

LITHIUM AND BORON OF SPRING WATER AND SALT CRUST FROM SALAR DE ASCOTÁN, SOUTHWESTERN ALTIPLANO

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ABSTRACT

Lithium is an essential element for humans and animals, it is bio accumulated by plants and it is a relatively uncommon element in the Earth's crust, on the contrary boron is widely distributed and it is micronutrient for plants. Boron and lithium are incorporated in fertilizers for agriculture and they used in many industries. Economically lithium is considered a strategic element because it is important in energy markets. There are two main economically recoverable sources of lithium, those being mineral ores and the evaporate deposits (playa lakes, called "salars" in Spanish). Direct extraction of lithium from brines at the salars is a low cost method and generates byproducts such as boron. Salars with high concentrations of Li have been reported in the Andean region near the borders of Chile, Bolivia, and Argentina. In Chile, the brines at Salar de Atacama are considered an important commercial source of lithium. To the northeast of Salar de Atacama it is located Salar de Ascotán (21°27'01, 9°S; 68°15'8,5''W) where the commercial boron extraction has been done for many decades but lacks published information about lithium extraction. In this study concentrations and distribution of lithium and boron in the water, sediment and salt crust were analyzed in some of the east-side springs which have a high endemic biodiversity. The concentrations in the salt crust were higher than in water and sediment. Geographically, the concentration of lithium in salt crust increases from north to south, but the boron concentration was higher in the extreme north and south, in the southernmost spring, N°11. The average concentration of B in the salt crust was 149 [mg/Kg] and for Li was 3000 [mg/Kg] at the east side of the salar, thus it is the area with the highest concentration of lithium and boron. The concentrations in the salt crust were high and geographically heterogeneous for using a non-invasive method, for environmental protection we propose an exploration superficial on the western side which lack spring water and present the higher concentration of lithium and boron of the salar.

Keywords: Lithium, Boron, springs, Salt crust and Brines.

1. INTRODUCTION

Lithium is an infrequent element in the Earth's crust ¹; it is an essential element for humans and animals. Until 1990 it was utilized by US armed forces in nuclear bombs and its extraction was only from mineral deposits. Recently it has acquired many applications: lithium nitrate is used in solar plants because of its thermal storage ability ², lithium carbonate has pharmaceutical applications to treat manic depression, although its action on the brain is still not fully understood; it is also used in the manufacture of glass, ceramics, rubber, allied with aluminum because it is hard as steel but lighter to be incorporated in modern aircraft and especially in the production of lithium-ion power batteries for mobile phones and other technologies³.

Boron is an element widely distributed in the earth's hydrosphere and lithosphere. It is a micronutrient because it is an essential element for plant development due to its participation in photosynthetic metabolism and calcium movement, but in concentrations of 0.3 to 0.5 (mg/L), because it is toxic above 1 (mg/L) ⁴. It is used in many industries, including agriculture, glass, electronics, ceramics, porcelains, cosmetics, semiconductors, leather, pharmaceuticals, insecticides, catalysts, fuels and cleaning products. The glass industry consumes more than half of the total production of boron compounds ⁵. Also, isotope boron-10 plays a crucial role in the nuclear industry because it absorbs neutrons and tends to make the nucleus less reactive, avoiding a nuclear explosion ⁶. However, elemental boron has not been found yet; it has been extracted with other elements, for years mainly as ulexite. Another way to do it is from brines; because it is a byproduct of the lithium industry.

There are two main types of lithium resource which are economically recoverable; first mineral ores were used and later the brines ³. Lithium from mineral resources accounts for 8.8 million tons; large deposits are located in the USA, Russia and China. Today attention centers in the southern desert regions; about 70% of the world's economically viable Li deposits are found in one small area, the so-called lithium triangle (Salar de Atacama, Salar de Uyuni and Salar del Hombre Muerto) located near the borders of Chile, Bolivia, and Argentina ⁷. The current lithium in this area is approximately 52.3 million tons, of which 23.2 million tons are recoverable ⁸. Besides, this area is called the Andean Boratiferous Province because in here is found the totality of known borate deposits in South America, deposits of B₂O₃, in Argentina with 100-20.5 million tons, in Bolivia with 59.5, in Peru with 20-5 million tons and in Chile with 76 million tons ⁹.

Formerly access was a negative factor for competitive economic exploitation of minerals; today extraction is possible because of technological development. Extraction of Li from brines is usually less expensive and entails lower energy consumption. Chile among other countries has been able to produce lithium compounds from brines ¹⁰. The Salar de Atacama in northern Chile has an estimated Li content of 6.3 million tons ¹¹; it is the planet's largest deposit of economically recoverable Li ⁷. These sites have many advantages: low cost of processing because it has less magnesium concentration compared to the Salar de Uyuni; they operate continuously because the weather is favorable all year and the solar conditions are ideal for high evaporation due to the annual global radiation value (2500 kWh/m²) and the index of direct normal irradiance (DNI, 3500 kWh/m²) ¹⁰. In the Salar de Atacama waterproofing evaporation ponds are used; they pump brines under a layer of salt crust with a thickness between 0.5 and 2.5 meters and obtain lithium carbonate, potassium chloride, potassium sulfate, boric acid and magnesium chloride from evaporation ¹².

There have been explorations in Chile to estimate the concentration of lithium near the Salar de Atacama, including the Salar de Maricunga, Pedernales, La Isla, Quisquiro, Punta Negra, Aguas Calientes Centro, Pajonales, Aguilar, Tara, Parinas, Pujsa, Aguas Calientes Norte, Talar and Aguas Calientes Sur ¹³. However, the Salar de Ascotán, which is also near the Salar de Atacama (about 200 km), has no reports up to date describing lithium extraction, only the historical extraction of boron. This exploitation started in 1883, in this place and the Salar de Surire, with a maximum of 36,000 metric tons in 1913, positioning Chile as the first world producer, of ulexite ⁹. Because lithium has a promising future in the technology industry and boron has a historical extraction in Chile, the objective of this study was to analyze the concentrations and distribution of boron and lithium in the water, sediment and salt crust in three eastern springs in the Salar de Ascotán.

2. MATERIALS AND METHOD

2.1 Study area

The Salar de Ascotán is located in the southern Chilean Altiplano at 3700 m elevation in the Antofagasta region. In the eastern border it has twelve springs with different degree of isolation that drain to the Salar. This study analyzed springs 1 (21°27'2.9'' S, 68°15'8.2''W), spring 6 (21°29'54.3'' S, 68°15'24.6''W) and spring 11 (21°41'16.3'' S, 68°12'53.8''W) at the eastern site. The western border does not have superficial water.



Figure 1. Geographical distribution of eastern springs 1, 6 and 11 in Salar de Ascotán.

2.2 Sampling processing

In May 2015 salt crust samples were collected at six random points around the springs. The water samples and sediment samples were collected at three points at different depths in a sequence from the source of the springs towards the center

of the Salar, at below 1.5 m, at 50 cm and at less 15 cm; the last depth corresponds to the dark zones in Figure 2. The sediment samples were dried at room temperature and sieved to 2 mm. The dilution factor was calculated in salt crust samples, which were dried at 100 °C.

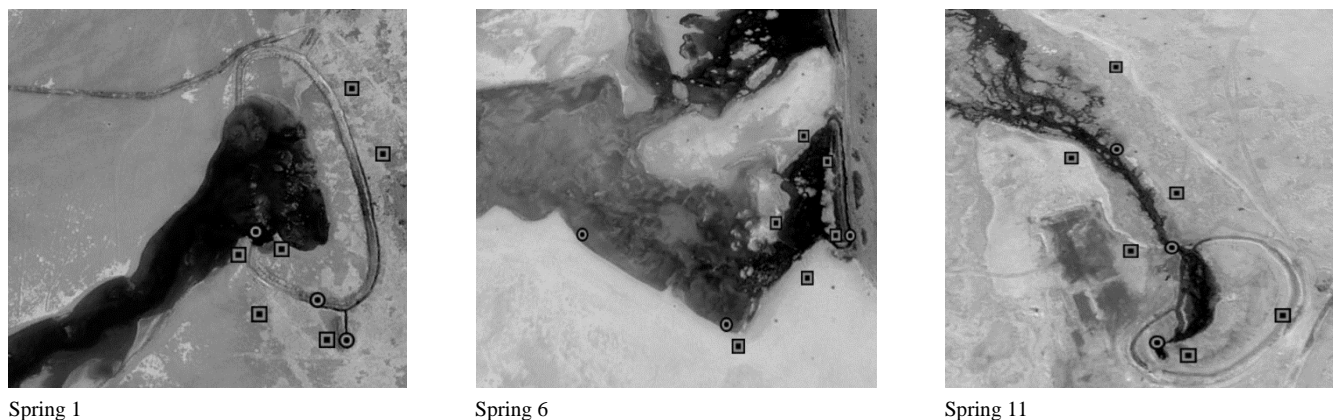


Figure 2. Six samples of salt crust are shown as red squares and three samples of sediment and water as in a green circles.

2.3 Chemical analysis

All chemicals used in the study were analytical grade. Aqueous solutions of the metals were prepared from standards (titrisol, Merck). Deionized water was used throughout the study (Millipore, milliQ grade). All glassware and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10% nitric acid (Merck Suprapur 65%) for 48 h and finally rinsed with deionized water several times prior to use. The calibration curves were constructed with a standard solution of 1 g/L Merck lithium chloride (LiCl) titrisol and 0.5716 g Merck boric acid (H_3BO_3) for analysis. We prepared white samples with 0.051 mg/L boric acid (absorbance 0.2810) and lithium at the low detection limit (absorbance 0.0029). Operational conditions were adjusted to yield optimal determination.

For lithium analyses sediment samples were prepared with a saturated extract with a solid-liquid ratio of 1:2¹⁴; salt crusts were prepared by diluting samples of 1 g salt crust in 100 mL deionized water. The pH and conductivity were obtained with a WTW model 3430 SET G multi parameter probe.

After these procedures all samples (water, sediment and salt crust) were filtered with a 0.22 μm pore (P-nitrocellulose membrane) and analyzed in an AAS (atomic absorption spectrophotometer) Shimadzu Model AA-6800 with Software WizAard at 670.8 λ . 0.1% KCl (Merck) was used as suppressor for lithium analysis.

Boron analyses in sediment and crust salt samples we extracted with hot water¹⁵. After this procedure all samples (water, sediment and salt crust) were filtered with a 0.45 μm pore filter (P-nitrocellulose membrane) and analyzed colorimetrically with azomethine-H [14] in a PharmaSpec UV-1700 spectrophotometer with a quartz cell at 420 λ .

2.4 Cluster analysis

In this study the statistical analysis of the results was based on Cluster Analysis (CA)¹⁶. CA was performed from the original data in order to reduce the variance biases. The nearest neighbor method was applied and dissimilarity by City-Block distance.

3. RESULTS

3.1 Characterization of water and sediment.

Table 1 shows water and sediment physical and chemical characteristics

Parameter	Matrix	Spring 1	Spring 6	Spring 11
EC (mS cm ⁻¹)	Water	14 ± 0.9	4.1 ± 0.2	2.5 ± 0.0
	Sediment	9.2 ± 1.6	6.6 ± 4.0	7.0 ± 1.8
pH	Water	8.2 ± 0.3	8.2 ± 0.2	8.4 ± 0.1
	Sediment	8.9 ± 0.5	9.3 ± 0.5	8.1 ± 0.8

The average pH in water ranged between 8.4-8.2 and in sediment 8.1-8.9, slightly alkaline probably due to the high concentration of salts in the area, specifically carbonates. The electrical conductivity of the water in the eastern springs decreased from north to south; from north to south the averages for each springs were 14, 4.1 and 2.5 (mS/cm). In sediments the electrical conductivity is lower in slopes 6 and 11 following the same trend observed in the water.

3.2 Lithium and boron concentrations.

The following figures show the concentrations of Li and B determined in water, sediment and salt crust of slopes 1, 6 and 11.

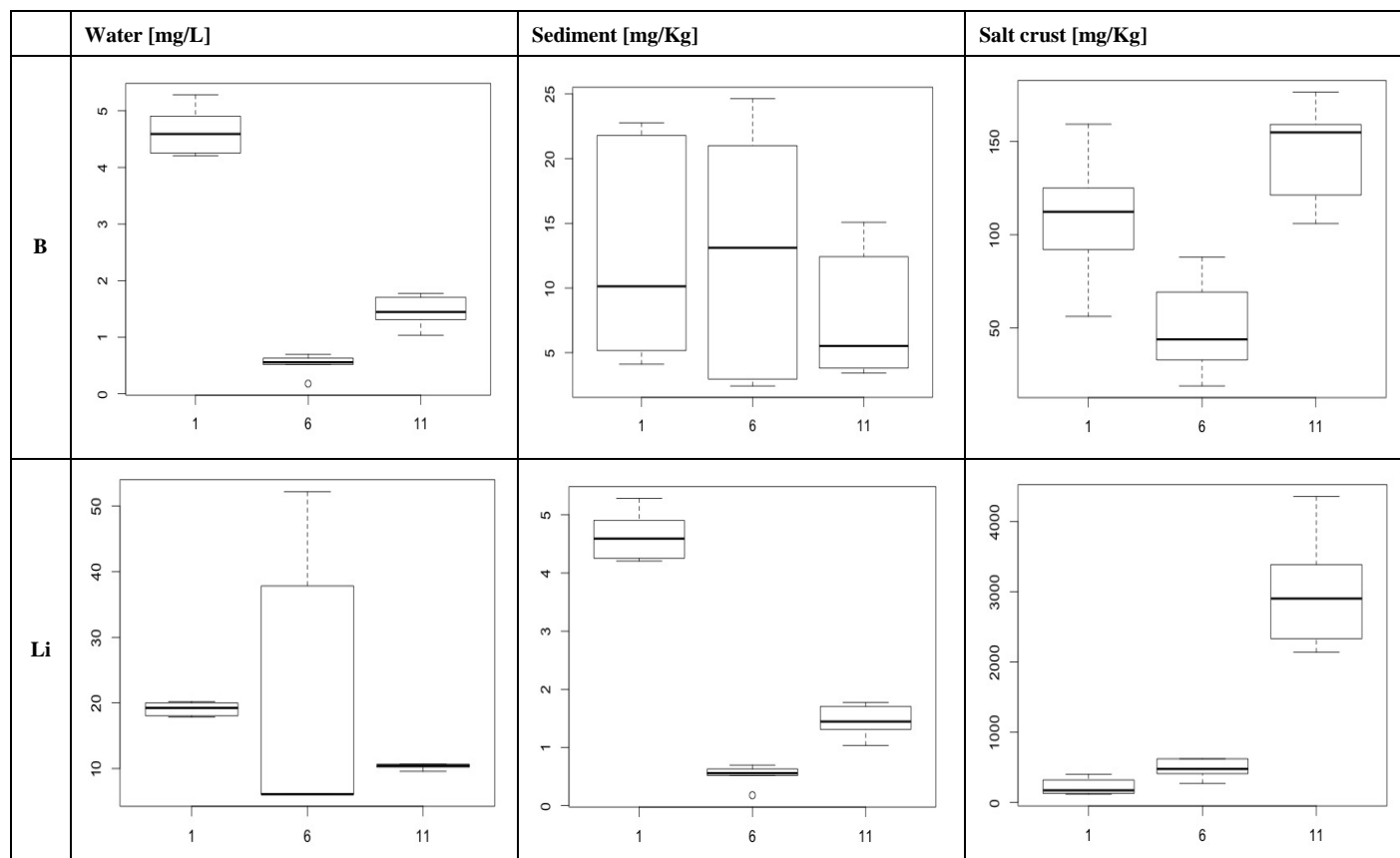


Figure 3. Boxplot of boron and lithium concentration in springs 1, 6 and 11.

Each spring has its own range of concentrations, except for the concentration of boron in the sediment. The concentrations of boron and lithium in water were higher in spring 1, but only boron was different in all springs. These concentrations were higher than those in Lauca National Park¹⁷ and the nearby Salars as in Salar de Aguas Calientes Sur, lithium is 8.5-17.5 (mg/L)¹³. In Salar de Carcote springs¹⁸, boron is lower than 4 (mg/L) and lithium is lower than 1 (mg/L). Figure 2 also shows that lithium concentration in salt crust increase from north to south and that boron concentrations were higher in the northern and southern extremes. Spring 11, located at the southern end of the Salar de Ascotán, had the highest concentration of these two elements average boron was 149 (mg/Kg) and lithium was 3000 (mg/Kg).

Differences between springs are shown in the next figures.

3.3 Cluster analysis

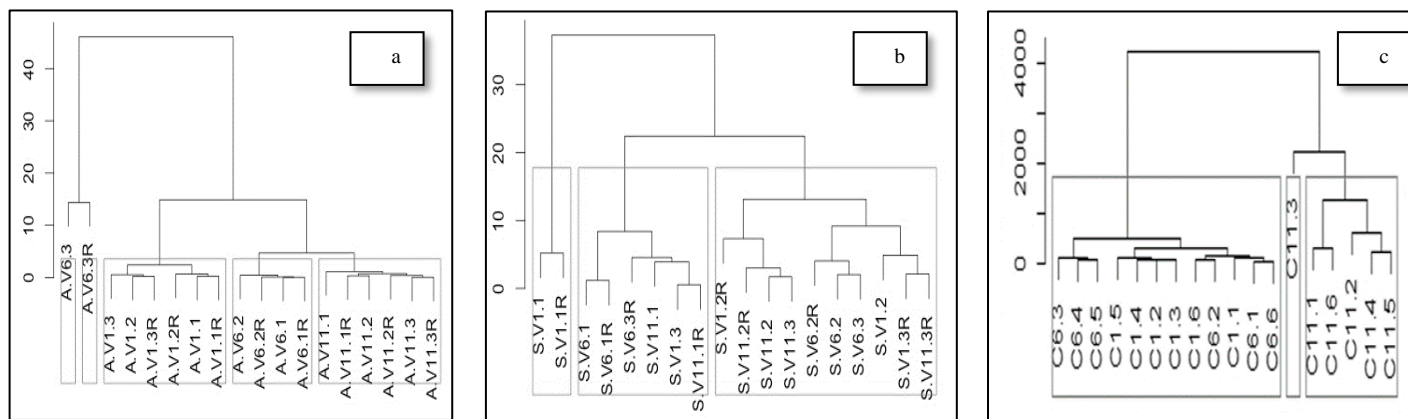


Figure 4. Cluster analysis for a: water; b: sediment c: salt crust.

To see the effect of the lithium and boron concentrations in the three strands, the cluster analysis of both elements in water shows similarity in the three springs, only site 3 of spring 6 shows a difference. In the sediment, slopes 1, 6

and 11 show similarity, only sites 1 of spring 1 show difference. In the salt crust there is only difference in site 4 of slope 6.

4. DISCUSSION

The commercial interest in lithium and boron in brines would affect the characteristics of the salar and its protection. The salars are very complex, dynamic and fragile ecosystems, which are important for fauna studies, because the endemic species are generally in danger due to these extreme environments. The springs located west of the Salar have been isolated for a long time. Morales et al., (2011)¹⁹ demonstrated genetic differences in the fish *Orestias ascotanensis Parenti* between springs as a consequence of a gradual and deep process of habitat fragmentation. This isolation could be the best explanation for these results and not only the current evaporation by itself, which effects were evaluated by collecting the samples from different depths. Another explanation could be the volcanism or soil composition, because the water of the springs has a contribution of groundwater coming from the Caldera de Pastos Grande, a Miocene-Pliocene ignimbrite center located in western Bolivia at an average altitude of 4,600 m²⁰.

For a complete analysis in the crust salt, in the future the magnesium should be considered, since the lowest Mg / Li ratios are considered adequate for the lithium recovery, in the Salar de Uyuni, where the ratio is 18.6; this ratio is three times greater than in the Atacama salar⁷. This is important because the magnesium may be associated with the chemicals of paleo-lake Minchin that covered the area 30,000 years ago, which flooded both Salar de Uyuni and Salar de Ascotán not reaching Salar de Atacama.

We are concerned about lithium extraction in the Salar because the global market that uses it in batteries has grown significantly over the last few years, reaching 23% in 2010²¹. It is considered as a strategic element²² and the demand for lithium is forecast to increase by 60%, from 102,000 tons to 162,000 tons as lithium carbonate equivalent, in the next 5 years. The application in batteries used a large percentage (40,000 tons) of this growth^{21,23}. Because of this its price has increased considerably; during 2008 the price of one ton was US\$3000, in 2011 it was US\$7000, during 2015 it was US\$12,000 and it is likely to continue to increase²⁴. This does not happen with boron, because it is a product with very stable commercialization that maintains a market niche that can be used favorably by small and medium enterprises⁹. Due to all this, is very important to know the lithium and boron concentration in the salars, especially in places where endemic species live, and to develop studies to protect them.

5. CONCLUSIONS

In this study, we prove that concentrations in the salar are irregular and scattered, the concentrations in salt crust were high and geographically heterogeneous. To use a non-invasive method, promoting the economic activity and benefits without harming the local biodiversity, we propose an exploration superficial of the western side without spring water due to the high conductivity recorded in this place, to find of higher concentration lithium and boron in salar. Besides, it is important to consider the updating of scientific information on salars incorporating concentrations of these commercial elements.

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