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Boron Industry, Sources, and Evaporitic Andean Deposits: Geochemical Characteristics and Evolution Paths of the Superficial Brines

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Abstract

This study accounts for boron deposits in Chile. In addition, a vision is given of the geochemical evolution of its waters that depend largely on the evaporation of water and various factors among which are the geomorphology, climate, and volcanic activity that favor the conditions for the deposition of various salts between that accentuate lithium, potassium, and boron. Borates are found in lenticular stratified bodies, known as “bars,” interspersed in detrital-saline sequences and always in the first meters of the saline surface part or as high-grade nodules (up to 30% B_2O_3) that can reach tens of centimeters. In the first part, a description is made of the saline deposits to coming of the salars of South America, because it is the most important reserves of boron-rich minerals known in this continent are directly related to this type of deposits. Subsequently, the deposits in Chile and their characteristics are described. The only mineral of economic recovery known in Chile is ulexite. The second part refers to the Pitzer ion interaction model that is applied to predict the precipitation of salts in multicomponent aqueous systems with high ionic strength in a temperature range of 0–60°C, using the three natural brines of Andean borates.

Keywords: deposits of borates, Andean salars, natural brines, Pitzer model, Salar de Quisquiro, Salar de Aguas Calientes, Salar de Surire

1. Introduction

The boron element does not exist by itself in nature; it appears in combination with oxygen and other elements in salts, commonly called “borates” and defined as a compound that contains boric oxide (B_2O_3). In Babylon, more than 4000 years ago, the use of borax was known because the Babylonians brought it from the Himalayas to use in the manufacture of jewelry. The Egyptians used borax for the mummification process, and by ~300 d.C. the Chinese were familiar with borax glazes, as were the Arabs three centuries later [1–3]. More than 230 minerals containing boron have been identified [2], with sodium, calcium, or magnesium salts being the most common. There are many minerals that contain boric oxide, but

four are the most important minerals from the commercial point of view: borax, kernite, ulexite, and colemanite. All are derived from continental evaporites that form the main commercial sources of borates. Deposits that contain these minerals are mined in a limited number of countries (**Figure 1**), dominated by the United States and Turkey, which together furnish 90% of the world's borate supplies, but the most important world reserves are in Turkey (borax, ulexite, and colemanite).

The main uses of borates and boron compounds are found in the enamel and ceramic industry (sanitary ware, crockery, ceramics, tiles), glass industry (crystals, glass fibers, fire-resistant Pyrex glasses, lamps and spotlights), and fertilizers. Kernite is used to produce boric acid, tincal is used to produce sodium borate, and ulexite is used as the principal ingredient in the manufacture of a variety of specialty glasses and ceramics. Boron is one of the seven essential micronutrients for plants; it is applied directly to the soil and also is utilized in the fertilizer-type specialty [4]. It is present in the chemical industry (preparation of detergents, bleach, fire retardants, abrasives, cosmetics), tanneries (prevents rot), pharmacy (mild antiseptic), and paints (fungicide) and is used as a wood preservative (because of its low toxicity) and in capacitors, alloys, catalysis, rubber (fire retardant), and cement (slows setting). Boron hydrides oxidize easily and release large amounts of energy and for that are being studied as a possible source of fuel (aircraft and rocket borane); also they are used for shielding against radiation and for the detection of neutrons. B-10 is used in the control of nuclear reactors, in optics, and in the production of semiconductors [5].

The majority of commercial borate deposits in the world are extracted by open-pit methods. Another main source is from saline lakes, whose deposits are associated with the volcanism of the Neogene age in tectonically active regions on plate boundaries with arid climates, such as in the Mojave Desert of the United States near Boron, California, the Tethyan belt in West Asia, and the Andean belt in South America. The most important continental borates are found in the United States,



Figure 1.

Places where borate deposits are found in the world. The South American borates are located in the 70° W latitude strip and around the 30° N longitude. Turkish borates, American borates, and Chinese Asians are located.

Argentina, Chile, Peru, and China. The world's largest known borate reserves are found in western Anatolia, Turkey [6].

The presence of borates in South America is interesting. Peru has only one site (Laguna Salinas, Arequipa) with reserves that exceed 10 million tons with a 25% law of boric anhydride (B_2O_3) [7]. Bolivia has reserves of ulexite in Coipasa, Empexa, Uyuni, Chiguana, Pastos Grandes, Capina, Mamacoma, Curuto, Chaviri, Luriques, and others, while Argentina has the borate salt flats of Hombre Muerto, Diablillos, Ratones, Centenario, Cauchari, Olaroz, and Salinas Grandes [7].

There are only four major important metallogenic provinces in the world of continental borates. In order of importance are Anatolia in Turkey; Nevada, California, United States; the Central Andes of South America; and Tibet in Central Asia [8] (**Figure 1**). The Andean Boratífera Province includes a part of the south of Peru, the central-eastern part of the Great North of Chile, the high plateau sectors of the northwest of Argentina, and the southwest of Bolivia that has been described by Alonso [9], corresponding to the region between 16 and 27° S and 66 and 70° W with its north-south major axis of the order of 1500 km and another east-west of 400 km. Argentina has the best reserves and production in South America [9].

The Central Andean volcanic province coincides with the normal subduction that accompanies the Altiplano-Puna plateau that has the anomaly in boron and other volcanogenic elements, such as lithium and arsenic. The Andean borate formation model was developed by Argentine investigators [9–11]. The concentration of boron that gave place to the formation of deposits of economic interest is related with the concurrence of several associated factors such as volcanism; presence of closed basins; semiarid climate; and thermal sources [7] of the Miocene and Quaternary.

The world production of borates is estimated at 5.75 million tons of different minerals [12], and the main producers are Turkey (2.50 mill ton), United States (1.15 mill ton), Argentina (600 mil ton), Chile (560 mil ton), Russia (400 mil ton), Peru (290 mil ton), and others (270 mil ton for the rest of the producers) [13]. The United States and Turkey are the largest producers of boron in the world. Boron is quoted and sold based on boron oxide (B_2O_3), which varies according to the mineral and the compound and with or without sodium and calcium.

In South America, the “Central Andean Boratífera Province” is located between the Cordillera de la Costa in Chile and the eastern edge of the Altiplano-Puna. The current production of Bolivia is based on the mineral reserves of boron from saline deposits in the south of the country and from the Salar de Uyuni. The reserves in these deposits have been estimated at 15 million tons (Mt) of B_2O_3 . The most important boron ore that is extracted is ulexite, associated with tincal [13]. In Peru, there is only one company that extracts natural borates from the Laguna Salinas deposit, where reserves are estimated at 10 Mt. of ore with 25–27% of B_2O_3 . The open-pit mine is about 80 km away from Arequipa at an altitude of 4100 m.a.s.l. The capacity of the mine is 120,000 tpa of ulexite and 8000 tpa of colemanite. There are two main types of borates in Puna, Argentina: borates in rocks and borates in salars. The borate deposits in rock are of the Tertiary and Quaternary, formed in the last 7 million years, being located with greater abundance and economic importance in the NOA region (Argentine Northwest). The main mineralogy that these deposits present are borates of sodium (tincal), calcium and sodium (ulexite), calcium (colemanite), and calcium and magnesium (hydroboracite). The reserves in the Tertiary deposits (hard borates) amount to 60 million tons of B_2O_3 and are represented by Tincalayu (Salar del Hombre Muerto, Salta), Sijes (Pastos Grandes, Salta), and Loma Blanca (Puna Jujena), while the reserves in the Quaternary deposits (soft borates) amount to 40 million tons of B_2O_3 and represent salt flats of Salta, Jujuy, and Catamarca, whose main mineral is ulexite. The brine reserves of borates from salars of La Puna are not all estimated [14].

Chile has been the main producer of borate in South America, and the production in 2017 reached 560,000 tons of ulexite; the largest ulexite salt deposit in the world is the Salar de Surire, with estimated reserves of 1.5 Mt. [12]. Chile has ulexite reserves that together exceed 35 million tons with a 25% grade in B_2O_3 , while world reserves are estimated at 380 million tons in B_2O_3 [12]. Canada, China, India, Japan, and Malaysia are the countries that imported the highest amounts of refined borates from the United States in 2018.

2. Review of boron deposits in Chile

The discovery and commercial development of borate deposits were accelerated in the nineteenth century. Chile started to mine borate from the Salar de Ascotán in 1852 (accounting for a quarter of the world's annual supply of ~16,000 tons) by the British company Borax Consolidated [15]. It is necessary to consider that at that time, the borate deposits were not part of the Chilean territory. Chile was the world's principal producer of boron, with its deposits located in the salars of Surire in the north of the country; Ascotán, Carcote, Aguas Calientes I, and Quisquiro, located in the second region; and Maricunga in the third region of Atacama. In 1836 the borates of the South American region were known, with existing records of the year 1852. The incipient exploitation of the Salar de Ascotán in 1883 was described with a production of 36,000 metric tons in 1913 and stopped working in 1967 [16, 17]. Currently, Chile is located after Argentina in reserves and installed treatment capacity among the Andean producing countries. Boron (ulexite) production in Chile increased by approximately 6%, from 518 tons in 2015 to 560 tons in 2017 [18].

The discovery of deposits of borates “hard” in Turkey of minerals with better economic performance, greater reserves, and comparative advantages of exploitation and benefit changed to become Chile a country with a status quo in this area, for more than 70 years. The final chapter seemed to be closed in 1967, when Borax Consolidated, an English monopoly producing company, which exploited the Surire (Chilcaya) deposits and, subsequently, Ascotán, abandoned its deposits and the country [15]. Subsequently, in 1980 it had a vigorous upturn, and in the coming years, the production of borates and boric acid will be considered strategic because boron is associated with lithium in these Andean saline deposits. This alternative is only a potential alternative because it will depend exclusively on market and non-technological factors.

The Andean sector known as the Code of Santa Cruz (**Figure 2**), localized between 14° and 27° south latitude and 68° 30' west longitude until the Pacific Ocean, has the greatest variety of deposits in relation to that of the neighboring countries. The Andean orogenic system can reach up to 600 km wide and is characterized by numerous closed basins that serve as local base levels for drainage systems in the High Cordillera, also known as Puna or Altiplano [18]. These basins can be of tectonic, volcanic, or other subordinate origin. Their maximum age is probably middle Tertiary, and they continue formed during the Quaternary. Some of them are in full evolution, today with few outcrops of Paleozoic and Mesozoic bases. Its axes, in general, have a meridian to submeridian orientation and, from the Tertiary, have had an active sedimentary development. Some of them can be big, as is the great Bolivian basin, which includes the Poopó and Titicaca lakes, and the great Salar de Uyuni. In Chile, we have the case of the Pampa del Tamarugal [18]. The most outstanding sedimentary aspect of this basin has been the development of lacustrine systems with fresh or saline waters that, in their terminal stages, have evolved into evaporitic basins that are known today as “salars.” These are located in the lower part of the basins and, often, asymmetrically within them. The salars

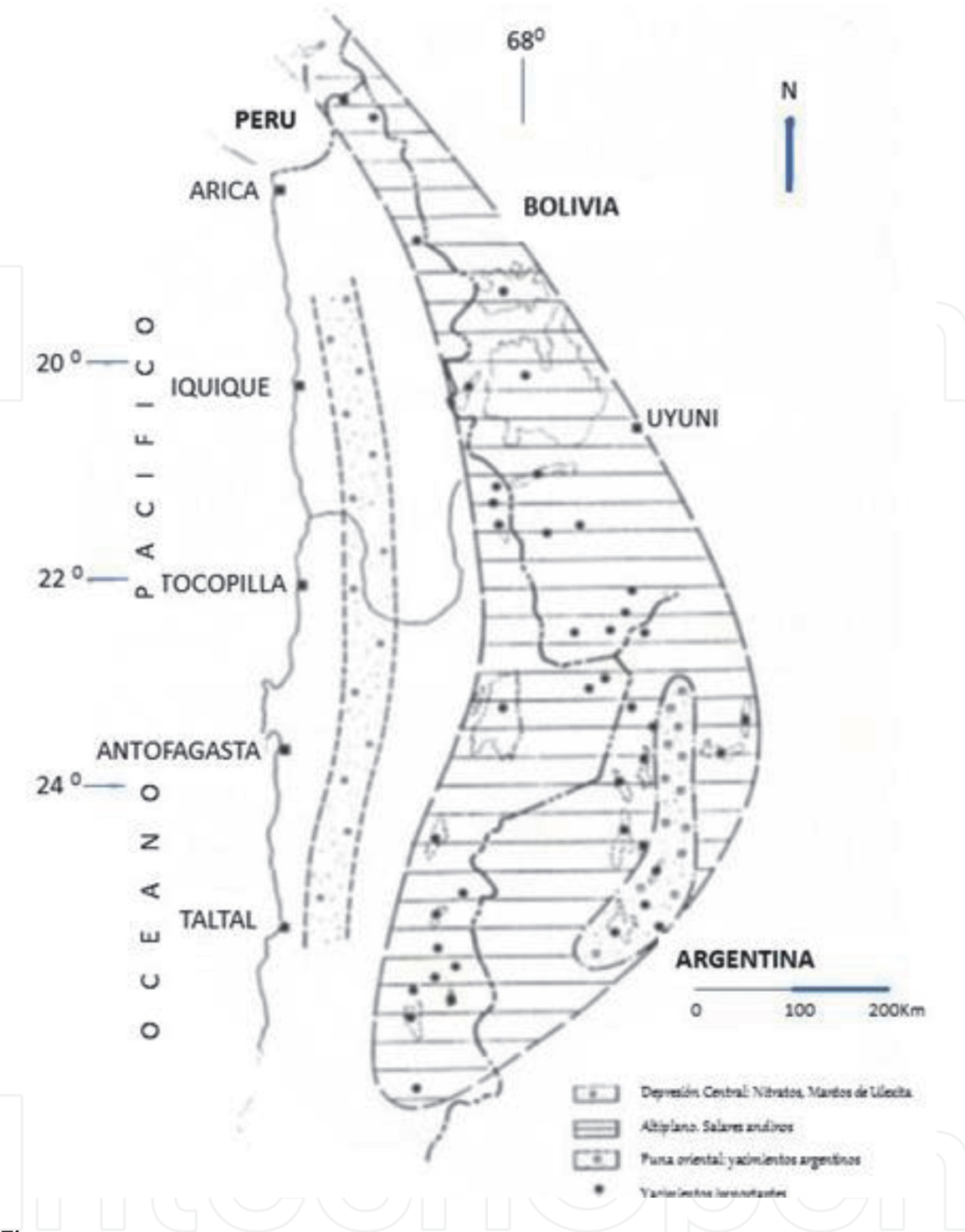


Figure 2. South American Boratífera Province [9]. The Andean sector is known as the Code of Santa Cruz, that is, approximately between 14° and 27° south latitude. The Andean orogenic system can reach up to 600 km wide and is characterized by numerous closed basins that serve as local base levels to systems of drains of the High Cordillera, also known as Puna or Altiplano. It comprises deposits of Neogenic and Quaternary borates, formed in the last 7 Ma.

result from the breakdown of the balance between the waters contributed to the basins and the evaporation and evapotranspiration processes. A salt flat (salar) is a saline detritic body located in the lower part of closed basins, formed in arid to semiarid environments. In its border, clastic deposits are formed, normally the distal parts of coalescent alluvial systems, which interdigitate with the salts that fill the basins themselves [19]. The contributions are both superficial and underground, with the latter predominant. The salts usually form concentric zones, due to their different solubility product, while the clastic materials are deposited according to their relative granulometry (gravel, sand, clays). Lagoons and groundwater levels

are common in salars. The surface of the salt flat (salar) is characterized by salt crusts and structures that reach a great variety, due to the dynamism of the salts. In the major basins, sub-basins with complex hydrological systems have differentiated over time. These basins, although in time and space are very varied, have as a common factor that most of their components, both detritic and chemical, have a majority volcanic origin of Cenozoic age [19]. This includes processes of erosion, weathering, and leaching of volcanic rocks, in addition to direct volcanic activity through the geothermal gradient, pyroclastic materials and lavas that enter the basins, and the contributions of the thermal sources. This is as true for salt flats inside eroded volcanic systems or boilers, such as those formed by tens or hundreds of kilometers of current volcanic systems [20]. The size of the salars varies, from up to thousands of square kilometers, such as the Salar de Uyuni that reaches about 9000 km², but its in-depth composition constitutes one of its most unknown aspects. In exceptional cases, such as the Salar de Atacama, it has been recognized that evaporitic bodies can reach more than 1 km of power [20].

The deposits of the high Andean subprovince of the Chilean sector are exclusively of the salar type, and to date, there are no described deposits associated with Miocene sedimentary sequences, as happens in Argentina. The latter are not related to salt flats and present a great mineralogical variety, becoming world-class reserves (subprovince of the eastern Puna) reaching the order of 100 million tons of B₂O₃ [15]. The only deposit described in Chile is the Salar de Maricunga, whose age would be in the “Miocene Superior to the Lower Pliocene” period [21].

The geomorphology of the region corresponds to the block systems in a tectonically active desert. The main blocks, in an integrated profile, from the west, and at a zero level to approximately at 6000 m altitude, are the mountain range of the coast (Cordillera de la Costa); the Central Depression, with its most characteristic section in the Pampa del Tamarugal; the precordillera, with the Cordillera Domeyko Mountain Range; and the Andean Mountain Range (Cordillera de los Andes), formed by the Altiplano and the Cordillera de los Andes. These morphological units may have limits, including sometimes obliterated, or they may be perfectly defined by regional structures [15]. This position geomorphologic to have permitted to classify the salars by your geographic position in Salars of the Coast, Central Depression Salars, Preandean Salars and Andean Salars [22]. The geological framework includes a wide stratigraphic record and igneous rocks, probably the most complete in the country, presenting a great variety of mineral deposits. In this region, the optimal conditions are present for the development of this saline deposits or salars, due to climatic conditions (desert to semidesert environment), geomorphology (abundance of closed basins), and a varied geological framework, both in age and in lithology, in addition to a relative abundance of outcrops [23, 24].

A striking characteristic of this area in southern Peru and northern Chile is the extreme aridity that has prevailed for several million years [25]. Due to this long-lived hyperaridity, the regional landscape experienced extremely low denudation rates ($<0.5 \text{ m Ma}^{-1}$), as supported by several cosmogenic nuclide studies [26, 27] in southern Peru and in northern Chile [25, 28, 29], allowing a long-term preservation of geomorphology [30].

Contributions to different basins correspond, mainly, to meteoric and “thermal” waters that, when they reach the basins, of saline composition, evolve into chlorinated brines with lower carbonate and sulfate contents, although the latter can be enriched in situ [31, 32]. The higher cations are sodium, calcium, potassium, magnesium, and lithium, with significant local amounts of arsenic and mercury, while the main anions are sulfates, chlorides, and carbonates, in addition to nitrates and borates [20, 33–35]. Additional factors that contribute in the formation of basins are erosion and leaching of different types of rocks; the transformation, in situ, of rocks

by the chemical and physical action of the salts, through “saline tectonics”; biological activity; photochemical reactions; and mists (“camanchacas”) and marine spray [36, 37].

It is evident that, from geological times and even in historical times, there is a polarization in aridity, from west to east. As a result, there are “fossilized” salt flats, in the western most part, as is the case of the Salar Grande de Tarapacá (salar of the coast); others receive occasional recharge such as the salars of the Central Depression and Salar de Llamara; others such as the Salar de Atacama (pre-Andean salar) receive contributions from ephemeral rivers and the eastern sector and others that, at present, are in the process of formation like those found in the Andean Mountain Range such as Salar de Loyoques or Salar de Surire (Andean salars).

Another source of boron and lithium are the geothermal fields. In the brines of geothermal fields, there are significant concentrations of salts, including borates. It has been proven that the brines of the Tatio geothermal field have values of the order of 200 ppm of boron, and in similar fields in the United States like Salton Sea, average values of the order of 250 ppm are detected [23, 24]. The basins of the andean salars have a structural control, some have been formed by entrapment flows of lava or inside ancient volcanic systems eroded, for example, boilers. The contributions to the basins are influenced by the volcanic activities that, in some salt flats, are evidenced in its interior by sources of thermal hot springs (Surire, Aguas Calientes I) [19, 35]. The volcanic activity provides a high geothermal gradient that directly affects the quantity and quality of the leached transported ions to the basins [20, 38]. The brines can have up to 220,000 g/l of dissolved solids and, compared to their environment, can reach values 100 times more than those found in meteoric waters and 10 times than those of thermal waters. The main contributions are related to the Cenozoic volcanic rocks, and the brines are mainly chlorides, having as main ions sodium, calcium, lithium, magnesium, chlorides, sulfates, borates, and carbonates [20]. They also have significant amounts of arsenic, mercury and significant strontium anomaly, and, at the level of traces, cesium and rubidium [33, 34, 39]. About 90% of the rocks where boron deposits are formed are volcanic or volcanoclastic, mainly ignimbritas [22].

3. The boron resource in Chilean salars

The different alternatives of exploitation of boron deposits in Chile, either as ore or by-products, in order of importance in terms of magnitude were described by Chong and Garcés [15] and subsequently expanded in Garcés and Chong [22] as:

- a. **Deposits in the Andean salars:** The salt flats are located in the high mountain range at altitudes between 4000 and 4500 m.a.s.l. These are distributed in the first three regions of the north. The boron deposits are the biggest reserves in the country, and the predominant geological framework is the Cenozoic volcanism illustrated by the presence of volcanoes and hot springs. The most important starting from the north are Surire, Carcote, Ascotán, Aguas Calientes Norte 2, Quisquiro, Aguas Calientes Sur, Pedernales, and Salar de Maricunga.

Ulexite in Chilean deposits comes in two forms:

- In lenses of powers ranging from centimeters to, in exceptional cases, 2 m. They can extend of a few tens to hundreds of square meters; however, the continuity is quite irregular, equal that its quality or law of mineral. These horizons are called bars.

- In irregularly distributed nodules in the clay sediments known as “potatoes,” which do not exceed 15–20 cm in diameter; mostly, these concretions are 10 cm in diameter and have the highest concentrations in B_2O_3 units.

Both types of deposits maintain a genetic relationship with waters from thermal sources. Among the companions of the ulexite are arsenic, gangue minerals such as calcium and sodium sulfates, sodium chloride, and varying amounts of clay minerals or other sulfates and silicates. The presence of other borates such as probertite, its anhydrous equivalent, is frequent, but in subordinate quantities, colemanite and borax have also been detected and don't represent economic importance [40].

The brines in these salt basins also have anomalous borate contents in some cases, which must be discarded from the point of view of eventual economic use. Subsequent works done by Garcés [19, 22, 24, 32], in the Salar de Ascotán, Quisquiro, and Huasco, show that the presence of boron in its brines reaches contents of 550 mg/l, 1627 g/l, and 507 mg/l, respectively.

The only ore mineral in those deposits is the ulexite, and its exploitation is carried out exclusively in the first 2 m of the salt crusts. This limitation is defined by the shallow position of groundwater levels. In the salars of Ascotán and Quisquiro, with the ulexite, probertite, hydroboracite, borax, and colemanite were found. The biggest composition of ulexite in units of B_2O_3 is presented in potatoes, reaching values of 34.74% B_2O_3 compared to 18–19% in B_2O_3 , which has the ulexite in bars of the Salar de Ascotán. For Quisquiro samples, potatoes reach 35.43% in B_2O_3 , while in bars they range from 9% to 23.8% in B_2O_3 . In the Salar de Huasco, a little further north than the previous ones (20°18'S and 68°50'W), probertite, hydroboracite, and ulexite are recognized in a subordinate way; despite the anomalous contents in some sampled points, the salar does not correspond to a boron deposit, since it consists mostly of sulfates, such as thenardite and gypsum, accompanied by halite [19].

b. Pre-Andean salars: Those saline deposits are located between the precordillera and the cordillera of Andes. They correspond exclusively to the Salar de Atacama and Punta Negra, both are the oldest, the first of these being the largest and most economically important in the country. Both are part of the Atacama-Punta Negra system. According to Alpers and Whittemore [41], the geological framework is varied with a predominance of Cenozoic, volcanic, and detritic rocks; both salt flats in the past were part of a single tectonically controlled basin. The Salar de Atacama is closed to a great volcanic activity on the eastern side, producing a drainage of the basin with great influence on the geochemistry of its waters, especially of underground origin, through the contribution of CO_2 of volcanic magma. The eastern edge of the salar presents horizons of ulexite, associated with gypsum, but in nonsignificant quantities as for its exploitation, usually the presence of the gypsum makes difficult the visual recognition of the ulexite. The brines of the Salar de Atacama are rich in trace elements such as lithium (0.15 g/l) and potassium (1.8 g/l), these being the highest contents that have been found in Chilean salt flats and are currently exploited jointly with boron and sulfates that water brings (see **Table 1**). These brines are concentrated until boric acid is obtained through a process of concentration by solar evaporation. The boric acid produced is a product of the recovery process of potassium sulfate that brine is extracted in boron concentration. Subsequently, the brine is acidified with sulfuric acid to obtain the crystallized boric acid. The crystals are filtered

| Species | Boron | Chloride | Sulphate | Sodium | Potassium | Lithium |
|-------------------------------------|--------|----------|----------|--------|-----------|--------------|
| S. Atacama© % p/p | 0.06 | 16 | 1.78 | 7.6 | 1.8 | 0.15 |
| S. Surire (mg/l) | 1627 | 144,028 | 13,583 | 82,225 | 13,500 | 472 |
| S. Punta Negra average value (mg/l) | 0.0377 | 54.125 | 4.17 | 34.2 | 0.845 | Not analyzed |
| S. Aguas Calientes N (mg/l) | 729 | 117,655 | 1984 | 71,581 | 1831 | 227 |
| S. Maricunga average value (mg/l) | 596 | 190,930 | 709 | 85,190 | 8237 | 1123 |

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Source: [19, 42, 48].

Table 1.
Chemical composition in mg per liter of the brines in Andean Salar's, except Atacama salar's.

and washed in counter current in three successive stages, to finally dry them and obtain the boric acid of high purity. For other parts, the Salar de Punta Negra is the second biggest in the country, located at an altitude of 2956 m, close to 200 km south of the Salar de Atacama, between the Cordillera de los Andes and the Cordillera de Domeyko. The salar drainage basin is approximately 4660 km². The closest volcanoes to the east edge are the Llullaillaco (6723 m) and the Socompa volcanoes (6031 m). The geological framework consists of lithostratigraphic units, which include almost all of the stratigraphic columns, since marine and continental, volcanic, metamorphic, and intrusive sedimentary rocks are present, ranging from Paleozoic to Recent. In some sectors in its eastern part, ulexite lenses, intercalated with sediments and crusts of calcium sulfate, show small-scale exploitation in the past, but today no eventual future of exploitation of this resource is estimated. Studies of Gannat and Schlund [42] indicate the western edge of the Salar de Punta Negra is mostly composed of halite and gypsum and in a subordinate way at the level of traces, glaserite, nitratite, potassium nitrate, humberstonite, silvite, darapskite, tenardite, glauberite, singenite, and polyhalite.

c. **Deposit saline of the Central Depression:** The Central Depression is a depressed relief that extends between the Cordillera de la Costa and the Precordillera. The salt flats found in this plateau are closed watersheds of the endorheic type, which receive water contributions from the east (Alta Cordillera), underground and surface. The salt concentration mechanism is based on the leaching of these materials, associated with mud flows or other irregular water avenues, which are transported to the Central Depression and are the formators of this type of salt flats in the distal part of alluvial cones or isolated bodies in some basins [22]. These deposits include, at the base, decimetric sequences of clays and saline silts and monomineral decimetric horizons of tenardite, humberstonite, bloedite, ulexite, and darapskite. It should be considered that the parts of these mud flows have volcanic origin. Characteristic deposits of this type are found in Cerros de la Joya and Cerro Antar in the southern part of the I Region of Tarapacá (21° 50' 32" S and 69° 27' 17" W), which were exploited with some intensity in the past. In the same area, in the upper part of some salt flats, lenticular bodies of centimeters thickness of ulexite are recognized. These have also been exploited sporadically, in the area of the Salar de Pintados in the first region was also exploited in the past, but in general, in all these deposits, they can consider the ulexite of subordinate economic importance. In the Pampa del Tamarugal

between coordinates 19° 40' S and 69° 40' W, the minerals found in boron correspond to ulexite, associated with halite, potassium salts, and carbonates, in beach-type deposits.

- d. **Deposits of borates and by-products from the salt industry:** This economic alternative to recover borates from the salt industry requires the exploitation of large volumes of nitrate ores, and the recovery of borates would be a by-product of this industry. The geology and mineralogy of these nitrate deposits are described in various authors [31, 43, 44]. George Ericksen studied these deposits in detail, from a structural, geological point of view, their history, mineralogy, and geochemistry. He found and described several iodine minerals he called brüggenite, hectorflorecite, fuenzalidite, and carlosruizite, among others. Ericksen [44] includes the presence of borax in the nitrate deposits, together with inyoita, kaliborita, and gowerita but in low relations. Inderite, ginorite, hydrochloroboracite, and hydroboracite have also been recognized, but all of them in minimal quantities. Minerals recognized in the field of nitrates are halite, silvite, sodium nitrate, potassium nitrate, darapskite, humberstonite, tenardite, anhydrite, bassanite, gypsum, kieserite, epsomite, glauberite, bloedite, apthitalite, picromerite, lautarite, ulexite, and probertite hydroboracite.

The minerals treated from caliche in the Pedro de Valdivia and María Elena plants contain contents in B_2O_3 units over 1%, of the minerals treated in plants, during the period from 1932 to 1967. Data are currently referenced in Wisniak and Garcés [45].

- e. **Brine by-products in geothermal fields:** It is known that the waters of geothermal fields, such as the case of Tatio, for example, are enriched with borates (183 mg/l) [46] as in other salts of economic importance (even of metallic elements). The economic recovery of borates must be considered in this case as secondary in all its aspects, since it depends on the initial exploitation of geothermal energy and the salts contained in the brines. Currently there is no project that estimates in the near term geothermal exploitation and would not involve large volumes of production.

4. Description of the area of the deposits studied

Chile only occupies a narrow strip, which extends from 18° to 27° south latitude and 68° 30' west longitude, from the South American Boratífera Province (**Figure 2**); but these appear in all the latitude of the northern part of the country, from the eastern limit to the coast. The westernmost part is a desert domain (Atacama Desert in the strict sense), while, to the east, it can be considered semi-desert (Puna or Altiplano). The aridity of this area, however, is very special, due to the winter rainfall of the Altiplano, added to those of the summer known as “Bolivian winter,” cyclically carrying large amounts of water to the east sector. This means a considerable recharge, in addition to mud currents and ephemeral lakes that can reach the coastal edge. All these waters drain into the interior drainage basins that have intermediate base levels. The geomorphology of the region corresponds to block systems in a tectonically active desert. The blocks, corresponding to main reliefs, are controlled by faults of meridian to submeridian heading, and another transversal EW. The main blocks, in an integrated profile, range from west to zero level up to 6000 m altitude.

Salar de Surire: The salar is located northeast of Chile at 18° 53' S and 69° 03' W at an altitude of 4300 m with a 140 km² closed basin. The most characteristic is in the central part because the volcano Oquecollo emerges to a height of 70 m on the surface cutting the saline cover [19]. The salar receives water from two forms, meteoric and groundwater, creating a very shallow body of brine in the south central area. The region is semiarid with an average annual rainfall of about 230 mm [19]. During the rainy season, the salar may be brine covered to a depth of 20 cm, but during the dry season, the brine water table in the dry season cements the upper crust pores. There are a number of saline thermal springs located on all southeast border of salar, the principal is Polloquere. Almost all the time the river is dry up during the dry season. This suggests that it is fed mainly by atmospheric precipitation. Each year rainwater partially recharges the groundwater system which in turn discharges in topographic depressions. Such waters don't undergo deep circulation, which would put them in contact with ancient evaporites. They owe their composition almost exclusive to the weathering of the volcanic rocks and the resolution of ancient buried evaporites.

The mean annual air temperature is estimated between 10 and 15°C. Air temperature ranges from -15°C in winter to 20°C in summer. Daily variations may reach 35°C. The potential evaporation is high 2500 mm/year [36]. The deposits that make up the salar correspond to carbonates, sulfates, chlorides, borates, and sinter deposits [19]. The Borax Chemical and Industrial Company operates the ulexite deposit in the Salar de Surire since 1985, producing a range of boron products, including boric acid, boron granules (known as granulex), and fertilizers and insecticides, which combine boron or boric acid with calcium sulfate and sodium borates [47]. The surface morphology of the salar is practically flat, although with a slight tilting toward the west, conditioning that the waters that access it go and accumulate in its western margin. Yellow and red colorations are observed that are assigned to arsenic sulfides [19] which reveals a markedly arid environment.

A relevant aspect of the hydrology of the Salar de Surire is the existence of a swampy halo rich in vegetation, which is in the marginal area of the saline body that constitutes the salt flat. It is a special ecosystem known as bofedal and that consists of a high-altitude wetland where varied and abundant vegetation develops. This ecosystem coexists in the middle of a large area of salts, mainly borates that affect the development of its vegetation and others such as arsenic that give it a certain toxic character. The importance of these bofedales is the water they contain, and that is essential for the varied biodiversity to exist into Andean altiplano.

Salar de Quisquiro o Loyoques: It is located in the Altiplano of the Antofagasta region between the latitudes of 23° 07' and 23° 30' south latitude and the longitudes 67° 10' and 67° 30' west, at 4430 m altitude. This saline deposit is a closed basin of about 80 km²; it is a beach-type salt flat with few surface lagoons of variable extension (around 5 km²) and a brine of a few decimeters deep. The main characteristic is that it presents in its center a borate mine with exploitable levels of ulexite, which in the past was exploited [22, 23]. The main surface contributions in this salar are the Salado River in the south and in the north the Loyoques estuary, in addition to the three-deep pass in the west (from north to south) Agua Escondida, Taina, and Quisquiro. The runoff (tributary to the salar) is 3500 l/s; the surface evaporation of the waters is 1500 mm/year, and the average annual rainfall is 150 mm [36]. These data show that the high evaporation rate is due to the high aridity in the area. The maximum average temperature ranges between 10 and 20° C, while the minimum average temperature is a few degrees below 0° [36]. The winds in the altiplano follow a pattern, which in the morning is of low intensity with north orientation, and in the afternoon they start from moderate to high intensity, with west to east orientation.

This saline deposit shows an overload exceeding a continuous horizon of ulexite that varies between 1 and 2 m of power with halite and small amounts of arsenic sulfide and native sulfur particles. In its upper part (30–40 cm), despite the homogeneous aspect of the mineralization, it presents a low grade not exceeding 12% in B_2O_3 in dry sample. At the same time, in its lower part, eliminating interstitial water can reach concentrations of up to 24% in B_2O_3 [4]. At the edges of the salt flat, the overload is dry and hardened presenting gypsum crystals and halite with clay and sand. The underlying ulexite, mixed with abundant gypsum, surpasses sterile clay horizons. The sections that do not contain mineralization are formed by hard salt crusts (20–30 cm) that overlap clays and sands with abundant organic material under which it is found, the water table [22, 23].

The hydrological characteristics are controlled by the conditions of zonal aridity and affected by summer rainfall from the Amazon Basin. This endorheic type basin is characterized by presenting potential resources for water use from its confined layers, as well as mineral species of commercial interest (B, Li, etc.).

Salar de Aguas Calientes I: Evaporitic deposits are located at coordinates 23° 07' 22° S and 67° 26' W, at an altitude of 4280 m and have an extension of approximately 15 km². It drains to an endorheic basin of about 281 km², with an orientation of its main axis NS of 6.5 km and that in its widest part reaches 2.4 km. It is a beach-type salt flat, with surface lagoons of variable extension which occupies a relatively small area of depression, and is covered by a crust of saline materials, mostly halite and gypsum [36, 48]. This situation is due to the current water balance, clearly deficient, since the rainfall received by the drainage basin is around 150 mm/year, with the estimated evaporation exceeding 1500 mm/year which reveals a clearly arid environment. The surface morphology of the salt flat is practically flat, although a slight tilting toward the west determines that the waters that access the salt run and accumulate in its western margin. The geological substrate of the area where the salt flat is located consists mainly of igneous rocks of the Pliocene age. The most important is the ignimbrite atana with a volume of about 2500 km³ of white, pink, and gray daffitic tuffs [48]. It belongs to the geological zone known as the Altiplanic Puna Volcanic Complex (APVC). This unit is stratigraphically located on other older ignimbrite units, associated with the igneous activity existing in this sector at least from the Upper Miocene [49, 50], associated with the La Pacana caldera, which has been interpreted as the oldest collapse boiler of the Cenozoic volcanism in this region. The combination of climatic aridity and high altitude translates into rigorous environmental conditions, among which the following stand out: low partial pressure of oxygen and carbon dioxide, high solar radiation, poorly developed soils with low nutrient availability, low temperatures with a sharp daily oscillation, irregular distribution of rainfall, and prolonged periods of aridity. Under these conditions, the salt flat and its surroundings constitute a crucial water reserve for the development of life.

From an economic point of view, the salar has important reserves of borates, highly soluble mineral salts, which are genetically related to the volcanic activity of the Tertiary Superior-Quaternary [10, 50]. The boron deposit in this salt flat has been prospected, but not exploited, leaving on the surface of its central zone a series of open calicatas of up to 2 m deep, at whose bottom the groundwater of the salar.

5. Geochemical modeling

The physical–chemical processes, including the solubility or deposition of various salts, are known to be determined by the ionic composition of the solutions. The

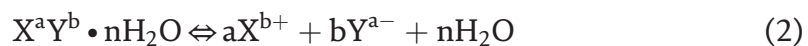
solubilities of minerals in brines can be calculated from thermodynamic considerations, provided the equilibrium constants are known and activity coefficients can be obtained. In this context, we have used Pitzer's ionic interaction model with the extension formulations of the Harvie and Weare model [51–53] to predict the precipitation of salts in multicomponent aqueous systems with high ionic strength in a temperature range of 0–60°C [54–56], using three salt natural brines of Andean borates.

The code used for the thermodynamic calculations of the brines studied in this work is the PHRQPITZ [57], which incorporates and extends to temperature ranges from 0 to 60°C with the Pitzer approximation and the parameterization performed by Harvie et al. [53] for the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system. The codes are subject to compliance with conditions of chemical equilibrium and conservation of mass and/or ionic. These conditions translate into a series of government equations in which knowledge of the activities of the species present is essential. This software calculates the individual ionic activities from the analytical concentration data, based on the specific interaction method. Subsequently, it evaluates the degree of saturation of the solutions with respect to the mineral phases of interest and compares the products of ionic activity (PAI) obtained against the equilibrium constants (K_{eq}) corresponding to the minerals, by means of the saturation index (IS) through the expression:

$$I.S. = \log (P.A.I./K_{eq}) \quad (1)$$

where P.A.I. represents the product of ionic activity and K_{eq} the corresponding equilibrium constant. If the I.S. shows zero value means that the solution is in equilibrium with respect to that phase, on the other hand, positive or negative values of the I.S., they determine a situation of supersaturation or subsaturation, respectively, whose magnitude is a direct function of the absolute value of the quantity.

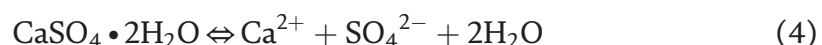
The solubility of a mineral in equilibrium is represented as:



If the solubility product of a mineral is defined as (K_{sp}, X^aY^b•nH₂O) and it is considered as the solid phase activity equal to 1, then.

$$K_{sp, X_a Y_b n H_2 O} \rightleftharpoons a^a X \cdot a^b Y \cdot a^n H_2 O \rightleftharpoons (m_{x,sat} \cdot \gamma_X)^a \cdot (m_{y,sat} \cdot \gamma_Y)^b \cdot a^n H_2 O \quad (3)$$

where m_{x,sat} and m_{y,sat} are the cation and anion mole concentrations, in the saturated liquid phase with respect to the solid phase. For example, for gypsum, Eq. (2) looks like:



The gypsum solubility product (K_{ps}, CaSO₄•2H₂O) depending on the activity is:

$$K_{ps} = (a_{Ca^{2+}} \cdot a_{SO_4^{2-}} \cdot a_{2H_2O}) / a_{CaSO_4 \cdot 2H_2O} \quad (5)$$

The activity of the solid (mineral) phase is defined as equal to 1 (a_{CaSO₄•2H₂O} = 1), where Eq. (5) is transformed to:

$$K_{ps} = (m_{Ca^{2+}} \cdot \gamma_{Ca^{2+}}) \cdot (m_{SO_4^{2-}} \cdot \gamma_{SO_4^{2-}}) \cdot a^2 H_2 O \quad (6)$$

This equation can be rewritten as:

$$K_{ps} = K_{ps}^* \cdot \gamma_{Ca^{2+}} \cdot \gamma_{SO_4^{2-}} \quad (7)$$

where K_{ps}^* is the stoichiometric solubility product, $K_{ps}^* = (m_{Ca^{2+}} \cdot m_{SO_4^{2-}})$. In the equilibrium, the K_{ps} depends on the thermodynamic and stoichiometric product. The activity coefficient (γ) and the solubility depend on several factors, the main one being the ionic force (F.I.). However, as the activity coefficients decrease with the ionic strength of the medium, the K_{ps} value should increase as a function of the ionic strength that the thermodynamic solubility constant does not vary. This increase in stoichiometric constant (K_{ps}) translates into an increase in solubility, as can be deduced from Eq. (7); this is known as the “saline effect” [58].

6. Material and methods

Sampling of surface was collected in the Salar de Surire, Quisquiro, and Aguas Calientes I. Samples of water are taken for analysis from river, springs, and pool, during two seasons, summer and end of winter, at the same previously labeled extraction points and geographically located with GPS. During transport to the laboratory, the samples were kept refrigerated, protected from light, and sealed. The pH, temperature, TdS, and Eh were measured in the field with portable devices pH-conductivity meter (Orion Star A325) which is periodically calibrated with buffer solutions. After making these measurements, the samples were filtered through 0.45 μm filter papers and preserved for analysis. Each sample was stored in two polyethylene bottles. One of them was acidified with 10 mL HCl for cation analysis. The other was kept unacidified for Cl, SO_4 , and HCO_3 analyses. Samples were stored at 4°C for being envoy to the laboratory analyses. In the laboratory the cations (K, Na, Ca, Mg, Li, and As) were determined by atomic absorption spectrophotometry (Perkin Elmer 2380), using the standard protocol, chlorides by the Mohr method, and SO_4 by gravimetry with BaCl and volumetric analysis (Cl, B_2O_3 , CO_3 , HCO_3). Sulfate determination was carried out by precipitation with BaCl₂, using the Mohr method for the analysis of chlorides [59] and the acid-base technique for borates [60].

The quality of the analytical data is evaluated by calculating the percentage of charge-balance error, by the expression of Ball and Nordstrom [61]. In parallel, samples of saline scabs and sediments are taken, in which, once dried, their mineralogy is analyzed with a atomic absorption diffractometer (Siemens, mod. D5000):

$$\% Error = \frac{\sum (m_i z_i)_{cationes} - \sum (m_i z_i)_{aniones}}{(\sum (m_i z_i)_{cationes} + \sum (m_i z_i)_{aniones})^{1/2}} * 100 \quad (8)$$

With the data of the chemical analysis of the brines, the geochemical modeling calculations are carried out, using a speciation code. The values of ionic strength (F.I.), water activity, ionic activities, and saturation indices (I.S.) of the solutions with respect to the salt phases of interest are determined. The geochemical modeling code PHRQPITZ [57] was used, the most suitable for the treatment of concentrated solutions. The values of the equilibrium constant of thenardite (Na_2SO_4) are included, because it was not in the original database of the software, being of great interest in natural brines with high concentrations. Similarly, the values, at different temperatures, of the equilibrium constants of other mineral phases are of interest such as glauberite ($Na_2Ca(SO_4)_2$), a mineral that appeared in the original database of the PHRQPITZ code only at 25°C.

The accuracy achieved in the calculation of saturation indices depends on the quality of both the thermodynamic parameters handled (included in the code database and those from the necessary extensions, such as those commented on the equilibrium constants) and the analytical results obtained. The criterion applied to assess uncertainty has been ± 0.15 units of I.S., implying that equilibrium situations cannot be determined with greater precision than defined [62]. In the case of carbonated minerals, a slightly higher range of uncertainty is considered, besides ± 0.4 units of I.S. This different treatment is due to the existence of important methodological problems related to the determination of pH in highly concentrated solutions [63, 64], because the use of conventional buffers for the calibration of the pH meter determines the measurement of this parameter in brines is not in the same scale of activity coefficients as the aqueous model used [57]. This type of problems related to the behavior of the carbonated system in high-concentration solutions has been manifested even in experimental studies [65].

The evaluation of the saturation status of the solutions against the selected mineral phases is performed by calculating the I.S. The equilibrium constants used are those that appear in the database of the code used. Examples of similar studies are [35, 66–68].

7. Results and discussion

The analysis of the data from the water samples collected in the different salt flats allows us to express certain considerations that are detailed below.

The representation of the chemical composition of the surface water samples is represented in **Figure 3**. It shows the similarity between the water contributed from the thermal springs and the surface brines of the salt, because the thermal waters arise from the interior of the salt flat and, when dissolving salts in their ascent, acquire ionic proportions similar to the surface brines sampled inside the salar. On the other hand, the diluted waters that provide the slopes show greater ionic variability, because the salt drainage basins are made up of different types of volcanic and sedimentary rocks, which give a different chemical signature to the waters that flow about them. The waters of the Salar de Surire present greater variability of chemical types (with a greater number of samples taken) as well as the Salar de Quisquiro, while the Salar de Aguas Calientes I presents the most homogeneous waters.

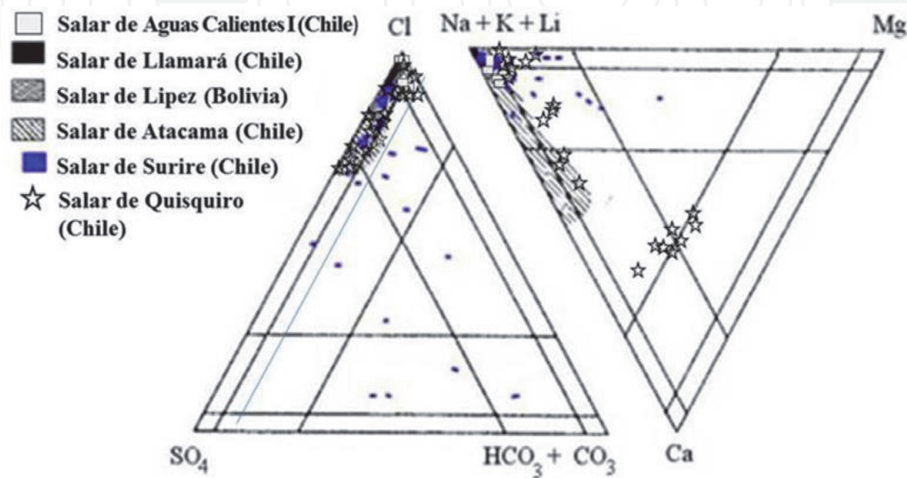


Figure 3.
Graphic comparison of the chemistry of the waters of the Salar de Surire, Quisquiro, and Aguas Calientes I with the Salar de Atacama and Bolivian salt flats.

In the Salar de Surire, the brines accumulated in its internal surface exhibit a lower variability, the anionic composition of the Cl-(SO₄) and Cl type, and the very homogeneous cationic of the Na type. On the other hand, the samples of springs present a high degree of variation in the distribution of both cations and anions. The anionic composition is of the HCO₃-(SO₄)-(Cl) and Cl-(SO₄) type, with virtually all intermediate types, and the cationic varies from the Mg-Na-(Ca) type to the Na-Mg type. These waters are slightly alkaline, with a pH ranging between 6.2 and 9.7. On the other hand, the waters of the Salar de Quisquiro are of the Na-Cl-SO₄ type. Its anionic relationship is $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{BO}_3^{3-} > \text{NO}_3^{3-} > \text{F}^-$, and its cationic relationship is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{As}^+ > \text{Li}^+$. The description of ionic compositions and their temporary changes in closed natural water bodies allows for an explanation of the formation mechanism and the development of enrichment of its brines. The flow of water that enters in this closed basin shows a considerable variety of ionic composition, like in this concentration, the pH varies between 7.2 and 9.02. Finally, the chemical representation of the waters of the Salar de Aguas Calientes I tells us that these are quite homogeneous; their anionic relationship is $\text{Cl}^- > \text{SO}_4^{2-} > \text{BO}_3^{3-} > \text{HCO}_3^-$, and their cationic concentration is $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Li}^+ > \text{As}^{3+}$. They are practically neutral waters, whose pH values range from 6.4 to 7.9. The chemical nature of these waters (**Figure 3**) shows that the salar belongs to the Na-Cl system, and if we consider the equimolar relationship between [Na] and [Cl], they are practically the same, which has a direct relationship with the saline composition of the salar; this suggests that the high concentrations of Na and Cl of the most saline waters come essentially from the solution of sodium chloride or halite (NaCl). Therefore, in the most saline contribution waters, the excess of Na and Cl (in relation to the more dilute waters) probably comes from the redissolution of old evaporites associated with sedimentary rocks covered by the extensive volcanic formations of the east and northeast of the basin. When comparing the chemical nature of the waters of the Salar de Aguas Calientes I with the Lipez Bolivian salars [39] on the diagram (**Figure 3**), it can be verified that the brines of the Lipez salars are of the type Na-(Ca)-Cl-(SO₄) and vary to Na-Cl type while the waters of the Salar de Aguas Calientes I, show little variability of the type Na-Cl-(Ca), which leads to suggest that their brines contain more calcium than sulfate. In short, the similarity and contrast of the chemistry of our study [48] with that carried out by Risacher et al. [36] 20 years later are complementary.

The thermal springs that emerge inside the Salar de Surire have an anionic composition between the types Cl-(SO₄), Cl-(HCO₃), and Cl, while its cationic composition varies between the types Na-(Ca) and Na. The values measured in the thermal springs in Surire range between 84°C, pH 6.82, and F.I. 0.0832 m and 32°C, pH of 7.84, and F.I. 0.0897 m, while the thermal springs located south of the Salar de Aguas Calientes (black lagoon) has a composition of the Cl-(SO₄) and Na type, with a concentration of 0.46 molal. It is the most acidic of all waters with a pH 6.4 to 47.3°C. From these data we can mention that the thermal springs that occur in the Salar of Surire and Aguas Calientes I are waters of low concentrations and rather neutral.

The evolution of the physicochemical conditions was evaluated with the PHRQPITZ code that allows to calculate the ionic activity coefficients (γ_i), activities of the species present, and the degree of water saturation (I.S.). **Figure 4** shows the evolution of the ionic activity coefficients as a function of the ionic strength. From these graphs it is observed that there is a first group, whose activity coefficients decrease to a minimum and then increase as it increases with the F.I. in the solution; they are γNa^+ , γMg^{2+} , γCa^{2+} , and Cl^- . The second group is the γK^+ , γSO_4^{2-} , and γHCO_3^- , which is characterized by a progressive behavior with the decrease in F.I.

The saline waters of the Salar de Surire are between 0.004 m to 5.03 m, with values in the calcite saturation index practically supersaturated in this mineral.

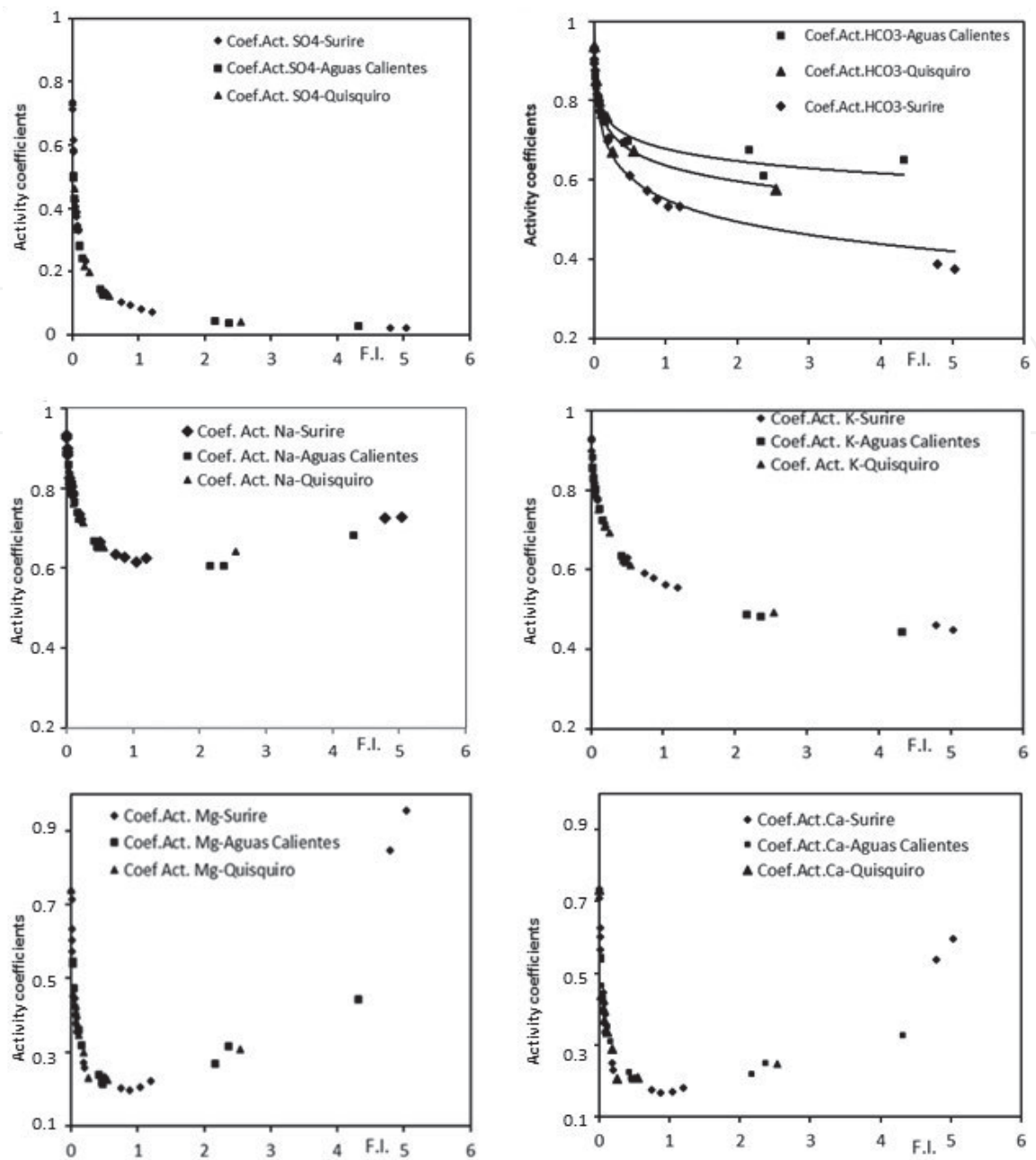


Figure 4.
Activity coefficients of major ions based on ionic strength, calculated from the speciation code PHRQPITZ.

Water samples with F.I. < 0.07 m is far from equilibrium. If we consider alkalinity, such as $(\text{alk}) > 2(\text{Ca}^{2+})$ in the initial water entering the salar, then the alkalinity should increase regularly during the evaporation process and only precipitate calcite, so the waters will follow the alkaline pathway (increasing the carbonate concentration and decreasing calcium). Our waters have a slightly alkaline pH, so the process goes in the direction of the precipitation of magnesium silicates, releasing H^+ ions, neutralizing a large part of the carbonate in the solution, and modifying the Ca/CO_3 ratio, therefore changing the alkaline pathway to the neutral saline pathway, while other waters (to a lesser extent) go through the alkaline pathway. It can be said that if the alkalinity of the initial solution is greater than the total concentration of the calcium (in milli-equivalents per liter: meq/l) [36], the solution will begin its evolution toward the alkaline route, raising the pH above 10. But, if the alkalinity is less than the sum of the calcium and magnesium concentrations (in meq/l), the solution will change its evolution toward the neutral saline route due to the precipitation of magnesium silicates, pH less than 9. Interestingly, it is possible

to determine immediately, from the analysis of the initial solution, which evolutionary path should theoretically follow the solution from the precipitation of calcite and magnesium silicates. For its part, as an explanation of the presence of calcium sulfate and gypsum, since there is a clear tendency to balance in the samples that have F.I. greater than 2 m, in this case the existence of the sulfate source is the additional sulfur brought to the waters of the aquifer where it is oxidized transforming into sulfate from the sulfated minerals in the area. But, if the alkalinity is less than the sum of the calcium and magnesium concentrations (in meq/l), the solution will change its evolution toward the neutral saline route due to the precipitation of magnesium silicates, pH less than 9. The interesting thing about this method is that it allows you to immediately determine, from the analysis of the initial solution, which evolutionary pathway should theoretically follow the solution from the precipitation of calcite and magnesium silicates. If all alkali cations such as sulfate are removed, the amount of oxidized sulfate would be the difference between the total loss of alkali cations and the apparent loss of sulfate. From the visual observation in the area, there is a very close native sulfur, which is transported by the winds; probably this is the process that generates the significant reduction of alkalinity.

The Salar de Quisquiro presents concentrations between F.I. 0.004 m and 2.54 m, and all sampled waters saturated in calcite and aragonite are presented. The other minerals closest to equilibrium are gypsum and later magnesite but far from precipitating. Since all waters are supersaturated in calcite, the next step is to consider alkalinity. If $(alc) > 2(Ca^{2+})$, in the initial inlet water, then it increases regularly during evaporation, if only calcite precipitates. In other words, the activity product of the Ca^{2+} ions in solution in relation to CO_3^{2-} must remain constant, as the concentration increases. If one of the solutes increases, then the other should decrease. In our case, the distribution of all incoming water must be converted into carbonate-rich brines. However, the evolution of the water represented in the triangular diagram (**Figure 3**) is of the Na-Cl- SO_4 type with a pH lower than 9. The usual explanation for this anomaly is the precipitation of Mg silicates [69]. This suggests that the distribution of the incoming waters should become alkaline but that they are neutral brines. This induces evaporitic waters to follow two evolution paths. If during the evaporative process they are enriched with carbonates, becoming an alkaline brine of sodium carbonate, they will have a pH greater than 10. The other way is when the waters of input present more calcium than carbonate so that the solution is concentrated in calcium producing neutral brines with pH less than 9, as it is in our case. Therefore, the fundamental relationship if $(alc) > 2((Ca^{2+}) + (Mg^{2+}))$ does not depend on the nature of the weak anion of the acid associated with Ca and Mg, during the evaporation concentration process. Another explanation of the data is the existence of an excess sulfate of origin. In this model, additional sulfur is put into the waters of the aquifer where it oxidizes to sulfate and removes sulfate minerals. If every alkali cation is removed as sulfate from the amount of oxidized sulfate would be the difference between the total loss of alkali cations and apparent loss of sulfate. In observing the area very close to it, there is native sulfur. This is transported by the winds. These processes give a significant reduction in alkalinity.

The Salar de Aguas Calientes I has concentration waters that vary between 0.0237 m and 4.3195 m. The chemical nature of the waters shows (**Figure 3**) that its waters are of the Na-Cl type and it is directly related to the salt composition of the salt, whose sediments are mainly halite accompanied by gypsum and with the presence of borates in its central zone. The composition of all its waters seems to be linked to the saline composition of the sediments of the salt flat, since its contact with both the surface waters that access the salars and the underground

contributions cause the enrichment in chloride and sodium, thus generating a more homogeneous composition of the solutions. The only samples that differ from this behavior are those of the northern sector, presenting a slightly higher anionic proportion in HCO_3 and SO_4 . According to the results of the samples, the highest concentration of As and B in the brines is in the central-western sector of the salt, which is due to the predominantly hydrothermal origin of the recharge solutions. The lagoons of the central western sector are waters with a variable degree of chemical concentration. These lagoons are located mainly in the western zone of the salar, due to a slight slope of its surface toward the sector W, accumulating in this margin the scarce rainfall and also the solutions coming from the subsurface flow of the salar like that of its internal zone.

The predominance of water from inside or outside the saline nucleus of the salar determines the greater or lesser degree of concentration of the solutions, although they all share the same chemical type. In the southernmost zone, thermal waters emerge with a degree of concentration in solution similar to that of the brines that accumulate in the nearby lagoons, from which it follows that the concentration of the solutions comes in this area controlled by the interaction with the saline sediments of the salar. The saturation conditions (I.S.) of the solutions analyzed with respect to saline minerals of interest show a variable behavior; in the northern sector, the waters are clearly subsaturated with respect to gypsum and halite, while the waters of the bofedal are saturated with respect to calcite. On the other hand, the hot springs are subsaturated with respect to these three main saline minerals, although the degree of subsaturation is lower than that of the nonthermal springs. Finally, of the samples collected in the lagoons of the central sector, the two most diluted are in equilibrium with calcite and subsaturated with respect to gypsum and halite, while the most concentrated appears to be supersaturated with respect to calcite and gypsum and subsaturated with respect to halite.

8. Conclusion

Chilean salt flats have only ulexite as an economic mineral, these deposits being related to a shallow saline lake, whose main contributions in boron are from thermal sources. Boron in Andean salars is mainly linked to the Cenozoic volcanic rocks that prevail in the eastern Andean territory, particularly in recent or latent volcanic centers, and there is an increase in boron in areas of active latent volcanism, such as the hot springs of Salar de Surire [47] and Salar de Aguas Calientes I [48].


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