the study area. The maximum recorded TDS value reaches approximately 13,479 mg/L at an elevation close to 3,450 m a.s.l. in the The Puna region. According to standard TDS classifications, this value corresponds to saline water, as it exceeds 10,000 mg/L. However, most samples display TDS values ranging between approximately 381 mg/L and 5,348 mg/L, corresponding mainly to fresh to brackish waters. In contrast, samples from the Pampean Ranges generally present lower TDS values, mostly below 3,000 mg/L.

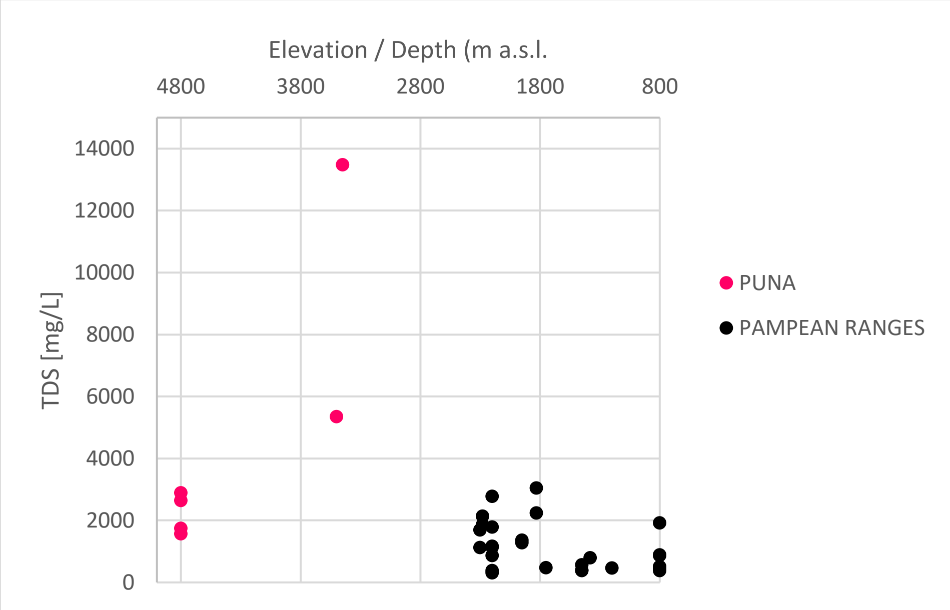

Figure 35. Relationship between total dissolved solids (TDS, mg/L) and elevation/depth (m a.s.l.) of thermal waters in the geological provinces of the study area (The Puna and Pampean Ranges).

In the analysis of Equivalent Concentration Ratios in meq/L (Figure 36) of the sodium-to-calcium ratio, distinctive patterns are observed at different altitudes grouped by geological provinces: in the The Puna, there is a significant presence of sodium in relation to calcium with maximum values of 30.38 meq/L at 4800 ma.s.l.

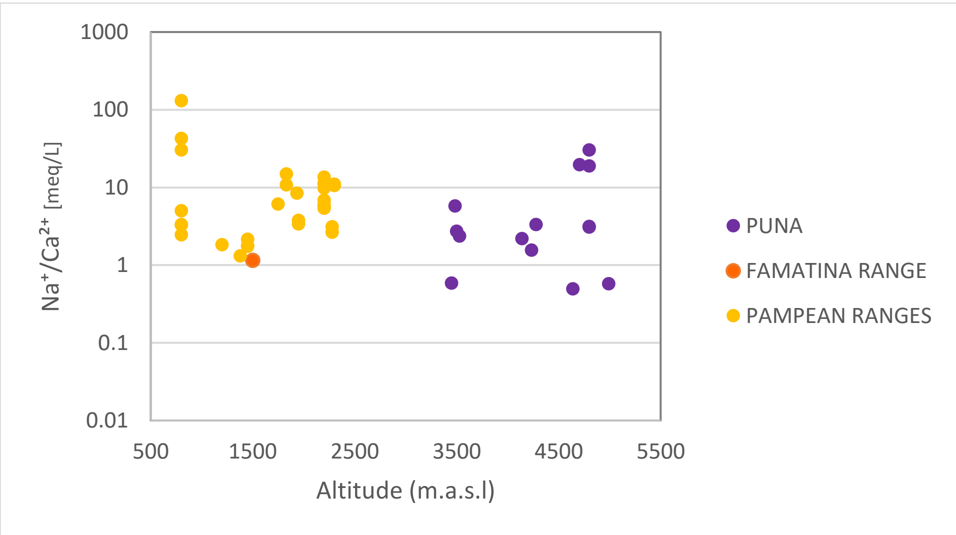

Figure 36. Na^+/Ca^{2+} [meq/L] in The Puna, Famatina Range and Pampean Ranges.

In the analysis of Equivalent Concentration Ratios in meq/L of magnesium-to-calcium (Figure 37), some minimal anomalies are observed with a slight predominance of magnesium over calcium in the The Puna 46.42 meq/L at 800 m a.s.l., but in the majority there is a predominance of calcium over magnesium, with maximum values of 0.023 meq/L at 1830 m a.s.l.

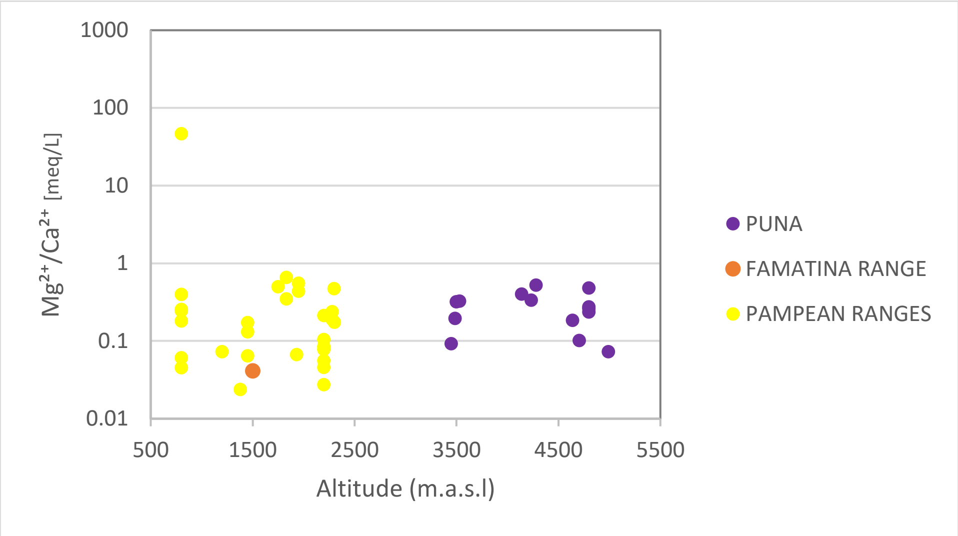

Figure 37. Mg^{2+}/Ca^{2+} [meq/L] according to altitude (m.a.s.l).

In the analysis of Equivalent Concentration Ratios in meq/L of chloride to sulfates (Figure 38), it is observed that in the The Puna, chloride values predominate over sulfates in most of the localities. The maximum concentration of chloride reaches 542.85 meq/L at 4800 m a.s.l. However, in general terms, chloride values vary between 150 meq/L and 1.07 meq/L. On the other hand, unlike most of the cases, there are some localities with minimum values in which sulfates predominate, reaching 0.082 meq/L.

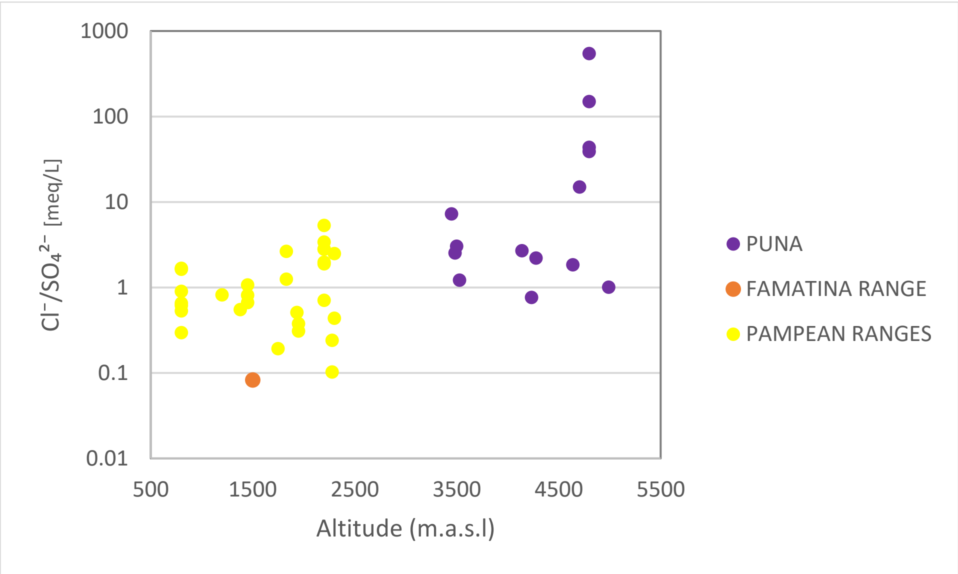

Figure 38. Cl^{-}/SO_4^{2-} [meq/L] according to altitude (m.a.s.l).

In the analysis of Equivalent Concentration Ratios in meq/L of chloride to bicarbonates (Figure 39), it is observed that in The Puna chlorides predominate over bicarbonates in most of the localities. The maximum concentration of chlorides reaches 32.52 meq/L at 1380 m a.s.l.. As for bicarbonates, the minimum values recorded are 0.14 meq/L at 2300 m asl.

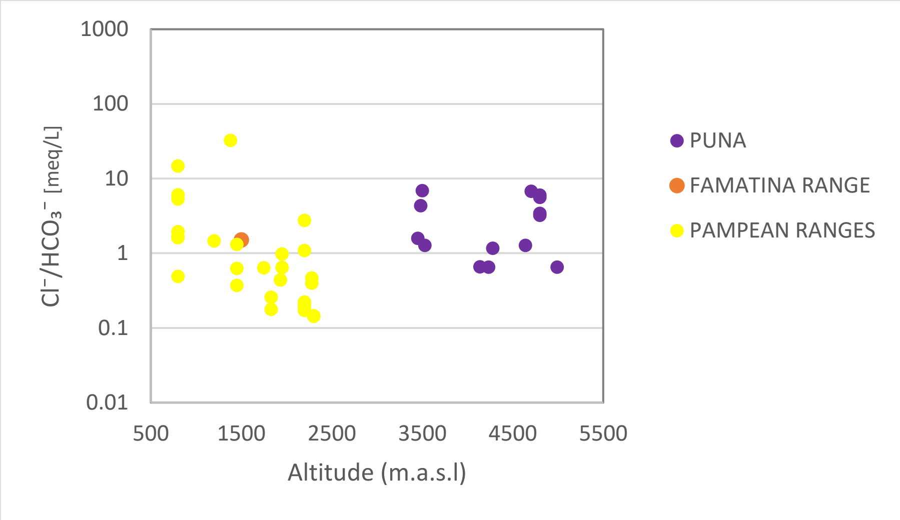

Figure 39. Cl^-/HCO_3^- [meq/L] according to altitude (m.a.s.l).

The calcite saturation index (Figure 40) reveals that it is supersaturated in the Volcanic (Undifferentiated) and Sedimentary (Siliciclastic).On the other hand, Metamorphic rocks (low to medium grade), together with Sedimentary (Siliciclastic), Volcanic (Undifferentiated) and Plutonic (Granitic), show undersaturated conditions. In general, subsaturation predominates, except in the above-mentioned cases where supersaturation is observed.

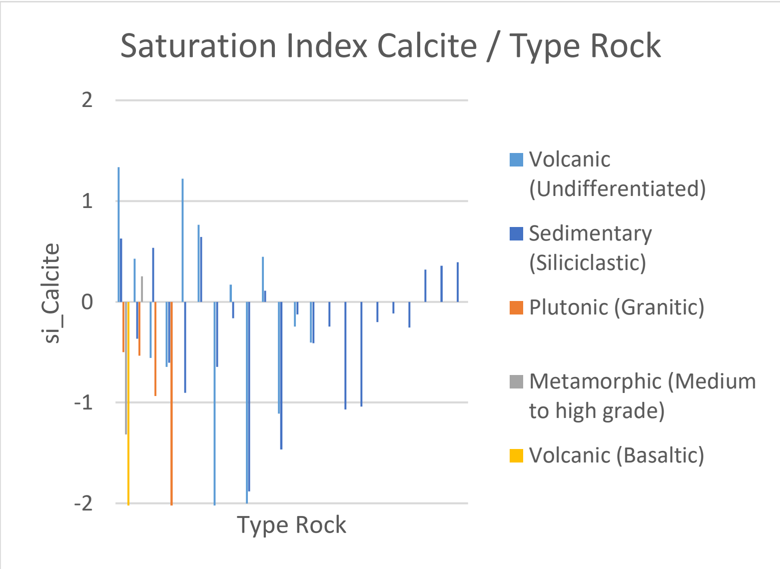

Figure 40. Saturation Index of Calcite phases according to type rocks.

The dolomite saturation index (Figure 41) indicates that the Volcanic (Undifferentiated), Sedimentary (Siliciclastic) formations, except in some samples of these same formations and Plutonic (Granitic), Metamorphic (Medium to high grade), where oversaturation is observed. In general, in the water samples there is subsaturation and supersaturation without predominance of one over the other.

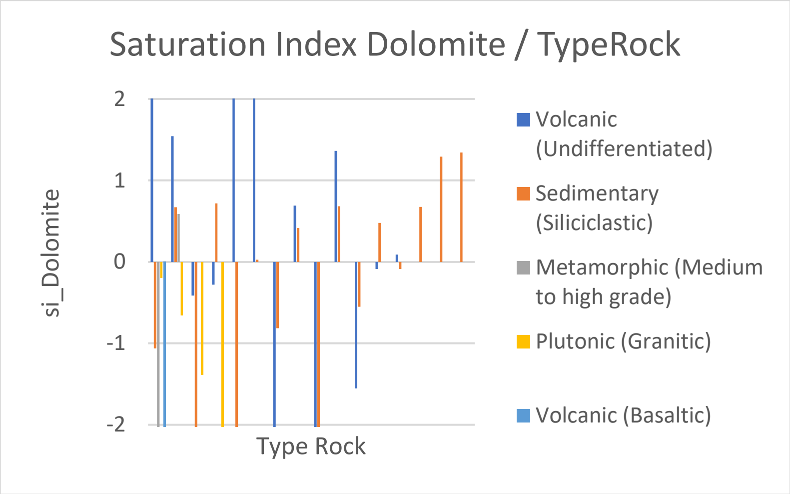

Figure 41. Saturation Index of Dolomite phases.

The saturation index (Figure 42 and 43) of halite and sylvite is unsaturated across all rock types and elevations. Additionally, the saturation index remains consistent, showing no significant dependence on changes in altitude.

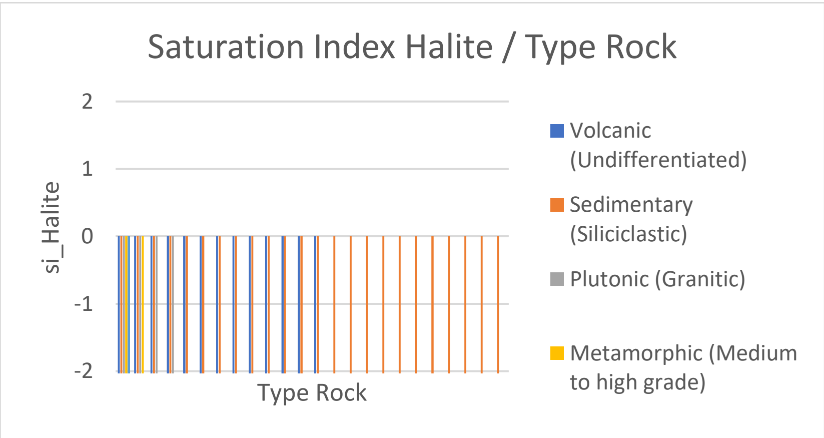

Figure 42. Saturation Index of Halite phases.

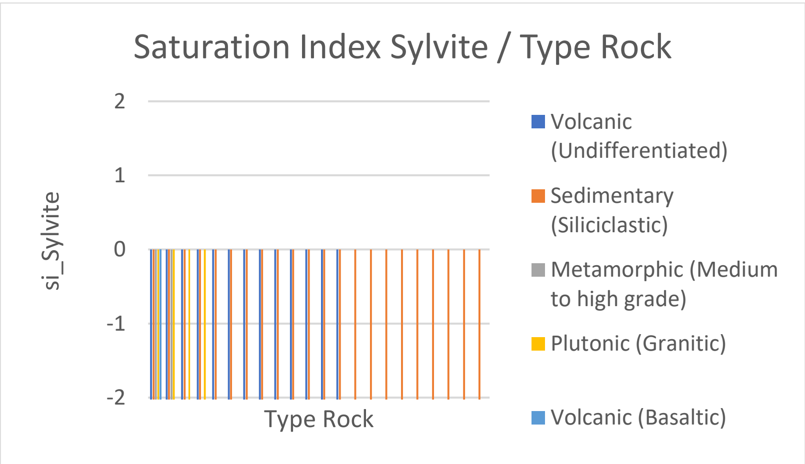

Figure 43. Saturation Index of Sylvite phases.

In the Piper diagram (Figure 44), which illustrates the distribution of water classifications according to rock type, distinctive patterns can be observed that reveal the geochemical characteristics of emerging waters in the different rock formations of Catamarca.

- Plutonic Granitic Rocks: These are primarily characterized by thermal waters with a dominant sodium bicarbonate (Na^+-HCO_3^-) composition.
- Undifferentiated Volcanic Rocks: The springs in these formations exhibit a sodium-calcium bicarbonate chloride (Na^+-Ca^{2+}-HCO_3^--Cl^-) composition.
- Metamorphic Rocks (low to medium grade): These show a variety of water compositions, predominantly sodium sulfate chloride (Na^+-SO_4^{2-}-Cl^-).
- Siliciclastic Sedimentary Rocks: Thermal waters emerging from these formations are classified as sodium-calcium sulfate bicarbonate chloride (Na^+-Ca^{2+}-SO_4^{2-}-HCO_3^--Cl^-).
- Basaltic Volcanic Rocks: The waters from these formations are characterized mainly by a sodium bicarbonate (Na^+-HCO_3^-) composition.

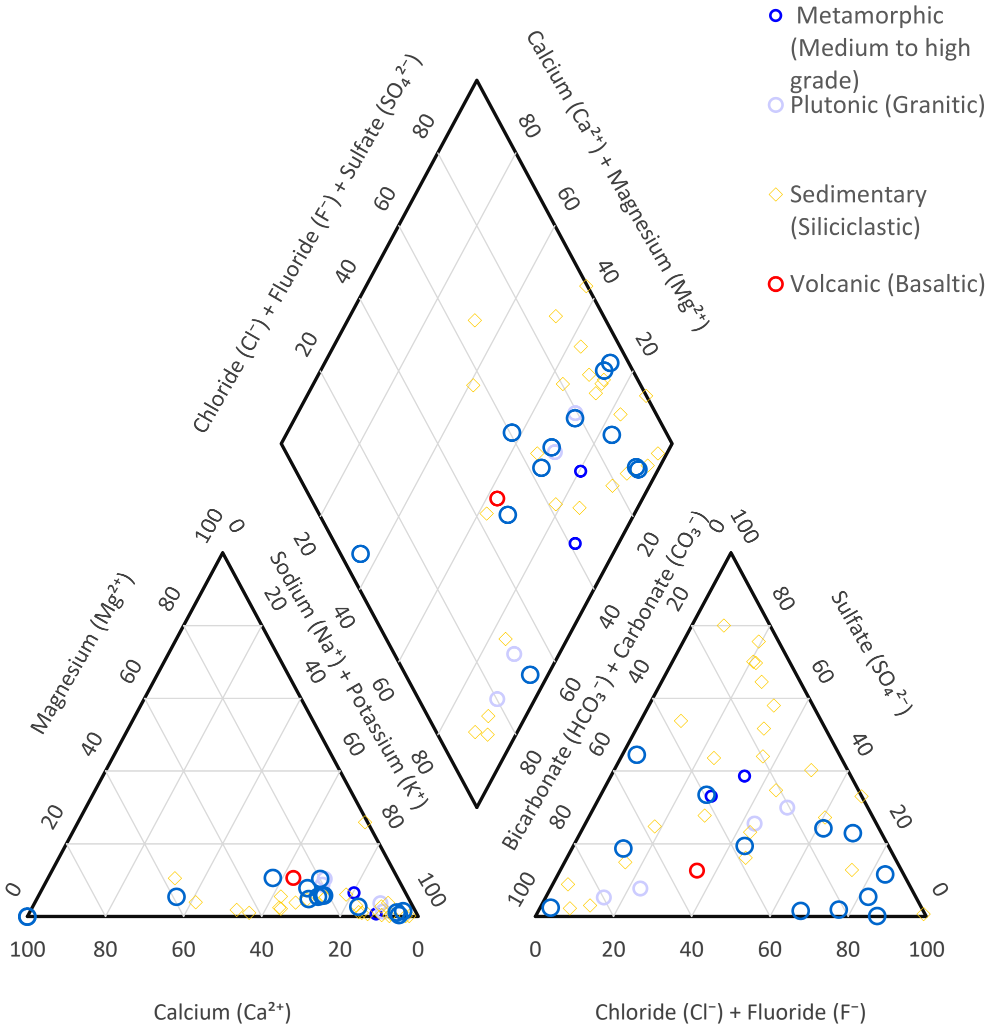

Figure 44. Piper plot of concentration in meq/L of springs in rock types.

En el diagrama de Piper (Figura 45), que refleja las clasificaciones de las aguas según las elevaciones de las provincias geológicas, se observan patrones distintivos que revelan la composición química de las aguas en las distintas zonas geográficas de Catamarca.

- The Puna: Las aguas termales de esta región presentan un predominio de la composición bicarbonatada clorurada sódica cálcica (HCO_3^--Cl^--Na^+-Ca^{2+}).
- Famatina Range: Las aguas emergentes en esta zona se caracterizan principalmente por una composición clorurada sódica (Cl^--Na^+).
- Pampean Ranges: Las aguas termales de esta región exhiben una composición sulfatada bicarbonatada clorurada sódica cálcica (SO_4^{2-}-HCO_3^--Cl^--Na^+-Ca^{2+}).

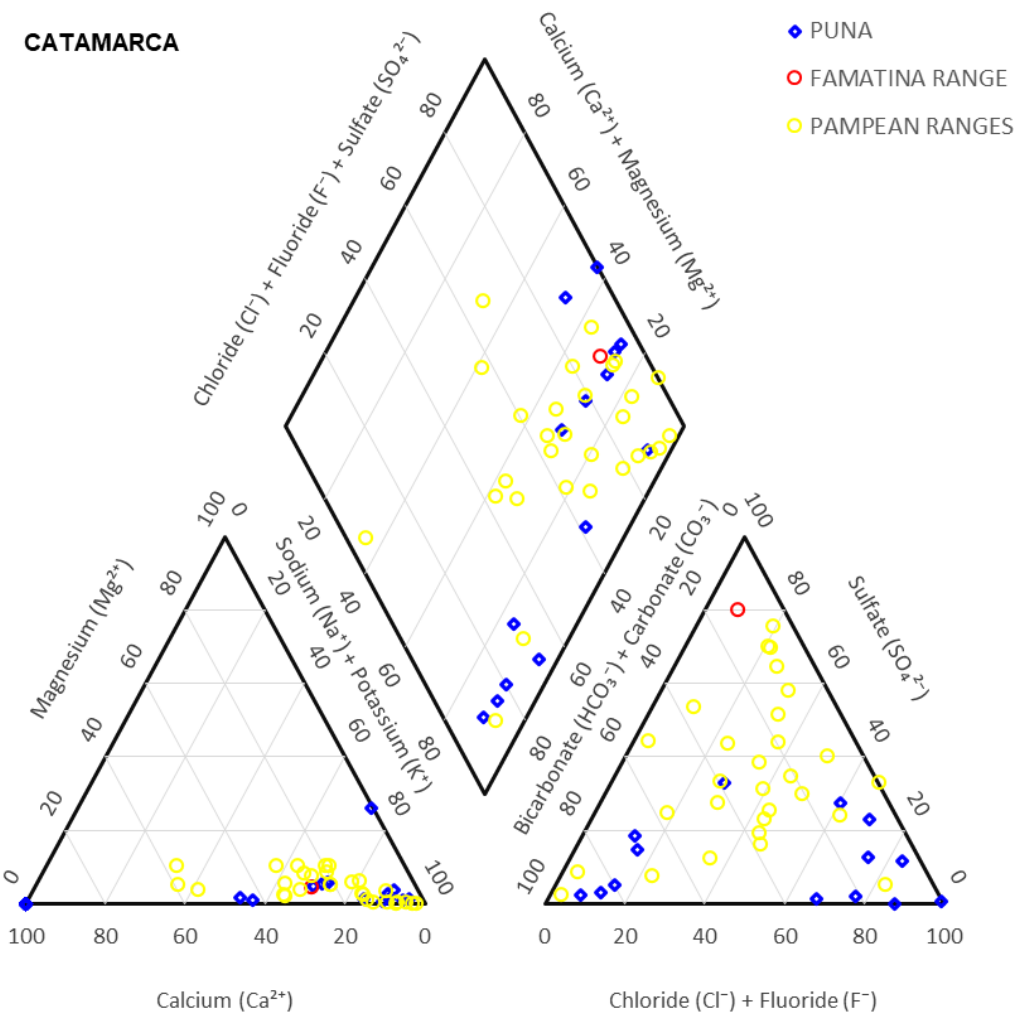

Figure 45. Piper plot of concentration in meq/L of springs in Catamarca..

Discussion: Hydrogeochemical classification of thermal waters in the three geological provinces of Catamarca.

In the present study, a hydrochemical characterization of thermal waters of the northern Argentinean Andes was carried out, particularly in the province of Catamarca, divided into three geological provinces: Frontal Cordillera, The Puna, Pampean Ranges and Famatina Ranges. The analysis of water samples is from these last three geological provinces. Through the analysis of the 35 samples collected, it was possible to classify thermal waters according to their ionic composition, and the relationship between the local rock formations and the chemical characteristics of the waters was observed. This relationship reflects how the interactions between groundwater and the geological materials present in each region contribute to the variability of its composition, in addition to the geological context of being located on a subduction edge, where tectonic dynamics and related structures, such as major faults, influence the circulation of fluids and the release of minerals that affect water chemistry.

1. The Puna

The six thermal water samples analyzed in the The Puna region, collected at altitudes ranging from 4,800 to 3,450 meters above sea level, reflect the significant geothermal activity in areas such as Teben Grande (sample 1), Vega Botijuela (sample 2), Aguas Calientes, and La Colcha. These samples predominantly exhibited a bicarbonate-chloride sodium-calcium and sodium chloride composition, reflecting significant hydrothermal activity in the region. The water temperatures ranged from 32 to 85°C, indicating active geothermal activity in the area. The average pH of the samples was 6.85, with values fluctuating between 6.4 and 7.3, suggesting that the waters are generally slightly acidic to neutral.

In thermal manifestations of the Cerro Galán caldera, hydrothermal activity is influenced by the interaction of a magmatic body, which serves as a heat source, with meteoric and volcanic fluids. This geothermal system is controlled by regional faults, which serve as preferential pathways for the upward migration of deep fluids to the surface. In areas such as La Colcha, Aguas Calientes, and Piscinas Burbujeantes, surface manifestations have been identified, including thermal springs with temperatures ranging from 25 to 99°C, whose waters show variability in composition, from slightly acidic to neutral pH (between 6.28 and 7.11). In particular, the studies by Massenzio et al. (2024) have shown that the anomalous CO_2 degassing in the areas of Aguas Calientes and La Colcha has a direct impact on the water chemistry, altering the balance between carbonate and bicarbonate ions and favoring the precipitation of minerals such as calcite and dolomite.

The concentration of total dissolved solids (TDS) in the samples ranged from 1,747 to 5,348 mg/L, classifying the waters as brackish, with the exception of one sample that showed a much higher value of 13,479 mg/L, corresponding to saline water. This high TDS concentration is related to hydrothermal activity and the presence of volcanic rocks in Teben Grande, located north of the Salar de Antofalla, which release chloride (Cl^-) and sodium (Na^+) ions into thermal fluids. The chemical composition of these waters reflects interactions between meteoric fluids, magma, and underground volcanic rocks.

In the La Colcha area, thermal waters, with temperatures between 35 and 85°C, have a sodium chloride composition and a pH between 6.28 and 7.05. These waters are responsible for the formation of salt and travertine deposits, a result of high temperatures and interaction with underground minerals. Aguas Calientes shows waters with temperatures between 25 and 65°C, also of sodium chloride type, with a pH between 6.41 and 7.11, also favoring the formation of saline deposits.

The anomalous CO_2 degassing detected in the areas of La Colcha and Aguas Calientes has a direct impact on the water chemistry. This phenomenon, enhanced by the low atmospheric pressure of the The Puna, facilitates the release of CO_2 from thermal waters into the atmosphere, altering the equilibrium between carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. This chemical change promotes the precipitation of calcium carbonate ($CaCO_3$), observed in the form of calcite in the mineral formations of these areas.

The mineralogy of soils near thermal springs reflects the hydrothermal processes occurring in the region. In the case of La Colcha, white and black salts are found in contact with thermal water, mainly calcite and halite, along with minerals such as borax and tincal. This finding coincides with the analysis performed using Phreeqc, which indicates that the waters in this area are oversaturated with calcite and dolomite, reinforcing the presence of these minerals in the formations. Furthermore, it is observed that the waters or springs in the area are undersaturated with halite and sylvite, suggesting a lack of precipitation of these salts under the current conditions of the hydrothermal system, coinciding with the classification of sodium chloride waters.

These results demonstrate a clear interaction between the mineralogical composition of thermal waters and the ongoing geothermal processes, reinforcing previous interpretations of the fluid dynamics in the Cerro Galán caldera. The interaction between the saline lake brines, hydrothermal fluids, and volcanic rocks is crucial for understanding the chemical and mineralogical processes in the region. The hydrothermal transport of brines from subduction zones to the surface contributes to the formation of salt deposits in thermal areas of the The Puna. These processes are also related to the formation of large deposits of lithium and boron, elements found in high concentrations in the brines and geothermal waters of the region, as discussed in previous studies (Durán, 2016).

In summary, thermal water samples analyzed and the information obtained from the hydrothermal manifestations of Cerro Galán, such as the hot springs and La Colcha, and from areas near the Salar de Antofalla, such as Vega Botijuela and Teben Grande, provide a detailed view of the geothermal processes occurring in the The Puna. The interaction between magmatic fluids, meteoric fluids, and volcanic and sedimentary rocks results in a wide variety of chemical compositions in thermal waters, reflecting the geological and geothermal dynamics of the region. Additionally, the low atmospheric pressure characteristic of the high altitude of the The Puna facilitates the degassing of CO_2, causing the release of this gas from geothermal fluids into the atmosphere, promoting the precipitation of minerals such as calcite and dolomite. This geothermal dynamics, combined with the interaction of gases, water, and underground minerals, contributes to the rich mineralogy observed in thermal areas of the region

2. Famatian Range

The Famatian Range is a geologically active region with a series of complex tectonic, hydrothermal and geochemical processes that shape both its geology and its natural resources, particularly its thermal waters. A sample of thermal water was collected from a spring called La Higuerita, located 1,500 meters above sea level, and it was found that the composition of The emergent waters in this area are mainly characterized by a sodium chloride composition (Cl--Na^+).

The water temperature was 29°C, reflecting moderate hydrothermal activity in the region. The pH was 7.2, indicating a nearly neutral environment. Additionally, the total dissolved solids (TDS) concentration was not detected. These data reflect the hydrothermal behavior in the region, suggesting that, although direct magmatic activity has ceased, the heat accumulated during past tectonic events continues to influence the circulation of groundwater.

Emerging waters in the area, such as those from La Higuerita and near Termas La Aguadita, are indications of ongoing geothermal heating in the region. Although the original magmatic arc has shifted westward and is no longer active, the accumulated heat remains relevant for the circulation of groundwater. This phenomenon is not associated with recent volcanic activity but with the circulation of meteoric water through tectonic faults. As the water descends to greater depths, it heats up due to contact with hot underground rocks, which causes an increase in the temperature of thermal waters. This process highlights how the remnants of accumulated heat from past tectonic events continue to play a crucial role in the region (Aceñolaza and Toselli, 1973; Ramos et al., 1984).

The Famatinian Cycle, a key orogenic event that occurred during the Ordovician and Silurian periods, has played a fundamental role in shaping the geology of the Eastern Cordillera. Cambrian-Ordovician sedimentation and volcanic processes during this cycle directly influenced the formation of rock structures, shaping the landscape we observe today. During the Ordovician, the region experienced the intrusion of large granitic bodies, associated with a subduction process due to the approach of the Precordillera terrain. This orogenic cycle also triggered a series of tectonic events that generated folded and faulted structures, observed in the Cordón de la Cumbre, and they are a testament to the complexity of tectonic processes influencing the region. However, the precise interpretation of the tectonic processes that formed the Eastern Cordillera remains a topic of debate. The lack of consensus on the exact dynamics of subduction and magmatism in the formation of the Sierra reflects the complexity of the geotectonic processes involved and the need for further research to fully understand the geological history of the region. The evolution of plate tectonics over time has transformed Famatina into part of a magmatic arc built on continental crust, leaving a clear imprint on its relief and geological structures (Pankhurst and Rapela, 1998; Dávila et al., 2001).

The chemical composition of thermal waters in the Eastern Cordillera reflects the interaction between water and the rock formations that predominate in the region. Calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}) dissolve as thermal water comes into contact with the siliciclastic sedimentary rocks that dominate the area. In particular, the presence of sulfate in the waters is a manifestation of the hydrothermal alteration of sulfide minerals, such as pyrite (FeS_2), which releases sulfate (SO_4^{2-}) and iron ions into solution. Additionally, calcium and magnesium ions are also released during this process, contributing to the concentrations observed in the water samples. The lower concentration of sodium chloride (NaCl) in the waters of the Eastern Cordillera may be related to the mixing of thermal waters with freshwater or less mineralized sources from nearby tributaries or meteoric waters. This mixing dilutes the concentrations of ions present in thermal waters, such as sodium (Na^+) and chloride (Cl^-), which are common in other areas of the The Puna, making the waters of the Eastern

Cordillera fresher and less saline compared to other bodies of water in the region (Astini, 1998; Dávila et al., 2001).

The geochemical phenomenon in the Eastern Cordillera is also reflected in the mineral saturation indices. Oversaturation in dolomite and calcite, and undersaturation in halite and sylvite are observed, indicating that thermal waters have the capacity to precipitate carbonates such as dolomite and calcite, but do not favor the formation of saline minerals such as halite or sylvite. This behavior could be linked to fluctuations in pH, temperature, or the chemical composition of the water. These geochemical aspects are relevant not only for understanding current thermal processes but also for evaluating the region's potential in terms of mineral deposit formation in the future. The capacity of thermal waters to precipitate these minerals reflects the current conditions of the geothermal environment and its potential evolution (Ramos et al., 1984).

The interaction between meteoric and thermal waters has a considerable impact on the water chemistry and its quality for various uses. The mixing of meteoric waters with thermal waters can alter both the temperature and the chemical composition of the water, which could influence its potential for medicinal, therapeutic, or tourism-related uses. This phenomenon highlights the importance of constant monitoring in the region to anticipate changes in water quality and its impact on the local ecosystem, as well as on human activities dependent on these waters. Additionally, climate change could alter precipitation patterns and the underground circulation of water, affecting the composition and properties of thermal waters, which has implications for both water quality and regional development.

In conclusion, the Eastern Cordillera presents a complex interaction between tectonic, hydrogeological, and geochemical processes that continue to shape its landscape and natural resources. Although direct volcanic activity has ceased, the region remains geothermally active due to the remnants of heat accumulated during past tectonic events. The region's geology, marked by the influence of the Famatinian Cycle, continues to be a topic of debate and a source of interest for future studies. The chemistry of thermal waters is a clear reflection of the interactions between water and rock formations, and the variations in mineral composition, as well as the mixing with meteoric waters, provide an interesting perspective on how these processes might evolve in the future (Aceñolaza and Toselli, 1973; Pankhurst and Rapela, 1998).

3. Pampean Ranges

The PAMPEAN RANGES present a great diversity in the ionic composition of their thermal waters. A total of 30 samples were collected from thermal springs located at altitudes ranging from 380 to 2930 meters above sea level. Thermal waters in this region exhibit a sulfate-bicarbonate-chloride-sodium-calcium composition (SO_4^{2-}-HCO_3^--Cl^--Na^+-Ca^{2+}).

The temperatures of thermal waters ranged from 20°C to 60°C, with the highest temperature recorded at the Villa Vil spring. The pH of the waters varied between 5.8 and 9.6, indicating a wide range of chemical conditions. Most of the waters were slightly acidic (around 6), neutral (around 7), and slightly alkaline (around 9.6).

According to San José Rodríguez (2008), the water samples collected in the study of the Pampean Sierras show a wide variety of chemical compositions, reflecting the interaction of the waters with the surrounding rocks over time. These waters, such as those from Villa Vil, present a combination of bicarbonate-sodium, sulfate-sodium, chloride, and silicate, with temperatures ranging from 25°C to 60°C, reaching up to 85°C in certain points. This behavior suggests that, although volcanic activity in the area has ceased, the structural conditions created by tectonic dynamics millions of years ago continue to influence the circulation and heating of the current thermal waters.

In this context, the concentrations of total dissolved solids (TDS) in the waters of the Pampean Sierras range from 306 mg/L to 3043 mg/L, classifying the waters into three types: fresh (low TDS), brackish (medium TDS). The main ions present include sodium (Na^{+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^{-}), bicarbonate (HCO_3^{-}), and sulfate (SO_4^{2-}), reflecting the interaction between the waters and the rocks in this process.

It is possible that the Pampean Sierras and Famatina Sierras share a common geothermal process that favors the formation of sulfate waters through the migration of underground fluids tah, as they ascend, interact with minerals in the fractured rocks and meteoric waters, giving them the chemical variability observed.

Currently, no significant magmatic activity is evident in the Pampean Sierras, but in the past, during the orogenic phases that shaped the region, tectonic and volcanic activity was significant. This historical activity is associated with the Pampean and Famatinian orogenies, processes that deeply marked the region's geology. The current elevation of the sierras is the result of the activation of large reverse faults with a high angle during the Tertiary period, which led to the current configuration of the region, although without recent volcanic activity.

Despite the lack of current magmatic activity, the Pampean Sierras remain a geothermally active area, particularly in its thermal manifestations. These thermal waters, such as those from Sierra de Hualfín, Villa Vil, Los Nacimientos, Colpa de Hualfín, Agua de Dionisio, Termas de Fiambalá, Suriyaco, Vis Vis, continue to be a manifestation of inherited geothermal activity, as the current thermal waters continue to circulate through structural faults that fracture the rocks, utilizing the residual heat from past tectonic and geothermal processes (Cosentino, Barcelona, & Ramos, 2022).

Discussion on Water Circulation in Geological Provinces

The regions of the The Puna, Eastern Cordillera, and Pampean Ranges exhibit complex geothermal interactions through thermal flows and subsurface waters. However, the available evidence allows for some conclusions, while also revealing the need for more data to fully understand the exact relationship between these regions.

In the The Puna, thermal waters show a clear presence of sodium chlorides, indicating strong interaction with volcanic rocks. Thermal flows in this region are clearly influenced by ancient volcanic activity, although there is no recent magmatic activity. The water temperatures in the The Puna can reach up to 60°C, suggesting active circulation of water through fractures in the region's rocks, utilizing the residual thermal flow generated by prior tectonic processes.

In the Eastern Cordillera, analysis of the only available sample indicates the presence of sodium (Na^{+}), calcium (Ca^{2+}), and sulfates (SO_4^{2-}) in thermal waters. This composition, although rich in sulfates, is different from that found in the The Puna and the Pampean Ranges, which show a higher presence of sodium chlorides. However, because only a single sample is available, it is not possible to definitively determine whether there is a match or direct connection between thermal flows of the Eastern Cordillera and the other two regions. The lack of additional samples prevents the confirmation of a solid relationship, as there could be variability in the water chemistry within this region itself.

In the Pampean Ranges, thermal waters present a more complex ionic composition, with a predominance of bicarbonates, sulfates, and sodium chlorides, similar to what is observed in the The Puna. The water temperatures in the Pampean Ranges also reach up to 60°C, indicating the presence of thermal flows associated with residual geothermal processes. These waters primarily originate from the circulation of fluids through structural fractures inherited from past tectonic and volcanic activity.

The analysis of thermal flows and water composition across the three regions suggests that while there is a clear geothermal relationship between the The Puna and the Pampean Ranges, the situation in the Eastern Cordillera is more uncertain due to the limited number of available samples. While the waters in the The Puna and Pampean Ranges share characteristics in temperature and ionic composition (particularly sodium chlorides), the sample from Eastern Cordillera shows a different composition (predominance of sulfates), which could suggest a difference in thermal flows of that region.

However, since the available information is limited to a single sample from Eastern Cordillera, it cannot be conclusively stated whether or not there is a direct connection between thermal flows of this region and the other two. This sample is not sufficient to establish clear evidence of coincidence or dissonance in thermal flows and subsurface waters between these three geographic areas.

Current evidence points to a greater match between the The Puna and Pampean Ranges in terms of thermal flows and water chemical composition, especially regarding the presence of sodium chlorides and temperatures up to 60°C. However, Eastern Cordillera presents a different composition in the few available samples, with a predominance of sulfates, suggesting that thermal flows in that region may follow different paths. Nonetheless, the lack of a representative sample from Eastern Cordillera prevents a conclusive statement about the connections between these three regions. More studies are needed to confirm or refute the existence of a direct relationship in thermal flows and subsurface waters between the The Puna, Eastern Cordillera, and Pampean Ranges.

IV.4. SAN JUAN

In the hydrogeological exploration of San Juan Province (Figure 46), significant patterns emerge when analyzing the relationship between temperature and altitude across its main geological provinces and associated intermontane valleys: Frontal Cordillera, Iglesia Valley, Precordillera, Bermejo Valley, and the Pampean Ranges (including Sierra Pie de Palo). For the purpose of regional interpretation, thermal springs of La Laja, Talacasto, Agua Hedionda, and nearby sectors of the Tulum Valley were grouped within the Precordillera geological province, as they are structurally and lithologically linked to this unit, which therefore provides the most appropriate framework for their hydrogeological analysis.

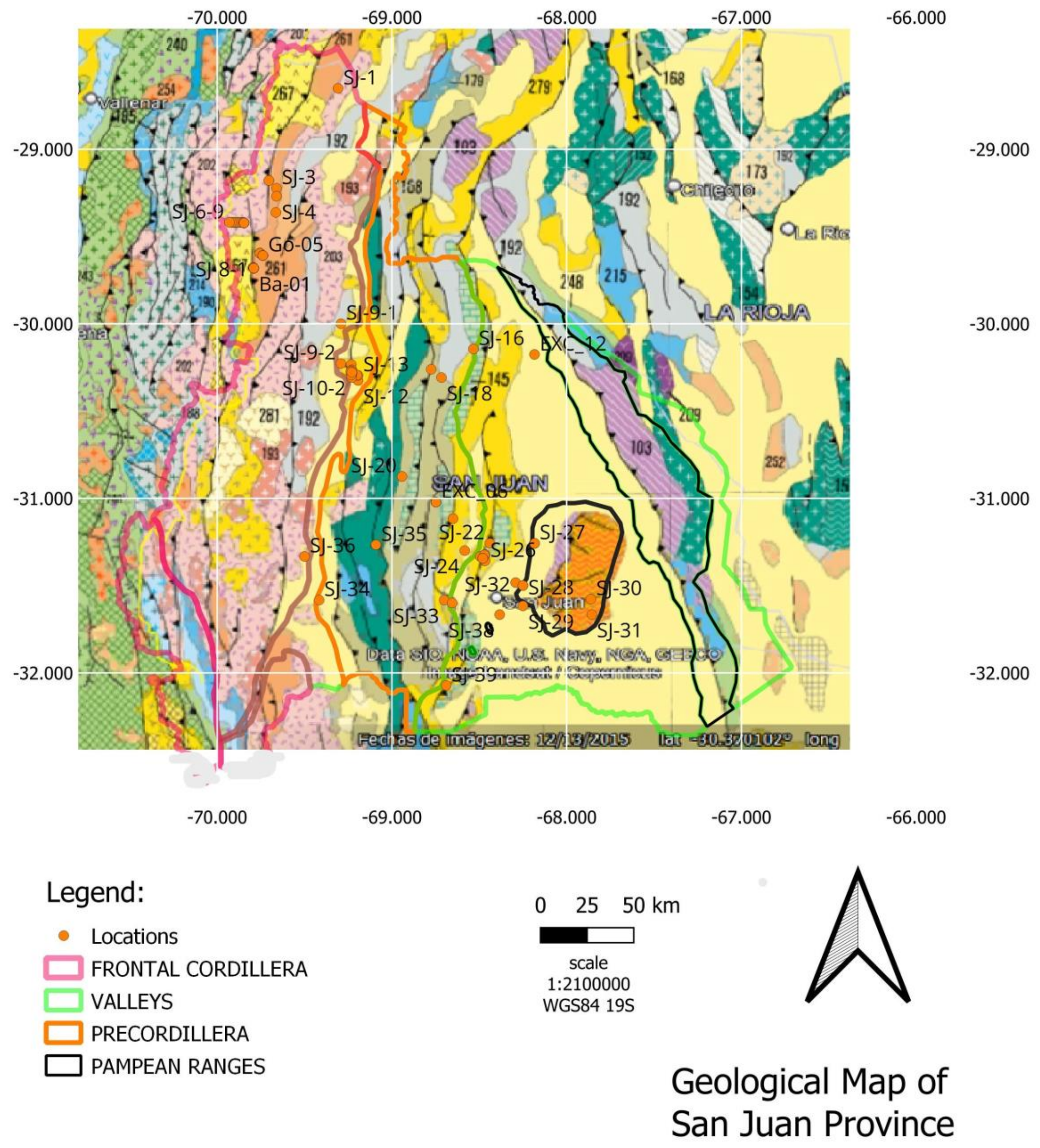

Figure 46. Location of the analyzed samples in San Juan Province.

The figure presents the distribution of over 120 thermal water and geothermal discharge samples in San Juan Province, classified by their location within the main geological provinces: Frontal Cordillera, Iglesia Valley, Precordillera, Bermejo Valley, and Pampean Ranges. The samples are georeferenced and labeled with prefixes such as “SJ-”, “Ba-”, “Des-”, “Go-”, and “EXC_”, and are plotted over a geological base map derived from the *Geological Map of South America* (CGMW, 2019), with main fault lines highlighted to show their structural influence on spring locations. In the Frontal Cordillera, most samples are concentrated over Tertiary siliciclastic sediments (code 261), Andesitic volcanic rocks and equivalents (code 267), Permian rhyolites (code 203), and Cretaceous sediments (code 252). Representative series include SJ-2, SJ-6, SJ-7, SJ-8, Des-01 to Des-11, Ba-01 to Ba-14, and Go-01 to Go-07. These thermal discharges align with active structural lineaments, indicating fault-controlled meteoric water flow and deep geothermal circulation. In the Iglesia Valley, all samples are located on Tertiary siliciclastic units (code 279), typical of foreland basins with active structural control. Samples SJ-9 to SJ-15 and

EXC_07 to EXC_24 exemplify geothermal discharge within valley fill zones influenced by fractures and potential Andean recharge. The Precordillera comprises Cambrian, Silurian, Carboniferous, and Tertiary formations (codes 145, 168, 192, 279), both carbonatic and siliciclastic, along with Quaternary sediments (292). Samples such as SJ-16 to SJ-35 and EXC_05-06 illustrate the connection between folded and faulted Paleozoic strata and deep hydrothermal systems.In the Bermejo Valley, Quaternary siliciclastic deposits (code 292) dominate, with samples SJ-22 to SJ-39 and EXC_01 to EXC_04 indicating discharge zones linked to basin-margin structures. Finally, samples in the Pampean Ranges (SJ-27 to SJ-31) are associated with Quaternary sediments (292) and Proterozoic metamorphic rocks (code 71), revealing spring emergence through fractured ancient basement. This figure enables the direct correlation between lithology, structural setting, and groundwater flow patterns, providing key insight into thermal water genesis, mineralization processes, and geothermal potential of the region. **Source**: Commission for the Geological Map of the World – CGMW (2019). *Geological Map of South America*. Paris: UNESCO-CGMW.

Figure 47 shows the relationship between temperature and elevation of thermal waters in the different geological provinces of San Juan, including the Frontal Cordillera, Iglesia Valley, Precordillera, Bermejo Valley and Pampean Ranges. The maximum recorded temperature reaches 78.6 °C at the Baños Los Despoblados hot spring, located at an elevation of approximately 3,657 m a.s.l. in the Frontal Cordillera.

In the Iglesia Valley, the maximum temperature reaches 45.1 °C at the Pismanta hot spring, located at an elevation of approximately 2,010 m a.s.l. In the Precordillera, temperatures reach up to 40 °C at the Agua Hedionda hot spring. In the Bermejo Valley, the highest recorded temperature is approximately 27 °C at the La Laja hot spring, located at about 650 m a.s.l. Finally, in the Pampean Ranges, a temperature of 27.5 °C was recorded at the Guayaupa hot spring at an elevation of approximately 690 m a.s.l.

Overall, the highest temperatures are observed in the Frontal Cordillera at elevations above approximately 3,600 m a.s.l., whereas lower temperatures are generally recorded in the Bermejo Valley and Pampean Ranges at elevations below 1,000 m a.s.l.

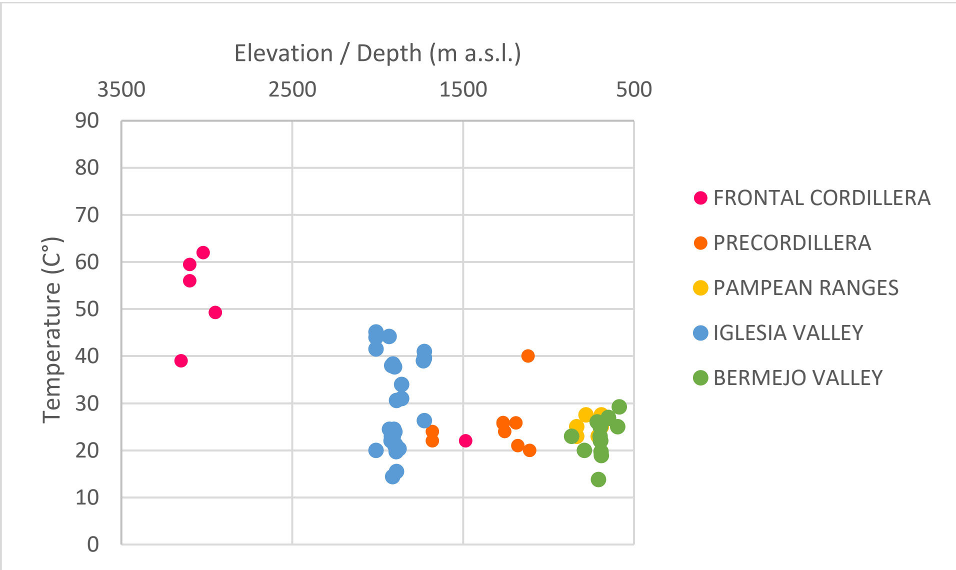

Figure 47. Relationship between temperature (°C) and elevation (m a.s.l.) of thermal springs in the geological provinces of San Juan (Frontal Cordillera, Iglesia Valley, Precordillera, Bermejo Valley and Pampean Ranges).

Figure 48 shows the relationship between total dissolved solids (TDS) and elevation of thermal waters in the geological provinces of San Juan. The maximum recorded TDS value reaches approximately 12,114 mg/L at the Bañitos de Chollay hot spring, located at an elevation of approximately 3,020 m a.s.l. in the Frontal Cordillera. According to standard TDS classifications, this value corresponds to saline water, as it exceeds 10,000 mg/L.

Minimum values of approximately 50.5 mg/L are also observed, indicating the presence of very fresh waters. In general, most samples display TDS values ranging between approximately 1,000 and 9,000 mg/L, corresponding mainly to brackish waters.

The dataset is dominated by samples from the Frontal Cordillera, as most available data correspond to this geological province. However, two samples from the Bermejo Valley are also included, showing very fresh waters with TDS values of approximately 229 mg/L and 80.6 mg/L.

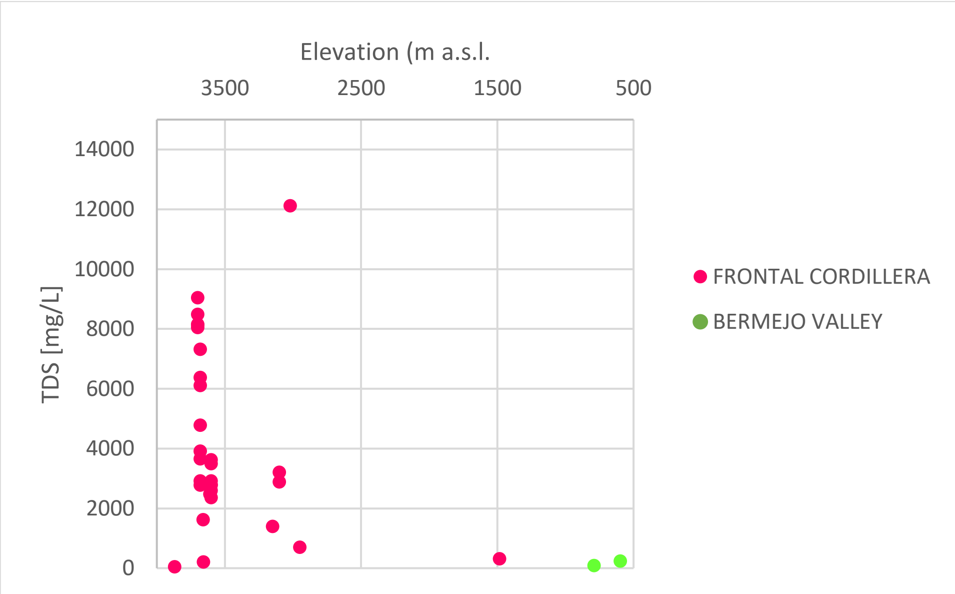

Figure 48. Relationship between total dissolved solids (TDS, mg/L) and elevation (m a.s.l.) of thermal waters in the geological provinces of San Juan, including the Frontal Cordillera and Bermejo Valley.

In the analysis of Equivalent Concentration Ratios in meq/L (Figure 49) of the sodium-to-calcium ratioIn the Frontal Cordillera, significantly high values are observed, reaching peaks such as 85.44 meq/L and 84.81 meq/L, indicating a prevalence of sodium relative to calcium, which may suggest specific geological processes, such as the dissolution of sodium-rich minerals in this region. However, the ratio also shows low values, such as 0.0483 meq/L, which could indicate local variability or influences from other hydrological factors. On the other hand, in the Iglesia Valley, the values are similarly high, with a maximum of 218.52 meq/L, reflecting a particular hydrochemical behavior in this area that could be associated with the interaction of groundwater with local minerals. These results contrast with those from the Bermejo Valley, where the values are generally lower, suggesting a greater homogeneity in the ionic composition of the water in that area. In the Pampanian Sierras and the Precordillera, the values are also variable, reinforcing the idea that each area has its own hydrochemical characteristics, related both to geological processes and local hydrogeological conditions. Overall, the distribution of Na^+/Ca^{2+} ratios shows complex patterns that should be interpreted in the context of the local geology and the predominant hydrochemical processes in each area.

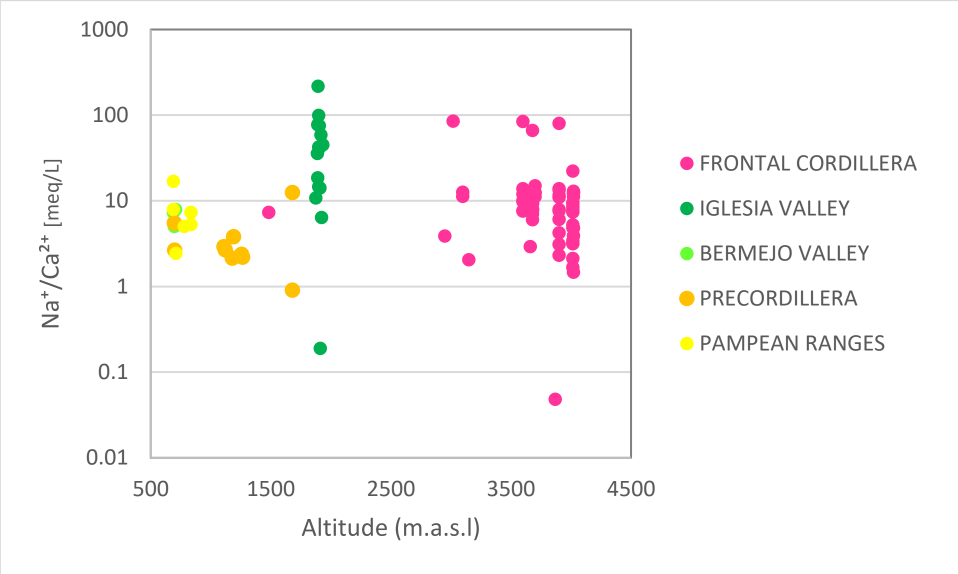

Figure 49. Na^+/Ca^{2+} [meq/L] according to Geological Provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of magnesium-to-calcium (Figure 50), In the Frontal Cordillera, the Mg^{2+}/Ca^{2+} ratios are generally low, with values such as 0.0023 meq/L and 0.0288 meq/L, indicating a relatively low presence of magnesium compared to calcium. This suggests that the geochemical processes in this region may be characterized by a greater availability of calcium relative to magnesium. However, the ratio also shows some variation with higher values, such as 1.5078 meq/L, indicating possible local differences or specific interactions with magnesium-rich minerals in certain areas. In the Iglesia Valley, the ratios are more variable, ranging from 0 to values like 1.0238 meq/L, which could reflect a complex hydrochemical behavior involving different mineral compositions and groundwater interactions. In the Precordillera, values such as 3.0550 meq/L are observed, suggesting a higher presence of magnesium compared to calcium in some areas, possibly linked to specific geological features or processes that promote the dissolution of magnesium-rich minerals. In contrast, the Bermejo Valley displays ratios that are often higher, such as 1.5791 meq/L, indicating a more pronounced presence of magnesium relative to calcium in this region. The Pampean Ranges exhibit lower values like 0.0737 meq/L, suggesting that magnesium levels are lower in comparison to other regions. Overall, the Mg^{2+}/Ca^{2+} distribution highlights significant spatial variability, with each area displaying unique hydrochemical characteristics influenced by local geological and hydrological factors.

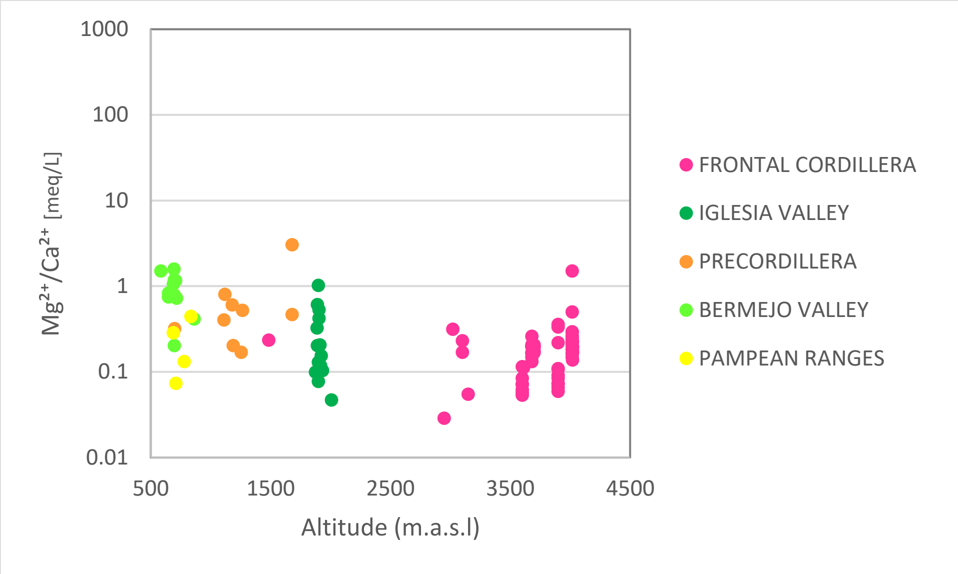

Figure 50. Mg^{2+}/Ca^{2+} [meq/L] according to geological provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of chloride to sulfates (Figure 51), in the Frontal Cordillera, the values were predominantly higher, reaching up to 21.48 meq/L, suggesting a greater presence of chlorides in this zone. On the contrary, in the Iglesia Valley, the values were notably lower, ranging between 0.0 and 1.87, reflecting a lower concentration of these compounds. On the other hand, in the Precordillera and Pampean Ranges, a moderate presence of chlorides and sulfates was observed, with values that did not exceed 4.66.

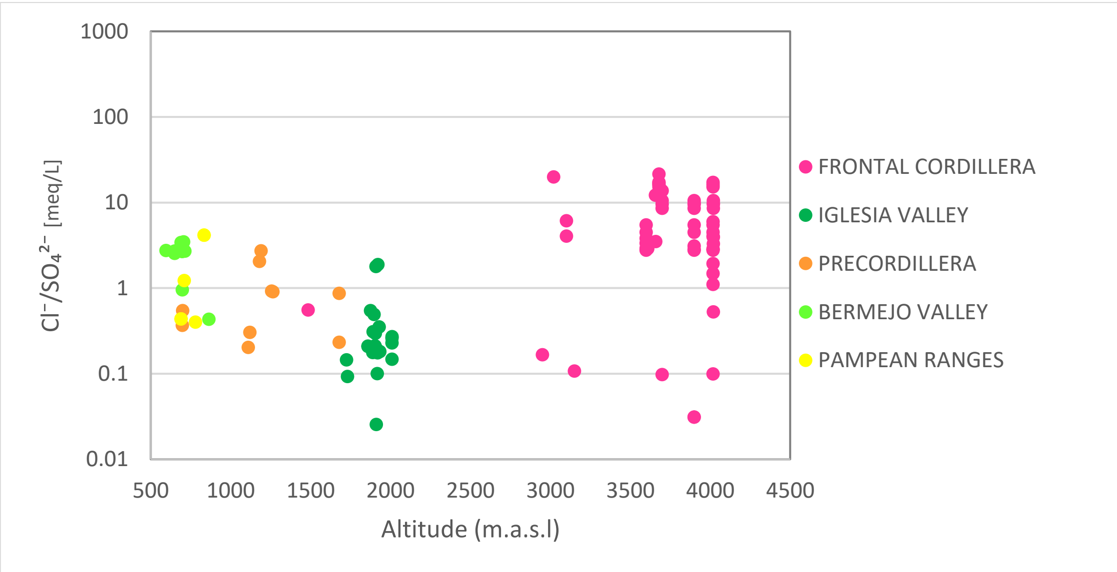

Figure 51. Cl^{-}/SO_4^{2-} [meq/L] according to geological provinces.

In the analysis of Equivalent Concentration Ratios in meq/L of chloride to bicarbonates (Figure 52), In the analysis of Equivalent Concentration Ratios in meq/L of chloride to bicarbonates (Figure 8), in the Frontal Cordillera, the values fluctuate significantly, with high peaks such as 1025.06, 472.70 and 651.77 meq/L suggesting a high concentration of chlorides compared to bicarbonates in that region. In the Iglesia Valley, values are lower, ranging from 0 to 55.45 meq/L, which could indicate a lower concentration of chlorides relative to bicarbonates, reflecting different hydrochemical or geological conditions. In the Precordillera, moderate values are also observed, reaching up to 454.47 and 411.78 meq/L, indicating an intermediate relationship between these two ions. In the Bermejo Valley, the values are significantly higher, with a maximum of 1311.5, which highlights a greater presence of chlorides compared to bicarbonates, which could be linked to the hydrological dynamics of the region. Finally, in the Pampean Ranges, high values are also presented, highlighting the value of 2593.07, which could be related to specific geological processes that favor the concentration of chlorides over bicarbonates. This behavior in the different regions suggests the importance of geological factors and hydrochemical processes in the distribution of these ions in groundwater.

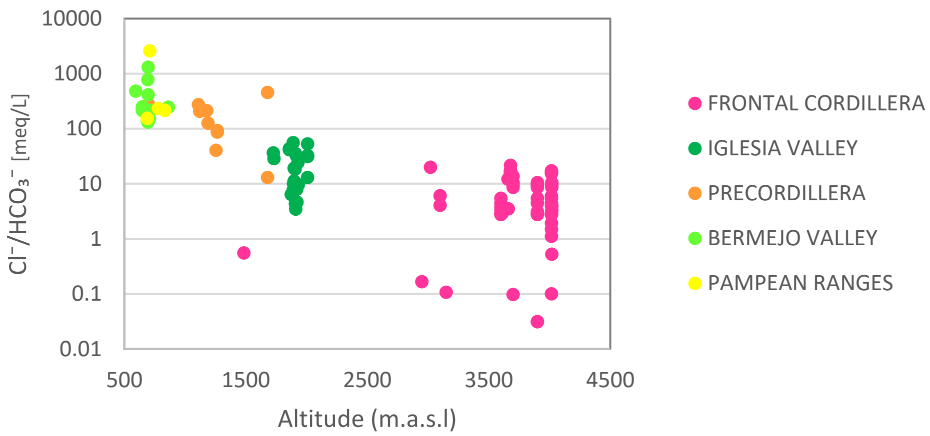

Figure 52. Cl^-/HCO_3^- [meq/L] according to geological provinces.

The calcite saturation index (Figure 53) reveals significant variability in the data and its relationship with rock types. Volcanic rocks, both rhyolitic and Andesitic, predominantly show negative values, indicating strong undersaturation with respect to calcite. In particular, Andesitic rocks and their related variants exhibit extremely low values, such as -18.642, -11.144, and -16.677 mg/L, reinforcing the idea that these volcanic formations are chemically unfavorable for calcite.

On the other hand, sedimentary rocks, particularly siliciclastic ones, display a wider range of values, from moderately negative to positive. This suggests greater diversity in sedimentary environments, where, depending on local conditions, there could be a tendency towards both undersaturation and oversaturation of calcite. In some cases, positive values are observed, such as 0.2636 mg/L in rhyolitic volcanic rocks and 0.8308 mg/L in siliciclastic sedimentary rocks, indicating that these rocks might be in oversaturation conditions or may favor calcite precipitation, consistent with sedimentary environments rich in calcium or carbonates. Additionally, some carbonate sedimentary rocks show positive values like 0.7068 mg/L and 0.1144 mg/L, reflecting their higher propensity to associate with calcite due to their compositional nature.

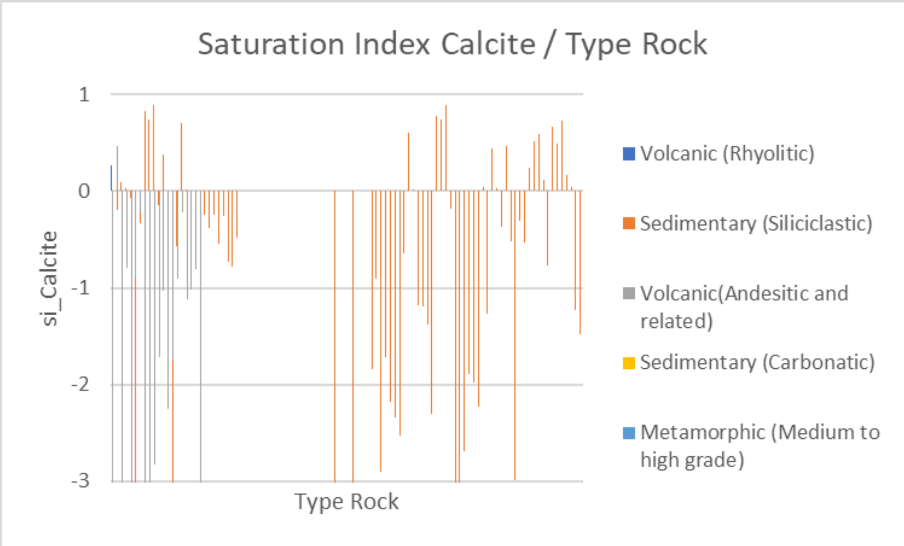

Figure 53. Saturation Index of Calcite phases.

The dolomite saturation index (Figure 54) shows a notable variability in the data and its relationship with rock types. Volcanic rocks, including rhyolitic and Andesitic varieties, predominantly exhibit negative values, indicating a strong undersaturation with respect to halite. In particular, Andesitic rocks and their related variants show extremely low values, such as -79.728, -70.481, and -72.469 mg/L, suggesting that these volcanic rocks are chemically unfavorable for halite formation.

In contrast, sedimentary rocks, particularly siliciclastic ones, display a wider range of values, mostly negative, but with some exceptions. This variability indicates the presence of diverse sedimentary environments where halite may be either undersaturated or oversaturated depending on local conditions. For instance, some siliciclastic sedimentary rocks show values like -48.383 mg/L and -47.352 mg/L, reflecting a tendency toward undersaturation, while other carbonatic sedimentary rocks, such as -75.512 mg/L and -40.052 mg/L, indicate the complex interaction between halite and the mineralogical composition of sedimentary environments.

Overall, the significant negative values in most rock types, particularly in volcanic rocks, highlight the trend toward halite undersaturation, while the variability in sedimentary rocks underscores the diverse conditions under which halite may precipitate or remain undersaturated.

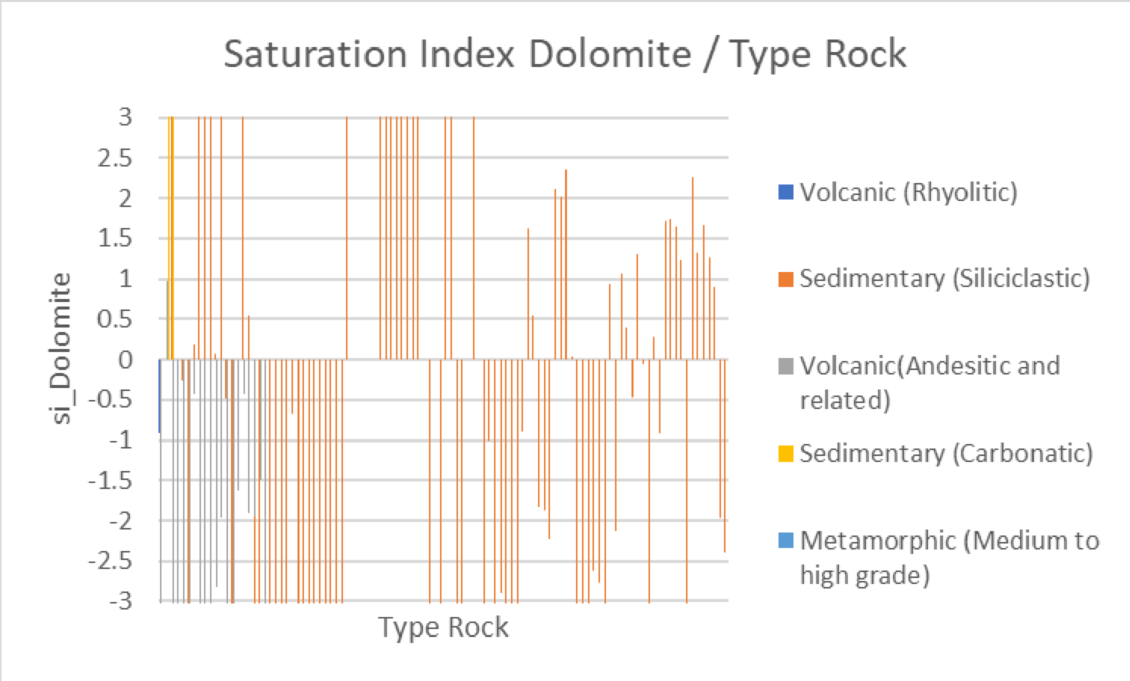

Figure 54. Saturation Index of Dolomite phases.

The saturation index (Figure 55 and 56) of halite and sylvite. The analysis shows that volcanic rocks, especially Andesitic varieties, predominantly exhibit negative values, indicating strong sub-saturation of both minerals. Halite values range from -9,999,990 mg/L to -87,332 mg/L, while sylvite values vary between -4.5311 mg/L and -5.5286 mg/L, suggesting that these rocks are unfavorable for the formation of these minerals.

In contrast, sedimentary rocks, particularly siliciclastic and carbonatic ones, show greater variability in their saturation values. Some display higher values, such as 25.027 mg/L and 23.569 mg/L for halite, indicating that local conditions might be more conducive to its formation. However, in general, both halite and sylvite tend to be sub-saturated in most samples, especially in volcanic rocks.

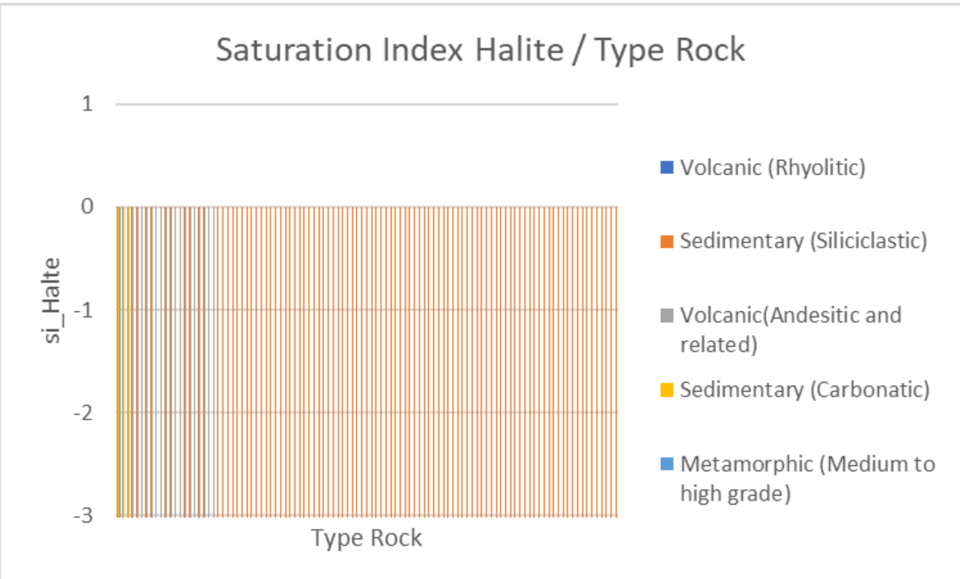

Figure 55. Saturation Index of Halite phases.

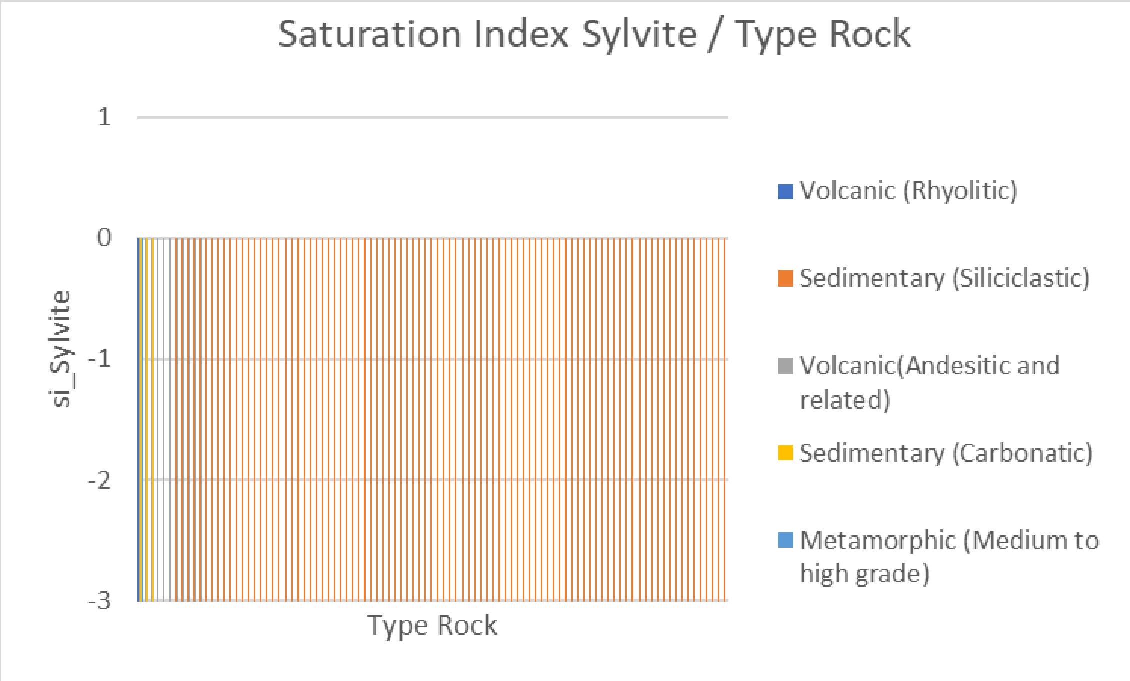

Figure 56. Saturation Index of Sylvite phases.

In the Piper diagram (Figure 57), illustrating the distribution of water classifications according to rock type, distinctive patterns can be observed revealing the geochemical characteristics of emerging waters in different types of rock formations in San Juan.

- Volcanic Rocks (Rhyolitic): Sodium chloride (Na^+-Cl^-) water is found.
- Sedimentary Rocks (Siliciclastic): Predominantly sodium chloride (Na^+-Cl^-). Sodium bicarbonate-chloride (Na^+-HCO_3^--Cl^-) and sodium sulfate (Na^+-SO_4^{2-}) waters are also observed. Calcium sodium sulfate (Ca^{2+}-Na^+-SO_4^{2-}) and sodium bicarbonate-sulfate (Na^+-HCO_3^--SO_4^{2-}) types appear in smaller proportions.
- Volcanic Rocks (Andesitic and related): Calcium sodium bicarbonate-sulfate (Ca^{2+}-Na^+-HCO_3^--SO_4^{2-}), sodium chloride (Na^+-Cl^-), and sodium bicarbonate-chloride (Na^+-HCO_3^--Cl^-) waters are found. Sodium sulfate (Na^+-SO_4^{2-}) is also present.
- Sedimentary Rocks (Carbonatic): Sodium bicarbonate, calcium, and calcium sulfate (Na^+-Ca^{2+}-HCO_3^--SO_4^{2-}) waters are found.
- Metamorphic Rocks (Medium to high grade): Sodium sulfate (Na^+-SO_4^{2-}) water is found.

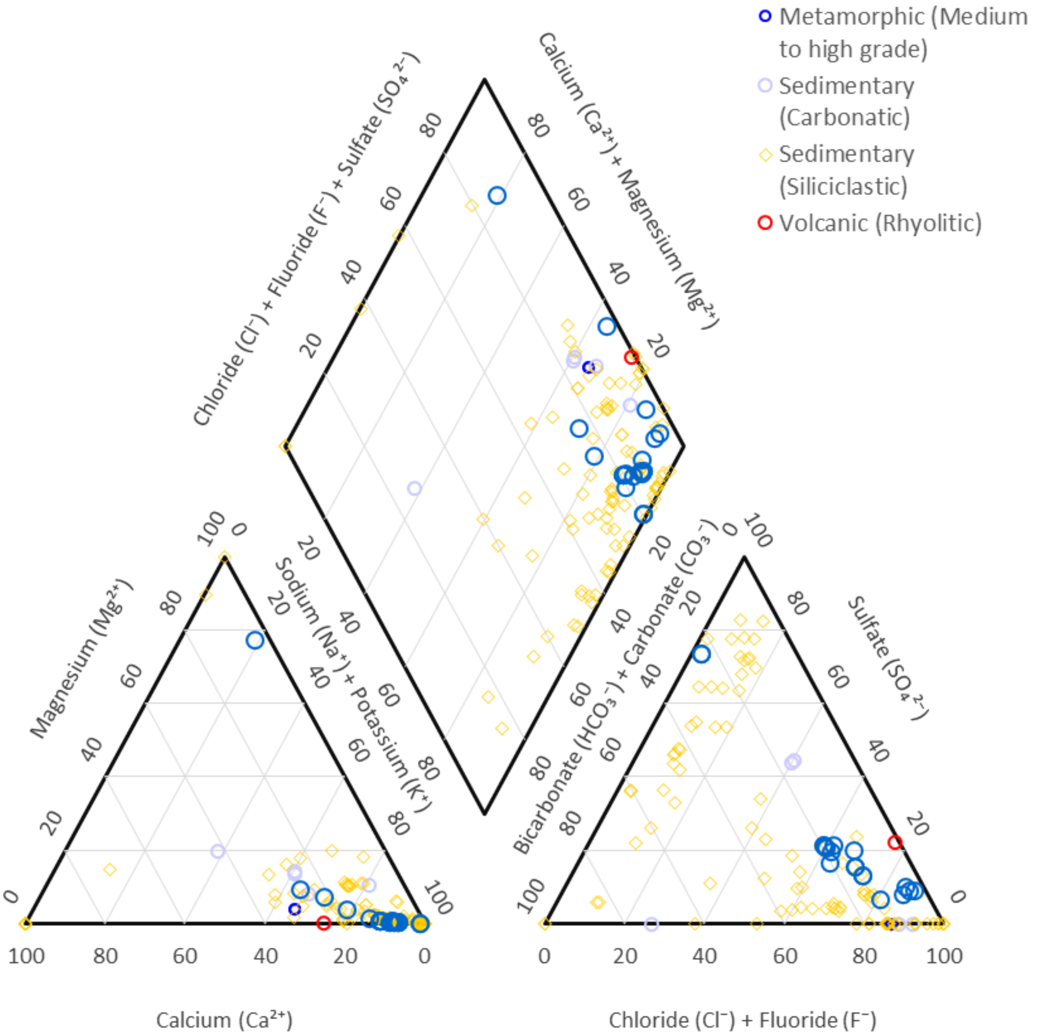

Figure 57. Piper plot of concentration in meq/L of springs in rock types.

In the Piper diagram (Figure 58), reflecting water classifications according to elevations in the geological provinces, distinctive patterns are observed revealing the chemical composition of waters in different geographical areas of San Juan.

- Frontal Cordillera: Primarily sodium chloride waters, with magnesium and sodium bicarbonate and sulfate compositions.
- Iglesia Valley: Sodium calcium bicarbonate and sulfate waters.
- Precordillera: Sodium calcium bicarbonate chloride waters.
- Bemejo Valley: Sodium chloride waters.
- Pampean Ranges: Sodium chloride waters.

This analysis highlights the variability in the chemical composition of thermal waters across elevations and geological regions in San Juan. The predominance of certain ions in different areas suggests the influence of underlying geology on the local hydrochemistry.

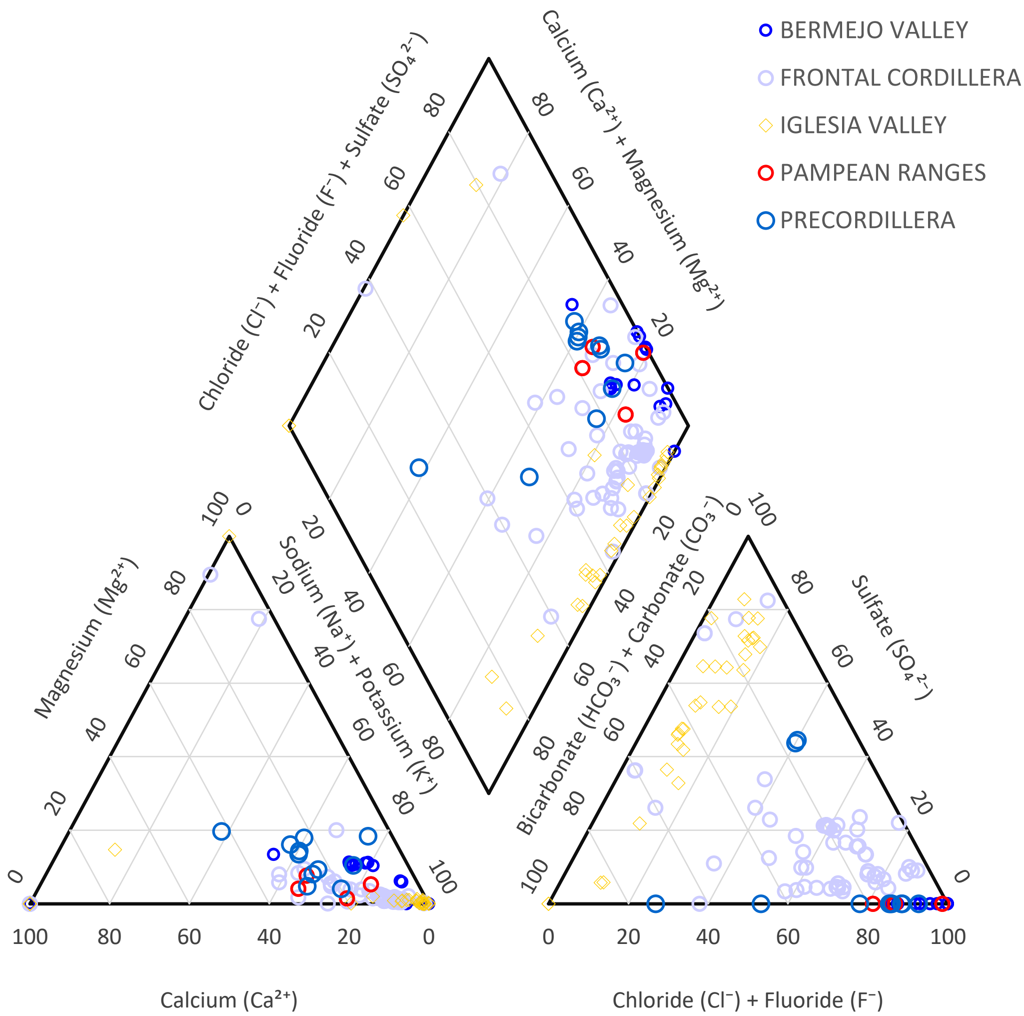

Figure 58. Piper plot of concentration in meq/L of springs in altitudinal regions of San Juan.

Discussion: Hydrogeochemical Classification of Thermal Waters in the Three Geological Provinces of San Juan and Its Intermountain Valleys

In the present study, a hydrochemical characterization of hot springs in the northern Andes of Argentina was carried out, particularly in the province of San Juan, which is divided into three geological provinces and their intermontane valleys: the Front Range, the Iglesia Valley, the Precordillera, the Bermejo Valley, and the Pampean Sierras, including the Sierra Pie de Palo. Through the analysis of the 126 collected samples, it was possible to classify thermal waters according to their ionic composition, observing the relationship between local rock formations and the chemical characteristics of the waters. This relationship reflects how interactions between groundwater and the geological materials present in each region contribute to the variability of their composition, in addition to the geological context of being located on a subduction edge, where tectonic dynamics and related structures, such as major faults, influence fluid circulation and the release of minerals that affect water chemistry.

1. Frontal Cordillera

In the Frontal Cordillera region, 62 thermal water samples were collected, which were classified mainly into seven categories based on their chemical composition. Most of the samples (33) are sodium chloride (Na^+-Cl^-), followed by a significant amount of sodium bicarbonate chloride (Na^+-HCO_3^--Cl^-) (20). There were also samples of sodium sulfate (Na^+-SO_4^{2-}) (5), sodium bicarbonate sulfate chloride (Na^+-HCO_3^--SO_4^{2-}) (6), sodium bicarbonate chloride (Na^+-HCO_3^-) (5), sodium bicarbonate sulfate (Na^+-HCO_3^--SO_4^{2-}) (1), and sodium calcium bicarbonate sulfate (Ca^{2+}-Na^+-HCO_3^--SO_4^{2-}) (2). The samples were collected at altitudes ranging from 3680 to 2950 meters above sea level. The water temperatures ranged from 2°C to 78.6°C, reflecting thermal activity of the region. The average pH was 6.53, with values ranging from 6 to 8.32, indicating that the waters are generally acidic to slightly alkaline, although some samples were neutral.

The total dissolved solids (TDS) concentration in the samples varied from 1000 to 12114 mg/L, indicating brackish water, except for one sample from the Baños del Gollete mine, which had a significantly lower value of 50.50 mg/L, corresponding to very fresh water. This classification as brackish water is due to the high concentrations of chloride (Cl^-) and sodium (Na^+) ions, associated with the rocks and hydrothermal activity in the region.

The ascending hydrothermal vapors contain a variety of minerals, including volatile elements such as sulfur (S^{2-}), fluorine (F^-), bromine (Br^-), and metallic elements like iron (Fe^{2+} or Fe^{3+}), magnesium (Mg^{2+}), and sodium (Na^+). The released minerals mainly include chlorides such as halite (NaCl) and sylvite (KCl), which are common in volcanic areas. As these vapors rise, the minerals condense and release ions that contribute to the ionic composition of the region's thermal waters. The high concentrations of sodium (Na^+) and chloride (Cl^-) in the water samples are a direct result of the dissolution of these minerals in the hydrothermal fluids, reflecting the influence of rock-water interaction.

The different solubilities of marine salts lead to the refinement of the types of salt. When they reach the seabed, hot brines cool in saline pools, eventually becoming saturated with salts, leading to their precipitation on the seabed. Dense brine layers protect the salts from re-dissolution by normal seawater. Magmatic processes associated with hydrothermal activity, especially those linked to subduction under the Andes, are associated with huge salt deposits. The brines are hydrothermally transported from the subduction zone and expelled at altitudes ranging from 3500 to 4000 meters above sea level.

On the surface, the brines evaporate due to the dry climate, which also helps protect the salts from re-dissolution. The brine feeding the hydrothermal systems above the subduction zone originates from the drainage of subducted slabs. This water causes fractional melting of the upper mantle wedge, initiating volcanism (Hovland, Rueslåtten & Johnsen, 2015).

The geothermal manifestations of the Cura Valley, located in the Frontal Cordillera of the Andes at approximately 29.5°S and 69.5°W, present notable features associated with evolved geothermal systems and magmatic activity in the region. The meteoric origin of thermal fluids, primarily derived from the melting of glaciers in the high mountains, highlights the influence of local climate and hydrological processes on the formation of these geothermal systems.

The structural and lithostratigraphic control of recharge zones is crucial for fluid infiltration. Faults and tectonic structures in the region, particularly those related to subhorizontal subduction, favor the deep circulation of thermal fluids. This is reflected in the presence of a conductive anomaly detected at more than 5 km depth, suggesting the existence of brines in the deep zones of the system, indicating active circulation in a high-enthalpy system.

The geothermal system in Valle del Cura is liquid-dominated and exhibits high temperatures in the reservoir, reaching 180°C in the Despoblados area. This temperature remains stable below 800 m depth, indicating a reservoir with significant thermal capacity and relative accessibility. However, as we move southward, in areas such as Gollete, an increase in the depth of the reservoir and a decrease in permeability are observed, suggesting a possible transition to a more closed system or one with lower accessibility to thermal fluids.

Interactions between thermal fluids and shallow aquifers are essential in the mixing and dilution processes, particularly in areas like Gollete and Bañitos. These processes result in the formation of springs, travertine terraces, and calcreted soils as stated by the PHREEQC software; the waters are oversaturated in calcite and dolomite, and undersaturated in halite and sylvite. These are typical characteristics associated with the geothermal manifestations in the region. Furthermore, the absence of acidic gases such as H2S and SO2, and the predominance of CO2, supports the idea of a mature, degassed system, likely related to a thermal anomaly linked to recent magmatic activity.

Regarding the saturation indices, thermal water samples in the region present values that indicate their degree of saturation with respect to various minerals. These indices are used to assess the stability of the minerals in the waters and their tendency to precipitate or dissolve. In most of the samples, the saturation indices reflect a high saturation in minerals such as carbonates, sulfates, and chlorides, suggesting a dynamic geothermal environment in which the dissolved minerals tend to precipitate as thermal fluids interact with shallow aquifers and conditions of pressure and temperature vary. The saturation values reach significant levels in areas such as Gollete and Bañitos, where the presence of precipitated minerals contributes to the formation of travertine and calcreted soils.

Magnetotelluric models have been key in interpreting the geometry of the upwelling system, revealing how faults act as natural conduits for thermal fluids. In particular, the upwelling zone in Despoblados is well-defined by a conductive anomaly with a plume-like geometry, suggesting an underground heat transfer channel. The interaction of these fluids with shallow aquifers, saturated with atmospheric components and dissolved minerals, leads to the precipitation of minerals and the formation of geothermal features at the surface.

A key finding of this study is the confirmation of a thermal anomaly associated with intracortical magmatic activity. This phenomenon, along with the fluid-rock interaction in the structural faults, contributes to a dynamic geothermal system. Effective permeability and local thermal gradient play a crucial role in controlling the prevalence of thermal convection over thermal conduction in thermal areas of Valle del Cura. This local convection, activated by thermal anomaly, facilitates the circulation of deep fluids and sustains the evolution of the geothermal system.

The magmatic origin of the CO2 in the gaseous emissions indicates that the geothermal system has formed over a degassed magmatic reservoir. This finding aligns with the characteristics of a mature geothermal system, which could be related to recent tectonic activity in the region. The presence of faults in the crust, moderate seismic activity, and the geomorphological processes observed in the area reinforce the importance of neotectonics in the evolution of these geothermal systems.

The geothermal system of Valle del Cura presents a series of geological, geothermal, and geochemical characteristics that position it as a relevant example of a deep hydrothermal system, with high enthalpy and associated magmatic activity. This case opens new perspectives for geothermal exploration in subhorizontal subduction segments, previously considered low-enthalpy, and suggests the need to reassess the geothermal potential of these segments in the Andes.

As Barcelona (2015) states, "The geothermal system of Valle del Cura is characterized by: a) the presence of a local thermal anomaly near the head of the Zancarrón Range, b) a slight local convection superimposed on the conductive heat transport of the gravity-driven fluid circulation system, c) medium to high enthalpy reservoirs of the liquid-dominated type below 800 meters depth, and d) circulation dominated by regional faults and fractures" (Barcelona, 2015).

2. Iglesia Valley

In Iglesia Valley, at altitudes ranging from 2010 to 1860 meters above sea level, 33 water samples were analyzed. These samples revealed an ionic composition dominated by sodium sulfate (Na_2SO_4), followed in frequency by sodium bicarbonate sulfate ($NaHCO_3$–SO_4). Three samples of sodium bicarbonate ($NaHCO_3$) and one sample of calcium bicarbonate sulfate ($CaHCO_3$–SO_4) were also identified. This distribution suggests that geochemical processes in the region favor the formation and dissolution of sulfates and bicarbonates, significantly influencing the water composition in this area. Dominant ions include sodium (Na^+), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}), which are related to the interaction of thermal waters with the local geological formations. The temperature of these waters ranged from 20°C to 45.1°C, reflecting moderate hydrothermal activity in the region. The average pH is 8.92, with values between 7.6 and 9.6, indicating a slightly alkaline environment.

The low concentration of sodium chloride (NaCl) could be linked to the mixing of thermal waters with less mineralized sources, such as nearby tributaries or meteoric waters. The predominant rocks in the region are mainly siliciclastic sedimentary, which explains the presence of ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and bicarbonate (HCO_3^-), which are released through the interaction of thermal waters with the rock formations. The presence of sulfate (SO_4^{2-}) is associated with the interaction of hydrothermal fluids with rocks rich in sulfur minerals, such as pyrite (FeS_2), which, when hydrothermally altered, can release sulfate and iron ions (Fe^{2+} or Fe^{3+}) into the solution.

The saturation index of the waters in Iglesia Valley shows that these waters are undersaturated in halite (NaCl), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and sylvite (KCl), suggesting that the conditions are not sufficient for the formation of these minerals under current conditions.

According to a study by Ilka Hinzer et al. (2021), Iglesia Valley contains a series of thermal springs, the most important of which are the Pismanta Baths, which release water at approximately 45°C. Despite the scarcity of water resources in the region, few detailed studies have been conducted on these springs. This work sought to improve understanding of the groundwater flow and its connections with fault systems and springs. The observed temperatures and ionic relationships are compatible with a deep hydraulic circulation system.

Studies carried out in the Pismanta geothermal system, located in the Iglesia basin, have provided a detailed understanding of the distribution and behavior of thermal waters, linking these phenomena to various geological and structural factors. According to field results, it is proposed that thermal activity in this area is primarily controlled by the interaction between the regional geothermal gradient, local tectonics, and the lithological characteristics of the subsurface.

A key factor is the structural control of NNE-oriented faults, which have created conditions of high permeability in the Neogene sequences of the Las Flores Member. These faults have not only facilitated the upward movement of groundwater from depths of up to 2500 meters but have also formed preferential pathways for thermal waters to reach the surface, manifesting at various temperatures. Geophysical interpretation through resistivity tomography and local gravity and magnetic data has revealed that these faults are high-permeability zones that allow efficient heat transfer to the surface, which is reflected in thermal manifestations observed in the Pismanta area.

In particular, a main fault zone has been identified beneath the Pismanta hotel, which appears to be crucial for the ascent of thermal waters from a depth of about 300 meters to the surface. This fault structure acts as a primary pathway for the ascent of thermal waters, reinforcing the hypothesis that local faults are determining factors in the distribution of thermal manifestations on the surface.

Although the Pismanta geothermal system has traditionally been associated with a non-magmatic model, where heat comes exclusively from the regional geothermal gradient and not from direct magmatic activity, the complex tectonic history of the Iglesia basin seems to have significantly influenced the concentration of thermal waters. Faults and tectonic structures, particularly those oriented NNE, facilitate the ascent of heat from deeper reservoirs to the surface, suggesting a significant interaction between the geothermal system and the region's tectonics.

Regarding lithology, the Neogene sedimentary deposits, especially the sandstones of the Las Flores Member, show characteristics that favor the transmission of groundwater. These sedimentary formations are partially lithified and permeable, which facilitates the ascent of thermal waters, further enhanced by fractures generated by tectonic activity. In contrast, silt and clay deposits act as impermeable barriers, restricting water flow in certain areas. This differential lithological behavior is crucial to understanding how the geothermal system is organized and how groundwater interacts with the geological formations in the Iglesia basin.

The connection between tectonic structures and the hydrogeological properties of the subsurface is evident, as a hypothesis has been proposed regarding the existence of groundwater ascent ramps in the roof of the Lomas del Campanario Member, possibly associated with sedimentary sequences deposited during the migration of the deposition center to the west. These ramps could be facilitating the movement of water toward surface areas, explaining the distribution of thermal springs both north and south of Pismanta.

In general terms, the geophysical analysis of the Iglesia basin has provided a surface geological model that explains the behavior of thermal waters in the first 300 meters of depth. The data obtained has allowed a precise characterization of the basin structure and the hydrogeological conditions that control the ascent of thermal waters. This model is not only useful for understanding the local dynamics of the Pismanta geothermal system but also for future research on the geothermal potential of the region.

The geothermal study of the Iglesia basin, particularly in the Pismanta area, has demonstrated that tectonic structures are key to the concentration of thermal waters on the surface. Faults and other local geological structures determine the permeability of the subsurface and facilitate the ascent of thermal water, enabling thermal springs observed in this area. These findings contribute to understanding the non-magmatic geothermal system of the region and open new opportunities for the use of geothermal energy in a well-understood hydrogeological and tectonic context (Clavel et al., 2023; Hinzer et al., 2021).

3. Precordillera

The Precordillera region exhibits a great diversity in the ionic composition of its thermal waters. Eleven samples were collected from thermal springs at altitudes ranging from 698 to 1680 meters above sea level. The waters are classified according to their ionic composition into the following types: Sodium Magnesium Sulfate Chloride, Calcium Sodium Sulfate, Sodium Chloride, Sodium Calcium Bicarbonate Calcium Sulfate, Sodium Chloride Sulfate, Sodium Sulfate, and Sulfated Sodium and Calcium Chlorurate Bicarbonate. These combinations reflect the diversity of thermal waters in the region, with a predominance of Sodium Sulfate and Sodium Chloride waters.

The main ions present in thermal waters of the region include sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}), reflecting the interaction between the waters and rock formations during their journey.

Temperatures range between 20°C and 25°C, with an exceptionally high value of 40°C in the "Hedionda" spring. The pH fluctuated between 6.7 and 7.6, with a predominance of slightly acidic (around 6), neutral (around 7), and slightly alkaline (around 7.6) waters. This pH variability is related to the interaction of thermal fluids with the rock formations and, especially, with the influence of dissolved gases. Gases such as carbon dioxide (CO_2), when dissolved in water, can lower the pH, making the waters more acidic in areas with greater gas accumulation. The dissolution of CO_2 also increases the concentration of bicarbonate (HCO_3^-), which can lead to acidic waters, especially in areas with high hydrothermal activity.

In these zones, the interaction of meteoric waters with underground rocks can lead to the dissolution of minerals, including sodium chlorides, due to the temperature and pressure conditions generated by tectonic activity. There is no precise information on the total dissolved solids (TDS) concentrations in the waters of the Precordillera. The main ions present include sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}), reflecting the interaction between the waters and the rocks in this process.

It is more plausible to assume that meteoric waters infiltrate deeply into the Precordillera, where they are heated and then rise due to the hydrostatic pressure generated by fractured siliciclastic sedimentary rocks. Along their path, these waters become loaded with various minerals, primarily calcium, magnesium, sulfates, and chlorides. This hydrothermal process, caused by the infiltration of meteoric waters and their heating as they ascend through fractures in the rocks, leads to the dissolution and release of various minerals in solution.

The geology of the region, dominated by siliciclastic sedimentary formations accumulated in the foreland basin and preserved in the Precordillera range, crossed by tectonic fault structures, favors the release of cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}) due to hydrothermal alteration in the subsurface. Vapors generated at great depths enrich the system with compounds like sulfate (SO_4^{2-}) and chloride (Cl^-), which react with the rocks, altering their mineral composition and releasing these ions into solution. These hydrothermal processes are responsible for the complexity of the ionic compositions observed, reflecting the interaction between the fluids and the rock formations.

Regarding saturation indices, it is observed that in most samples, the saturation indices for calcite, halite, and sylvite are in sub-saturation conditions, indicating that these minerals are not completely present in the solution but could precipitate if conditions change. However, dolomite is supersaturated in most samples, suggesting that this mineral is more likely to precipitate under certain temperature and ion concentration conditions. This supersaturation of dolomite could be related to the high concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in the waters, which favors its formation and precipitation.

In the comparative analysis of the hydrochemical data obtained for the Talacasto spring, both the results of Villarroel et al. and my own research show common characteristics and some notable differences that warrant discussion.

Regarding temperature, the values obtained in both measurements were quite similar, with a range between 25.7°C and 25.9°C in my data, compared to 25.9°C reported by Villarroel et al. This consistency in temperature suggests that thermal conditions of the spring remain relatively stable during the sampling period, which is relevant for interpreting the hydrochemical dynamics, as temperature can influence the solubility of minerals and the biological activity of the aquatic system.

However, there is a significant difference in electrical conductivity. According to Villarroel et al., the electrical conductivity in the Talacasto spring is 3.08 µS/cm, while in my research, the values were considerably higher, with a range between 3320 µS/cm and 3560 µS/cm. This difference could reflect a higher concentration of dissolved ions in the samples I collected, suggesting that the spring water may have a higher concentration of soluble salts such as sulfates, chlorides, and bicarbonates. This discrepancy could also be explained by spatial or temporal variations in the water composition or differences in sampling methods or the exact location within the spring where measurements were taken.

Regarding pH, the values in my research ranged between 6.77 and 6.95, indicating slightly acidic or neutral waters, while the pH reported by Villarroel et al. was 7.13, indicating more neutral waters. The slight acidity observed in my measurements could be related to the dissolution of acidic minerals or biochemical processes occurring in the hydrochemical system of the spring. This difference could also be influenced by local factors, such as interactions with rock formations or the presence of biogeochemical processes that affect the acid-base balance of the water.

Regarding total dissolved solids (TDS), Villarroel et al. report a value of 2073 ppm, while my conductivity measurements suggest that the TDS content in my samples is also relatively high, although the exact TDS value was not specified in my research. However, the high electrical conductivity observed in my measurements supports the idea that the ion concentrations in my samples are significant, which is consistent with the TDS values reported by Villarroel et al.

In terms of ionic classification, both data sets seem to agree that the waters of Talacasto contain a mixture of sodium and calcium sulfates and bicarbonates, reflecting an interaction between the water and the minerals present in the area. However, the differences in conductivity and pH could indicate that the waters of Talacasto have a more complex or variable composition than previously observed in earlier studies.

In conclusion, although the general data on temperature, pH, and ionic composition of the Talacasto waters show some similarities, the differences in electrical conductivity and pH suggest significant variability in the hydrochemical characteristics of the spring. Local and temporal conditions are likely to play an important role in this variability, which highlights the need for more detailed and frequent monitoring to better understand the hydrochemical dynamics of the spring and its possible contribution to the recharge of the Matagusanos aquifer.

La Laja Region and Tectonic Activity

La Laja, located in the Precordillera of the Andes, presents a geological context that facilitates the circulation of thermal waters, influenced by local tectonic activity. In this area, tectonic faults serve as natural conduits for underground waters, which are heated and enriched with minerals before rising to the surface. These fractures and escarpments generated by tectonic movements create high permeability zones that are essential for the flow of hydrothermal waters. In particular, seismic activity in the region, such as the 1944 earthquake, played a key role in reactivating these faults, which increased the permeability of the affected zones and facilitated the ascent of thermal waters. This earthquake generated visible fractures in the terrain, suggesting that seismic events can directly influence the circulation of underground waters, especially thermal ones, by activating or creating new fractures that allow them to rise from deeper layers.

Thus, the La Laja faults not only serve as channels for the circulation of thermal waters but also play a crucial role in the mineralization of these waters. The interaction of these waters with underground minerals, along with tectonic and seismic activity, is what gives La Laja springs their particular thermal characteristics. The presence of faults and fractures in the region, which facilitate the ascent of hydrothermal fluids, explains the high temperature and mineral richness of the waters in this area, underscoring the importance of tectonic activity in the hydrogeology of the Precordillera.

4. Bermejo Valley

In the Bermejo Valley, located at altitudes ranging from 790 to 585 meters above sea level, analyses were conducted on 15 water samples. The results revealed a clear predominance of sodium chloride (NaCl), present in 12 of the analyzed samples. Singular samples of sodium chlorosulfate ($NaCl\text{-}SO_4^{2-}$), sodium and calcium bicarbonate chlorosulfate ($Na\text{-}Ca\text{-}HCO_3^-\text{-}Cl\text{-}SO_4^{2-}$), and sodium chlorosulfate ($NaCl\text{-}SO_4^{2-}$) were also identified, suggesting the influence of various geochemical processes on the water composition of the region.

The temperatures of the analyzed waters ranged between 22°C and 29°C, reflecting moderate hydrothermal activity in the area. Regarding pH, the average value obtained was 7.24, with a range between 6.5 and 8.2, indicating a slightly alkaline environment. The total dissolved solids (TDS) concentration exceeds 10,000 mg/L in some samples, classifying the waters in this area as saline, although no information is available on the concentrations in the other samples.

The high concentration of sodium chloride (NaCl) in the waters of Bermejo Valley could be associated with the mixing of groundwater from the frontal mountain range, with limited interaction with meteoric waters or fresh inflows. The predominant rocks in the region are mainly siliciclastic sedimentary, which is linked to the presence of ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-). These ions dissolve due to the interaction of thermal waters with the rock formations. Other ions, such as sulfate (SO_4^{2-}) and chloride (Cl^-), are also abundant, further enriching the composition of thermal waters.

The presence of sulfate (SO_4^{2-}) in the waters is directly associated with the interaction of hydrothermal fluids with rocks rich in sulfur minerals. A typical example of these minerals is pyrite (FeS_2), which, when hydrothermally altered, can release sulfate (SO_4^{2-}) and iron ions (Fe^{2+} or Fe^{3+}) into solution, contributing to the complex chemical composition of thermal waters in Bermejo Valley (Jordan et al., 1990, 1993a).

The interaction between tectonic processes and thermal waters in Bermejo Valley is key to understanding the genesis of these waters. Tectonic activity in the region favors the circulation of groundwater and thermal waters, being one of the most relevant factors in the composition of these waters. The high concentration of sodium chloride (NaCl) in thermal waters could be related to the mixing of groundwater from flows originating from the frontal mountain range. This mixing occurs mainly with geothermal groundwater, and to a lesser extent with fresh meteoric or inflowing waters, highlighting the influence of tectonic processes on the local hydrogeology.

The tectonic origins of thermal waters in Bermejo Valley are closely linked to the geological movements occurring in the region. Hydrothermal fluids rise to the surface through fractures and geological faults formed by tectonic dynamics. This fluid ascent, facilitated by the geological structure of the area, allows thermal waters to emerge at the surface, leading to thermal springs observed in the region (Jordan et al., 1990, 1993a).

Studies conducted by Jordan et al. (1990, 1993a) indicate that the foreland basin of Bermejo was formed during the Oligocene, with a thick deposit of approximately 6,000 meters of synorogenic sediments. The interaction between tectonics, basin subsidence (due to tectonic loads or infill), and sedimentation plays a crucial role in the hydrogeological configuration of the region. This interaction is associated with the tectonic movements that uplifted the Precordillera, creating favorable conditions for groundwater circulation and the concentration of minerals such as sodium chloride.

In the Piper diagram, the water from Bermejo Valley is classified as sodium chloride water. The saturation index reveals that dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) are oversaturated, while halite (NaCl) and sylvite (KCl) are undersaturated in most samples. This indicates that thermal waters are in equilibrium with certain mineral phases, while others, such as halite and sylvite, have not yet reached equilibrium and remain undersaturated

The presence of thermal waters in Bermejo Valley is a direct consequence of the tectonic processes occurring in the region. Seismic and tectonic activity, along with the circulation of hydrothermal fluids through geological fractures, enables the modification of the water's chemical composition, enriched with dissolved minerals originating from the interactions between the waters and the underlying rocks

4. Pampean Ranges

In the Pampean Sierras, located at altitudes ranging from 835 to 690 meters above sea level, analyses were conducted on 5 thermal water samples. The results revealed a clear predominance of sodium sulfate, indicating the influence of various geochemical processes on the water composition in this region. Additionally, waters containing a mix of sodium sulfate, sodium chloride, and calcium sulfate were found. This ionic composition reflects a complex interaction between the fluids and rocks in the area.

The temperatures of the analyzed waters ranged from 23°C to 27.5°C, reflecting moderate hydrothermal activity in the region. Regarding the pH, the average value obtained was 7.74, with a range between 7.2 and 8, indicating a slightly alkaline environment. Although data on the concentration of total dissolved solids (TDS) is not available, the saturation index for dolomite and calcite is oversaturated, while that for halite is undersaturated, which explains the high concentrations of sodium chloride water in the samples.

From a geological perspective, the Pampean Sierras are marked by a history of tectonic collisions and subduction events during the Cambrian period. According to C. W. Rapela et al., the Pampean orogeny took place during the Cambrian, between 535 and 520 million years ago, and was characterized by a cycle of subduction, magmatic arc formation, and continent-continent collision. Although there is no magmatic or volcanic activity observed in the region today, the fault structures formed by these tectonic events may have acted as conduits for the paths of groundwater flows. These faults, created during the collisions, likely facilitate the circulation and heating of groundwater, contributing to the current geothermal composition of the area.

It is important to note that, although there is no evidence of recent magmatism or volcanism in the geological past, the fault structures formed by the tectonic events could be responsible for the paths followed by groundwater in the region. These structural faults, inherited from past tectonic processes, continue to play a crucial role in the circulation and heating of groundwater, allowing current thermal waters to follow patterns influenced by these historical processes.

In summary, the Pampean Sierras present a complex interaction of geological, geothermal, and groundwater factors, with tectonic history playing a fundamental role. Despite the lack of current magmatic activity, the fault structures inherited from ancient subduction events remain key to the geothermal behavior of the region. The chloride and sodium sulfate waters in the area reflect this interaction of groundwater with fractured rocks and the influence of residual geothermal processes.

Discussion: Hydrogeochemical and Geological Connection between the The Puna, Frontal Cordillera, Eastern Cordillera, Iglesia Valley, Precordillera, Sub-Andean System, Pampean Ranges, and Bermejo Valley.

In the region encompassing the Frontal Cordillera, Iglesia Valley the Precordillera, Pampean Ranges, and Bermejo Valley, a complex hydrogeological connection is observed, influenced by tectonic and geothermal processes. Although there are no active volcanoes in the area, the geothermal heat that heats the underground waters is related to a mature magmatism. This magmatism is associated with the degassing of a deep magmatic body in the Frontal Cordillera, leading to the ascent of sodium-chloride fluids. These fluids, resulting from the interaction between the groundwater and the chloride sediments deposited in the subduction zone, ascend through tectonic faults that act as escape routes for the heat and ions present in the subsurface. Additionally, the subduction of the Nazca Plate beneath the South American Plate generates salts like sodium chloride (NaCl), originating from marine sediments of the subducting plate. These sediments contain water that is released at depth during the subduction process, contributing to the concentrations of Na^+ and Cl^- in thermal waters.

The The Puna (Jujuy, Salta, and Catamarca) and the Frontal Cordillera (San Juan) show clear differences in the origin of the heating of the groundwater. In the The Puna, the presence of active volcanoes like Socompa, Tocomar, Llullaillaco, Atofalla, Antuco, Cerro Galán, Tuzgle, among others, clearly relates to the subduction of the Nazca Plate beneath the South American Plate. This subduction generates a high thermal gradient that drives volcanic activity and affects the circulation of hydrothermal fluids. In contrast, in the Frontal Cordillera of San Juan, there are no active volcanoes, but mature magmatism generates a thermal gradient in the subsurface due to the cooling of a deep magmatic body, which heats the underground waters without generating superficial volcanic activity.

Geochemical Connection of the Waters

Regarding the geochemical composition, both thermal springs of the The Puna and the Frontal Cordillera share similar characteristics in terms of predominant ions such as Na^+, Cl^-, and SO_4^{2-}, indicating that both areas are influenced by interactions with deep geothermal rocks and fluids. However, as these waters flow eastward toward the Precordillera, the Famatina System, and the Eastern Cordillera, the composition of the waters becomes enriched with additional ions such as calcium (Ca^{2+}), sodium (Na^+), and sulfate (SO_4^{2-}), reflecting their contact with different geological formations along the way.

Specifically, in the Eastern Cordillera, the Famatina System, and Iglesia Valley, there is a higher concentration of calcium sulfate ($CaSO_4$) and sodium sulfate (Na_2SO_4), reflecting a geochemical change as the waters move toward lower and more distal regions. This enrichment with sulfates is indicative of the interaction of the waters with geological formations rich in soluble minerals, such as sulfates, which favor the dissolution of these compounds into the fluids.

As the underground waters move from the Andes (The Puna and Frontal Cordillera) toward the Pampean Ranges, the Bermejo Valley, and the Sub-Andean System, the presence of sodium chloride ions (NaCl) increases, reflecting the impact of tectonic faults and the circulation of fluids from deeper zones, with higher concentrations of sodium

(Na^+) and chlorine (Cl^-) ions. This highlights how the waters, driven by the degassing of the magmatic body in the Frontal Cordillera, interact with different geological units that contain chloride salts, similar to the volcanic activity in the The Puna.

Temperature Variation

As the underground waters move from the higher and warmer areas of the Frontal Cordillera toward the Pampean Ranges and the Bermejo Valley, the temperatures gradually decrease. In the The Puna, the temperatures of thermal waters range between 56°C and 85°C, showing the intense geothermal heat associated with volcanic activity in the region. In the Eastern Cordillera and the Famatina System, with no active volcanic activity, the waters show temperatures in the range of 30°C, indicating that although the fluid circulation from the The Puna toward the east does not maintain a gradual temperature decrease, both regions (The Puna and Pampean Ranges) have high temperatures. This hydrothermal circulation reflects a complex geothermal interaction, where the waters in the The Puna maintain their elevated temperature due to volcanic influence, while the waters in the Eastern Cordillera and Precordillera remain relatively cooler and later increase again in the Pampean Ranges in Catamarca and San Juan. Here, a temperature jump or break is observed, going from high to low and then back to high.

This temperature pattern shows a gradual decrease as the waters move from west to east. In areas closer to the Frontal Cordillera, temperatures are higher, while temperatures decrease gradually when reaching Iglesia Valley, the Precordillera, the Pampean Ranges, and the Bermejo Valley.

The hydrogeological and geochemical connection along this longitudinal stretch, from the The Puna to the Frontal Cordillera, through the Eastern Cordillera, Famatina System, Iglesia Valley, Precordillera, and ultimately the Sub-Andean System and Pampean Ranges, shows a pattern of underground water circulation driven by geothermal and tectonic processes. The waters, enriched with sodium chloride ions, follow a trajectory driven by tectonic faults, connecting the different geological provinces, from the The Puna to the Eastern Cordillera, Famatina Range, Precordillera, Iglesia Valley, Pampean Ranges, and Bermejo Valley.

This hydrogeological system is influenced by the geothermal heat generated by the sub-horizontal and oblique subduction of the Nazca Plate, which facilitates the circulation of sodium chloride hydrothermal fluids and their interaction with the rock formations, leading to a complex and dynamic chemistry in the underground water path.

CHAPTER V: CONCLUSIONS

I. Main Conclusions

The hydrogeochemical analysis conducted in this thesis allows the identification of consistent structural, geological, and climatic controls on the distribution and evolution of thermal waters in the northern part of the Argentine Andes. Based on the integration of hydrochemical data, geological context, and altitudinal gradients, the following main conclusions can be established:

1. A total of 280 thermal water samples were selected from an initial dataset of 388 records based on strict quality criteria, including completeness of physicochemical parameters and a maximum ionic charge balance error of ±10 %, ensuring the reliability of the hydrogeochemical dataset.
2. Hydrochemical facies and ionic relationships demonstrate that thermal waters in the study area are controlled primarily by geological provinces and structural domains rather than administrative or political boundaries.
3. The integration of temperature and total dissolved solids (TDS) with elevation reveals a clear regional organization of hydrothermal systems across the Andes, with distinct patterns corresponding to western, central, and eastern structural domains.
4. The western Andean domain (The Puna and Frontal Cordillera) is characterized by high-elevation thermal systems, predominantly Na–Cl waters with high salinity and evidence of deep groundwater circulation and long residence times.
5. The central Andean domain (Eastern Cordillera, Famatina Range, Precordillera, and Bermejo Valley) shows mixed hydrochemical facies and intermediate salinity, reflecting groundwater mixing processes and medium-depth circulation influenced by structural permeability.
6. The eastern domain (Pampean Ranges and Sub-Andean System) is dominated by Ca–HCO_3 waters with lower TDS values, indicating shallow groundwater circulation and strong meteoric recharge under wetter climatic conditions.
7. The longitudinal structural model proposed in this thesis demonstrates that hydrogeochemical evolution across the study area is controlled by altitudinal gradients, tectonic structures, lithology, and climatic conditions.
8. San Juan province represents the most complete regional example of this hydrogeological framework, as it contains geological provinces belonging to the three structural domains, allowing the observation of the full hydrochemical gradient across the Andean system.
9. The conceptual framework based on Mountain Block Recharge (MBR) and Mountain Front Recharge (MFR) provides a coherent explanation for the coexistence of shallow meteoric flows and deep geothermal circulation in the studied regions.

II. Regional Hydrogeochemical Synthesis and Interpretation

1. Data validation and hydrogeochemical analysis

This work presented a detailed hydrogeochemical characterization of thermal waters in the provinces of Jujuy, Salta, Catamarca and San Juan, integrating a total of 280 samples selected for their analytical quality, regional representativeness and reliability, from an original set of 388 records. The selection was based on strict criteria: completeness of essential physicochemical parameters (temperature, altitude, electrical conductivity, in situ pH, concentration of carbonates, anions and major cations), a reliable pH measurement performed in the field -key to interpret dissolution processes, precipitation and redox conditions- and a maximum margin of ±10 % error in the ionic charge balance to ensure the electrical consistency of the data (Appelo & Postma, 2005; Parkhurst & Appelo, 2013).

PHREEQC was used to calculate mineral saturation indices (calcite, dolomite, silica, halite and sylvite), which allowed us to identify in each sample whether the minerals were in a state of oversaturation (with precipitation potential) or undersaturation (with a tendency to dissolve). This information was key to characterize the geochemical processes active in the different regions of the study.

The hydrogeochemical facies were classified using Piper diagrams, constructed from the meq/L equivalents of the main anions and cations. Likewise, ionic ratios such as Na^+/Ca^{2+}, Mg^{2+}/Ca^{2+}, Cl^-/SO_4^{2-} and Cl^-/HCO_3^- were calculated and plotted to visualize regional patterns associated with lithology and altitude.

2. Regional synthesis of temperature and total dissolved solids (TDS) as a function of elevation

The regional integration of temperature and total dissolved solids (TDS) data as a function of elevation allows the spatial distribution of thermal and mineralization characteristics of thermal waters to be visualized across the main geological provinces of the northern part of the Andes of Argentina (Figures 59 and 60). The graphs reveal a clear west–east spatial organization, consistent with the regional arrangement of the geological units that compose the Andean system in the study area (Ramos, 1999; SEGEMAR, 2019).

In the western sector, represented by the The Puna, the Frontal Cordillera, and the Iglesia Valley, the highest elevations of the dataset are recorded, with thermal springs located between approximately 3500 and more than 4500 m a.s.l. In these geological provinces a wide dispersion of temperatures is observed, ranging from moderate values to high temperatures approaching or exceeding 70–80 °C, particularly in the The Puna region, where such temperatures occur in natural springs at high elevations. In terms of mineralization, this sector also presents some of the highest TDS values, including concentrations exceeding 10,000 mg/L, which correspond to saline waters.

Toward the intermediate sector of the Andean system lie geological provinces such as the Eastern Cordillera, the Famatina Range, the Precordillera, and the Bermejo Valley, where elevations progressively decrease and recorded temperatures are generally intermediate. In these units low to moderate TDS values predominate, mainly within the range of fresh waters (250–1000 mg/L) to brackish waters (1000–10,000 mg/L).

Finally, in the eastern sector of the study area are the Pampean Ranges and the Sub-Andean System, where elevations are significantly lower. In these regions recorded temperatures are generally moderate; however, in some cases high temperatures associated with deep boreholes are observed, indicating hydrothermal conditions at greater depth that are not necessarily expressed by surface springs.

According to the hydrogeochemical classification based on total dissolved solids concentration, the ranges observed in the study area extend from very fresh waters (<250 mg/L) to saline waters (>10,000 mg/L), although most samples fall within the fresh to brackish water range (Domenico & Schwartz, 1990; Hem, 1985).

Overall, the distribution observed in the graphs reveals a clear regional organization of thermal and mineralization characteristics of thermal waters, associated with both altitudinal gradients and the structural arrangement of the geological provinces of the Andean system (Ramos, 1999; SEGEMAR, 2019). These spatial trends allow the recognition of regional groupings of hydrothermal behavior, which will be analyzed in the following section through the integration of geological provinces into western, central, and eastern structural domains.

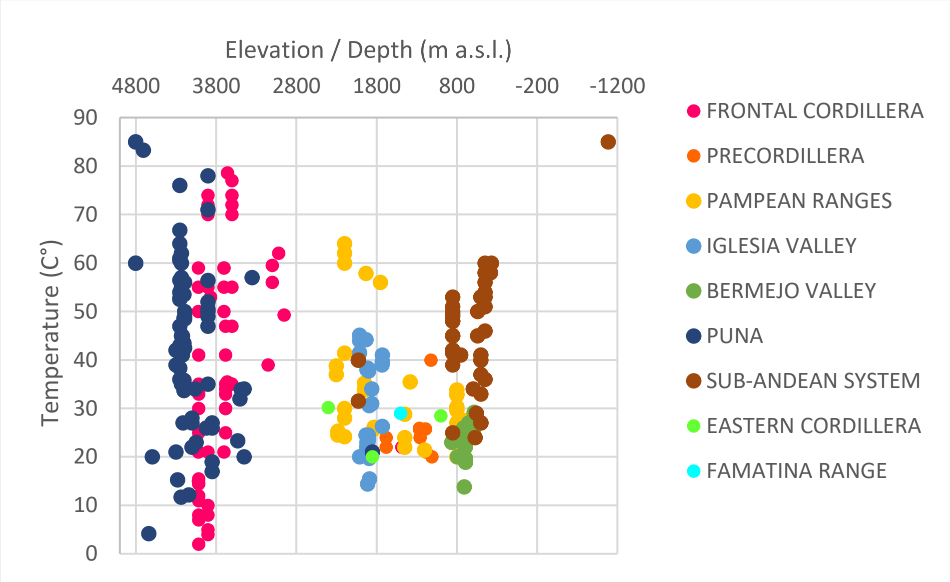

Figure 59. Distribution of thermal water temperature (°C) as a function of elevation (m a.s.l.) across the main geological provinces of the northern part of the Andes of Argentina.

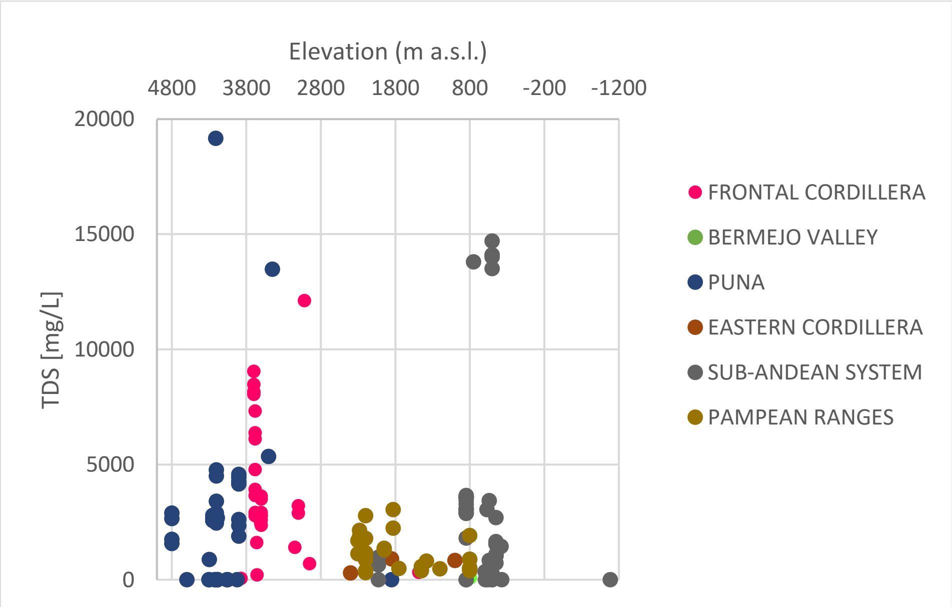

Figure 60. Distribution of total dissolved solids (TDS, mg/L) as a function of elevation (m a.s.l.) across the main geological provinces of the northern part of the Andes of Argentina.

3. **A longitudinal interpretation of the northern part of the Andes of argentina**

Building upon the regional synthesis of temperature and total dissolved solids (TDS) presented in the previous section, the hydrogeochemical analysis developed in this thesis demonstrates that thermal waters do not follow political or administrative boundaries, but instead respond to structural, lithological, and climatic controls operating at a regional scale.

To enable comparative analysis, a longitudinal reading of the Andean system was adopted, organizing the study area into three major structural domains: western, central, and eastern. This classification is based on factors such as altitude, predominant rock type, water salinity (TDS), spring temperature, main geochemical facies, and precipitation regime.

Western Domain

The western domain includes the geological provinces of the The Puna and the Frontal Cordillera, where sodium-chloride waters with high TDS predominate. These waters are associated with deep groundwater flow, prolonged interaction with volcanic and evaporitic rocks, and long residence times. The Iglesia Valley is also included in this domain. Although it is located at lower elevations (~1900–2200 m a.s.l.), it presents sodium-sulfate waters with lower TDS, linked to more active meteoric recharge and shorter flow paths. The inclusion of the Iglesia Valley in this domain is justified by its structural connection to the Frontal Cordillera and its intermediate position between high thermal energy systems and transitional zones toward the central domain.

Central Domain

The central domain encompasses the Eastern Cordillera, the Famatina Range, the Precordillera, and the Bermejo Valley. These regions exhibit intermediate altitudes (1500–3000 m a.s.l.), mixed lithologies, and evidence of medium-depth groundwater flows. In particular, the Bermejo Valley shows a marked predominance of sodium-chloride waters, similar to those observed in the Frontal Cordillera, reinforcing the hypothesis of deep groundwater circulation dominated by long pathways, prolonged mineral dissolution, and extended residence times. The mixed facies observed in the rest of the domain — such as Na^{+}–SO_4^{2-} or Ca^{2+}–HCO_3^{-} — reflect moderate hydrogeochemical evolution related to interactions with sedimentary and volcanic rocks.

Eastern Domain

The eastern domain comprises the Sub-Andean System and the Pampean Ranges, where sodium-bicarbonate-sulfate waters predominate. These waters are characterized by lower TDS (<1000 mg/L), shallow circulation, and greater meteoric influence. Altitudes in this domain range from 400 to 1500 m a.s.l., and annual precipitation can exceed 800 mm. The observed facies indicate faster flows, shorter residence times, and the predominance of direct recharge.

Among the provinces analyzed, San Juan stands out as the most comprehensive example in terms of data availability and geostructural diversity. The province includes all the domains mentioned above: the Frontal Cordillera and Iglesia Valley (western), the

Precordillera and Bermejo Valley (central), and the Pampean Ranges (eastern). This coverage allows for a clear observation of how hydrochemical facies vary according to structural domains — from sodium-chloride waters in elevated areas (Frontal Cordillera), to sodium-sulfate waters in intermediate zones (Precordillera), and sodium-bicarbonate-sulfate waters in lower regions (Pampean Ranges). The official altitudinal sequence between these sectors ranges from over 4500 m a.s.l. in the Frontal Cordillera to less than 600 m a.s.l. in the Pampean Ranges, reinforcing the value of this gradient for analyzing flow patterns, recharge processes, and mineralization. This model, validated in San Juan, may serve as a guide to replicate or adjust hydrogeological and hydrogeochemical interpretations in other geological provinces and valleys of northwestern Argentina.

The interpretative framework adopted here is supported by the use of conceptual diagrams such as Mountain Front Recharge (MFR) and Mountain Block Recharge (MBR), which help explain the coexistence of shallow and deep flows based on altitude, lithology, tectonic structure, and climatic conditions (see Figure 6). In particular, regions such as Iglesia Valley and Bermejo Valley exhibit structural and topographic settings analogous to these models, supporting the hypothesis of a combined MFR–MBR dynamic. In these areas In these areas, the hydrogeochemical dataset analyzed in this study suggests the presence of recharge zones at high elevations, groundwater flow through fractured formations, fault-controlled discharges, and geochemical facies consistent with long residence times and ionic enrichment. The correlation between sodium-chloride waters in the Frontal Cordillera and Bermejo Valley serves as a clear example of deep circulation within this conceptual framework.

This longitudinal conceptual model, represented in Figure 61, integrates in a single scheme the observed flow path, structural domains, facies types, and altitudinal and thermal gradients across the studied Andean region. Along with Table 1, which summarizes the comparative characteristics by structural domain, it constitutes the visual and interpretative synthesis of the results obtained in this thesis.

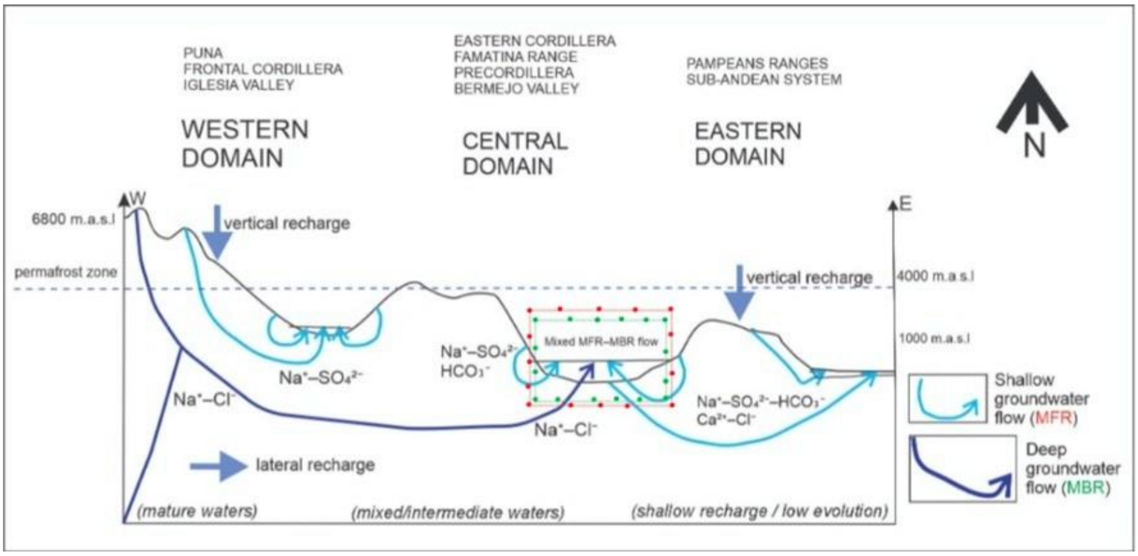

Figure 61. Regional hydrogeochemical conceptual model: trajectories, facies, and structural domains

This figure presents a conceptual longitudinal cross section that summarizes the structural, hydrogeological, and hydrogeochemical organization of groundwater thermal systems in the northern Argentine Andes. It integrates field data, geochemical analyses, and structural interpretations into three main domains: western, central, and eastern.

The western domain (The Puna, Frontal Cordillera, Iglesia Valley) is characterized by high-altitude recharge (>5000 m a.s.l.), cold climatic conditions (including permafrost zones), and deep groundwater flow trajectories. Dominant facies include Na^{+}–Cl^{-}, indicating mature waters with long residence times, intense evaporation, and significant water–rock interaction with volcanic and evaporitic formations. Flow occurs laterally, driven by gravitational and thermal gradients. These waters are classified as mature, reflecting advanced hydrochemical evolution. In contrast, Iglesia Valley exhibits shallower flows and sodium–sulfate facies, suggesting shorter residence times, partial evolution, and greater recharge renewal due to its intermediate altitude and structural permeability. Precipitation in this domain is typically <200 mm/year.

The central domain (Eastern Cordillera, Famatina Range, Precordillera, Bermejo Valley) features a combination of lateral and vertical flows, enhanced by faulting and tectonic complexity. Waters show mixed or transitional facies, such as Na^{+}–SO_4^{2-} and Na^{+}–SO_4^{2-}–HCO_3^{-}, indicating moderate geochemical development and interaction with sedimentary rocks. This domain is structurally permeable and marked by hydrochemical mixing. Bermejo Valley, in particular, presents Na^{+}–Cl^{-} facies with high salinity and structural confinement, suggesting the accumulation of evolved waters in low-permeability zones. The presence of a deep upward flow (represented by a dark blue arrow rising from the bottom of the figure) indicates two possible origins for these chloride-rich waters:

(1) a deep magmatic source associated with residual degassing from the Frontal Cordillera and migration through tectonic faults (e.g., Bermejo Fault), or

(2) lateral transport from high-elevation, hyperarid zones (e.g., the The Puna), where extreme evaporation enhances sodium and chloride accumulation.

Precipitation in this domain ranges from 200 to 400 mm/year.

The eastern domain (Pampeans Ranges and Sub-Andean System) is defined by lower elevations (<2000 m a.s.l.), higher precipitation (>400 mm/year), and predominantly vertical recharge. Aquifers are shallow, with low residence times and limited water–rock interaction. Dominant facies include Ca^{2+}–HCO_3^{-} and Na^{+}–SO_4^{2-}–HCO_3^{-}, characteristic of low-evolution waters. This domain is labeled as "surface recharge/low evolution", indicating rapid aquifer renewal in a more humid climatic setting.

Overall, this conceptual model illustrates the hydrogeochemical transition from deep, saline, and mature waters in the western arid zones to recently recharged, low-salinity waters in the more humid eastern regions. Flow trajectories are shown with light blue arrows (shallow flow) and dark blue arrows (deep flow). Recharge mechanisms are labeled as Mountain Front Recharge (MFR – red dotted lines) and Mountain Block Recharge (MBR – green dotted lines).
Mixed recharge zones—where both MFR and MBR processes coexist—are highlighted in green and red dotted outlines, illustrating the overlapping recharge dynamics in structurally complex areas such as the Iglesia and Bermejo valleys.

Source: Adapted by the author based on Bresciani et al. (2018), in Somers & McKenzie (2020), WIREs Water.
https://wires.onlinelibrary.wiley.com/doi/10.1002/wat2.1475

Tabla 1. Flow Depth and Recharge Type by Domain

Classification based on chloride concentration as tracer, according to Bresciani et al. (2018).

Structural Domain	Flow Circulation Pattern	Conceptual Recharge Model (MFR/MBR)
Western	Deep circulation (Cl^--enriched waters)	MBR dominant (Frontal Cordillera); MFR–MBR mixed (Iglesia)
Central	Intermediate to deep circulation	MBR dominant (Bermejo); transitional elsewhere
Eastern	Shallow circulation (low Cl^-, HCO_3^- dominance)	MFR dominant

Note: The presence of chloride-rich waters has been used in this table as a qualitative indicator of deep groundwater flow (MBR), while facies with low chloride content are associated with shallower flow pathways and recent recharge (MFR). This interpretation is based on the methodology proposed by Bresciani et al. (2018), who demonstrate that mountain block recharge systems (MBR) tend to have higher chloride concentrations due to prolonged interaction between rock and water and the accumulation of solutes, while mountain front recharge systems (MFR) are characterized by lower chloride levels and less advanced hydrochemical evolution. This distinction is particularly relevant in arid mountainous regions, where recharge processes are limited and groundwater flow is strongly influenced by structural controls.

4. Geochemical interpretation using Piper diagrams

Piper diagrams were fundamental to classify water types and visualize ionic composition as a function of geochemical evolution. The distribution of samples in these diagrams validated the proposed structural zonation and allowed establishing key inferences for each geological domain:

- In the **western domain** (The Puna and Cordillera Frontal), most samples were concentrated in the sodium chloride field (Na^+-Cl^-), with high TDS (>5000 mg/L), alkaline pH and oversaturation in calcite and dolomite. This pattern is associated with advanced evolution, long residence time, deep circulation and strong interaction with evaporite and volcanic rocks. The waters reflect accumulation processes in endorheic basins and the action of marked thermal gradients.

- In the **central domain** (Eastern Cordillera, Famatina Range, Precordillera), samples are grouped in mixed fields, mainly Na^{+}-SO_4^{2}- and Ca^{2+}-HCO_3-, indicating higher meteoric recharge, dissolution of sedimentary rocks and intermediate flows. TDS vary between 1000-5000 mg/L, and mixing processes between young and aged waters are recorded, in contexts of less confinement.
- In the **eastern domain** (Sub-Andean System and Pampean Ranges), the calcium bicarbonate field (Ca^{2+}-HCO_3-) predominates, with lower TDS (<250-1000 mg/L) and greater meteoric influence. The diagrams show young waters, with incipient geochemical evolution and shallow circulation, reflecting wetter climatic conditions, higher precipitation and shorter residence time.

This integrated reading of the Piper diagrams not only confirms the longitudinal segmentation of thermal systems, but also illustrates how water geochemistry responds to deep structural factors, tectonic history and environmental gradients. The ionic composition is, in this sense, a faithful reflection of the subterranean journey of the waters through the geological provinces of the northern part of the arid Andes.

Both **Iglesia Valley** and **Bermejo Valley** exhibit distinctive hydrogeochemical characteristics that may be associated with deep ascending flows of common origin. In the case of Iglesia Valley, although sodium–bicarbonate facies (Na^{+}–HCO_3^{-}) predominate—suggesting an intermediate evolution or mixing system—the elevated sodium and chloride content in some samples, combined with its geological location adjacent to the Frontal Cordillera, supports the hypothesis of a possible underground connection with deeper and more saline aquifers originating in the western domain.

Indeed, the Frontal Cordillera—with its ancient volcanic systems, deep tectonic structures, and significant geothermal gradients—may act as a source of heat and pressure that drives the ascent of evolved waters toward structurally lower areas such as Iglesia and Bermejo. This ascending flow may be facilitated by a network of regional tectonic faults, including the Iglesia Fault, La Laja Fault, and Bermejo Fault (

SEGEMAR; 2019). These deep-seated structures traverse the basin and act not only as conduits for vertical fluid migration but also as pressure-release zones that enable long-term hydrogeological connectivity across domains.

In Bermejo Valley, the predominance of sodium–chloride waters, with high TDS and neutral to alkaline pH, further reinforces this hypothesis. These waters may represent the distal expression of a deep lateral flow path, originating in the Frontal Cordillera or The Puna, and migrating eastward across domains until they accumulate in more confined, topographically depressed settings.

This interpretation adds significant value to the understanding of the San Juan groundwater system, as it illustrates the co-existence of the three major structural domains—western, central, and eastern—along with two intermontane valleys (Iglesia and Bermejo) that exemplify the possibility of interconnected deep groundwater flow across lithological and tectonic boundaries.

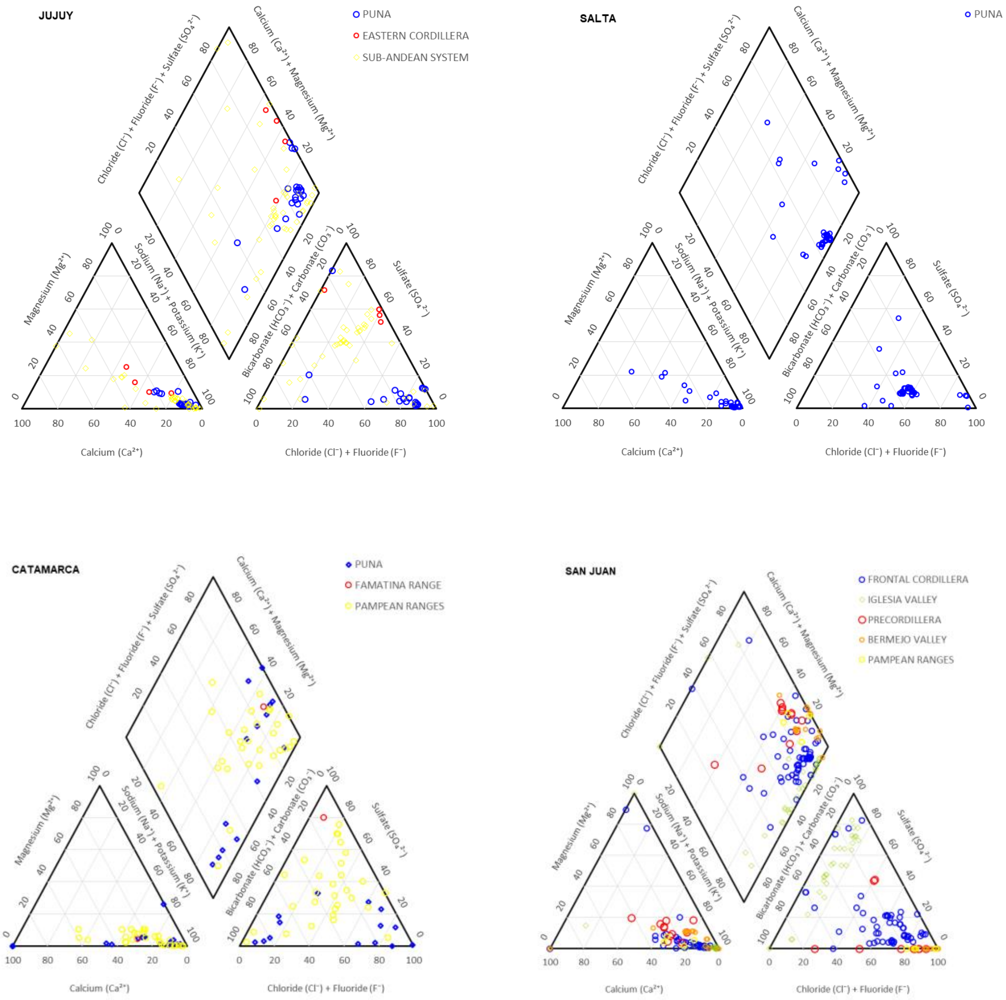

Figure 60. Comparative Piper diagrams by geological province (Jujuy, Salta, Catamarca, and San Juan)

Distribution of hydrochemical facies of thermal waters across the different geological provinces analyzed in the study area: The Puna, Eastern Cordillera, Frontal Cordillera, Iglesia Valley, Precordillera, Pampean Ranges, Bermejo Valley, and Famatina Range. The Piper diagrams are presented in a comparative format to emphasize differences and similarities between structural domains and intermontane valleys across the provinces of Jujuy, Salta, Catamarca, and San Juan.

In the Western Domain (The Puna and Frontal Cordillera), sodium-chloride waters with high salinity and geochemically evolved signatures are predominant. In the Central Domain (Eastern Cordillera, Famatina Range, and Precordillera), mixed facies dominate—mainly sodium-bicarbonate and calcium-sulfate waters—indicating processes such as carbonate dissolution, hydrochemical mixing, and interaction with evaporitic lithologies. The Eastern Domain (Pampean Ranges and Sub-Andean System) is characterized by low mineralization and a predominance of calcium-bicarbonate facies, associated with recent meteoric recharge.

The intermontane valleys show intermediate patterns: Iglesia Valley reflects transitional hydrochemical characteristics between the western and central domains, while Bermejo Valley displays sodium-chloride facies, suggesting the accumulation of deep ascending brines with advanced chemical evolution.

These comparative Piper diagrams provide a visual synthesis of the hydrogeochemical patterns discussed throughout this chapter, supporting the proposed model of longitudinal structural zoning in the northwestern Argentine Andes.

4. Altitudinal gradients and groundwater geochemical evolution

The analysis of altitudinal trajectories revealed a hydrogeochemical pattern consistent with the defined structural domains. In the **western domain** (The Puna and Frontal Cordillera), a systematic increase in salinity with altitude was observed, linked to low meteoric recharge, high evaporation rates, structural confinement and prolonged residence time. Sodic chloride waters (Na^{+}-Cl^{-}), supersaturated in carbonates and amorphous silica, dominate this environment. The high concentration of solutes and the predominance of low ionic ratios ($Na^{+}/Cl^{-} < 1$; $SO_4^{2-}/Cl^{-} < 1$) suggest a strong influence of dissolution of deep brines or evaporitic deposits, which may ascend by density gradients or active tectonic structures (Clavel et al., 2023). In the **central domain** (Eastern Cordillera, Famatina Ranges and Precordillera), subsurface flow paths adopt downward directions with evidence of mixing between young and old waters, as shown by the intermediate patterns in the Piper diagrams. Here, a greater diversity of facies (Na^{+}-SO_4^{2-}, Ca^{2+}-HCO_3^{-}) is recorded, consistent with active meteoric infiltration, dissolution of sedimentary and Andean rocks, and presence of permeable structures that facilitate circulation. The higher volume of annual precipitation (200-600 mm) and the lower relative altitude favor the inflow of fresh water, which reduces the relative salinity. In the **eastern domain** (Sub-Andean System and Pampean Ranges), the flow is shallower and meteorically influenced. The waters present low TDS and a predominance of calcic bicarbonate facies, revealing a superficial origin with limited rock-water interaction and less geochemical evolution. However, in certain upwellings, more evolved Na^{+}-SO_4^{2-} facies are identified, which could indicate mixing with older flows from higher or confined areas.

In all domains, altitudinal, thermal and chemical gradients are clearly expressed in the ionic composition of the water, which allows inferring processes such as differentiated infiltration, structurally guided vertical and horizontal flow, and the existence of orographic barriers that regulate the water regime. Precipitation, which increases from the arid west (<150 mm/yr) to the wetter east (>800 mm/yr), marks a decisive climatic control on the hydrogeochemical evolution and renewal of regional thermal systems.

Altitudinal analysis showed that salinity tends to increase with altitude in the western domain, a product of low recharge and long residence of confined waters. The central domain shows downward flow paths with progressive mixing, while the eastern domain shows shallow, meteorically influenced flows. This distribution reflects gradients of temperature, pressure, geothermicity, fluid density, as well as the action of orographic barriers that regulate precipitation (Viale et al., 2019; Bookhagen and Strecker, 2008).

5. Final Integrative Conclusion

The study developed in this thesis identified consistent structural, hydrogeochemical, and climatic patterns across the northern part of the Argentine Andes, confirming that thermal waters are distributed according to geological and altitudinal domains rather than administrative boundaries. This organization reveals a close correspondence between geological and hydrogeological provinces, thereby validating the longitudinal analytical approach adopted.

The integration of multiple lines of evidence, including hydrochemical facies, molar ratios, mineral saturation indices, and altitudinal and climatic gradients, made it possible to delineate groundwater flow paths, identify connections between deep groundwater flows and meteoric recharge—which, upon infiltration, connects with shallower groundwater flows—and gain a better understanding of the role of regional fault systems as fluid conduits. In addition, the role of intermontane valleys was confirmed as key zones of accumulation and hydrochemical transition.

These findings highlight the need to approach hydrothermal systems from an integrated hydrogeological and hydrogeochemical basin perspective, one that considers both groundwater quality and quantity. This vision is essential not only for interpreting the resource's dynamics but also as a preventive tool for its use, monitoring, and conservation in the face of increasing environmental and water demand pressures.

The conceptual model proposed, supported by empirical evidence and recent scientific literature, provides a solid foundation for future research and the development of sustainable management strategies for geothermal systems in tectonically active regions. In contexts of growing environmental pressure—marked by climate change in arid zones, agricultural expansion, mining development, and aquifer overexploitation—it is a priority to consolidate an integrated research framework based on hydrogeological and hydrogeochemical basins.

Understanding both the quality and availability of groundwater is key not only to deciphering the dynamics of thermal systems but also to ensuring their sustainable use, protection, and long-term planning. In this regard, it is recommended to establish a groundwater baseline that includes regular sampling campaigns (ideally on an annual basis) to monitor geochemical evolution, validate flow models using stable isotope and geophysical techniques, and generate continuous data that reflect the system's response to climatic, seismic, and anthropogenic variables.

The conceptual model presented in this thesis offers a valuable framework for future research and interventions aimed at the sustainable management of hot springs in tectonically active regions of the Andes.

CAPITULO VI: REFERENCES

- Abraham de Vázquez, E. M., Garleff, K., Liebricht, H., Regairaz, A. C., Schäbitz, F., Squeo, F. A., Stingl, H., Veit, H., & Villagrán, C. (2000). Geomorphology and paleoecology of the arid diagonal in southern South America. Zeitschrift für Angewandte Geologie, Sonderheft 1, 55–61. https://www.researchgate.net/publication/230777610_Geomorphology_and_paleoecology_of_the_arid_diagonal_in_Southern_South_America
- Appelo, C. A. J., & Postma, D. J. (2005). *Geochemistry, groundwater and pollution* (2da ed.). CRC Press/Balkema https://www.taylorfrancis.com/books/mono/10.1201/9781439833544/geochemistry-groundwater-pollution-dieke-postma-appelo
- Auge, M. P., Wetten, C., Baudino, G., Bonorino, A. G., Gianni, R., González, N., Grizinik, M. M., Hernández, M. A., Rodríguez, J., Sisul, A. C., Tineo, A., & Torres, C. (2006). Hydrogeology of Argentina. Geological and Mining Bulletin, 117(1), 7-23. Geological and

Mining Institute of Spain. Retrieved from institution repositor https://ri.conicet.gov.ar/handle/11336/76016

- Aceñolaza, F. G., & Toselli, A. J. (1973). Geology of the Famatina System. *Revista de la Asociación Geológica Argentina*.
- Astini, R. A. (1998). *The Ordovician Proto-Andean basins of Argentina: evolution of a complex margin*. Sedimentary Geology.
- Astini, R. A., Benedetto, J. L., & Vaccari, N. E. (2005). *The Early Paleozoic evolution of the Argentine Precordillera as a Laurentian rifted, drifted and collided terrane: A geodynamic model*. In V. A. Ramos & J. D. Keppie (Eds.), *Laurentia–Gondwana Connections Before Pangea* (pp. 43–62). Geological Society of America.
- Allmendinger, R. W., Jordan, T. E., Kay, S. M., & Isacks, B. L. (1997). The evolution of the Altiplano–The Puna Plateau of the Central Andes. *Annual Review of Earth and Planetary Sciences*, 25, 139–174. https://www.researchgate.net/publication/257652703_The_evolution_of_the_Altiplano-The Puna_Plateau_of_the_Central_Andes_Annual_Reviews_of_Earth_and_Planetary_Sciences_v_25_139-17
- Bresciani, E., Cranswick, R. H., Banks, E. W., Batlle-Aguilar, J., Cook, P. G., & Batelaan, O. (2018). Using hydraulic head, chloride and electrical conductivity data to distinguish between mountain-front and mountain-block recharge to basin aquifers. *Hydrology and Earth System Sciences, 22*(2), 1629–1648. https://www.researchgate.net/publication/318797875_Using_hydraulic_head_chloride_and_electrical_conductivity_data_to_distinguish_between_mountain-front_and_mountain-block_recharge_to_basin_aquifers#:~:text=MFR%20and%2015-,MBR%20is%20typically%20difficult.,concentrations%20using%20an%20empirical%2020
- Bookhagen, B., & Strecker, M. R. (2008). Orographic barriers, high-resolution TRMM rainfall, and relief structure of the Andes. *Geophysical Research Letters*, 35(6), L06403. https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2007GL032011
- Bookhagen, B., & Strecker, M. R. (2008). *Modern Andean rainfall variation during ENSO cycles and its impact on the Amazon drainage basin*. Geophysical Research Letters, 35(5), L05703. https://bodobookhagen.github.io/pdf/bookhagen10_enso_rainfall_color.pdf
- Barcelona, H. (2015). *Sistema geotérmico del Valle del Cura, provincia de San Juan*. Revista de la Asociación Geológica Argentina, 72(3), 349–367. https://bibliotecadigital.exactas.uba.ar/download/tesis/tesis_n5699_Barcelona.pdf
- Center for Research, Development and Innovation for Integrated Water Management in Arid Regions (CIGIAA). (2024). *Water resources status report for the province of San Juan: From hydrological drought to socio-economic crisis*. Interinstitutional technical document. Cámara Minera de San Juan. Retrieved from https://camaramínerasj.com.ar/wp-content/uploads/2024/03/INFORME-CIGIAA.pdf
- Christiansen, R. O., Clavel, F., Gonzalez, M., Garcia, H. P. A., Ortiz, D. A., Ariza, J. P. A., Martinez, M. P., & Wohnlich, S. (2021). *Low-enthalpy geothermal energy resources in the Central Andes of Argentina: A case study of the Pismanta system.* Energy Reports, 7, 309–316 https://ri.conicet.gov.ar/handle/11336/155027
- Comisión de Sitios de Interés Geológico de la República Argentina (CSIGA). (2008). *Inventario de sitios geológicos de interés científico*. SEGEMAR. http://repositorio.segemar.gov.ar/handle/308849217/2022
- CGMW (2019) – *Geological Map of South America*. Commission for the Geological Map of the World, Paris.
- Data collected during Master's Program Excursions in Applied Geothermics (2015–2018), Argentina. (Used in field surveys and updated sample campaigns).

- Domenico, P. A., & Schwartz, F. W. (1990). *Physical and chemical hydrogeology*. John Wiley & Sons. ISBN: 978-0471507444 https://health.hawaii.gov/heer/files/2021/07/Domenico1990.pdf
- Ecological Restoration in the Arid Diagonal of Argentina (2018). Arid Diagonal of Argentina. In Daniel Pérez (Ed.), Ecological Restoration in the Arid Diagonal Argentina 3. Retrieved from https://restauremos-ra.blogspot.com/2016/08/diagonal-arida.html
- Forte, A. P., Villarroel, C. D., & Angillieri, M. Y. E. (2016). Impact of natural parameters on rock glacier development and conservation in subtropical mountain ranges, northern Argentine Central Andes. *The Cryosphere Discussions*, 1–24. [Access via ResearchGate/profile https://scholar.google.com/citations?view_op=view_citation&hl=es&user=tCol1qwAAAAJ&citation_for_view=tCol1qwAAAAJ:2osOgNQ5qMEC
- Furque, G., González, P. D., & Caballé, M. F. (2003). Geologic Sheet 3169-II San José de Jáchal (Bulletin Nº 259). National Program for Geological Maps of the Argentine Republic. https://repositorio.segemar.gob.ar/handle/308849217/176
- Gómez, J., Schobbenhaus, C., & Montes, N. E. (2019). *Geological Map of South America 2019* (Scale 1:5,000,000). Commission for the Geological Map of the World, Geological Service of Colombia & Geological Service of Brazil. https://repositorio.segemar.gov.ar/handle/308849217/3420
- Giggenbach, W. F. (1992). Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth and Planetary Science Letters, 113(4), 495–510. https://www.sciencedirect.com/science/article/abs/pii/0012821X9290127H
- GeoXnet. (n.d.). New model for salt formation: Accumulation of salt as a result of hydrothermal processes associated with Wilson cycles. Retrieved from https://www.geoxnet.com/nuevo-modelo-de-formacion-de-sal-acumulacion-de-sal-como-consecuencia-de-procesos-hydrotermales-asociados-con-los-ciclos-de-wilson/#:~:text=Las%20salmueras%20se%20transportan%20hydrotermalmente,la%20sal%20de%20la%20redisoluci%C3%B3n
- Hydroproyectos S.A., Stec SRL & Sepic S.C. (1985). *Second phase geothermal prefeasibility study of the Despoblados area, Frontal Cordillera, San Juan* [Unpublished report]. (Used in and Miranda (2003) & Miranda, 2003 compilation).
- Hem, J. D. (1985). *Study and interpretation of the chemical characteristics of natural water* (3rd ed.). U.S. Geological Survey Water-Supply Paper 2254. https://pubs.usgs.gov/publication/wsp2254
- Houston, J., Butcher, A., Ehren, P., Evans, K., & Godfrey, L. (2011). The evaluation of brine prospects and the requirement for modifications to existing codes. *Economic Geology*, 106(7), 1225–1239.*Economic Geology*, 106(7), 1225–1239. https://www.researchgate.net/publication/256371148_The_Evaluation_of_Brine_Prospects_and_the_Requirement_for_Modifications_to_Filing_Standards
- Hochstein, M. P. (1990). Classification and assessment of geothermal resources. In Dickson, M. H., & Fanelli, M. (Eds.), *Small Geothermal Resources: A Guide to the Development and Use of Resources* (pp. 31–57). https://www.researchgate.net/publication/316876669_Classification_and_assessment_of_geothermal_resources
- Hinzer, I., Altherr, M., Christiansen, R., Schreuer, J., & Wohnlich, S. (2021). *Characterisation of an artesian groundwater system in the Valle de Iglesia in the Central Andes of Argentina.* Environmental Earth Sciences, 80, 457 https://link.springer.com/article/10.1007/s00531-021-02058-0
- IANIGLA-CONICET. (n.d.). *National Glacier Inventory of Argentina: Interactive map viewer* [Web map]. Argentine Institute of Snow Research, Glaciology and Environmental Sciences (IANIGLA-CONICET). Retrieved July 28, 2025, from

http://maping.glaciaresargentinos.gob.ar/visor_ing_v122024/index.html?zoom=4&lat=-40.8803&lng=-60.6445&layers=argenmap,glaciares_pais_v12,glaciares_pnlg_v2,limite_subcuencas_pais_v17

- IANIGLA–CONICET (Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales – CONICET). (2018). *Inventario Nacional de Glaciares y Ambiente Periglacial: Resultados preliminares*. Mendoza: IANIGLA–CONICET. https://www.glaciaresargentinos.gob.ar
- INTA (2023):
- Instituto Nacional de Tecnología Agropecuaria (INTA). (2023). Atlas of Soils and Natural Resources of the Argentine Republic. Buenos Aires: INTA Ediciones. Retrieved from https://inta.gob.ar/documentos/atlas-de-suelos
- Jordan, T. E., Allmendinger, R. W., Damanti, J. F., & Drake, R. E. (1993). Chronology of motion in a complete thrust belt: The Precordillera, 30–31° S, Andes Mountains. *Geological Society of America Special Paper*, (281), 1–34. https://www.journals.uchicago.edu/doi/10.1086/648213
- Lavel, F. G., González, M., Sottile, A. L., Christiansen, R. O., Gianni, G. M., Winocur, D. A., Ortiz, D. A., Garcia, H. P. A., Lince Klinger, F. G., & Martinez, P. (2023). Geophysical studies on shallow structures linked to the rise of the Pismanta hot springs, Iglesia Valley, San Juan, Argentina. *Revista de la Asociación Geológica Argentina*.
- Manning, A. H., & Solomon, D. K. (2003). Using noble gases to investigate mountain-front recharge. *Journal of Hydrology, 275*(3–4), 194–207. https://www.sciencedirect.com/science/article/abs/pii/S002216940300043X?via%3Dihub
- Mon, R., Monaldi, C. R., & Salfity, J. A. (2005). Curved structures and interference fold patterns associated with lateral ramps in the Eastern Cordillera, Central Andes of Argentina. *Tectonophysics, 399*(1–4), 173–179. https://www.sciencedirect.com/science/article/abs/pii/S0040195105000223?via%3Dihub
- Mon, R. (2005). Tectonics of the Eastern Cordillera and Santa Barbara System. Revista de la Asociación Geológica Argentina, 60(4), 682-702. https://revista.geologica.org.ar/raga/article/view/1098
- Pesce and Miranda (2003), *Catalogue of Thermal Manifestations of the Argentine Republic. Volume I: Northwestern Region (Provinces of Jujuy, Salta, Catamarca, Tucumán, Santiago del Estero, La Rioja and San Juan)* (Anales 36). Buenos Aires: Servicio Geológico Minero Argentino, Instituto de Geología y Recursos Minerales. Retrieved from http://repositorio.segemar.gov.ar/308849217/2424
- Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water-analyses. *Transactions, American Geophysical Union*, 25, 914–923. https://agupubs.onlinelibrary.wiley.com/doi/10.1029/TR025i006p00914
- Peruca, L. P., & Paredes, J. de D. (2003). Quaternary faulting in the La Laja area and its relation to the 1944 earthquake, Albardón Department, San Juan, Argentina. *Revista Mexicana de Ciencias Geológicas, 20*(1), 20-26. https://rmcg.geociencias.unam.mx/index.php/rmcg/article/view/952
- Restauremos Argentina. (2016). Argentina's Arid Diagonal. Retrieved from https://restauremos-ra.blogspot.com/2016/08/diagonal-arida.html
- Ramos, V. A. (1999). *Los sistemas orogénicos del Paleozoico en el margen occidental de Gondwana*. Revista de la Asociación Geológica Argentina, 54(4), 305–315 https://www.researchgate.net/publication/285423150_Evolucion_tectonica_de_la_Argentina
- Ramos, V. A. (1999). Plate tectonic setting of the Andean Cordillera. In C. J. Kay, V. A. Ramos & W. R. Allmendinger (Eds.), *Geology and Ore Deposits of the Central Andes* (pp. 31–56). Society of Economic Geologists. https://doi.org/10.5382/SP.07

- Rapela, C. W., Casquet, C., Baldo, E., Dahlquist, J., Pankhurst, R. J., Galindo, C., & Saavedra, J. (2001). Early Paleozoic orogeny in the proto-Andean margin of South America, Sierras Pampeanas, Argentina. *Journal of Iberian Geology, 27*, 23-41.
- Somers, L. D., & McKenzie, J. M. (2020). *A review of groundwater in high mountain environments*. WIREs Water, 7(6), e1475. https://wires.onlinelibrary.wiley.com/doi/epdf/10.1002/wat2.1475
- SEGEMAR. *Hojas Geológicas de la República Argentina*. Instituto de Geología y Recursos Minerales. https://repositorio.segemar.gov.ar/
- SEGEMAR (2012) – *Mapa Geológico de la República Argentina 1:1.000.000*. Instituto de Geología y Recursos Minerales.
- Servicio Geológico Minero Argentino (SEGEMAR). (2019). Geological Map of the Argentine Republic, scale 1:2,500,000. Buenos Aires: SEGEMAR. Retrieved from https://geologia.segemar.gov.ar
- Taillant, J. D. (2012). *El ambiente periglacial y la minería en Argentina*. Center for Human Rights and Environment (Center-HRE). https://center-hre.org/wp-content/uploads/2012/11/El-Ambiente-Periglacial-y-la-Mineria-en-la-Argentina-English.pdf
- Tapia-Baldis, C., & Trombotto-Liaudat, D. (2020). Permafrost model in coarse-blocky deposits for the Dry Andes, Argentina (28°–33° S). *Cuadernos de Investigación Geográfica*, 46(1), 33–58. https://publicaciones.unirioja.es/ojs/index.php/cig/article/view/3802
- Trombotto Liaudat, D., & Sileo, N. (2020). Periglacial water paths within a rock glacier–dominated catchment in the Stepanek area, Central Andes of Mendoza, Argentina. *Permafrost and Periglacial Processes, 31*(2), 311–323. https://onlinelibrary.wiley.com/doi/10.1002/ppp.2044
- Taillant, J. D. (2012, November 9). The periglacial environment and mining in the Argentine Republic: The Glacier Law and frozen soils. Human Rights and Environment Center (CEDHA). http://www.geo.uzh.ch/microsite/cryodata/pf_global/GlobalPermafrostZonationIndexMap.kmz
- Villarroel, C. D., Forte, A. P., Ortiz, D. A., Tamburini Beliveau, G., & Güell, A. (2020). Active layer and permafrost thickness in rock glaciers derived from geophysical methods in the semiarid Andes of Argentina. *Geomorphology*, 365, 107249. https://www.sciencedirect.com/science/article/abs/pii/S0169555X2030221X?via%3Dihub
- Villarroel, C. D., Ortiz, D. A., Forte, A. P., Tamburini Beliveau, G., & López, A. (2021). Internal structure of a large, complex rock glacier and its significance in hydrological and dynamic behavior: A case study in the semi-arid Andes of Argentina. *Permafrost and Periglacial Processes*, 33(1), 78–95. https://onlinelibrary.wiley.com/doi/10.1002/ppp.2132
- Villarreal, C., Estévez, G., Ortiz, A., Ponce, D., Ocaña, E., Forte, A. P., & Gianni, R. (n.d.). Hydrochemistry and water quality in the Matagusanos groundwater basin and the Talacasto alluvial fan sector, San Juan. In *Chemistry, Quality, and Contamination of Water Volume I*.